# ARMY DRAFT

# UFP-QAPP

# RCRA FACILITY INVESTIGATION - PARCEL 3 SWMUs (SWMUS 14, 15, 33 AND 74) AND AOCs (AOCS 89, 90, 91, AND 92)

**Fort Wingate Depot Activity**
**McKinley County, New Mexico**

**October 23, 2015**

**Contract No. W912DY-10-D-0025**
**Task Order No. DS02**
**Modification No. 1**

***Prepared for:***

**United States Army Corps of Engineers**
**CESWF-PEC-TM**
**819 Taylor St.**
**Room 3A12**
**Ft. Worth, TX 76102**

***Prepared by:***

PIKA
ARCADIS MALCOLM PIRNIE
A JOINT VENTURE

**12723 Capricorn Drive, Suite 500**
**Stafford, TX 77477**

## Table of Contents

**Tables**



**Appendices**

## Acronyms and Abbreviations

| | |
|---|---|
| AOC | area of concern |
| bgs | below ground surface |
| BRAC | Base Realignment and Closure |
| CA | corrective action |
| CCV | continuing calibration verification |
| CESWF | United States Corps of Engineers, Fort Worth District |
| CESWT | United States Corps of Engineers, Tulsa District |
| COC | chain of custody |
| COPC | constituent of potential concern |
| COR | Contracting Officers Representative |
| CVAA | cold vapor atomic absorption |
| DL | Detection Limit |
| DoD | Department of Defense |
| DQI | data quality indicator |
| DQO | data quality objective |
| EB | equipment blank |
| EDD | electronic data deliverable |
| ELAP | Environmental Laboratory Accreditation Program |
| FB | field blank |
| ft | feet/foot |
| FTR | Functional Test Range |
| FWDA | Fort Wingate Depot Activity |
| GC/MC | Gas chromatography / Mass spectroscopy |
| GPS | Global Positioning System |
| HI | Hazard Index |
| HMX | High Melting Point Explosive/octahydro-1,3,5,7-tetranitro-1,3,5,7 tetrazocine |
| HPLC | high performance liquid chromatography |
| IAW | in accordance with |

| | |
|---|---|
| ICAL | initial calibration |
| ICP-AES | inductively coupled plasma – atomic emission spectrometry |
| ICP-OES | inductively coupled plasma – optical emission spectrometry |
| ICS | interference check sample |
| ICV | initial calibration verification |
| ID | identification |
| ISM | incremental sampling methodology |
| JV | PIKA-Pirnie Joint Venture, LLC |
| KOA | Kickout Area |
| LCS | laboratory control sample |
| LOD | limit of detection |
| LOQ | limit of quantitation |
| MB | method blank |
| MC | munitions constituents |
| MEC | munitions and explosives of concern |
| mg/kg | milligram per kilogram |
| MPPEH | Material Potentially Presenting an Explosive Hazard |
| MS | matrix spike |
| MSD | matrix spike duplicate |
| NA | Not Applicable/Available |
| NMED | New Mexico Environment Department |
| OB/OD | open burn /open detonation |
| OE | ordnance and explosives |
| PE | Professional Engineer |
| PIKA | PIKA International, Inc. |
| PM | Project Manager |
| PMP | Project Management Professional |
| QA | quality assurance |
| QAPP | Quality Assurance Project Plan |
| QA/QC | quality assurance/quality control |

| | |
|---|---|
| QC | quality control |
| QSM | Quality Systems Manual |
| RCRA | Resource Conservation and Recovery Act |
| RDX | Royal or Research Department Explosive/hexahydro-1,3,5-trinitro-1,3,5-triazine, cyclonite |
| RFI | Resource Conservation and Recovery Act Facility Investigation |
| RPD | relative percent difference |
| RSD | relative standard deviation |
| RSL | Regional Screening Level |
| SOP | standard operating procedure |
| SSL | Soil Screening Level |
| SVOC | semi-volatile organic compound |
| SWMU | solid waste management unit |
| TBD | to be determined |
| the Army | United States Army |
| UFP-QAPP | Uniform Federal Policy for Quality Assurance Project Plans |
| U.S. | United States |
| USACE | United States Army Corps of Engineers |
| USEPA | United States Environmental Protection Agency |
| WMM | Waste Military Munitions |
| % | percent |
| %R | percent recovery |

## 1. Introduction

This Uniform Federal Policy for Quality Assurance Project Plan (UFP-QAPP) addresses constituents of potential concern (COPCs) associated with Resource Conservation and Recovery Act (RCRA) Facility Investigation of Solid Waste Management Units (SWMUs) 14, 15, 33, and 74, and Areas of Concern (AOCs) 89, 90, 91, and 92, within Parcel 3, Fort Wingate Depot Activity, McKinley County, New Mexico. The purpose of this UFP-QAPP is to document the planning processes for collecting analytical data, describe the implementation of the field activities, and describe the quality assurance (QA) and quality control (QC) activities developed for this project. The objectives of this UFP-QAPP are to generate data that are technically valid, legally defensible, and are useful in meeting the project goals, as well as to integrate the technical and QC requirements for future remedial alternative development activities. This UFP-QAPP addresses four primary elements:

- Project Management
- Measurement and Data Acquisition
- Assessment and Oversight
- Data Validation and Usability

The UFP-QAPP workbook format used herein implements the systematic planning process for environmental sampling and was developed via collaboration between the United States Environmental Protection Agency (USEPA), Department of Defense (DoD), and the Department of Energy. In 2010, a subgroup comprised of members from the participating agencies was established to review and optimize the UFP-QAPP workbook in close coordination with USEPA's update of QA/G-5, *Guidance for Quality Assurance Project Plans* (CIO 2106-G-05 QAPP. Draft January 2012). The optimized workbook format is used for this UFP-QAPP. The information contained in the worksheets captures the elements that would be otherwise included in related project-planning documents, such as a Sampling and Analysis Plan and a Field Sampling Plan. Table 1 is a crosswalk between the optimized UFP-QAPP worksheet numbers and titles and the CIO 2106-G-05 QAPP Guidance (USEPA, 2012a).

| Table 1. Crosswalk: UFP-QAPP Workbook to 2106-G-05 QAPP | | | |
|---|---|---|---|
| **Optimized UFP-QAPP Worksheets** | | **2106-G-05 QAPP Guidance Section** | |
| 1 & 2 | Title and Approval Page | 2.2.1 | Title, Version, and Approval/Sign-Off |
| 3 & 5 | Project Organization and QAPP Distribution | 2.2.3 | Distribution List |
| | | 2.2.4 | Project Organization and Schedule |
| 4 , 7 & 8 | Personnel Qualifications and Sign-off Sheet | 2.2.1 | Title, Version, and Approval/Sign-Off |
| | | 2.2.7 | Special Training Requirements and Certification |
| 6 | Communication Pathways | 2.2.4 | Project Organization and Schedule |
| 9 | Project Planning Session Summary | 2.2.5 | Project Background, Overview, and Intended Use of Data |
| 10 | Conceptual Site Model | 2.2.5 | Project Background, Overview, and Intended Use of Data |
| 11 | Project/Data Quality Objectives | 2.2.6 | Data/Project Quality Objectives and Measurement Performance Criteria |
| 12 | Measurement Performance Criteria | 2.2.6 | Data/Project Quality Objectives and Measurement Performance Criteria |
| 13 | Secondary Data Uses and Limitations | Chapter 3 | QAPP Elements for Evaluating Existing Data |
| 14 & 16 | Project Tasks & Schedule | 2.2.4 | Project Organization and Schedule |
| 15 | Project Action Limits and Laboratory-Specific Detection / Quantitation Limits | 2.2.6 | Data/Project Quality Objectives and Measurement Performance Criteria |
| 17 | Sampling Design and Rationale | 2.3.1 | Sample Collection Procedure, Experimental Design, and Sampling Tasks |
| 18 | Sampling Locations and Methods | 2.3.1 | Sample Collection Procedure , Experimental Design, and Sampling Tasks |
| | | 2.3.2 | Sampling Procedures and Requirements |
| 19 & 30 | Sample Containers, Preservation, and Hold Times | 2.3.2 | Sampling Procedures and Requirements |
| 20 | Field QC | 2.3.5 | Quality Control Requirements |
| 21 | Field Standard Operating Procedures (SOPs) | 2.3.2 | Sampling Procedures and Requirements |
| 22 | Field Equipment Calibration, Maintenance, Testing, and Inspection | 2.3.6 | Instrument/Equipment Testing, Calibration and Maintenance Requirements, Supplies and Consumables |

| Table 1. Crosswalk: UFP-QAPP Workbook to 2106-G-05 QAPP | | | |
|---|---|---|---|
| **Optimized UFP-QAPP Worksheets** | | **2106-G-05 QAPP Guidance Section** | |
| 23 | Analytical SOPs | 2.3.4 | Analytical Methods Requirements and Task Description |
| 24 | Analytical Instrument Calibration | 2.3.6 | Instrument/Equipment Testing, Calibration and Maintenance Requirements, Supplies and Consumables |
| 25 | Analytical Instrument and Equipment Maintenance, Testing, and Inspection | 2.3.6 | Instrument/Equipment Testing, Calibration and Maintenance Requirements, Supplies and Consumables |
| 26 & 27 | Sample Handling, Custody, and Disposal | 2.3.3 | Sample Handling, Custody Procedures, and Documentation |
| 28 | Analytical Quality Control and Corrective Action | 2.3.5 | Quality Control Requirements |
| 29 | Project Documents and Records | 2.2.8 | Documentation and Records Requirements |
| 31, 32 & 33 | Assessments and Corrective Action | 2.4 | Assessments and Corrective Action |
| | | 2.5.5 | Reports to Management |
| 34 | Data Verification and Validation Inputs | 2.5.1 | Data Verification and Validation Targets and Methods |
| 35 | Data Verification Procedures | 2.5.1 | Data Verification and Validation Targets and Methods |
| 36 | Data Validation Procedures | 2.5.1 | Data Verification and Validation Targets and Methods |
| 37 | Data Usability Assessment | 2.5.2 | Quantitative and Qualitative Evaluations of Usability |
| | | 2.5.3 | Potential Limitations on Data Interpretation |
| | | 2.5.4 | Reconciliation with Project Requirements |

## QAPP Attachments

A. Field forms and Field SOPs

B. Laboratory Quality Assurance Management Plans, SOPs and Certifications

## 2. Project Authorization

In accordance with (IAW) Contract No. W912DY-10-D-0025, Task Order DS02, Modification No. 1 PIKA-Pirnie Joint Venture, LLC (JV) will conduct a RCRA Facility Investigation (RFI) at SWMUs 14, 15, 33, and 74,and AOCs 89, 90, 91, and 92, within Parcel 3 of the Fort Wingate Depot Activity (FWDA). This QAPP is included as Appendix D of the Parcel 3 RFI Work Plan. Parcel 3 is located entirely within the boundaries of the Kickout Area (KOA). Removal actions to remove Munitions and Explosives of Concern (MEC) and Material Potentially Presenting an Explosive Hazard (MPPEH) within the KOA is currently performed IAW the New Mexico Environment Department (NMED)-approved *Final Work Plan Kickout Area Munitions and Explosives of Concern Removal and Surface Clearance* (PIKA-Pirnie JV, 2015a). The JV also plans to perform interim measures to remove waste military munitions (WMM) and WMM scrap in AOCs and SWMUs within the KOA IAW the *Interim Measures Work Plan* (PIKA-Pirnie JV, 2015b), currently under review by the United States Army Corps of Engineers (USACE). The RFI Work Plan is written for the Army to comply with and implement the FWDA RCRA Permit Number NM6213820974-1 (the Permit), which became effective December 31, 2005 and was modified in 2014. The JV will perform this work under the direction of the USACE, Tulsa District (CESWT), and USACE, Fort Worth District (CESWF) to implement the Army's Base Realignment and Closure (BRAC) mission to close FWDA and revert this property to the Navajo Nation and Pueblo of Zuni. Throughout this work plan, the JV, the CESWT, the CEWSF, and the Army will be collectively referred to as the "Army". An Explosive Safety Submission Amendment and Certificate of Risk Assessment have been approved by the USACE according to Army and DoD policy.

This UFP-QAPP was developed IAW USACE Data Item Description Worldwide Environmental Remediation Services 001.01, Work Plans, USACE Engineering Manual (EM) 385-1-97, Change 1, and the FWDA RCRA Permit (dated December 2005 and revised in 2014).

## 3. Project Scope

The project scope is to assess the impact of previous site activities at SWMUs 14, 15, 33, and 74, and AOCs 89, 90, 91, and 92 within Parcel 3 at FWDA, as discussed in the RFI Work Plan, to which this QAPP is included as Appendix D. A separate Work Plan and QAPP covers confirmation soil sampling to be conducted within the burial pits of SWMUs 14, 15, and 33, and AOC 92 following munitions and explosives removal which is discussed in the *Interim Measures Work Plan AOCs and SWMUs in the KOA* (PIKA-Pirnie JV, 2015a).

## 4. Project Setting

The FWDA installation is located approximately seven miles east of Gallup, New Mexico, and currently occupies approximately 24 square miles (approximately 15,277 acres) of land in in McKinley County in northwestern New Mexico. FWDA contained facilities used to operate a reserve storage activity providing for the care, preservation, and minor maintenance of assigned commodities, primarily conventional military

munitions. FWDA is almost entirely surrounded by federally owned or administered lands, including both National Forest and Tribal lands. The installation can be divided into several sub-areas based on location and historical land use.

The FWDA installation was originally established by the U.S. Army in 1862 at the southern edge of the Navajo territory. The mission of the FWDA changed from tribal issues to World War I related activities. Beginning in 1940, the FWDA's mission was primarily to receive, store, maintain, and ship explosives and military munitions, as well as to disassemble and dispose of unserviceable or obsolete explosives and military munitions. In 1975, the installation came under the administrative command of Tooele Army Depot, located near Salt Lake City, Utah.

In January 1993, the active mission of the FWDA ceased and the installation closed as a result of the Defense BRAC Act of 1990. Beginning in 2002, the U.S. Army reassigned many FWDA functions to the BRAC Division, including caretaker duties, property transfer, and performance of environmental compliance and restoration activities. Command and control responsibilities were retained by Tooele Army Depot until January 31, 2008, when these responsibilities were transferred to White Sands Missile Range.

An area known as the Closed Open Burn/Open Detonation (OB/OD) Area was used from 1948 to 1955. Residues and debris from OB/OD operations were placed at various locations within the Closed OB/OD Area. Because the period of operations in the Closed OB/OD Area predated RCRA by approximately 25 years, the Closed OB/OD Area was not permitted under RCRA. Therefore, when the Permit was issued, the area previously known as the Closed OB/OD Area was identified as three separate SWMUs.

- SWMU 14, also described as Old Burning Ground and Demolition Landfill Area;
- SWMU 15, also described as Old Demolition Area; and
- SWMU 33, also described as Waste Pile KP1.

From approximately 1948 until installation closure in January 1993, burning and detonation operations were performed within an area known as the Current OB/OD Area also located within Parcel 3. The OB/OD Hazardous Waste Management Unit is an area within the Current OB/OD Area. The current OB/OD area is not included within the scope of this RFI

In addition to the OB/OD Unit Hazardous Waste Management Unit and three Closed OB/OD Area SWMUs listed above, Parcel 3 contains one additional SWMU and four AOCs, as follows:

- SWMU 74, also described as Area 16 or Site 16 (Proposed Burning Ground);
- AOC 89, also described as Features 30 and 34 on the 1973 Aerial Photo API-5;
- AOC 90, also described as Feature 36 on the 1973 Aerial Photo API-5;

- AOC 91, also described as Feature 41 on the 1973 Aerial Photo API-5 and Feature 27 on the 1978 Aerial Photo API-7; and
- AOC 92, is also described as Feature 31 on the 1973 Aerial Photo API-5 and Feature 21 on the 1978 Aerial Photo API-7.

## 5. Planned RFI

The JV will perform a RFI to determine the presence or absence of COPCs in SWMUs and AOCs identified within Parcel 3.

Data collected as part of this RFI effort will include surface soil samples used to complete the RCRA Facility Investigation Report and determine the presence and lateral extent of the COPCs at SWMUs 14, 15, 33, and 74 and AOCs 89, 90, 91, and 92. Analysis for metals will be limited to the RCRA 8 metals: arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver. The full suite of semi-volatile organic compounds (SVOCs), explosives and perchlorate will also be analyzed, as necessary. Samples will include both incremental sampling methodology (ISM) and composite samples.

## QAPP Worksheet #1&2 – Title and Approval Page

| | |
|---|---|
| **Project Identifying Information:** | Fort Wingate Depot Activity RCRA Facility Investigation, Parcel 3 SWMUs and AOCs<br>McKinley County, New Mexico<br>W912DY-10-D-0025, DS02, Modification No. 1 |
| **Lead Organization:** | USACE (Contract Executor and Project Technical Support) |
| **Contracting Organization Project Manager (PM):** | |
| | Signature/Date |
| | Shahrukh Kanga, PE, PMP, PIKA-PIRNIE JV |
| **Contracting Organization Contracting Officer's Representative (COR):** | |
| | Signature/Date |
| | Dennis Myers, PM, USACE Fort Worth District |
| **State Regulatory Organization:** | New Mexico Environment Department |
| **State Regulatory Agency PM:** | |
| | Signature/Date |
| | To Be Determined (TBD) |

## QAPP Worksheet #1&2 – Title and Approval Page

| | |
|---|---|
| **List plans and reports from previous investigations relevant to this project:** | • Soil Background Study and Data Evaluation Report (Shaw, 2010)<br>• Hydrogeologic Summary Report (TPMC, 2006)<br>• Aerial Photographic Analysis (ERI, 2006)<br>• Final Risk Assessment Technical Memorandum, Open Burning/Open Detonation Areas (PMC, 2000)<br>• Final OE Location and Removal Report, Fort Wingate Depot Activity, New Mexico (EHSI, 2000)<br>• Final Open Burning/Open Detonation Area RCRA Interim Status Closure Plan Phase IA – Characterization and Assessment of Site Conditions for the Soils/Solid Matrix (Phase IA Report) (PMC, 1999a)<br>• Final Open Burning/Open Detonation Area RCRA Interim Status Closure Plan Phase IB – Characterization and Assessment of Site Conditions for the Groundwater Matrix (Phase IB Report) (PMC, 1999b)<br>• Removal Report, OE Sampling and Removal Action, Fort Wingate Depot Activity (CMS, 1998)<br>• Archive Search Report (USACE, 1995)<br>• Unexploded Ordnance Survey Report, Fort Wingate Depot Activity, (ERM, 1994)<br>• Interim Status Closure Plan (ERM, 1993 and 1994)<br>• Final Work Plan Munitions and Explosives of Concern Removal and Surface Clearance Kickout Area (PIKA-Pirnie Joint Venture, 2015a) |

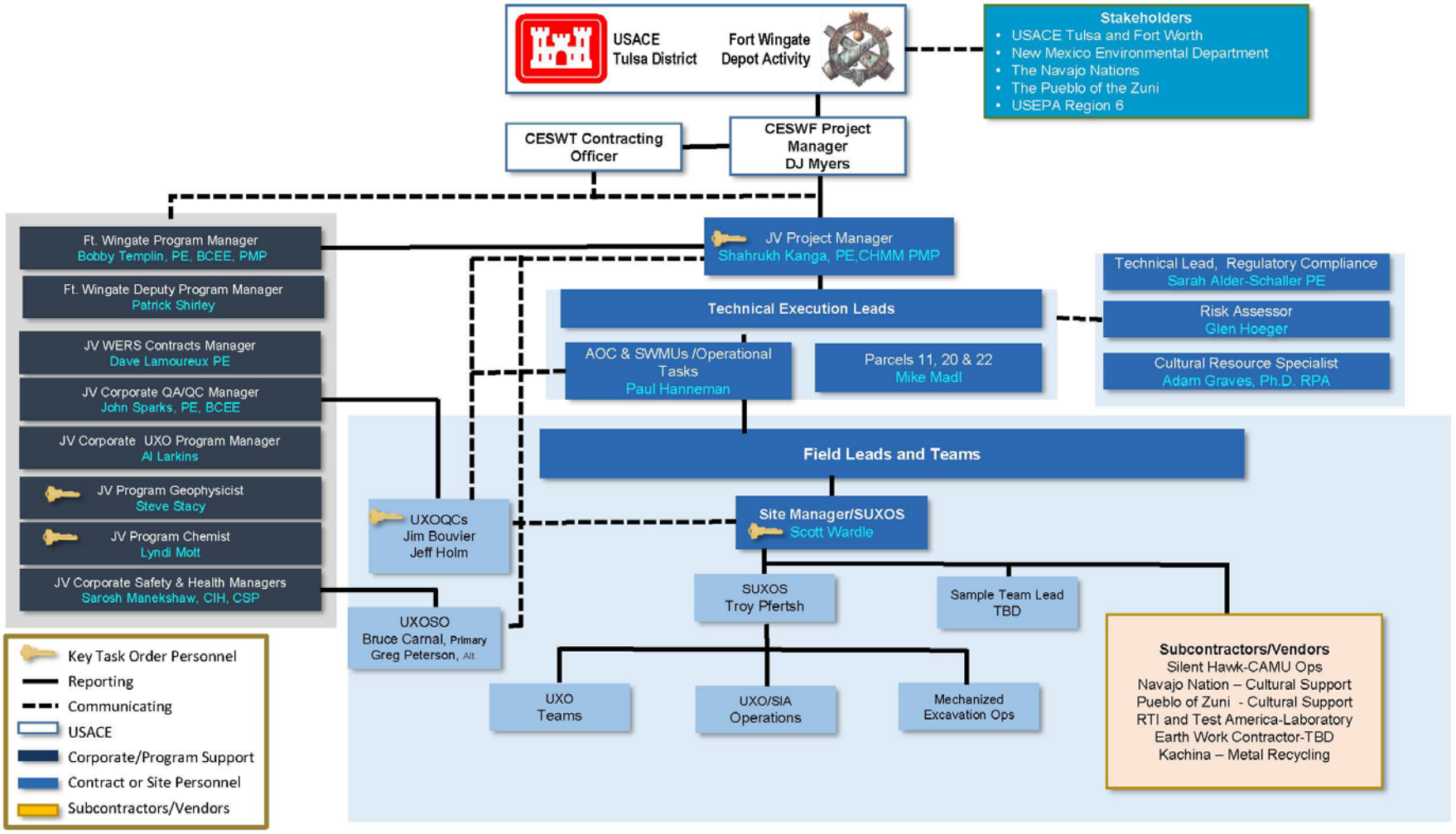
## QAPP Worksheet #1&2 – Title and Approval Page

| | |
|---|---|
| **List dates that scoping sessions were held** | Army Kickoff Conference Call: September 22, 2014<br><br>FWDA Team Meeting: November 4, 2014 |
| **List organizational partners (stakeholders) and identify the connection with lead organization** | CESWF: Project Technical Support<br><br>US Army BRAC-D: BRAC oversight<br><br>JV: Contractor<br><br>NMED: State Regulatory Organization<br><br>The Navajo Nation: Stakeholder<br><br>The Pueblo of Zuni: Stakeholder<br><br>FWDA: Installation / Site Owner / RCRA Permittee |

## QAPP Worksheet #3&5: Project Organization and QAPP Distribution

| QAPP Recipients | Title | Organization | Telephone Number | E-mail Address |
|---|---|---|---|---|
| Steve Smith | Program Manager | USACE, Fort Worth | 817.886.1879 | Steve.w.smith@usace.army.mil |
| Scottie Fiehler | COR | USACE, Tulsa | 918-669-7232 | Scottie.Fiehler@usace.army.mil |
| Dennis Myers | PM | USACE, Fort Worth | 817-609-5014 | Dennis.j.myers@usace.army.mil |
| Mark Patterson | FWDA BEC | U.S. Army BRACD | 330-358-7312 | mark.c.patterson.civ@mail.mil |
| TBD | PM | NMED | | |
| Shahrukh Kanga, CHMM, PMP | PM | JV | 281-340-5525 | skanga@pikainc.com |
| Mike Madl, PMP | Technical Lead | JV | 817-877-9978 ext. 102 | Mike.Madl@arcadis-us.com |
| Paul Hanneman | Technical Lead | JV | 303-770-1501 | phanneman@pikainc.com |
| Scott Wardle | Site Manager | JV | 713299-2918 | swardle@pikainc.com |

| QAPP Recipients | Title | Organization | Telephone Number | E-mail Address |
|---|---|---|---|---|
| Lyndi Mott | Program Chemist | JV | 713.953.4829 | Lyndi.Mott@arcadis-us.com |
| David Vesey | Laboratory PM | RTI Laboratories | 734.422.8000 | dvesey@rtilab.com |
| Charles O'Bryan | Laboratory QA Manager | RTI Laboratories | 734.422.8000 | cobryan@rtilab.com |
| Erika Gish | Laboratory PM | TestAmerica | 314.298.8566 | erika.gish@testamericainc.com |
| Marti Ward | Laboratory QA Manager | TestAmerica | 314.298.8566 | marti.ward@testamericainc.com |


USACE
Tulsa District
Fort Wingate
Depot Activity
Stakeholders
USACE Tulsa and Fort Worth
New Mexico Environmental Department
The Navajo Nations
The Pueblo of the Zuni
USEPA Region 6
CESWT Contracting Officer
CESWF Project Manager
DJ Myers
Ft. Wingate Program Manager
Bobby Templin, PE, BCEE, PMP
Ft. Wingate Deputy Program Manager
Patrick Shirley
JV WERS Contracts Manager
Dave Lamoureux PE
JV Corporate QA/QC Manager
John Sparks, PE, BCEE
JV Corporate UXO Program Manager
Al Larkins
JV Program Geophysicist
Steve Stacy
JV Program Chemist
Lyndi Mott
JV Corporate Safety & Health Managers
Sarosh Manekshaw, CIH, CSP
JV Project Manager
Shahrukh Kanga, PE,CHMM PMP
Technical Execution Leads
AOC & SWMUs /Operational Tasks
Paul Hanneman
Parcels 11, 20 & 22
Mike Madl
Technical Lead, Regulatory Compliance
Sarah Alder-Schaller PE
Risk Assessor
Glen Hoeger
Cultural Resource Specialist
Adam Graves, Ph.D. RPA
Field Leads and Teams
UXOQCs
Jim Bouvier
Jeff Holm
Site Manager/SUXOS
Scott Wardle
UXOSO
Bruce Carnal, Primary
Greg Peterson, Alt.
SUXOS
Troy Pfertsh
Sample Team Lead
TBD
UXO Teams
UXO/SIA Operations
Mechanized Excavation Ops
Subcontractors/Vendors
Silent Hawk-CAMU Ops
Navajo Nation – Cultural Support
Pueblo of Zuni - Cultural Support
RTI and Test America-Laboratory
Earth Work Contractor-TBD
Kachina – Metal Recycling
Key Task Order Personnel
Reporting
Communicating
USACE
Corporate/Program Support
Contract or Site Personnel
Subcontractors/Vendors

## QAPP Worksheet #4, 7 & 8 – Personnel Qualifications and Sign-off Sheet

| Name | Project Title/Role | Education/Experience | Signature/Date |
|---|---|---|---|
| ORGANIZATION: JV | | | |
| Bobby Templin, PE | Program Manager | B.S. / M.S. Civil/Environmental Engineering, 30 years of experience. Program/PM for numerous Military Munitions Response Program and Hazardous, Toxic and Radioactive Waste sites. Involved with numerous projects for the Army, Navy, and Air Force. | Signature on file |
| Shahrukh Kanga, CHMM, PMP | PM | M.S., Civil/Environmental Engineering; M.B.A., Business Administration; M.M.M., Marketing Management; B.E., Mechanical Engineering, 19 years of experience. Principal with PIKA International Inc., Program Manager, and PM on numerous munitions response projects including MEC Remedial Actions, Site Inspections, and Remedial Investigations / Feasibility Study projects for remediation and investigation projects with extensive working knowledge of Department of Transportation and Occupational Safety and Health administration regulations, federal, state, and local environmental compliance regulations, including Comprehensive Environmental Response, Compensation and Liability Act, RCRA, and TSCA, and USACE and U.S. Army health and safety requirements and quality assurance protocols. | Signature on file |
| Mike Madl, PMP | Technical Lead | B.S. Biology/Environmental Science, M.S. Environmental Engineering and Science, 15 years of experience. Project manager on numerous munitions response project, including Site Inspection and Remedial Investigations / Feasibility Study projects for Army sites. | Signature on file |

## QAPP Worksheet #4, 7 & 8 – Personnel Qualifications and Sign-off Sheet

| | | | |
|---|---|---|---|
| Paul Hanneman | Technical lead | Mr. Paul Hanneman, Bachalors Degree, Biology, 35 years environmentala experience. Authored RFI Addendums for FWDA Parcels 21 and 22 and served as the PM on the NMED-accepted Parcel 16 RFI conducted in 2013. | Signature on file |
| Lyndi Mott | Program Chemist | B.S. Chemistry/M.B.A. Business Administration. 31 years of experience. | Signature on file |
| ORGANIZATION: RTI Laboratories (RTI) (primary laboratory) | | | |
| David Vesey | Laboratory PM | Representative for project laboratory. | |
| Charles O'Bryan | Laboratory QA Manager | Representative for project laboratory.<br><br>M.S. Environmental and Industrial Health; B.S. Medical Technology; B.S. Biology; 37 years of experience | |
| ORGANIZATION: TestAmerica (QA laboratory) | | | |
| Erika Gish | Laboratory PM | Representative for project laboratory.<br><br>B.A Biology; 10 years of experience | |
| Marti Ward | Laboratory QA Manager | Representative for project laboratory.<br><br>B.S.; 25 years of experience | |

*Signatures indicate personnel have read and agree to implement this QAPP as written (signatures required for Final submittal only)

## QAPP Worksheet #6 – Communication Pathways

| Communication Drivers | Organization | Name/Role | Phone Number | Procedure (timing, pathways, documentation, etc.) |
|---|---|---|---|---|
| Point of Contact with USACE | USACE, CESWT | Dennis Myers, USACE PM | 817-609-5014 | USACE PM will be notified by JV if analytical data or field sampling irregularities are observed, or problems with analytical data or sampling are encountered. |
| Technical lead decisions and modifications | JV | Mike Madl<br>Paul Hanneman<br>Shahrukh Kanga<br>JV PM | 817-877-9978 ext. 102<br>303-770-1501<br>281-340-5525 | Communicate technical leads decisions and modifications to USACE and/or the JV, as necessary. All approved modifications will be included in the amendments to the UFP-QAPP by the JV and signed within 7 working days. |
| Project issues | JV | Mike Madl<br>Paul Hanneman<br>Shahrukh Kanga<br>JV PM | 817-877-9978 ext. 102<br>303-770-1501<br>281-340-5525 | Notify Scottie Fiehler (USACE COR) and Dennis Myers (USACE PM) of project issues within 7 days by telephone or email. |
| Point of Contact with NMED | NMED PM | TBD | | NMED Project Manager will be notified by USACE PM if analytical data or field sampling irregularities are observed, or problems with analytical data or sampling are encountered. The USACE PM has the primary lead on coordination with NMED, unless otherwise directed. |
| Stop work due to safety issues | Mike Madl<br>JV | Mike Madl<br>JV | 817-877-9978 ext. 102<br><br>281-340-5525 | Work may be stopped at any time by any member of the field team for any safety concern. Refer to the Accident Prevention Plan (APP) for specifics related to health and safety. Persons other than the responsible entity may also stop work for safety concerns. All stop work issues will be recorded in the Daily Quality Control Report. The JV PM will notify USACE PM by phone, within 24 hours of a stop work situation. |
| UFP-QAPP changes prior to field work | JV | Mike Madl<br>Paul Hanneman or<br>Shahrukh Kanga<br>JV PM | 817-877-9978 ext. 102<br>303-770-1501<br>281-340-5525 | Submit documented amendments within 10 working days for transmittal to USACE for approval. |

## QAPP Worksheet #6 – Communication Pathways

| Communication Drivers | Organization | Name/Role | Phone Number | Procedure (timing, pathways, documentation, etc.) |
|---|---|---|---|---|
| UFP-QAPP changes during project execution | JV | Mike Madl<br>Paul Hanneman or Shahrukh Kanga<br>JV PM | 817-877-9978 ext. 102<br>303-770-1501<br>281-340-5525 | Secure same-day approval from Site Superintendent. JV will secure approval for modifications to the UFP-QAPP from the USACE technical manager. The JV will also contact the NMED to notify them of changes to field data collection procedures which differ from the procedures documented in the UFP-QAPP. |
| Field corrective actions | JV | Mike Madl<br>Paul Hanneman or Shahrukh Kanga<br>JV PM | 817-877-9978 ext. 102<br>303-770-1501<br>281-340-5525 | Field corrective actions will be communicated by JV to the USACE PM (by phone followed by a confirming email) within 24 hours of the action. The USACE PM will contact the NMED to notify them of changes to field data collection procedures which differ from the procedures documented in the UFP-QAPP. |
| Sample receipt variances | RTI/ TestAmerica | David Vesey<br>RTI PM<br><br>Erika Gish<br>TestAmerica PM | 734.422.8000<br><br>314-298-8566 | All project field sample variance issues will be reported by the laboratory PM to the JV Program Chemist within two business days of identification of the technical concern. The JV PM will report all field sample variance issues to the USACE PM within 24 hours (by phone followed by a confirming email) of notification from the laboratory. |
| Laboratory quality control variances | RTI/ TestAmerica | David Vesey<br>RTI PM<br><br>Erika Gish<br>TestAmerica PM | 734.422.8000<br><br>314-298-8566 | All QA/QC issues with project field samples will be reported by the laboratory PM to the JV PM and Program Chemist within two business days of identification of the technical concern. The JV PM will report all QA/QC issues with project field samples to the USACE PM within 24 hours (by phone followed by a confirming email) of notification by the laboratory. |
| Data verification issues, e.g., incomplete records | JV | Lyndi Mott<br>JV Program Chemist | 713-953-4829 | All verification issues will be reported by the JV Program Chemist to the JV PM via email within 24 hours of identification of the technical concern. The JV PM will report verification issues to the USACE PM via email within 24 hours (by phone followed by a confirming email) of notification. |

## QAPP Worksheet #6 – Communication Pathways

| Communication Drivers | Organization | Name/Role | Phone Number | Procedure (timing, pathways, documentation, etc.) |
|---|---|---|---|---|
| Data validation issues, e.g., non-compliance with procedures | JV | Lyndi Mott<br>JV Program Chemist | 713-953-4829 | All validation issues will be reported by the data validator to the JV PM and Program Chemist via email within 24 hours of identification of the technical concern. The JV PM will report all validation issues to the USACE PM within 24 hours (by phone followed by a confirming email) of notification. |
| Data review corrective actions | JV | Lyndi Mott<br>JV Program Chemist | 713-953-4829 | The need for data review corrective actions will be determined by the JV Program Chemist and/or data validator, as appropriate, and will be documented in a memorandum to the JV PM. Data review corrective actions will be reported by the JV PM to the USACE PM within 24 hours (by phone followed by a confirming email) of notification. |

## QAPP Worksheet #9 – Project Planning Session Summary

**FWDA Team Meeting: November 4, 2014**
**Environmental Remediation Efforts, Fort Wingate Depot Activity, New Mexico**

A project team meeting was held on 4 November 2014 at the FWDA, New Mexico.

The purpose of the meeting was to:

- Introduce JV and Army team members and define responsibilities
- Discuss project safety issues
- Discuss project schedule
- Review project challenges and risks

Meeting Attendees were:

Mark Patterson, BRACD Environmental Coordinator
DJ Myers, PM CESWF
Christy Esler, Sundance
Angela Makin, Sundance
Steve Smith, FWDA Project Manager CESWF
Jackie Smith, Lead OESS
Joseph Murphey, Historical Architect, CESWF
Shahrukh Kanga, JV Project Manager
Eric Kirwan, Geophysicist & Technical lead, CESWF
Mike Madl, JV Technical Lead
Karan Holmes, JV Task Lead
Sarah Alder-Schaller, JV Regulatory Specialist
Adam Graves, JV Cultural Resources Lead
Shawn Corcoran, JV UXO Program Manager
Paul Hanneman, JV Technical Lead
Scott Wardle, JV Site Manager

## QAPP Worksheet #10 – Conceptual Site Model

### Background information

Background information for FDWA is discussed in detail in the RFI Work Plan – Parcel 3 SWMUs and AOCs.

### Nature and Extent of Contamination

Visual inspection performed during the site reconnaissance found numerous MEC items and there have been a limited number of soil investigations conducted at the SWMUs and AOCs within Parcel 3, which have not fully characterized the parcel. The first task will be to perform surface and subsurface clearance of the KOA area MEC and MPPEH. This will be followed by the interim measures to remove WMM and WMM scrap at SWMUs 14, 15, 33, the arroyo adjacent to SWMUs 14 and 15, and AOC 92. Following the interim measures, confirmation samples will be collected for analysis from the burial pits in SWMU 14 and15, and the waste piles in SWMU 33.

The interim measures will be followed by RFI work within Parcel 3 SWMUs and AOCs. Following the completion of the RFI at AOC 92, soil removal activities will be performed and followed by soil confirmation sampling at AOC 92 within the soil removal areas.

### Fate and Transport

If soils are affected at SWMUs 14, 15, 33, and 74, and AOCs 89, 90, 91, and 92, there is a potential for threat to human health and the environment through exposure to surface soils.

If munitions constituents (MC) are found to be present during the RFI activities, then a threat to human health and the environment exists.

### Data Gaps

Surface soils where probable COPCs are present need to be investigated. Additional surface soil samples need to be collected to characterize the SWMUs and AOCs within Parcel 3.

Further subsurface investigation that may be required to characterize groundwater transport pathways is not covered under this RFI Work Plan and will be performed under a separate contract.

## QAPP Worksheet #11 – MC Project/Data Quality Objective

Parcel 3 and its associated SWMUs and AOCs are located entirely within the defined boundaries of the KOA. There are three primary environmental issues at the KOA from past operations are:

- MEC and MPPPEH contamination (all AOCs and SWMUs non-burial pit areas): The surface and subsurface oil of these areas are potentially contaminated with MEC and MPPEH resulting from past operations. The MEC and MPPEH items are currently being addressed via surface and subsurface clearance of MEC and munitions debris within the KOA IAW the NMED-approved *Final Work Plan MEC Removal and Surface Clearance KOA* (PIKA-Pirnie JV, 2015b).
- Burial pits contain waste debris, and are potentially contaminated with MEC, MPPEH and metallic scrap related to munitions disposal. This waste will be removed IAW the *Interim Measures Work Plan AOCs and SWMUs in the KOA* (PIKA-Pirnie JV, 2015a), currently under review by the USACE.
- Potential soil contamination in the burial pits resulting from long-term burial of waste and debris. The presence or absence of COPCs related to past operations at SWMUs and AOCs is currently unknown.

For the RFI work, data quality objectives (DQOs) have been developed for characterization of COPCs within surface soils at the SWMUs and AOCs at Parcel 3 and for reporting to NMED. For AOC 92, the characterization data will also be used to determine soil removal requirements (to be performed IAW the *Interim Measures Work Plan AOCs and SWMUs in the KOA, October 2015*.)

### Statement of Problem

There is one primary problem associated with MC within the AOCs and SWMUs which will involve soil sampling activities: The presence or absence of MC in soil related to past site operations is unknown. If MC are present in soil, the current data is not sufficient to define the lateral and vertical extent of contamination.

### Identification of a Decision Addressing the Problem

The decision addressing the primary problem is identified as follows:

To comply with Section VII of the RCRA Permit, the lateral extent of COPCs in the soils at the SWMUs and AOCs at Parcel 3 will be determined by collecting and analyzing surface soil samples and evaluating the presence and/or absence of COPCs at concentrations greater than approved screening levels. Soil characterization samples collected

using ISM and composite sampling techniques will be analyzed for MC. The COPCs associated with MC include explosives, RCRA 8 metals, perchlorate, and SVOCs.

The COPCs identified above were determined based on planning documents approved by NMED for similar sites.

## Identification of Inputs Affecting the Decision

Inputs affecting the decision of whether or not MC in soil samples from the SWMUs and AOCs exceed approved screening levels include the validated analytical results for collected soil samples, site specific background concentrations for metals, the NMED Residential Soil Screening Levels (SSLs) or USEPA Region 6 Regional Screening Levels (RSLs), and the two step approach for assessing arsenic in soils recommended by the NMED in their December 18, 2003 letter (Attachment C of the Soil Investigation Work Plan). The evaluation of metals background and the risk/hazard-based screening level for each analyte will be determined as follows:

## Metals Background

The FWDA soil background for metals (with the exception of arsenic and antimony), are based on the Soil Background Study and Data Evaluation Report Version 2 (Shaw, 2010). IAW NMED's Evaluation of Background Levels for Arsenic in Soil, dated December 18, 2013, 5.6 milligrams per kilogram (mg/kg) will be used for arsenic. If the arsenic value of 5.6 mg/kg is exceeded, then consideration of the detected site range compared to the background range of 0.2-11.2 mg/kg is appropriate. The background value (0.23 mg/kg) for antimony is the 95% Upper Tolerance Limit for soil unit 350ss based on the 2012 background study. Metals determined to be at or below background are eliminated from further consideration and are not considered for estimation of potential risk/hazard.

## Risk/Hazard-Based Screening Level Hierarchy

The risk/hazard-based screening levels have been determined in accordance with the FWDA soil cleanup levels as defined by the Permit (December 2005, Revised April 2014). The following hierarchy will be used to determine the risk/hazard-based screening level for each analyte:

- The current NMED residential SSL per the NMED Risk Assessment Guidance for Site Investigations and Remediation (December 2014) is used (with the exception of arsenic) (http://www.nmenv.state.nm.us/HWB/documents/RA_Guidance_for_SI_and_Remediation_12-24-2014.pdf ) is used.

- A site-specific background level of 5.6 mg/kg will be used for arsenic in lieu of the NMED Residential SSL in accordance with NMED's Evaluation of Background Levels for Arsenic in Soil, dated December 18, 2013. If the arsenic value of 5.6 mg/kg is exceeded, then consider the site range compared to the background range of 0.2-11.2 mg/kg. If it is determined arsenic is above background, the NMED residential SSL of 4.25 mg/kg (cancer endpoint) is used for assessment of potential risk.
- If an NMED Residential SSL has not been established, the most recent (currently January 2015) USEPA Residential RSL (http://www.epa.gov/region9/superfund/prg/) is used. USEPA RSLs based on a cancer endpoint are adjusted to a cancer risk of $1x10^{-5}$ consistent with NMED guidance.
- If an analyte does not have an NMED SSL or USEPA RSL, appropriate surrogates may be used with NMED approval.

**Potential Cumulative Risk/Hazard**

Potential cumulative risk/hazard is assessed as follows:

- For metals the initial comparison will be made to background levels. Metals determined to be at or below background will be eliminated from further consideration. If it is determined that background is exceeded then comparison will be made to the appropriate risk/hazard-based screening level (NMED Residential SSL or USEPA Residential RSL, as appropriate) to estimate potential cumulative risk/hazard.
- Potential cumulative risk is assessed by summing potential risks for each individual analyte. The risk threshold is $1x10^{-5}$.
- For potential cumulative hazard estimates, individual hazard quotients are summed to provide a cumulative hazard index (HI). The target hazard is 1. The HI is compared to 1. If the HI is less than 1 then unacceptable hazard is not expected. If the HI is greater than 1 then unacceptable hazard is possible. When the HI for a data set exceeds 1, but an individual hazard quotients does not exceed 1, then it may be appropriate to perform further assessment by assessing the toxic endpoint (target organ) of the analytes that contribute to the HI exceeding 1. The critical toxicity and secondary toxicity should be assessed.
- Lead is assessed separately.

**Specification of the Domain of the Decision**

The domain of the decision of whether or not soil at the SWMUs/AOCs have been negatively impacted is restricted to the evaluation of only those parameters for which samples are analyzed and for which a screening level has been defined (NMED SSL or USEPA RSLs).

**Development of a Logic Statement**

If the validated analytical data for samples collected during RFI exceed background and the NMED Residential SSL, the area from which the sample was collected will be considered affected. Additional horizontal and/or vertical delineation may then be required until data indicates non-contaminated soil is encountered.

**Establishment of Constraints on Uncertainty**

Uncertainty in the data used to evaluate the logic statement will be constrained by following the QA/QC guidelines specified in this UFP-QAPP; selecting the appropriate analytical support level for the soil sample data; and by adhering to both the field and laboratory data quality indicator objectives (precision, accuracy, representativeness, comparability, and completeness). All reasonable attempts will be made to ensure laboratory reporting limits and/or detection limits are below the SSLs.

**Optimization of Design for Obtaining Data**

To optimize the quality of data collected for evaluation, the RFI Work Plan has been developed to be used as guidance during field activities. QA/QC procedures associated with the field activities described in the RFI Work Plan are presented in this UFP-QAPP.

## QAPP Worksheet #12-1 – Measurement Performance Criteria (Semi-volatile Organic Compounds by SW846 8270D)[1]

Matrix: Soil

Concentration Level: Low

Analytical Method: SW846 8270D

Laboratory SOP[2]: L-1 (RTI) / L-6 (TestAmerica)

| Data Quality Indicators (DQIs) | QC Sample of Measurement Performance Activity | Measurement Performance Criteria |
|---|---|---|
| Overall Precision | Field Duplicate | Relative percent difference (RPD) < 50% for soil |
| Sensitivity | Detection Limit (DL) / Limit of Quantitation (LOQ) | Sufficiently low to support project specified screening criteria as specified in QAPP Worksheet #15 |
| Accuracy/Bias | Laboratory control sample (LCS) containing all analytes to be prepared in the same manner as field samples. | Percent recovery (%R) %R, See Appendix C, Table 25 DoD Quality Systems Manual (QSM) V5.0 |
| Contamination | Method Blank (MB), Field Blank (FB), and Equipment Blank (EB) if collected | No target analyte > ½ LOQ. See QAPP Worksheet #15 for project specific LOQs |
| Accuracy/Bias | MS/MSD | %R %R, See Appendix C, Table 25 DoD QSM V5.0; RPD of all analytes ≤30% |
| Accuracy/Bias | Surrogate added to all field samples and QC samples | %R, See Table 25 DoD QSM V5.0 |

## QAPP Worksheet #12-1 – Measurement Performance Criteria (Semi-volatile Organic Compounds by SW846 8270D)[1]

Matrix: Soil

Concentration Level: Low

Analytical Method: SW846 8270D

Laboratory SOP[2]: L-1 (RTI) / L-6 (TestAmerica)

| Control Limits from Table 25 DoD QSM ver. 5.0 | | | |
|---|---|---|---|
| **Analyte** | **CAS Identification (ID)** | **Soil (8270D)** | |
| | | **Lower Control Limit** | **Upper Control Limit** |
| 1,2,4-Trichlorobenzene | 120-82-1 | 34 | 118 |
| 1,2-Dichlorobenzene | 95-50-1 | 33 | 117 |
| 1,2-Diphenylhydrazine [Azobenzene] | 122-66-7 | 41 | 125 |
| 1,3-Dichlorobenzene | 541-73-1 | 30 | 115 |
| 1,4-Dichlorobenzene | 106-46-7 | 31 | 115 |
| 1-Methylnaphthalene | 90-12-0 | 40 | 119 |
| 2,4,5-Trichlorophenol | 95-95-4 | 41 | 124 |
| 2,4,6-Trichlorophenol | 88-06-2 | 39 | 126 |
| 2,4-Dichlorophenol | 120-83-2 | 40 | 122 |
| 2,4-Dimethylphenol | 105-67-9 | 30 | 127 |
| 2,4-Dinitrotoluene | 121-14-2 | 48 | 126 |
| 2,6-Dinitrotoluene | 606-20-2 | 46 | 124 |
| 2-Chloronaphthalene | 91-58-7 | 41 | 114 |
| 2-Chlorophenol | 95-57-8 | 34 | 121 |
| 2-Methylnaphthalene | 91-57-6 | 38 | 122 |
| 2-Methylphenol (o-Cresol) | 95-48-7 | 32 | 122 |

| Control Limits from Table 25 DoD QSM ver. 5.0 | | | |
|---|---|---|---|
| **Analyte** | **CAS Identification (ID)** | **Soil (8270D)** | |
| | | **Lower Control Limit** | **Upper Control Limit** |
| 2-Nitroaniline | 88-74-4 | 44 | 127 |
| 2-Nitrophenol | 88-75-5 | 36 | 123 |
| 3,3'-Dichlorobenzidine | 91-94-1 | 22 | 121 |
| 3-Nitroaniline | 99-09-2 | 33 | 119 |
| 3/4-Methylphenol [m/p-Cresol] | 65794-96-9 | 34 | 119 |
| 4,6-Dinitro-2-methylphenol | 534-52-1 | 29 | 132 |
| 4-Bromophenyl phenyl ether | 101-55-3 | 46 | 124 |
| 4-Chloro-3-methylphenol | 59-50-7 | 45 | 122 |
| 4-Chloroaniline [p-Chloroanlinie] | 106-47-8 | 17 | 106 |
| 4-Chlorophenyl phenyl ether | 7005-72-3 | 45 | 121 |
| 4-Nitrophenol | 100-02-7 | 30 | 132 |
| Acenaphthene | 83-32-9 | 40 | 123 |
| Acenaphthylene | 208-96-8 | 32 | 132 |
| Anthracene | 120-12-7 | 47 | 123 |
| Azobenzene | 103-33-3 | 39 | 125 |
| Benz(a)anthracene | 56-55-3 | 49 | 126 |
| Benzo(a)pyrene | 50-32-8 | 45 | 129 |
| Benzo(b)fluoranthene | 205-99-2 | 45 | 132 |
| Benzo(g,h,i)perylene | 191-24-2 | 43 | 134 |
| Benzo(k)fluoranthene | 207-08-9 | 47 | 132 |
| Benzyl alcohol | 100-51-6 | 29 | 122 |
| bis(2-Chloroethoxy)methane | 111-91-1 | 36 | 121 |
| Bis(2-chloroethyl) ether | 111-44-4 | 31 | 120 |
| bis(2-Chloroisopropyl) ether | 39638-32-9 | 33 | 131 |
| Bis(2-ethylhexyl) phthalate | 117-81-7 | 51 | 133 |

| Control Limits from Table 25 DoD QSM ver. 5.0 | | | |
|---|---|---|---|
| **Analyte** | **CAS Identification (ID)** | **Soil (8270D)** | |
| | | **Lower Control Limit** | **Upper Control Limit** |
| bis(2-Ethylhexyl)adipate | 103-23-1 | 61 | 121 |
| Butyl benzyl phthalate | 85-68-7 | 48 | 132 |
| Carbazole | 86-74-8 | 50 | 123 |
| Chrysene | 218-01-9 | 50 | 124 |
| Di-n-butyl phthalate | 84-74-2 | 51 | 128 |
| Di-n-octyl phthalate | 117-84-0 | 45 | 140 |
| Dibenzo(a,h)anthracene | 53-70-3 | 45 | 134 |
| Dibenzofuran | 132-64-9 | 44 | 120 |
| Diethyl phthalate | 84-66-2 | 50 | 124 |
| Dimethyl phthalate | 131-11-3 | 48 | 124 |
| Fluoranthene | 206-44-0 | 50 | 127 |
| Fluorene | 86-73-7 | 43 | 125 |
| Hexachlorobenzene | 118-74-1 | 45 | 122 |
| Hexachlorobutadiene | 87-68-3 | 32 | 123 |
| Hexachloroethane | 67-72-1 | 28 | 117 |
| Indeno(1,2,3-cd)pyrene | 193-39-5 | 45 | 133 |
| Isophorone | 78-59-1 | 30 | 122 |
| N-Nitrosodi-n-propylamine | 621-64-7 | 36 | 120 |
| N-Nitrosodiethylamine | 55-18-5 | 41 | 124 |
| N-Nitrosodimethylamine | 62-75-9 | 23 | 120 |
| N-Nitrosodiphenylamine | 86-30-6 | 38 | 127 |
| Naphthalene | 91-20-3 | 35 | 123 |
| Nitrobenzene | 98-95-3 | 34 | 122 |
| Pentachlorophenol | 87-86-5 | 25 | 133 |
| Phenanthrene | 85-01-8 | 50 | 121 |

| Control Limits from Table 25 DoD QSM ver. 5.0 | | | |
|---|---|---|---|
| **Analyte** | **CAS Identification (ID)** | **Soil (8270D)** | |
| | | **Lower Control Limit** | **Upper Control Limit** |
| Phenol | 108-95-2 | 34 | 121 |
| Pyrene | 129-00-0 | 47 | 127 |

## Notes:

1. The laboratory is DoD Environmental Laboratory Accreditation Program (ELAP) accredited for the test method and is expected to meet the Measurement Performance Criteria specified in DoD QSM version 5.0.
2. Reference number from QAPP Worksheet #23. The laboratory SOPs are provided in Appendix B.

## QAPP Worksheet #12-2 – Measurement Performance Criteria (Explosives/Nitroaromatics and Nitramines by SW846 8330B)[1]

Matrix: Soil (ISM)

Concentration Level: Low

Analytical Method: SW846 8330B

Laboratory SOP[2]: L-2 (RTI) / L-7 (TestAmerica)

| Data Quality Indicators (DQIs) | QC Sample of Measurement Performance Activity | Measurement Performance Criteria |
|---|---|---|
| Precision - Overall | Field Duplicate | All target compounds RPD ≤50% |
| Precision | Three subsamples taken from a sample expected to contain the highest levels of explosives within calibration range. | Relative Standard Deviation (RSD) <20% for detects in sample triplicates |
| Sensitivity | DL/LOQ | Sufficiently low to support project specified screening criteria as specified in QAPP Worksheet #15 |
| Accuracy/Bias | LCS containing all analytes to be prepared in the same manner as field samples. | %R See Appendix C, Table 37 DoD QSM V5.0 |
| Contamination | MB, FB, and EB if collected | No target analyte > ½ LOQ, includes grinding blanks between sample grinds, if required. See QAPP Worksheet #15 for project specific LOQs |
| Accuracy/Bias | MS/MSD | %R See Appendix C, Table 37 DoD QSM V5.0;<br>RPD of all analytes ≤20% |
| Accuracy/Bias | Surrogate added to all field samples and QC samples | %R See Appendix C, Table 37 DoD QSM V5.0 |
| Confirmation of positive results | All positive results must be confirmed on a second column | RPD between results ≤ 40% |

## QAPP Worksheet #12-2 – Measurement Performance Criteria (Explosives/Nitroaromatics and Nitramines by SW846 8330B[1])

Matrix: Soil (ISM)

Concentration Level: Low

Analytical Method: SW846 8330B

Laboratory SOP[2]: L-2 (RTI) / L-7 (TestAmerica)

| Control Limits from Table 37 DoD QSM ver. 5.0 | | | |
|---|---|---|---|
| **Analyte** | **CAS Identification (ID)** | **Soil (8330B)** | |
| | | **Lower Control Limit** | **Upper Control Limit** |
| 1,3,5-Trinitrobenzene [1,3,5-TNB] | 99-35-4 | 80 | 116 |
| 1,3-Dinitrobenzene [1,3-DNB] | 99-65-0 | 73 | 119 |
| 2,4,6-Trinitrotoluene | 118-96-7 | 71 | 120 |
| 3,5-Dinitroaniline | 618-87-1 | 86 | 118 |
| 2,4-Dinitrotoluene | 121-14-2 | 75 | 121 |
| 2,6-Dinitrotoluene | 606-20-2 | 79 | 117 |
| 2-Amino-4,6-dinitrotoluene | 35572-78-2 | 71 | 123 |
| 2-Nitrotoluene [o-Nitrotoluene] | 88-72-2 | 70 | 124 |
| 3-Nitrotoluene [m-Nitrotoluene] | 99-08-1 | 67 | 129 |
| 4-Amino-2,6-dinitrotoluene | 19406-51-0 | 64 | 127 |
| 4-Nitrotoluene [p-Nitrotoluene] | 99-99-0 | 71 | 124 |
| Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) | 121-82-4 | 67 | 129 |
| Nitrobenzene | 98-95-3 | 67 | 129 |
| Nitroglycerin | 55-63-0 | 73 | 124 |

| Control Limits from Table 37 DoD QSM ver. 5.0 | | | |
|---|---|---|---|
| **Analyte** | **CAS Identification (ID)** | **Soil (8330B)** | |
| | | **Lower Control Limit** | **Upper Control Limit** |
| Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) | 2691-41-0 | 74 | 124 |
| PETN | 78-11-5 | 72 | 128 |
| Tetryl | 479-45-8 | 68 | 135 |

## Notes:

1. The laboratory is DoD ELAP accredited for the test method and is expected to meet the Measurement Performance Criteria specified in DoD QSM version 5.0.
2. Reference number from QAPP Worksheet #23. The laboratory SOPs are provided in Appendix B.

## QAPP Worksheet #12-3 – Measurement Performance Criteria (Perchlorate by SW846 6850)[1]

Matrix: Soil (ISM)

Concentration Level: Low

Analytical Method: SW846 6850

Laboratory SOP[2]: L-3 (RTI) / L-8 (TestAmerica)

| Data Quality Indicators (DQIs) | QC Sample of Measurement Performance Activity | Measurement Performance Criteria |
|---|---|---|
| Precision - Overall | Field Duplicate | RPD ≤50% |
| Sensitivity | DL/LOQ | Sufficiently low to support project specified screening criteria as specified in QAPP Worksheet #15 |
| Accuracy/Bias | Isotope ratio $^{35}Cl/^{37}Cl$ | Must fall within 2.3 to 3.8. |
| Accuracy/Bias | LCS containing all analytes to be prepared in the same manner as field samples. | Percent recovery (%R) See Appendix C, Table 7 DoD QSM V5.0 |
| Contamination | MB, FB, and EB if collected | No target analyte > ½ LOQ;<br>See QAPP Worksheet #15 for project specific LOQs |
| Accuracy/Bias | MS/MSD | %R See Appendix C, Table 7 DoD QSM V5.0;<br>RPD ≤30% |
| Accuracy/Bias | Interference Check Sample (ICS) | %R, See Table 13 DoD QSM V5.0 |
| Accuracy/Bias | Internal Standard | $^{18}O$ IS area within ±50% of the value from the average of the IS area counts of the initial calibration; relative retention time of the perchlorate ion must be 1.0 ±2% (0.98-1.02) |

Notes:

1. The laboratory is DoD ELAP accredited for the test method and is expected to meet the Measurement Performance Criteria specified in DoD QSM version 5.0.
2. Reference number from QAPP Worksheet #23. The laboratory SOPs are provided in Appendix B.

## QAPP Worksheet #12-3 – Measurement Performance Criteria (Perchlorate by SW846 6850[1])

Matrix: Soil (ISM)

Concentration Level: Low

Analytical Method: SW846 6850

Laboratory SOP[2]: L-3 (RTI) / L-8 (TestAmerica)

| Control Limits from Tables 36 and 37 DoD QSM ver. 5.0 | | | |
|---|---|---|---|
| **Analyte** | **CAS Identification (ID)** | **Soil (6850)** | |
| | | **Lower Control Limit** | **Upper Control Limit** |
| Perchlorate | 14797-73-0 | 84 | 121 |

**Notes:**

1. The laboratory is DoD ELAP accredited for the test method and is expected to meet the Measurement Performance Criteria specified in DoD QSM version 5.0.
2. Reference number from QAPP Worksheet #23. The laboratory SOPs are provided in Appendix B.

## QAPP Worksheet #12-4 – Measurement Performance Criteria (Metals by SW846 6010C/7471B)

Matrix: Soil (ISM)

Concentration Level: Low

Analytical Method: SW846 6010C/7471B

Laboratory SOP[3]: L-4, L-5 (RTI) / L-9, L-10 (TestAmerica)

| Data Quality Indicators (DQIs) | QC Sample of Measurement Performance Activity | Measurement Performance Criteria |
|---|---|---|
| Precision - Overall | Field duplicate | RPD ≤50% |
| Sensitivity | DL/LOQ | Sufficiently low to support project specified screening criteria as specified in QAPP Worksheet #15 |
| Sensitivity | Low-level Calibration Check Standard [Low-level initial calibration verification (ICV)]. Low level calibration check standard should be less than or equal to the LOQ. | Recovery within ±20% of true value |
| Accuracy/Bias | LCS containing all analytes to be prepared in the same manner as field samples | %R See Appendix C, Table 3 (6010/6020) and Table 11 (7471), DoD QSM V5.0 |
| Contamination | MB, FB, and EB if collected | No target analyte > ½ LOQ, See QAPP Worksheet #15 for project specific LOQs |
| Accuracy/Bias | MS containing all analytes to be prepared in the same manner as field samples | %R See Appendix C, Table 3 (6010/6020) and Table 11 (7471), DoD QSM V5.0 |
| Precision | MSD or matrix duplicate | MSD: %R See Appendix C, Table 3 (6010/6020) and Table 11 (7471), DoD QSM V5.0<br>MSD or matrix duplicate: RPD of all analytes ≤ 20% |
| Accuracy/Bias | Interference check sample (A and AB) | See Table 8 DoD QSM V5.0 (6010) |
| Precision | Serial Dilution Test; (Only applicable for samples with concentrations > 50 x LOQ) | Five-fold dilution must agree within ±10% of the original measurement |

Matrix: Soil (ISM)

Concentration Level: Low

Analytical Method: SW846 6010C/7471B

Laboratory SOP[3]: L-4, L-5 (RTI) / L-9, L-10 (TestAmerica)

| Data Quality Indicators (DQIs) | QC Sample of Measurement Performance Activity | Measurement Performance Criteria |
|---|---|---|
| Accuracy/Bias | Post-digestion spike addition | %R within 80-120% |

**Notes:**

1. Metals will include the RCRA metals list: arsenic, barium, cadmium, chromium, lead, mercury, selenium and silver.
2. The laboratory is DoD ELAP accredited for the test method and is expected to meet the Measurement Performance Criteria specified in DoD QSM version 5.0.
3. Reference number from QAPP Worksheet #23. The laboratory SOPs are provided in Appendix B.

## QAPP Worksheet #12-4 – Measurement Performance Criteria (Metals[1] by SW846 6010C/7471B)[2]

| | |
|---|---|
| Matrix: | Soil (ISM) |
| Concentration Level: | Low |
| Analytical Method: | SW846 6010C/ 7471B |
| Laboratory SOP[2]: | L-4, L-5 (RTI) / L-9, L-10 (TestAmerica) |

| **Control Limits from Tables 3 DoD QSM ver. 5.0** | | | |
|---|---|---|---|
| **Analyte** | **CAS ID** | **Soil (6010C)** | |
| | | **Lower Control Limit** | **Upper Control Limit** |
| Arsenic | 7440-38-2 | 82 | 111 |
| Barium | 7440-39-3 | 83 | 113 |
| Cadmium | 7440-43-9 | 82 | 113 |
| Chromium | 7440-47-3 | 85 | 113 |
| Lead | 7439-92-1 | 81 | 112 |
| Selenium | 7782-49-2 | 78 | 111 |
| Silver | 7440-22-4 | 82 | 112 |
| **Control Limits from Table 11 DoD QSM ver. 5.0** | | | |
| **Analyte** | **CAS ID** | **Soil (7471B)** | |
| | | **Lower Control Limit** | **Upper Control Limit** |
| Mercury | 7439-97-6 | 80 | 124 |

**Notes:**

1. Metals will include the RCRA metals list: arsenic, barium, cadmium, chromium, lead, mercury, selenium and silver for discrete and ISM samples.
2. The laboratory is DoD ELAP accredited for the test method and is expected to meet the Measurement Performance Criteria specified in DoD QSM version 5.0.
3. Reference number from QAPP Worksheet #23. The laboratory SOPs are provided in Appendix B.

## QAPP Worksheet #13 – Secondary Data Uses and Limitations

| Secondary Data | Data Source (originating organization, report title and date) | Data Generator(s) (originating organization, data types, data generation / collection dates) | How Data Will Be Used | Limitations on Data Use |
|---|---|---|---|---|
| Past site uses | Final Report Installation Assessment of Fort Wingate Depot Activity, 1980 | | Review of Historical Use | None |
| Past site uses | Environmental Survey of Ft. Wingate Depot Activity, Gallup, New Mexico, 1981 | | This Environmental Assessment provided a summary of all facets of the FWDA which may have environmental significance | None |
| Past site uses | FWDA RCRA Facility Assessment Report,1990 | | Review of historical use and historical reports of Functional Test Range (FTR). | None |
| Background concentrations | Fort Wingate Depot Activity, Gallup, New Mexico, Final Remedial Investigation/Feasibility Study & RCRA Corrective Action Program Document | ERM Program Management Company November 1997 | Established background concentrations and Preliminary Remediation Goals. | None |
| Site clearance information | Final Removal Report OE Sampling and Removal Action, 1998 | CMS Environmental, Inc. | Completed unexploded ordnance clearance at FTR 1 in 1998 in which a 100% surface clearance and a subsurface | None |

| Secondary Data | Data Source (originating organization, report title and date) | Data Generator(s) (originating organization, data types, data generation / collection dates) | How Data Will Be Used | Limitations on Data Use |
|---|---|---|---|---|
| | | | clearance of over 16% of the site was performed. | |
| Data gap review | Further Site Characterization of Functional Test Range 1, 2000 | Tetra Tech NUS, Inc. | Further Site Characterization at FTR 1 in 2000 to determine if explosives, metals, and diesel fuel had been released to soils and sediments.<br>Data Gap: To be implemented - Additional evaluation of the northern portion of FTR 1. | None |
| Site clearance information | Final Report on Airborne Geophysical Survey at Fort Wingate Depot Activity, McKinley County, New Mexico, January, 2009 | | Summary of results of an airborne geophysical survey to acquire vertical magnetic gradient data to provide an indication of the level of unexploded ordnance contamination and areas of pits and trenches, and to localize potential sources with sufficient positional accuracy to permit ground-based reacquisition of targets.<br>A high-resolution vertical magnetic gradient system was developed for FWDA.<br>Anomalies were identified at FTR 1. | None |

| Secondary Data | Data Source (originating organization, report title and date) | Data Generator(s) (originating organization, data types, data generation / collection dates) | How Data Will Be Used | Limitations on Data Use |
|---|---|---|---|---|
| | | | Data Gap: To be implemented - Ground truthing of anomalies. Additional soil characterization. | |
| Background concentrations | Soil Background Study and Data Evaluation Report, 2010 | | Background Study of soil to be used to make a statistical determination on the nature and occurrence of inorganic constituents in soil at the FWDA based on site-to-background comparisons. | None |

## QAPP Worksheet #14&16 – Project Tasks and Schedule

| Activity | Responsible Party | Deliverable(s) | Deliverable Due Date |
|---|---|---|---|
| Army Draft RFI Work Plan Submittal | JV | Army Draft RFI Work Plan Submittal | Upon completion of task |
| Draft Final (NMED/Tribal) RFI Work Plan Submittal | JV | Draft Final Work Plan Submittal | Four weeks after receipt of comments from USACE |
| Final RFI Work Plan Submittal | JV | Final RFI Work Plan Submittal | Five weeks after receipt of NMED/Tribal comments |
| RFI Field Work | JV | Field notes, weekly progress report, and daily QC report | Begin 90 days after receipt of NMED approval of Work Plan. Weekly submittals due Friday of the week following for which the activity was performed. |
| Army Draft RFI Report | JV | Army Draft RFI Report | 60 days following the receipt of validated laboratory data |
| Draft Final (NMED/Tribal) RFI Report | JV | Draft Final RFI Report | Four weeks after receipt of comments from USACE |
| Final RFI Report | JV | Final RFI Report | 30 days after receipt and resolution of comments on RFI Report from tribes and NMED |

## Summary of Project Tasks

| **Data Management Tasks** |
|---|
| The purpose of data management is to confirm the necessary data are accurate and readily accessible to meet the analytical and reporting objectives of the project. The soil investigation activities will include a number of samples requiring a structured, comprehensive and efficient program for management of data.<br><br>The data management program established for the project includes field documentation and sample QA/QC procedures, methods for tracking and managing the data, and a system for filing all site-related information. More specifically, data management procedures will be employed to efficiently process the information collected, such that the data are readily accessible and accurate. These procedures are described in detail in the following section.<br><br>The data management plan has five elements: 1) sample designation system, 2) field activities, 3) sample tracking and management, 4) data management system, and 5) document control and inventory. |
| **Sample Designation System** |
| A concise and easily understandable sample designation system is an important part of project sampling activities. It provides a unique sample number that will facilitate both sample tracking and easy resampling of select locations to evaluate data gaps, if necessary. The sample designation system to be employed during the sampling activities will be consistent, yet flexible enough to accommodate unforeseen sampling events or conditions. A combination of letters and numbers will be used to yield a unique sample number for each field sampled collected, as outlined below. |
| **Sample Codes** |
| Each sample will be identified by a unique sample identification number in the logbook, sampling log, and chain-of-custody (COC) record using an alphanumeric code. Field samples will be linked to geographic location via location codes. Where possible, location codes will link historical sample data with new data. All field samples will be identified using the following convention in the order presented below.<br><br>The sample identification will consist of a combination of the Parcel number, SWMU or AOC number, additional site identifier, source of sample, Decision Unit (DU), type of sample, and depth of sample collection in accordance with the latest version of the FWDA Environmental Information Management Plan (USACE, 2007). Additional description of the proposed sample nomenclature system is as follows: |

| | |
|---|---|
| Parcel: | 3 |
| SWMU: | 14 |
| Additional Site Identifier: | AF (arroyo floor), AW (arroyo wall), R (soil removal of DU) |
| Burial Pit Excavation No. (as needed): | BP1 |
| Source of Sample: | SS (surface soil), SW (side wall), B (excavation bottom) |
| DU Number (as needed): | XX or XXX, increment number as appropriate |
| Depth Range (as needed): | 0.0-0.5 or 0.5-1.0 (applicable to discrete sampling only) |
| Type of Sample: | IS (incremental sample), C (composite), ES (excavation screening), EC (excavation composite), ED (excavation discrete), D (discrete) |
| Matrix: | SO (Soil) |

QA/QC samples will carry the same sample nomenclature as the parent sample with a unique suffix and numeral (if required) to distinguish individual samples. The sampling point associations for field duplicates must be recorded in the field log. Blind duplicate samples will be labeled sequentially per sampling event, starting at 01 and followed with the date in "mmddyy" (e.g., FD01-013015). The collection time is for the field duplicate is not recorded on the COC so that the parent sample is blind to the laboratory. QA/QC designations are:

- Field Duplicate Sample – "FD"
- Matrix Spike and Matrix Spike Duplicate – "MS" and MSD"

Sample identification and labeling procedures may be modified as needed to supplement specific investigation objectives and any deviations identified in site-specific work plans.

**Field Activities**

Field activities require consistent documentation and accurate record keeping. During site activities, standardized procedures will be used for documentation of field activities, data security and QA/QC. These procedures are described in further detail in the following subsections.

**Field Documentation**

Complete and accurate record keeping is a critical component of the field investigation activities. When interpreting analytical results and identifying data trends, investigators realize that field notes are an important part of the review and assessment process. To confirm that the field investigation is thoroughly documented, several different information records, each with its own specific reporting requirements, will be maintained, including:

- Sample collection forms;
- COC forms; and
- instrument calibration records.

Each of these types of field documentation is described below.

**Field Logs**

Personnel performing the field activities will keep field logs that detail observations and measurements made during the site work. Data will be recorded directly into site-dedicated, bound notebooks, with each entry dated and signed. To determine, at a future date, that notebook pages are not missing, each page will be sequentially numbered. Erroneous entries will be corrected by crossing out the original entry, initialing it and then documenting the proper information.

**Chain-of-Custody Forms**

COC forms are used to document and track sample possession from time of collection to the time of disposal. A COC form will accompany each field sample collected, and one copy of the form will be filed in the project files. Field personnel will be briefed on the proper use of the COC procedure.

**Instrument Calibration Records**

As part of data QA procedures, field monitoring and detection equipment will be routinely calibrated. Instrument calibration confirms that equipment used is of the proper type, range, accuracy and precision to provide data compatible with the specified requirements and desired results. Calibration procedures for the various types of field instrumentation are described in Worksheet #22. To demonstrate that established calibration procedures have been followed, calibration records will be prepared and maintained to include, as appropriate, the following:

- calibration date and time;
- type and identification number of equipment;
- calibration frequency and acceptable tolerances;
- identification of individual(s) performing calibration;
- reference standards used;
- calibration data; and
- information on calibration success or failure.

The calibration record will serve as a written account of monitoring or detection equipment QA. Erratic behavior or failures of field equipment will be subsequently recorded in the calibration log.

**Data Security**

Measures will be taken during the field investigation to confirm that samples and records are not lost, damaged or altered. When not in use, field notebooks will be stored at the field office or locked in the field vehicle. Access to these files will be limited to the field personnel who use them.

**Sample Management and Tracking**

A record of all field documentation will be maintained to confirm the validity of data used in the site analysis. To effectively execute such documentation, specific sample tracking and data management procedures will be used throughout the sampling program.

Sample tracking will begin with the completion of COC forms. The completed COC forms associated with samples collected will be maintained by the appropriate Task Manager. Copies of all completed COC forms will be maintained in the project file. If samples are not hand delivered, the laboratory will verify receipt of the samples electronically (via e-mail) on the following day.

When analytical data are received from the laboratory, the Program Chemist will review the incoming analytical data packages against the information on the COCs to confirm that the correct analyses were performed for each sample and that results for all samples submitted for analysis were received. Any discrepancies noted will be promptly followed up by the Program Chemist.

**Data Management System**

In addition to the sample tracking system, a data management system will be implemented. The central focus of the data management system will be the development of a personal computer-based project database. The project database will combine pertinent geographical, field and analytical data. Information that will be used to populate the database will be derived from field observations and analytical results. Each of these sources is discussed in the following sections.

**Computer Hardware**

The database will be constructed on personal computer work stations connected through a network server. The network will provide access to various hardware peripherals, such as laser printers, backup storage devices, image scanners and modems. Computer hardware will be upgraded to industrial and corporate standards, as necessary, in the future.

**Computer Software**

The data will be warehoused in EQuIS 5 database and provided to USACE in Microsoft Access. Geographic information system applications will be developed in ESRI ArcGIS. Tables and other database reports will be generated through EQuIS in conjunction with Microsoft Excel. These software products will be upgraded to current industrial standards, as necessary.

**Field Observations**

An important part of the information that will ultimately reside in the data management system for use during the project will originate in the observations that are recorded in the field. Following each sampling event, the sample collection forms will be prepared by the field personnel who performed the sampling activities. The purpose of the sample collection forms is to summarize and provide a record of the sampling event. Topics

to be discussed include the locations sampled, the sampling methodologies used, QA/QC procedures, blind duplicate and MS/MSD sample identification numbers, personnel involved in the activity, and any other noteworthy events that occurred.

Tables are typically attached to the memorandum or email and are used to summarize measurements that were recorded in the field books. It is anticipated that these tables will be developed using a personal computer spreadsheet program to reduce possible transcription error and to facilitate the transfer of information to the data management system.

All pertinent field data will be manually entered into the appropriate database tables from the COC forms and field notebooks.

**Analytical Results**

Analytical results will be provided by the laboratory in both a digital, and a hard copy or pdf format. The data packages will be examined to confirm that the correct analyses were performed for each sample submitted and that all of the analyses requested on the COC form were performed. If discrepancies are noted, the Program Chemist will be notified and will promptly follow up with the laboratory to resolve any issues.

Each data package will undergo a usability assessment in accordance with procedures outlined in Worksheet #37. Data that do not meet the specified standards will be flagged pending resolution of the issue. The flag will not be removed from the data until the issue associated with the sample results is resolved. Although flags may remain for certain data, the use of the data may not necessarily be restricted.

Following completion of the usability assessment, the digital files will be used to populate the appropriate database tables. This format specifies one data record for each constituent for each sample analyzed. Specific fields include:

- sample identification number;
- date sampled;
- date analyzed;
- parameter name;
- analytical result;

- units;
- detection limit; and
- qualifier(s).

The individual electronic data deliverables (EDDs), supplied by the laboratory in Staged Electronic Data Delivery (SEDD) packages, and EQuIS 5 format, will be loaded into the appropriate database table. Any subcontracted laboratory is required to submit the same EDD formats. Any analytical data that cannot be provided by the laboratory in electronic format will be entered manually. After entry into the database, the EDD data will be compared to the field information previously entered into the database to confirm that all requested analytical data have been received.

**Data Analysis and Reporting**

The database management system will have several functions to facilitate the review and analysis of project data. Data entry screens will be developed to assist in the keypunching of field observations. Routines will also be developed to permit the user to scan analytical data from a given site for a given medium. Several output functions that have been developed will be appropriately modified for use in the data management system.

A valuable function of the data management system will be the generation of tables of analytical results from the project database. The capability of the data management system to directly produce tables reduces the redundant manual entry of analytical results during report preparation and precludes transcription errors that may occur otherwise. This data management system function creates the ability to process the data and generate a table of rows and columns. Tables of analytical data will be produced as part of data interpretation tasks, the reporting of data and generation of reports. The table will include the following information: Sample identification, date collected, analytical method, matrix, CAS number, analyte, result, reporting limit, units, lab qualifier, screening level source, screening level value, units, and if the screening level has been exceeded using a yes or no entry.

Another function of the data management system will be to create digital files of analytical results and qualifiers suitable for transfer to mapping/ presentation software. The digital file will consist of sample location number, state plane coordinates, sampling date and detected constituents, and associated concentrations and analytical qualifiers. The file is then transferred to an AutoCAD work station, where another program has been developed to plot a location's analytical data in a "box" format at the sample location (represented by the state plane coordinates). This routine greatly reduces the redundant keypunching of analytical results and facilitates the efficient production of interpretative and presentation graphics.

The data management system also has the capability of producing a digital file of select parameters that exists in one or more of the databases. This type of custom function is accomplished on an interactive basis and is best used for transferring select information into a number of analysis tools, such as statistical or graphing programs.

**Documentation and Records**

**Field Sample Identification**. This is described above in the Sample Codes section.

**Field Documentation**. Field personnel will provide comprehensive documentation covering all aspects of field sampling, field analysis and sample COC. This documentation constitutes a record that allows reconstruction of all field events to aid in the data review and interpretation process. All documents, records and information relating to the performance of the field work will be retained in the project file. The various forms of documentation to be maintained throughout the project are described below.

- *Daily Production Documentation.* A field notebook consisting of a waterproof, bound notebook that will contain a record of all activities performed at the site.
- *Sampling Information*. Detailed notes will be made as to the exact sampling location, physical observations and weather conditions (as appropriate).
- *Sample COC*. The COC forms will provide the record of responsibility for sample collection, transport and submittal to the laboratory. COC forms will be filled out at each sampling site, at a group of sampling sites or at the end of each day of sampling by field personnel designated to be responsible for sample custody. If the samples are relinquished by the designated sampling person to other sampling or field personnel, the COC form will be signed and dated by the appropriate personnel to document the sample transfer. The original COC form will accompany the samples to the laboratory, and copies will be forwarded to the project files.

  Persons will have custody of samples when the samples are in their physical possession, in their view after being in their possession, or in their physical possession and secured so they cannot be tampered with. In addition, when samples are secured in a restricted area accessible only to authorized personnel, they will be deemed to be in the custody of such authorized personnel.
- *Field Equipment, Calibration and Maintenance Logs*. To document the calibration and maintenance of field instrumentation, calibration and maintenance logs will be maintained for each piece of field equipment that is not factory-calibrated.

**Laboratory Project Files**. The laboratory will establish a file for pertinent data. The file will include correspondence, faxed information, phone logs and COC forms. The laboratory will retain project files and data packages for a period not less than five years.

**Laboratory Logbooks**. Workbooks, bench sheets, instrument logbooks and instrument printouts will be used to trace the history of samples through the analytical process and to document important aspects of the work, including the associated QCs. As such, logbooks, bench sheets, instrument logs and instrument printouts will be part of the permanent record of the laboratory. Each page or entry will be dated and initialed by the analyst at the time of entry. Errors in entry will be crossed out in indelible ink with one stroke, corrected without the use of white-out or by obliterating or writing directly over the erroneous entry, and initialed and dated by the individual making the correction. Pages of logbooks that are not used will be completed by lining out unused portions. Information regarding the sample, analytical procedures performed and results of the testing will be recorded on laboratory forms or personal notebook pages by the analyst. These notes will be dated and will also identify the analyst, instrument used and instrument conditions. Laboratory notebooks will be periodically reviewed by the laboratory group leaders for accuracy, completeness and compliance with this QAPP. All entries and calculations will be verified by the laboratory group leader. If all entries on the pages are correct, the laboratory group leader will initial and date the pages. Corrective action will be taken for incorrect entries before the laboratory group leader signs.

**Computer and Hard Copy Storage**. All electronic files and deliverables will be retained by the laboratory for not less than five years; hard copy data packages (or electronic copies) will also be retained for not less than five years.

**Field Data Reporting**. Information collected in the field through visual observation, manual measurement and/or field instrumentation will be recorded in field notebooks or data sheets and/or on forms. Such data will be reviewed by the Site Manager for adherence to the associated plan and for consistency. Concerns identified as a result of this review will be discussed with the field personnel, corrected if possible and (as necessary) incorporated into the data evaluation process. If applicable, field data forms and calculations will be processed and included in appendices to the appropriate reports (when generated). The original field logs documents and data reductions will be kept in the project files.

**Laboratory Data Reporting**. Data reports for all parameters will include, at a minimum, the following:

**Narrative:** Summary of activities that took place during sample analysis including the following information:

- laboratory name and address;
- date of sample receipt;
- cross reference of laboratory identification number to contractor sample identification;
- analytical methods used;
- deviations from specified protocol; and
- corrective actions (if any) taken.

Included with the narrative will be any sample handling documents, including field and internal COC forms, air bills, and shipping tags.

**Analytical Results:** These will be reported according to analysis type and include the following information, as applicable:

- sample ID;
- laboratory ID;
- date of collection;
- date of receipt;
- date of extraction;
- date of analysis; and
- detection limits, limit of detection, and limit of quantitation.

Sample results on the report forms will be corrected for dilutions. Soil data will be reported on a dry weight basis. Unless otherwise specified, all results will be reported uncorrected for blank contamination.

The analytical analyses will be performed using USEPA approved methodology. These data will be reported as Stage 3, as defined in DoD QSM Appendix A, Section 7.0.

Data reporting levels are as follows:

- Stage 3 as defined in DoD QSM Appendix A, Section 7.0

**Assessment/Audit Tasks**

Performance and systems audits will be completed in the field and laboratory during the site investigations, as described below and in Worksheets #31 and #32.

1. **Field Audits. The following field performance and systems audits will be completed during this project.**
   The Site Manager (or their designee), will monitor field performance. Field performance audit summaries will contain an evaluation of field activities to verify that the activities are performed according to established procedures as described in field sampling SOPs located in Appendix A of this QAPP. Field performance audits may also be performed by the appropriate PM (or their designee). The auditor(s) will review field reports and communicate concerns to the PM and/or Site Manager, as appropriate.

The number and frequency of field performance audits conducted will be determined independently by the Project Manager and Site Manager. The observations made during field performance audits and any recommended changes/deviations to the field procedures will be recorded and documented.

In addition, systems audits comparing scheduled QA/QC activities from this QAPP with actual QA/QC activities completed will be performed. The Site Manager and/or Program Chemist will periodically confirm that work is being performed consistent with this QAPP.

**2. Laboratory Audits**

Internal laboratory audits are conducted periodically by the Laboratory QA Manager. As part of the audit, the overall performance of the laboratory staff is evaluated and compared to the performance criteria outlined in the laboratory QA manual and SOPs. Results of the audits are summarized and issued to each department supervisor, Laboratory Manager and Laboratory Director. A systems audit of each laboratory may be performed by the Program Chemist to determine whether the procedures implemented by each laboratory comply with the QA manual and SOPs.

As a participant in state and federal certification programs, the laboratory(ies) are audited by representatives of the regulatory agency issuing certification, in addition to the laboratory's internal audits. Audits are usually conducted annually and focus on laboratory conformance to the specific program protocols for which the laboratory is seeking certification. The auditor reviews sample handling and tracking documentation, analytical methodologies, analytical supportive documentation and final reports. The audit findings are formally documented and submitted to the laboratory for corrective action, if necessary.

The JV reserves the right to conduct an on-site audit of the laboratory(ies) prior to the start of analyses for the project. Additional audits may be performed during the project, as deemed necessary.

**3. Corrective Action**

Corrective actions are required when field or analytical data are not within the objectives specified in this QAPP. Corrective actions include procedures to promptly investigate, document, evaluate and correct data collection and/or analytical procedures. Field and laboratory corrective action procedures for the actions are described below.

**a. Field Procedures**

If, during field work, a condition is noted by the field crew that would have an adverse effect on data quality, corrective action will be taken so as not to repeat this condition. Condition identification, cause and corrective action implemented by the Site Manager or a designee will be documented on a corrective action form and reported to the appropriate Project Manager.

Examples of situations that would require corrective actions are as follows:

- protocols as defined by the QAPP have not been followed;
- equipment is not in proper working order or is not properly calibrated;
- QC requirements have not been met; and
- issues resulting from performance or systems audits have not been resolved.

Project personnel will continuously monitor ongoing work performance as part of daily responsibilities.

**b. Laboratory Procedures**

In the laboratory(ies), when a condition is noted to have an adverse effect on data quality, corrective action will be taken so as not to repeat this condition. Condition identification, cause and corrective action taken will be documented and reported to the Project Manager and Program Chemist.

Corrective action may be initiated, at a minimum, under the following conditions:

- protocols as defined by this QAPP have not been followed;
- predetermined data acceptance standards are not obtained;
- equipment is not in proper working order or calibrated;
- sample and test results are not completely traceable;
- QC requirements have not been met; and
- issues resulting from performance or systems audits have not been resolved.

Laboratory personnel will continuously monitor ongoing work performance as part of daily responsibilities. Corrective action will be initiated at the point where the problem has been identified. At whatever level this occurs (analyst, supervisor, data review, or quality control), it will be brought to the attention of the Laboratory QA Manager and, ultimately, the Laboratory Director. Final approval of any action deemed necessary is subject to the approval of the Laboratory Director.

Any corrective action deemed necessary based on system or performance audits, the analytical results of split samples, or the results of data review will be implemented. The corrective action may include sample re-extraction, re-preparation, re-analysis, cleanup, dilution, matrix modification or other activities.

# QAPP Worksheet #15-1 Project Action Limits-Specific Detection/Quantitation Limits (RTI Laboratory - Soil)

| Analyte | CAS # | Soil Screening Levels[1] | Screening Level Source | Laboratory LOQ[3] | Laboratory LOD | Laboratory DL[4] |
|---|---|---|---|---|---|---|
| **Semi-volatile Organic Compounds (8270D)[5] (mg/kg)** | | | | | | |
| Acenaphthene | 83-32-9 | 3480 | NMED SSL | 0.160 | 0.0167 | 0.0074 |
| Acenaphthylene | 208-96-8 | -- | -- | 0.160 | 0.0167 | 0.0071 |
| Aniline | 62-53-3 | 93 | EPA RSL | 0.160 | 0.0333 | 0.0246 |
| Anthracene | 120-12-7 | 17400 | NMED SSL | 0.160 | 0.0167 | 0.0081 |
| Benzo(a)anthracene | 56-55-3 | 1.53 | NMED SSL | 0.160 | 0.0167 | 0.0110 |
| Benzo(a)pyrene | 50-32-8 | 0.153 | NMED SSL | 0.160 | 0.0167 | 0.0101 |
| Benzo(b)fluoranthene | 205-99-2 | 1.53 | NMED SSL | 0.160 | 0.0167 | 0.0091 |
| Benzo(g,h,i)perylene | 191-24-2 | -- | NMED SSL | 0.160 | 0.0167 | 0.0118 |
| Benzo(k)fluoranthene | 207-08-9 | 15.3 | NMED SSL | 0.160 | 0.0333 | 0.0173 |
| Benzoic acid | 65-85-0 | 250,000 | EPA RSL | 1.000 | 0.333 | 0.135 |
| Benzyl alcohol | 100-51-6 | 6200 | EPA RSL | 0.660 | 0.0167 | 0.0080 |
| 4-Bromophenyl phenyl ether | 101-55-3 | -- | -- | 0.200 | 0.0833 | 0.0425 |
| Butyl benzyl phthalate | 85-68-7 | 280 | EPA RSL | 0.160 | 0.0333 | 0.0197 |
| Carbazole | 86-74-8 | -- | -- | 0.160 | 0.0167 | 0.0115 |
| 4-Chloro-3-methyl phenol | 59-50-7 | 6200 | EPA RSL | 0.160 | 0.0167 | 0.0085 |
| 4-Chloroaniline | 106-47-8 | 2.7 | EPA RSL | 0.160 | 0.0833 | 0.0251 |
| bis(2-Chloroethoxy)methane | 111-91-1 | 180 | EPA RSL | 0.160 | 0.0167 | 0.0069 |
| bis(2-Chloroethyl)ether | 111-44-4 | 3.11 | NMED SSL | 0.160 | 0.0333 | 0.0179 |
| bis(2-Chloroisopropyl)ether | 108-60-1 | 99.3 | NMED SSL | 0.160 | 0.0167 | 0.0076 |
| bis(2-Ethylhexyl)phthalate | 117-81-7 | 380 | NMED SSL | 0.160 | 0.0333 | 0.0244 |
| 2-Chloronaphthalene | 91-58-7 | 6260 | NMED SSL | 0.160 | 0.0167 | 0.0111 |
| 2-Chlorophenol | 95-57-8 | 391 | NMED SSL | 0.160 | 0.0167 | 0.0069 |
| 4-Chlorophenyl phenyl ether | 7005-72-3 | -- | -- | 0.160 | 0.0167 | 0.0101 |
| Chrysene | 218-01-9 | 153 | NMED SSL | 0.160 | 0.0167 | 0.0094 |
| Di-n-butyl phthalate | 84-74-2 | 6160 | NMED SSL | 0.160 | 0.0333 | 0.0180 |
| Di-n-octylphthalate | 117-84-0 | 620 | EPA RSL | 0.160 | 0.0167 | 0.0114 |
| Dibenzo(a,h)anthracene | 53-70-3 | 0.153 | NMED SSL | 0.160 | 0.0333 | 0.0264 |
| Dibenzofuran | 132-64-9 | 72 | EPA RSL | 0.160 | 0.0167 | 0.0085 |
| 1,2-Dichlorobenzene | 95-50-1 | 2150 | NMED SSL | 0.160 | 0.0167 | 0.0072 |
| 1,3-Dichlorobenzene | 541-73-1 | -- | -- | 0.160 | 0.0167 | 0.0069 |
| 1,4-Dichlorobenzene | 106-46-7 | 32.8 | NMED SSL | 0.160 | 0.0167 | 0.0053 |
| 3,3'-Dichlorobenzidine | 91-94-1 | 11.8 | NMED SSL | 1.000 | 0.667 | 0.426 |
| 2,4-Dichlorophenol | 120-83-2 | 185 | NMED SSL | 0.160 | 0.0167 | 0.0113 |
| 2,6-Dichlorophenol | 87-65-0 | -- | -- | 0.160 | 0.0167 | 0.0057 |
| Diethylphthalate | 84-66-2 | 49300 | NMED SSL | 0.160 | 0.0167 | 0.0122 |
| Dimethyl phthalate | 131-11-3 | -- | -- | 0.160 | 0.0167 | 0.0111 |
| 2,4-Dimethylphenol | 105-67-9 | 1230 | NMED SSL | 0.160 | 0.0167 | 0.0130 |
| 4,6-Dinitro-2-methylphenol | 534-52-1 | 4.93 | NMED SSL | 0.320 | 0.0833 | 0.0479 |
| 2,4-Dinitrophenol | 51-28-5 | 123 | NMED SSL | 0.830 | 0.333 | 0.225 |
| 2,4-Dinitrotoluene | 121-14-2 | 17.1 | NMED SSL | 0.160 | 0.0167 | 0.0145 |
| 2,6-Dinitrotoluene | 606-20-2 | 3.56 | NMED SSL | 0.160 | 0.0167 | 0.0158 |
| Fluoranthene | 206-44-0 | 2320 | NMED SSL | 0.160 | 0.0167 | 0.0160 |
| Fluorene | 86-73-7 | 2320 | NMED SSL | 0.160 | 0.0167 | 0.0094 |
| Hexachlorobenzene | 118-74-1 | 3.33 | NMED SSL | 0.160 | 0.0167 | 0.0090 |
| Hexachlorobutadiene | 87-68-3 | 61.6 | NMED SSL | 0.160 | 0.0167 | 0.0152 |
| Hexachlorocyclopentadiene | 77-47-4 | 370 | NMED SSL | 0.160 | 0.0833 | 0.0385 |
| Hexachloroethane | 67-72-1 | 43.1 | NMED SSL | 0.160 | 0.0167 | 0.0077 |
| Indeno(1,2,3-c,d)pyrene | 193-39-5 | 1.53 | NMED SSL | 0.160 | 0.0333 | 0.0086 |

| Analyte | CAS # | Soil Screening Levels[1] | Screening Level Source | Laboratory LOQ[3] | Laboratory LOD | Laboratory DL[4] |
|---|---|---|---|---|---|---|
| Isophorone | 78-59-1 | 5600 | NMED SSL | 0.160 | 0.0167 | 0.0069 |
| 2-Methylnaphthalene | 91-57-6 | 230 | EPA RSL | 0.160 | 0.0167 | 0.0082 |
| 2-Methylphenol | 95-48-7 | 3100 | EPA RSL | 0.160 | 0.0167 | 0.0065 |
| 3 & 4-Methylphenol | 108-39-4 /106-44-5 | 3100 | EPA RSL | 0.160 | 0.0333 | 0.0158 |
| **N-Nitrosodiethylamine** | **55-18-5** | **0.0079** | NMED SSL | 0.160 | 0.0333 | 0.0230 |
| N-Nitrosodimethylamine | 62-75-9 | 0.023 | NMED SSL | 0.160 | 0.0167 | 0.0081 |
| N-Nitrosodi-n-propylamine | 621-64-7 | 0.076 | EPA RSL | 0.160 | 0.0167 | 0.0093 |
| N-Nitrosodiphenylamine (Diphenylamine) | 86-30-6 | 1090 | NMED SSL | 0.160 | 0.0167 | 0.0081 |
| Naphthalene | 91-20-3 | 49.7 | NMED SSL | 0.160 | 0.0167 | 0.0065 |
| 2-Nitroaniline | 88-74-4 | 610 | EPA RSL | 0.320 | 0.0167 | 0.0081 |
| 3-Nitroaniline | 99-09-2 | -- | -- | 0.320 | 0.0167 | 0.0117 |
| 4-Nitroaniline | 100-01-6 | 27 | EPA RSL | 0.320 | 0.0833 | 0.0240 |
| Nitrobenzene | 98-95-3 | 60.4 | NMED SSL | 0.160 | 0.0167 | 0.0103 |
| 2-Nitrophenol | 88-75-5 | -- | -- | 0.160 | 0.0167 | 0.0112 |
| 4-Nitrophenol | 100-02-7 | -- | -- | 0.830 | 0.333 | 0.239 |
| Pentachlorophenol | 87-86-5 | 9.85 | NMED SSL | 0.160 | 0.0833 | 0.0627 |
| Phenanthrene | 85-01-8 | 1740 | NMED SSL | 0.160 | 0.0167 | 0.0088 |
| Phenol | 108-95-2 | 18500 | NMED SSL | 0.160 | 0.0167 | 0.0089 |
| Pyrene | 129-00-0 | 1740 | NMED SSL | 0.160 | 0.0167 | 0.0102 |
| Pyridine | 110-86-1 | 78 | EPA RSL | 0.160 | 0.0833 | 0.0353 |
| 1,2,4-Trichlorobenzene | 120-82-1 | 82.9 | NMED SSL | 0.160 | 0.0167 | 0.0093 |
| 2,4,5-Trichlorophenol | 95-95-4 | 6160 | NMED SSL | 0.160 | 0.0167 | 0.0109 |
| 2,4,6-Trichlorophenol | 88-06-2 | 61.6 | NMED SSL | 0.160 | 0.0167 | 0.0123 |
| **Explosives (8330B)[5] (mg/kg)** | | | | | | |
| HMX | 2691-41-0 | 3850 | NMED SSL | 0.080 | 0.040 | 0.0027 |
| RDX | 121-82-4 | 60.4 | NMED SSL | 0.080 | 0.040 | 0.0034 |
| 1,3-Dinitrobenzene | 99-65-0 | 6.2 | EPA RSL | 0.080 | 0.040 | 0.0177 |
| 2,4-Dinitrotoluene | 121-14-2 | 17.1 | NMED SSL | 0.080 | 0.040 | 0.0108 |
| 2,6-Dinitrotoluene | 606-20-2 | 3.56 | NMED SSL | 0.080 | 0.040 | 0.0128 |
| 2-Amino-4,6-dinitrotoluene | 35572-78-2 | 150 | EPA RSL | 0.080 | 0.040 | 0.0136 |
| 4-Amino-2,6-dinitrotoluene | 19406-51-0 | 150 | EPA RSL | 0.080 | 0.040 | 0.0089 |
| Nitrobenzene | 98-95-3 | 60.4 | NMED SSL | 0.080 | 0.040 | 0.0089 |
| 2-Nitrotoluene | 88-72-2 | 31.6 | NMED SSL | 0.080 | 0.040 | 0.0103 |
| 3-Nitrotoluene | 99-08-1 | 6.16 | NMED SSL | 0.080 | 0.040 | 0.0104 |
| 4-Nitrotoluene | 99-99-0 | 246 | NMED SSL | 0.080 | 0.040 | 0.0147 |
| Tetryl | 479-45-8 | 156 | NMED SSL | 0.080 | 0.040 | 0.0029 |
| 1,3,5-Trinitrobenzene | 99-35-4 | 2200 | EPA RSL | 0.080 | 0.040 | 0.0070 |
| 2,4,6-Trinitrotoluene | 118-96-7 | 36.0 | NMED SSL | 0.080 | 0.040 | 0.0045 |
| Nitroglycerine | 55-63-0 | 6.16 | NMED SSL | 0.160 | 0.080 | 0.0185 |
| PETN | 78-11-5 | 120 | EPA RSL | 0.400 | 0.200 | 0.050 |
| **Perchlorate (6850)[5] (mg/kg)** | | | | | | |
| Perchlorate | 14797-73-0 | 54.8 | NMED SSL | 0.0020 | 0.0010 | 0.00047 |
| **Metals (6010C)[5] (mg/kg)** | | | | | | |
| Arsenic [6] | 7440-38-2 | 5.6 | Background | 2.0 | 1.0 | 0.726 |
| Barium | 7440-39-3 | 15,560 | NMED SSL | 10.0 | 5.0 | 0.297 |
| Cadmium | 7440-43-9 | 70.5 | NMED SSL | 0.25 | 0.05 | 0.033 |
| Chromium | 7440-47-3 | 96.6 | NMED SSL | 0.50 | 0.40 | 0.082 |
| Lead | 7439-92-1 | 400 | NMED SSL | 5.0 | 1.0 | 0.623 |
| Selenium | 7782-49-2 | 391 | NMED SSL | 2.0 | 1.5 | 1.16 |
| Silver | 7440-22-4 | 391 | NMED SSL | 1.0 | 0.25 | 0.082 |

| Analyte | CAS # | Soil Screening Levels[1] | Screening Level Source | Laboratory LOQ[3] | Laboratory LOD | Laboratory DL[4] |
|---|---|---|---|---|---|---|
| **Mercury (7471B)[5] (mg/kg)** | | | | | | |
| Mercury | 7439-97-6 | 23.8 | NMED SSL | 0.010 | 0.005 | 0.0007 |

**Abbreviations:**
DL = detection limit
LOD = limit of detection
LOQ = limit of quantitation

mg/kg = milligrams per kilogram

**Notes:**

1. Soil screening criteria reflect New Mexico Soil Screening Criteria for Resident Soil, December 2014. Soil screening criteria is from USEPA RSL for Resident Soil January 2015. The NMED Soil Screening Criteria is listed for all analytes. If screening criteria isn't specified by NMED, then the USEPA RSL is listed as the soil screening level criteria.
2. Screening levels shown as bold are less than the DL.
3. The target reporting limits are based on wet weight. Actual reporting limits will vary based on sample weight and moisture content.
4. Concentrations detected less than the LOQ but greater than the DL will be reported with the appropriate qualifier.
5. USEPA. Office of Solid Waste and Emergency Response. *Test Methods for Evaluating Solid Waste SW-846* Third Edition, as updated by Updates I, II, IIA, IIB, III, IIIA, IIIB, IVA and IVB, Revision 6, February 2007.
6. Arsenic screening value is the background value determined by December 18, 2013 NMED letter. The background value is used because it is higher than the NMED SSL. If the arsenic value of 5.6 is exceeded then consider the site range compared to 0.2-11.2mg/kg. If the result exceeds 5.6, then the NMED SSL of 4.25 will be used to estimate potential risk.

# QAPP Worksheet #15-2 Project Action Limits-Specific Detection/Quantitation Limits (TestAmerica - Soil)

| Analyte | CAS # | Soil Screening Levels[1] | Screening Level Source | Laboratory LOQ[3] | Laboratory LOD | Laboratory DL[4] |
|---|---|---|---|---|---|---|
| **Semi-volatile Organic Compounds (8270D)[5] (mg/kg)** | | | | | | |
| Acenaphthene | 83-32-9 | 3480 | NMED SSL | 0.330 | 0.0990 | 0.0333 |
| Acenaphthylene | 208-96-8 | -- | -- | 0.330 | 0.0990 | 0.0333 |
| Anthracene | 120-12-7 | 17400 | NMED SSL | 0.330 | 0.0990 | 0.0333 |
| Benzo(a)anthracene | 56-55-3 | 1.53 | NMED SSL | 0.330 | 0.0990 | 0.0333 |
| Benzo(a)pyrene | 50-32-8 | 0.153 | NMED SSL | 0.330 | 0.0990 | 0.0333 |
| Benzo(b)fluoranthene | 205-99-2 | 1.53 | NMED SSL | 0.330 | 0.0990 | 0.0333 |
| Benzo(g,h,i)perylene | 191-24-2 | -- | NMED SSL | 0.330 | 0.0990 | 0.0333 |
| Benzo(k)fluoranthene | 207-08-9 | 15.3 | NMED SSL | 0.330 | 0.0990 | 0.0333 |
| 4-Bromophenyl phenyl ether | 101-55-3 | -- | -- | 0.330 | 0.0990 | 0.0333 |
| Butyl benzyl phthalate | 85-68-7 | 280 | EPA RSL | 0.330 | 0.0990 | 0.0333 |
| Carbazole | 86-74-8 | -- | -- | 0.330 | 0.0990 | 0.0333 |
| 4-Chloro-3-methyl phenol | 59-50-7 | 6200 | EPA RSL | 0.330 | 0.0990 | 0.0333 |
| 4-Chloroaniline | 106-47-8 | 2.7 | EPA RSL | 0.330 | 0.0990 | 0.0333 |
| bis(2-Chloroethoxy)methane | 111-91-1 | 180 | EPA RSL | 0.330 | 0.0990 | 0.0333 |
| bis(2-Chloroethyl)ether | 111-44-4 | 3.11 | NMED SSL | 0.330 | 0.0990 | 0.0334 |
| bis(2-Chloroisopropyl)ether | 108-60-1 | 99.3 | NMED SSL | 0.330 | 0.0990 | 0.0333 |
| bis(2-Ethylhexyl)phthalate | 117-81-7 | 380 | NMED SSL | 0.330 | 0.0990 | 0.0453 |
| 2-Chloronaphthalene | 91-58-7 | 6260 | NMED SSL | 0.330 | 0.0990 | 0.0333 |
| 2-Chlorophenol | 95-57-8 | 391 | NMED SSL | 0.330 | 0.0990 | 0.0333 |
| 4-Chlorophenyl phenyl ether | 7005-72-3 | -- | -- | 0.330 | 0.0990 | 0.0333 |
| Chrysene | 218-01-9 | 153 | NMED SSL | 0.330 | 0.0990 | 0.0333 |
| Di-n-butyl phthalate | 84-74-2 | 6160 | NMED SSL | 0.330 | 0.0990 | 0.0333 |
| Di-n-octylphthalate | 117-84-0 | 620 | EPA RSL | 0.330 | 0.0990 | 0.0333 |
| Dibenzo(a,h)anthracene | 53-70-3 | 0.153 | NMED SSL | 0.330 | 0.0990 | 0.0333 |
| Dibenzofuran | 132-64-9 | 72 | EPA RSL | 0.330 | 0.0990 | 0.0333 |
| 1,2-Dichlorobenzene | 95-50-1 | 2150 | NMED SSL | 0.330 | 0.0990 | 0.0333 |
| 1,3-Dichlorobenzene | 541-73-1 | -- | -- | 0.330 | 0.0990 | 0.0333 |
| 1,4-Dichlorobenzene | 106-46-7 | 32.8 | NMED SSL | 0.330 | 0.0990 | 0.0333 |
| 3,3'-Dichlorobenzidine | 91-94-1 | 11.8 | NMED SSL | 1.600 | 0.660 | 0.330 |
| 2,4-Dichlorophenol | 120-83-2 | 185 | NMED SSL | 0.330 | 0.0990 | 0.0333 |
| Diethylphthalate | 84-66-2 | 49300 | NMED SSL | 0.330 | 0.0990 | 0.0333 |
| Dimethyl phthalate | 131-11-3 | -- | -- | 0.330 | 0.0990 | 0.0333 |
| 2,4-Dimethylphenol | 105-67-9 | 1230 | NMED SSL | 0.330 | 0.0990 | 0.0333 |
| 4,6-Dinitro-2-methylphenol | 534-52-1 | 4.93 | NMED SSL | 1.600 | 0.660 | 0.330 |
| 2,4-Dinitrophenol | 51-28-5 | 123 | NMED SSL | 1.600 | 0.660 | 0.330 |
| 2,4-Dinitrotoluene | 121-14-2 | 17.1 | NMED SSL | 0.330 | 0.0990 | 0.0333 |
| 2,6-Dinitrotoluene | 606-20-2 | 3.56 | NMED SSL | 0.330 | 0.0990 | 0.0333 |
| Fluoranthene | 206-44-0 | 2320 | NMED SSL | 0.330 | 0.0990 | 0.0333 |
| Fluorene | 86-73-7 | 2320 | NMED SSL | 0.330 | 0.0990 | 0.0333 |
| Hexachlorobenzene | 118-74-1 | 3.33 | NMED SSL | 0.330 | 0.0990 | 0.0333 |
| Hexachlorobutadiene | 87-68-3 | 61.6 | NMED SSL | 0.330 | 0.0990 | 0.0333 |
| Hexachlorocyclopentadiene | 77-47-4 | 370 | NMED SSL | 1600 | 660 | 330 |
| Hexachloroethane | 67-72-1 | 43.1 | NMED SSL | 0.330 | 0.0990 | 0.0333 |
| Indeno(1,2,3-c,d)pyrene | 193-39-5 | 1.53 | NMED SSL | 0.330 | 0.0990 | 0.0333 |
| Isophorone | 78-59-1 | 5600 | NMED SSL | 0.330 | 0.0990 | 0.0333 |
| 2-Methylnaphthalene | 91-57-6 | 230 | EPA RSL | 0.330 | 0.0990 | 0.0333 |
| 2-Methylphenol | 95-48-7 | 3100 | EPA RSL | 0.330 | 0.0990 | 0.0333 |

# QAPP Worksheet #15-2 Project Action Limits-Specific Detection/Quantitation Limits (TestAmerica - Soil)

| Analyte | CAS # | Soil Screening Levels[1] | Screening Level Source | Laboratory LOQ[3] | Laboratory LOD | Laboratory DL[4] |
|---|---|---|---|---|---|---|
| 3 & 4-Methylphenol | 108-39-4 /106-44-5 | 3100 | EPA RSL | 660 | 99.0 | 66.6 |
| N-Nitrosodi-n-propylamine | 621-64-7 | **0.076** | EPA RSL | 0.330 | 0.0990 | 0.0333 |
| N-Nitrosodiphenylamine (Diphenylamine) | 86-30-6 | 1090 | NMED SSL | 0.330 | 0.0990 | 0.0333 |
| Naphthalene | 91-20-3 | 49.7 | NMED SSL | 0.330 | 0.0990 | 0.0333 |
| 2-Nitroaniline | 88-74-4 | 610 | EPA RSL | 1.600 | 0.0990 | 0.0333 |
| 3-Nitroaniline | 99-09-2 | -- | -- | 1.600 | 0.0990 | 0.0333 |
| 4-Nitroaniline | 100-01-6 | 27 | EPA RSL | 1.600 | 0.660 | 0.330 |
| Nitrobenzene | 98-95-3 | 60.4 | NMED SSL | 0.330 | 0.0990 | 0.0333 |
| 2-Nitrophenol | 88-75-5 | -- | -- | 0.330 | 0.0990 | 0.0333 |
| 4-Nitrophenol | 100-02-7 | -- | -- | 1.600 | 0.660 | 0.330 |
| Pentachlorophenol | 87-86-5 | 9.85 | NMED SSL | 1.600 | 0.330 | 0.330 |
| Phenanthrene | 85-01-8 | 1740 | NMED SSL | 0.330 | 0.0990 | 0.0333 |
| Phenol | 108-95-2 | 18500 | NMED SSL | 0.330 | 0.0990 | 0.0333 |
| Pyrene | 129-00-0 | 1740 | NMED SSL | 0.330 | 0.0990 | 0.0333 |
| 1,2,4-Trichlorobenzene | 120-82-1 | 82.9 | NMED SSL | 0.330 | 0.0990 | 0.0333 |
| 2,4,5-Trichlorophenol | 95-95-4 | 6160 | NMED SSL | 0.330 | 0.0990 | 0.0333 |
| 2,4,6-Trichlorophenol | 88-06-2 | 61.6 | NMED SSL | 0.330 | 0.0990 | 0.0333 |
| **Explosives (8330)[5] (microgram per kilogram)** | | | | | | |
| HMX | 2691-41-0 | 3850 | NMED SSL | 0.250 | 0.0800 | 0.0388 |
| RDX | 121-82-4 | 60.4 | NMED SSL | 0.250 | 0.0800 | 0.0622 |
| 1,3-Dinitrobenzene | 99-65-0 | 6.2 | EPA RSL | 0.250 | 0.0800 | 0.0435 |
| 2,4-Dinitrotoluene | 121-14-2 | 17.1 | NMED SSL | 0.250 | 0.0800 | 0.0377 |
| 2,6-Dinitrotoluene | 606-20-2 | 3.56 | NMED SSL | 0.250 | 0.0800 | 0.0637 |
| 2-Amino-4,6-dinitrotoluene | 35572-78-2 | 150 | EPA RSL | 0.250 | 0.0800 | 0.0428 |
| 4-Amino-2,6-dinitrotoluene | 19406-51-0 | 150 | EPA RSL | 0.300 | 0.120 | 0.0933 |
| Nitrobenzene | 98-95-3 | 60.4 | NMED SSL | 0.250 | 0.0800 | 0.0432 |
| 2-Nitrotoluene | 88-72-2 | 31.6 | NMED SSL | 0.250 | 0.0800 | 0.0651 |
| 3-Nitrotoluene | 99-08-1 | 6.16 | NMED SSL | 0.250 | 0.0800 | 0.0556 |
| 4-Nitrotoluene | 99-99-0 | 246 | NMED SSL | 0.250 | 0.120 | 0.0813 |
| Tetryl | 479-45-8 | 156 | NMED SSL | | | |
| 1,3,5-Trinitrobenzene | 99-35-4 | 2200 | EPA RSL | 0.250 | 0.0800 | 0.0274 |
| 2,4,6-Trinitrotoluene | 118-96-7 | 36.0 | NMED SSL | 0.250 | 0.0800 | 0.0357 |
| Nitroglycerine | 55-63-0 | 6.16 | NMED SSL | 1.250 | 0.375 | 0.270 |
| PETN | 78-11-5 | 120 | EPA RSL | 2.500 | 0.375 | 0.344 |
| **Perchlorate (6850)[5] (mg/kg)** | | | | | | |
| Perchlorate | 14797-73-0 | 54.8 | NMED SSL | 0.0050 | 0.0050 | 0.0020 |
| **Metals (6010C)[5] (mg/kg)** | | | | | | |
| Arsenic [6] | 7440-38-2 | 5.6 | Background | 1.0 | 1.0 | 0.236 |
| Barium | 7440-39-3 | 15,560 | NMED SSL | 5.0 | 0.7 | 0.110 |
| Cadmium | 7440-43-9 | 70.5 | NMED SSL | 0.5 | 0.1 | 0.034 |
| Chromium | 7440-47-3 | 96.6 | NMED SSL | 1.5 | 1.0 | 0.138 |
| Lead | 7439-92-1 | 400 | NMED SSL | 1.0 | 0.5 | 0.129 |
| Selenium | 7782-49-2 | 391 | NMED SSL | 1.5 | 0.8 | 0.206 |
| Silver | 7440-22-4 | 391 | NMED SSL | 1.0 | 0.7 | 0.070 |

# QAPP Worksheet #15-2 Project Action Limits-Specific Detection/Quantitation Limits (TestAmerica - Soil)

| Analyte | CAS # | Soil Screening Levels[1] | Screening Level Source | Laboratory LOQ[3] | Laboratory LOD | Laboratory DL[4] |
|---|---|---|---|---|---|---|
| **Mercury (7471B)[5] (mg/kg)** | | | | | | |
| Mercury | 7439-97-6 | 23.8 | NMED SSL | 0.04 | 0.03 | 0.011 |

**Abbreviations:**
DL = detection limit
LOD = limit of detection
LOQ = limit of quantitation
mg/kg = milligrams per kilogram

**Notes:**

1. Soil screening criteria reflect New Mexico Soil Screening Criteria for Resident Soil, December 2014. Soil screening criteria is from USEPA RSL for Resident Soil November 2014. The NMED Soil Screening Criteria is listed for all analytes. If screening criteria isn't specified by NMED, then the USEPA RSL is listed as the soil screening level criteria.
2. Screening levels shown as bold are less than the DL.
3. The target reporting limits are based on wet weight. Actual reporting limits will vary based on sample weight and moisture content.
4. Concentrations detected less than the LOQ but greater than the DL will be reported with the appropriate qualifier.
5. USEPA. Office of Solid Waste and Emergency Response. *Test Methods for Evaluating Solid Waste SW-846* Third Edition, as updated by Updates I, II, IIA, IIB, III, IIIA, IIIB, IVA and IVB, Revision 6, February 2007.
6. Arsenic screening value is the background value determined by December 18, 2013 NMED letter. The background value is used because it is higher than the NMED SSL. If the arsenic value of 5.6 is exceeded then consider the site range compared to 0.2-11.2mg/kg. If the result exceeds 5.6, then the NMED SSL of 4.25 will be used to estimate potential risk.

# QAPP Worksheet #17 –Sampling Design and Rationale

## Sampling Design and Rationale

The soil investigation field activities are intended to determine the presence and lateral extent of the presence of COPCs in surface soil at SWMUs 14, 15, 33, and 74, and AOCs 89, 90, 91, and 92. For SWMUs 14, 15, and 33, the investigation will be focused only on those areas located outside of the burial pits and waste piles. Applicable field SOPs are located in Appendix A of this UFP-QAPP.

## Sampling Design

ISM samples will be collected in the areas suspected to be impacted by historical uses. The ISM sampling program will follow the guidance provided in Interim Guidance 09-02: Implementation of Incremental Sampling of Soil for the Military Munitions Response Program (USACE, 2009) and Technical and Regulatory Guidance Incremental Sampling Methodology (ITRC, 2011). Collecting and combining a large number of increments from a DU to produce one incremental sample is the physical analog of collecting and separately analyzing an equal number of discrete samples from the DU and arithmetically averaging the results. The ISM provides an unbiased and representative estimate of the mean concentration of COPCs in the DU.

Composite soil sampling will be conducted during ISM sampling activities to determine the presence and lateral extent the presence of SVOCs in surface soils at SWMUs 14, 15, 33, and 74, and AOCs 89, 90, 91, and 92. The composite sample will be comprised of 6 subsamples, collected from within the DU.

Sampling procedures for the above are discussed in the RFI Work Plan, and the Field Sampling SOPs located in Appendix A of this UFP-QAPP.

## Chemistry Analyses

Project-specific DQOs (QAPP Worksheet #11) for sampling and analysis and the QA/QC objectives by collecting the proper quantities and types of samples will be met by using the correct analytical methodologies, implementing field and laboratory QA/QC procedures, and using various data validation and evaluation processes.

## Analytical Methods

Analytical reference limits are included in QAPP Worksheet #15. Sampling locations are included in QAPP Worksheet #18. Analytical SOP references are listed in QAPP Worksheet #23.

## Quality Assurance/Quality Control Samples

The QA and QC procedures are documented in QAPP Worksheets #12 and #28. Samples are analyzed for the purpose of assessing the quality of the sampling effort and the analytical data.

**Field Quality Control Samples**

The QC for any analytical samples will be provided through the use of temperature blanks, EBs (if applicable), duplicates (composite samples), and replicates (ISM samples). The QC samples will be handled as regular samples.

- Equipment Blanks: EB will be collected for ISM and discrete sampling when non-dedicated equipment is used for sample collection. Samples will be taken during each sampling episode (one per day) to verify that decontamination procedures being employed are effective. The samples will be collected by pouring laboratory provided deionized water through decontaminated sampling equipment into the appropriate sample container. The COPCs for this sampling method include semi-volatile organic compounds (8270D), explosives (8330B), perchlorate (6850, when appropriate), and metals (6010B/7471A) which include arsenic, barium, cadmium, chromium, lead, mercury, selenium and silver.

- Field Duplicates: Blind Field Duplicate samples will be collected for composite samples in a quantity equal to at least 10 percent of the DUs for the study area. The Blind Field Duplicate will be analyzed for SVOCs.

- Triplicates: For ISM sampling, QC samples will be collected at a frequency of 10% of the DUs in the form of triplicate samples. The triplicate sample will include the primary ISM sample plus two replicate ISM samples. The replicate samples will be collected from the DU at the same time as the primary ISM sample is being collected.

**Quality Assurance Samples**

For composite characterization samples (see Worksheet #18), a QA sample will be taken as a split from the same primary sample each QC field duplicate is taken from (i.e., the sample will be homogenized and split into three aliquots: the primary sample, the Blind Field Duplicate (QC) sample, and the QA sample). The QA split sample will be sent to the secondary laboratory and analyzed for SVOCs.

## QAPP Worksheet #18 –Sampling Locations and Methods/Standard Operating Procedure Requirements

| Sample ID | Matrix | Depth (ft bgs) | Type | Analyte/ Analytical Group | Sampling SOP | Comments |
|---|---|---|---|---|---|---|
| **SWMU 14** | | | | | | |
| Example for DU Location 30:<br>Primary: 314SS-30-IS-SO<br>R1: 314SS-30-IS-SO-R1<br>R2: 314SS-30-IS-SO-R2 | Soil | 0-0.5 | ISM | Explosives, RCRA 8 metals, and perchlorate | MC SOP 1 through MC SOP 7 | ISM samples to be collected from 33 DUs [10% of DUs to be sampled in triplicate comprised of the Primary sample and two Replicate samples (R1/R2)] |
| Example for DU Location 5:<br>314SS-5-C-SO<br>QC: 314SS-x-C-SO-FD1<br>QA: 314SS-5-C-SO-QA1 | Soil | 0-0.5 | Composite | SVOCs | MC SOP 2 through MC SOP 7 | 1 composite sampled to be collected from 33 DUs (for 10% of DUs, the sample will be split into 3 aliquots: Primary, Field Duplicate, and QA) |
| **SWMU 15** | | | | | | |
| Example for DU Location 10:<br>Primary: 3-15-SS-10-IS-SO<br>R1: 315SS-10-IS-SO-R1<br>R2: 315SS-10-IS-SO-R2 | Soil | 0-0.5 | ISM | Explosives, RCRA 8 metals, and perchlorate | MC SOP 1 through MC SOP 7 | ISM samples to be collected from 14 DUs [10% of DUs to be sampled in triplicate comprised of the Primary sample and two Replicate samples (R1/R2)] |
| Example for DU Location 5:<br>315SS-5-C-SO<br>QC: 315SS-x-C-SO-FD1<br>QA: 315SS-5-C-SO-QA1 | Soil | 0-0.5 | Composite | SVOCs | MC SOP 2 through MC SOP 7 | 1 composite sampled to be collected from 14 DUs (for 10% of DUs, the sample will be split into 3 aliquots: Primary, Field Duplicate, and QA) |
| **SWMU 33** | | | | | | |

## QAPP Worksheet #18 –Sampling Locations and Methods/Standard Operating Procedure Requirements

| Sample ID | Matrix | Depth (ft bgs) | Type | Analyte/ Analytical Group | Sampling SOP | Comments |
|---|---|---|---|---|---|---|
| Example for DU Location 1:<br>Primary: 333SS-1-IS-SO | Soil | 0-0.5 | ISM | Explosives, RCRA 8 metals, and perchlorate | MC SOP 1 through MC SOP 7 | ISM samples to be collected from 1 DU |
| **SWMU 74** | | | | | | |
| Example for DU Location 4:<br>Primary: 3-74-SS-4-IS-SO<br>R1: 374SS-4-IS-SO-R1<br>R2: 374SS-4-IS-SO-R2 | Soil | 0-0.5 | ISM | Explosives, RCRA 8 metals, and perchlorate | MC SOP 1 through MC SOP 7 | ISM samples to be collected from 4 DUs [10% of DUs to be sampled in triplicate comprised of the Primary sample and two Replicate samples (R1/R2)] |
| Example for DU Location 4:<br>374SS-4-C-SO<br>QC: 374SS-x-C-SO-FD1<br>QA: 374SS-4-C-SO-QA1 | Soil | 0-0.5 | Composite | SVOCs | MC SOP 2 through MC SOP 7 | 1 composite sampled to be collected from 4 DUs (for 10% of DUs, the sample will be split into 3 aliquots: Primary, Field Duplicate, and QA) |
| **AOC 89** | | | | | | |
| Example for DU Location 4:<br>Primary: 389SS-4-IS-SO<br>R1: 389SS-4-IS-SO-R1<br>R2: 389SS-4-IS-SO-R2 | Soil | 0-0.5 | ISM | Explosives, RCRA 8 metals, and perchlorate | MC SOP 1 through MC SOP 7 | ISM samples to be collected from 6 DUs [10% of DUs to be sampled in triplicate comprised of the Primary sample and two Replicate samples (R1/R2)] |
| Example for DU Location 4:<br>389SS-4-C-SO<br>QC: 389SS-x-C-SO-FD1<br>QA: 389SS-4-C-SO-QA1 | Soil | 0-0.5 | Composite | SVOCs | MC SOP 2 through MC SOP 7 | 1 composite sampled to be collected from 6 DUs (for 10% of DUs, the sample will be split into 3 |

## QAPP Worksheet #18 –Sampling Locations and Methods/Standard Operating Procedure Requirements

| Sample ID | Matrix | Depth (ft bgs) | Type | Analyte/ Analytical Group | Sampling SOP | Comments |
|---|---|---|---|---|---|---|
| | | | | | | aliquots: Primary, Field Duplicate, and QA) |
| **AOC 90** | | | | | | |
| Example for DU Location 4:<br>Primary: 390SS-4-IS-SO<br>R1: 390SS-4-IS-SO-R1<br>R2: 390SS-4-IS-SO-R2 | Soil | 0-0.5 | ISM | Explosives, RCRA 8 metals, and perchlorate | MC SOP 1 through MC SOP 7 | ISM samples to be collected from 4 DUs [10% of DUs to be sampled in triplicate comprised of the Primary sample and two Replicate samples (R1/R2)] |
| Example for DU Location 4:<br>390SS-4-C-SO<br>QC: 390SS-x-C-SO-FD1<br>QA: 390SS-4-C-SO-QA1 | Soil | 0-0.5 | Composite | SVOCs | MC SOP 2 through MC SOP 7 | 1 composite sampled to be collected from 4 DUs (for 10% of DUs, the sample will be split into 3 aliquots: Primary, Field Duplicate, and QA) |

## QAPP Worksheet #18 –Sampling Locations and Methods/Standard Operating Procedure Requirements

| Sample ID | Matrix | Depth (ft bgs) | Type | Analyte/ Analytical Group | Sampling SOP | Comments |
|---|---|---|---|---|---|---|
| **AOC 91** | | | | | | |
| Example for DU Location 20:<br>Primary: 391SS-20-IS-SO<br>R1: 391SS-20-IS-SO-R1<br>R2: 391SS-20-IS-SO-R2 | Soil | 0-0.5 | ISM | Explosives, RCRA 8 metals, and perchlorate | MC SOP 1 through MC SOP 7 | ISM samples to be collected from 32 DUs [10% of DUs to be sampled in triplicate comprised of the Primary sample and two Replicate samples (R1/R2)] |
| Example for DU Location 4:<br>391SS-20-C-SO<br>QC: 391SS-x-C-SO-FD1<br>QA: 391SS-20-C-SO-QA1 | Soil | 0-0.5 | Composite | SVOCs | MC SOP 2 through MC SOP 7 | 1 composite sampled to be collected from 32 DUs (for 10% of DUs, the sample will be split into 3 aliquots: Primary, Field Duplicate, and QA) |
| **AOC 92** | | | | | | |
| Example for DU Location 20:<br>Primary: 392SS-20-IS-SO<br>R1: 392SS-20-IS-SO-R1<br>R2: 392SS-20-IS-SO-R2 | Soil | 0-0.5 | ISM | Explosives, RCRA 8 metals, and perchlorate | MC SOP 1 through MC SOP 7 | ISM samples to be collected from 80 DUs [10% of DUs to be sampled in triplicate comprised of the Primary sample and two Replicate samples (R1/R2)] |
| Example for DU Location 4:<br>392SS-20-C-SO<br>QC: 392SS-x-C-SO-FD1<br>QA: 392SS-20-C-SO-QA1 | Soil | 0-0.5 | Composite | SVOCs | MC SOP 2 through MC SOP 7 | 1 composite sampled to be collected from 80 DUs (for 10% of DUs, the sample will be split into 3 aliquots: Primary, Field Duplicate, and QA) |

**Notes:**

1. One blind duplicate sample will be collected for every 10 samples. FD = Field duplicate
2. One QA sample will be collected for every 10 samples and submitted to the QA lab. QA = Quality Assurance
3. Triplicate samples will be comprised of the Primary sample and two Replicate samples (R1/R2)]
4. Sampling SOP reference number from QAPP Worksheet #21.
5. ft bgs = feet below ground surface

## QAPP Worksheet #19 & 30: Sample Containers, Preservation, and Holding Times

This worksheet is applicable to the MC investigation only.

Laboratory (Name, sample receipt address, POC, email, and phone numbers)

RTI Laboratories (Primary Laboratory)
31628 Glendale Street
Livonia, MI 48150
31628 Glendale Street
Contact: David Vesey
Phone: 734.422.8000
Email: dvesey@rtilab.com

TestAmerica St. Louis (QA Laboratory)
13715 Rider Trail North
Earth City, MO 63045
13715 Rider Trail North
Contact: Erika Gish
Phone: 314.787.8276
Email: Erika.gish@testamericainc.com

DoD QSM Stage 3 data packages to be delivered within 21 calendar days
Sample Delivery Method: Federal Express
RTI will serve as the primary laboratory. TestAmerica St. Louis will serve as the QA laboratory and will analyze 10% of samples.
DoD ELAP and National Environmental Laboratory Accreditation Program Certifications are included in Attachment B.

| Parameter | Analytical and Preparation Method/SOP Reference | Method | Bottle Type | Preservation | Holding Time [2] |
|---|---|---|---|---|---|
| **Soil** | | | | | |
| Semi-volatile Organic Compounds (SVOCs) | SW846 8270D/L-1 (RTI), L-6 (TA) | 8270D [1] | 1 x 4-oz glass jar with Teflon®-lined lid | Cool to <6°C | 14 days to extraction<br>40 days to analysis |
| Explosives | SW846 8330B/L-2 (RTI)/L-7 (TA) | 8330B [1] | 1 x 4-oz glass jar with Teflon®-lined lid | Cool to <6°C; store in dark | 14 days to extraction<br>40 days to analysis |
| Explosives (ISM preparation) | SW846 8330B/L-2 (RTI)/L-7 (TA) | 8330B [1] | 1 x 1-gal plastic zip-lock bag | Cool to <6°C; store in dark | 14 days to extraction<br>40 days to analysis |
| Perchlorate | SW846 6850/L-3 (RTI)/L-8 (TA) | 6850 [1] | 1 x 4-oz glass jar with Teflon®-lined lid | Cool to <6°C; store in dark. containers should only be filled 2/3s of the way | 28 days to extraction and analysis |
| Metals | SW846 6010C/L-4 (RTI)/L-9 (TA) | 6010C [1] | 1 x 4-oz glass jar with Teflon®-lined lid | Cool to <6°C | 180 days to analysis |
| Mercury | SW846 7471B/L-5 (RTI)/L-10 (TA) | 7471B [1] | | | 28 days to analysis |
| Metals (ISM preparation) | SW846 6010C/L-4 (RTI)/L-9 (TA) | 6010C [1] | 1 x 1-gal plastic zip-lock bag | Cool to <6°C | 180 days to analysis |
| Mercury (ISM preparation) | SW846 7471B/L-5 (RTI)/L-10 (TA) | 7471B [1] | | | 28 days to analysis |
| Cyanide | SW846 9012/L-14 | 9012 [1] | 1 x 8-oz glass jar with Teflon®-lined lid | Cool to <6°C | 14 days to analysis |

| Parameter | Analytical and Preparation Method/SOP Reference | Method | Bottle Type | Preservation | Holding Time [2] |
|---|---|---|---|---|---|
| Nitrate-N | SW846 9056A/L-15 | 9056A [1] | | | 14 days to extraction; 48 hours from extraction to analysis |

**Abbreviations:**
°C = degree Celsius
oz = ounce
ISM = incremental sampling method

**Notes:**
1. USEPA. Office of Solid Waste and Emergency Response. *Test Methods for Evaluating Solid Waste SW-846.* Third Edition, as updated by Updates I, II, IIA, IIB, III, IIIA, IIIB, IVA and IVB, Revision 6, February 2007.
2. All holding times are measured from date of collection.

## QAPP Worksheet #20 –Sample Quantities and Control Frequencies

| Matrix/ Analysis | Laboratory[1] | Analytical and Preparation SOP[2] | Estimated Environ. Sample Quantity[3] | Field QC samples | | | | Laboratory QC Samples | | | | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Field Duplicate | | Field Replicates - ISM only | | MS | | MSD | | |
| | | | | Freq. [5] | No. | Freq. [5] | No. | Freq. [4] | No. | Freq. [4] | No. | |
| **Soils-Composite** | | | | | | | | | | | | |
| SVOCs | RTI | L-1 | 174 | 1/10 | 20 | NA | -- | 1/20 | 12 | 1/20 | 12 | 218 |
| | TA | L-5 | 20 | 1/10 | -- | NA | -- | 1/20 | -- | 1/20 | -- | 20 |
| **Soils-ISM** | | | | | | | | | | | | |
| Explosives | RTI | L-2 | 174 | 1/10 | 20 | 1/10 | 20 | 1/20 | 12 | 1/20 | 12 | 238 |
| Perchlorate | RTI | L-3 | 174 | 1/10 | 20 | 1/10 | 20 | 1/20 | 12 | 1/20 | 12 | 238 |
| RCRA Metals | RTI | L-4 | 174 | 1/10 | 20 | 1/10 | 20 | 1/20 | 12 | 1/20 | 12 | 238 |
| Mercury | RTI | L-5 | 174 | 1/10 | 20 | 1/10 | 20 | 1/20 | 12 | 1/20 | 12 | 238 |

**Abbreviations:**

Freq. = frequency

QC = quality control

NA = not applicable

TBD = to be determined

No. = number of samples

**Notes:**

1. See QAPP Worksheet #19/30 for contact information.
2. See QAPP Worksheet #23 for SOP title, revision number, date details.
3. Sample quantities are approximate
4. Frequency for MS/MSD samples is 1 per 20 field samples.
5. Frequency of field duplicates, and ISM replicate samples is 1 per 10 samples.

## QAPP Worksheet #21 –Field Standard Operating Procedure References

| SOP# or Reference | Title, Revision, Date and URL (if available) | Originating Organization | SOP Option of Equipment Type (if SOP provides different options) | Modified for Project Work? (Yes/No) | Comments |
|---|---|---|---|---|---|
| MC SOP 1 | Incremental Sampling Methodology, January 2015 | JV | Incremental Sampling Tool | No | NA |
| MC SOP 2 | Surface and Subsurface Soil Sampling Using Manual Methods, Revision 1, March 6, 2009 | ARCADIS | Stainless Steel Hand Augers | No | NA |
| MC SOP 3 | Documenting Sample Locations with a Global Positioning System (GPS) | NA | NA | No | NA |
| MC SOP 4 | Field Log Book Entries, Revision 0, August 11, 2009. | ARCADIS | Field Log Book | No | NA |
| MC SOP 5 | Chain of Custody, Revision 0, March 31, 2004. | NA | Chain of Custody Record Form | No | NA |
| MC SOP 6 | Investigation-Derived Waste Handling and Storage, Revision 2, March 6, 2009 | ARCADIS | 55-gallon steel drums, Department of Transportation 1A2 or equivalent | No | NA |
| MC SOP 7 | Sample Handling, Packaging and Shipping, Revision 0, March 31, 2004. | NA | Analysis Request and Chain of Custody Record | No | NA |

Note: All field SOPs are listed for discrete, ISM and confirmation sampling for continuity.

## QAPP Worksheet #22 – Field Equipment Calibration, Maintenance, Testing and Inspection

Field equipment will be maintained, inspected, and tested as presented in the table below.

| Field Equipment | Activity | Frequency | Acceptance Criteria | Corrective Action | Responsible Person | SOP Reference[1] |
|---|---|---|---|---|---|---|
| GPS | Number of satellites acquired and quality of data will be checked periodically while collecting GPS data. | Daily, prior to use | Per equipment manual | Contact the JV equipment facility manager for direction. | Field Team Leader | MC SOP 3 |
| Hand trowel | Daily instrument check | Daily, prior to use | Per equipment manual | Contact the JV equipment facility manager for direction. | Field Team Leader | MC SOP 2 |
| Incremental Sampling Method sampling equipment (use of hand trowel based on surface conditions) | Daily instrument check | Daily, prior to use | Per equipment manual | Contact the JV equipment facility manager for direction. | Field Team Leader | MC SOP 1 |

**Notes:**

[1]SOP reference numbers correspond to the field sampling SOPs in QAPP Worksheet #21.

# QAPP Worksheet #23 – Analytical Standard Operating Procedure References

| SOP # | Title, Revision Date and/or Number | Definitive or Screening Data | Matrix/Analytical Group | Instrument | Organization Performing Analysis | Modified for Project Work? (Yes/No) |
|---|---|---|---|---|---|---|
| **RTI Laboratories (Primary laboratory)** | | | | | | |
| L-1 | SOP 8270D_110713_R13: Analysis of Semi-Volatile Organics by SW-846 270D, 11/7/2013, and SOP 3550C_022814_R8: Sonication Extraction Procedure for Semi-volatile organic compounds by EPA SW-846 3550C, 2/28/2014 | Definitive | SVOCs in soil | Gas chromatography/ Mass spectroscopy (GC/MS) | RTI | No |
| L-2 | SOP 8330B_022114_R4.1: Analysis of Explosives by HPLC, SW-846 8330B, 8/28/2013. The sample preparation procedure for all ISM samples is located in Section 9.0 Sample Preparation of this SOP. | Definitive | Explosives in soil | High performance liquid chromatography (HPLC) | RTI | No |
| L-3 | SOP 6850_071513)R0.1: Analysis of Perchlorate by HPLC/MS/MS, SW-846 6850, 7/15/2013 | Definitive | Perchlorate in soil | HPLC with a tandem mass spectrometry (HPLC/MS/MS) | RTI | No |
| L-4 | SOP 6010C_100713_R3.2: Analysis of Elements by Inductively Coupled Plasma – Optical Emission Spectrometry by SW-846 6010C, 8/11/2014, and SOP 3050_110512_R11: Acid Digestion of Solid Samples for the Analysis of Total Metals by SW-846 3050B, 11/05/2012 The sample preparation procedure for all ISM samples is located in Section 9.0 Sample Preparation of SOP 8330B_022114_R4.1. | Definitive | Metals in soil | Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES) | RTI | No |
| L-5 | SOP 7470A_7471B_022014_R7: Analysis for Mercury by SW-846 7470A, 7471B, 2/20/2014 | Definitive | Mercury in soil | Cold vapor atomic absorption (CVAA) | RTI | No |
| **TestAmerica St. Louis (QC laboratory)** | | | | | | |
| L-6 | SOP ST-MS-0001: GC/MS Semi-volatiles Analysis [SW-846 8270D: EPA 625], Rev 17, 9/16/2014 and SOP ST-OP-0002: Extraction and Cleanup of Organic Compounds from Waters and Soils, Rev 23, 9/16/2014 | Definitive | SVOCs in soil | GC/MS | TestAmerica St. Louis | No |

Note: All analytical SOPs are listed for discrete, ISM and confirmation samples for continuity.

# QAPP Worksheet #24 – Analytical Instrument Calibration

| Instrument | Calibration Procedure | Frequency of Calibration | Acceptance Criteria | Corrective Action | Person Responsible for Corrective Action | SOP Reference[1] |
|---|---|---|---|---|---|---|
| GC/MS (SW846 8270D) | Instrument performance check (tune). | Prior to initial and continuing calibration. | Specific ion abundance criteria of BFB (8260) or DFTPP (8270) from method. | Retune instrument. | Laboratory Analyst | L-1, L-6 |
| | Initial Calibration (ICAL): Minimum of 5 calibration levels for linear and 6 calibration levels for quadratic. | At instrument setup and after ICV or continuing calibration verification (CCV) failure, prior to sample analysis. | ICAL must meet one of the three options below: *Option 1:* RSD for each analyte ≤15%; *Option 2:* linear least squares regression for each analyte: $r^2 \geq 0.99$; *Option 3:* non-linear least squares regression (quadratic) for each analyte: $r^2 \geq 0.99$. | Correct problem, then repeat ICAL. | | |
| | ICV | Once after each ICAL, analysis of a second source standard prior to sample analysis. | All reported analytes and surrogates within ±20% of true value. | Correct problem. Rerun ICV. If that fails, repeat ICAL. | | |
| | CCV | Before sample analysis, after every 12 hours of analysis time, and at the end of the analysis sequence. | All reported analytes and surrogates within ±20% of true value. All reported analytes and surrogates within ± 50% for end of analytical batch CCV. | Recalibrate, and reanalyze all affected samples since the last acceptable CCV; or Immediately analyze two additional consecutive CCVs. If both pass, samples may be reported without reanalysis. If either fails, take corrective action(s) and re-calibrate; then reanalyze all affected samples since the last acceptable CCV. | | |
| HPLC (SW846 8330B) | ICAL: Minimum of 5 calibration levels for linear and 6 calibration levels for quadratic. | At instrument setup and after i ICV or CCV failure, prior to sample analysis. | ICAL must meet one of the three options below: *Option 1:* RSD for each analyte ≤15%; *Option 2:* linear least squares regression for each analyte: $r^2 \geq 0.99$; *Option 3:* non-linear least squares regression (quadratic) for each analyte: $r^2 \geq 0.99$. | Correct problem, then repeat ICAL. | Laboratory Analyst | L-2, L-7 |

# QAPP Worksheet #24 – Analytical Instrument Calibration

| Instrument | Calibration Procedure | Frequency of Calibration | Acceptance Criteria | Corrective Action | Person Responsible for Corrective Action | SOP Reference[1] |
|---|---|---|---|---|---|---|
| | ICV | Once after each ICAL, analysis of a second source standard prior to sample analysis. | All reported analytes and surrogates within ±20% of true value. | Correct problem. Rerun ICV. If that fails, repeat ICAL. | | |
| | CCV | Before sample analysis, after every 10 field samples, and at the end of the analysis sequence. | All reported analytes and surrogates within ±20% of true value. | Recalibrate, and reanalyze all affected samples since the last acceptable CCV;<br>or<br>Immediately analyze two additional consecutive CCVs. If both pass, samples may be reported without reanalysis. If either fails, take corrective action(s) and re-calibrate; then reanalyze all affected samples since the last acceptable CCV. | | |

# QAPP Worksheet #24 – Analytical Instrument Calibration

| Instrument | Calibration Procedure | Frequency of Calibration | Acceptance Criteria | Corrective Action | Person Responsible for Corrective Action | SOP Reference[1] |
|---|---|---|---|---|---|---|
| HPLC/MS/MS (SW846 6850) | Mass Calibration | Instrument must have a valid mass calibration prior to any sample analysis. The mass calibration is updated on an as-needed basis (e.g., QC failures, ion masses show large deviations from known masses, major instrument maintenance is performed, or the instrument is moved). | Mass calibration range must bracket the ion masses of interest. The most recent mass calibration must be used for an analytical run, and the same mass calibration must be used for all data files in an analytical run. Mass calibration must be verified by acquiring a full scan continuum mass spectrum of a perchlorate stock standard. | If the mass calibration fails, recalibrate. If it still fails, consult manufacture instructions on corrective maintenance. | Laboratory Analyst | L-3, L-8 |
| | Tune Check | Prior to ICAL and after any mass calibration or maintenance is performed. | Tuning standard must span the mass range of the analytes of interest and meet acceptance criteria outlined in the laboratory SOP. | Retune instrument and verify. If the tune check will not meet acceptance criteria, an instrument mass calibration must be performed and the tuning redone. | | |
| | ICAL: Minimum of 5 calibration levels for linear and 6 calibration levels for quadratic. | At instrument setup or after ICV or CCV failure, prior to sample analysis. | ICAL must meet one of the two options below:<br>*Option 1:* RSD for each analyte ≤15%;<br>*Option 2:* linear least squares regression for each analyte: $r^2 \geq 0.995$. | Correct problem then repeat ICAL. | | |
| | ICV | Once after each ICAL. | Perchlorate concentration must be within ±15% of true value. | Correct problem. Rerun ICV. If that fails, repeat ICAL. | | |
| | CCV | On days an ICAL is performed, after every 10 field samples and at the end of the analytical sequence. On days an ICAL is performed, at the beginning of the sequence, after every 10 field samples, and at the end of the analytical sequence. | Perchlorate concentration must be within ±15% of true value. | Recalibrate, and reanalyze all affected samples since the last acceptable CCV;<br>or<br>Immediately analyze two additional consecutive CCVs. If both pass, samples may be reported without reanalysis. If either fails, take corrective action(s) and re-calibrate; then reanalyze all affected samples since the last acceptable CCV. | | |

# QAPP Worksheet #24 – Analytical Instrument Calibration

| Instrument | Calibration Procedure | Frequency of Calibration | Acceptance Criteria | Corrective Action | Person Responsible for Corrective Action | SOP Reference[1] |
|---|---|---|---|---|---|---|
| HPLC/MS/MS (SW846 6850) continued | Isotope Ratio 35Cl/37Cl | Every sample, batch QC sample, and standard. | Monitor for either the parent ion at masses 99/101 or the daughter ion at masses 83/85 depending on which ions are quantitated. Must fall within 2.3 to 3.8. | If criteria are not met, the sample must be rerun. If the sample was not pretreated, the sample must be reextracted using cleanup procedures. If, after cleanup, the ratio still fails, use alternative techniques toconfirm presence of perchlorate, e.g, a post spike sample or dilution to reduce any interference. | Laboratory Analyst | L-3, L-8 |
| ICP-AES (SW846 6010C) | ICAL Minimum one high standard and a calibrationblank. | Daily ICAL prior to sample analysis. | If more than one calibration standard is used, $r^2 \geq 0.99$. | Correct problem, then repeat ICAL. | Laboratory Analyst | L-4, L-9 |
| | ICV | Once after each ICAL, analysis of a second source standard prior to sample analysis. | All reported analytes within ±10% of true value. | Correct problem. Rerun ICV. If that fails, repeat ICAL. | | |

# QAPP Worksheet #24 – Analytical Instrument Calibration

| Instrument | Calibration Procedure | Frequency of Calibration | Acceptance Criteria | Corrective Action | Person Responsible for Corrective Action | SOP Reference[1] |
|---|---|---|---|---|---|---|
| ICP-AES (SW846 6010C) continued | CCV | After every 10 field samples, and at the end of the analysis sequence. | All reported analytes within ±10% of true value. | Recalibrate, and reanalyze all affected samples since the last acceptable CCV; or Immediately analyze two additional consecutive CCVs. If both pass, samples may be reported without reanalysis. If either fails, take corrective action(s) and re-calibrate; then reanalyze all affected samples since the last acceptable CCV. | Laboratory Analyst | L-4, L-9 |
| | Low-Level Calibration Check Standard (Low-Level ICV) | Daily | All reported analytes within ±20% of true value. | Correct problem and repeat ICAL. | | |
| | Initial and Continuing Calibration Blank (ICB/CCB) | Before beginning a sample run, after every 10 field samples, and at the end of the analysis sequence. | No analytes detected > LOD. | Correct problem and repeat ICAL. All samples following the last acceptable calibration blank must be reanalyzed. | | |
| | Interference Check Sample (ICS) | After ICAL and prior to sample analysis. | *ICS-A:* Absolute value of concentration for all non-spiked project analytes < LOD (unless they are a verified trace impurity from one of the spiked analytes); *ICS-B:* Within ±20% of true value. | Terminate analysis; locate and correct problem; reanalyze ICS and all samples. | | |
| CVAA (SW846 7471B) | ICAL: Minimum of 5 calibration levels and a calibration blank | Daily ICAL prior to sample analysis. | $r^2 \geq 0.99$. | Correct problem, then repeat ICAL. | Laboratory Analyst | L-5, L-10 |
| | ICV | Once after each ICAL, analysis of a second source standard prior to sample analysis. | All reported analytes within ±10% of true value. | Correct problem. Rerun ICV. If that fails, repeat ICAL. | | |

# QAPP Worksheet #24 – Analytical Instrument Calibration

| Instrument | Calibration Procedure | Frequency of Calibration | Acceptance Criteria | Corrective Action | Person Responsible for Corrective Action | SOP Reference[1] |
|---|---|---|---|---|---|---|
| CVAA (SW846 7471B) continued | CCV | After every 10 field samples, and at the end of the analysis sequence. | All reported analytes within ±10% of true value. | Recalibrate, and reanalyze all affected samples since the last acceptable CCV; or Immediately analyze two additional consecutive CCVs. If both pass, samples may be reported without reanalysis. If either fails, take corrective action(s) and re-calibrate; then reanalyze all affected samples since the last acceptable CCV. | Laboratory Analyst | L-5, L-10 |
| | ICB/CCB | Before beginning a sample run, after every 10 field samples, and at the end of the analysis sequence. | No analytes detected > LOD. | Correct problem and repeat ICAL. All samples following the last acceptable calibration blank must be reanalyzed. | | |

Note:
1SOP reference numbers correspond to analytical SOPs in QAPP Worksheet #23.

# QAPP Worksheet #25 – Analytical Instrument and Equipment Maintenance, Testing and Inspection

| Instrument/ Equipment | Maintenance Activity | Testing Activity | Inspection Activity | Frequency | Acceptance Criteria | Corrective Action | Responsible Person | SOP Reference[1] |
|---|---|---|---|---|---|---|---|---|
| GC/MS | • Replace pump oil as needed<br>• Change gas line dryers as needed<br>• Perform ion source cleaning and filament replacement<br>• Replace injection port liner weekly or as needed<br>• Clip column<br>• Replace gas chromatography (GC) column as needed<br>• Manual tuning<br>• Replace electron multiplier<br>• Check that gas supply is sufficient and delivery pressure is adequate<br>• Bake out lines and column | Semi-volatile Organic Compounds by SW846 8270D | Check connections, replace worn equipment | Daily or as needed | Acceptable instrument quality control and sensitivity | Inspect system, correct problem, rerun calibration and affected samples | Analyst | L-1, L-6 |
| HPLC<br>HPLC/MS/MS | • Check column flow<br>• Check gas and liquid lines for leaks<br>• Check or replace solvent inlet filters<br>• Check pump seals<br>• Check for injector leaks<br>• Check and clean liquid lines and detector<br>• Check and replace pump oil | Explosives by SW846 8330B<br><br>Perchlorate by SW846 6850 | Check connections, replace worn equipment | Daily or as needed | Acceptable instrument quality control and sensitivity | Inspect system, correct problem, rerun calibration and affected samples | Analyst | L-2, L-3, L-7, L-8 |

# QAPP Worksheet #25 – Analytical Instrument and Equipment Maintenance, Testing and Inspection

| Instrument/ Equipment | Maintenance Activity | Testing Activity | Inspection Activity | Frequency | Acceptance Criteria | Corrective Action | Responsible Person | SOP Reference[1] |
|---|---|---|---|---|---|---|---|---|
| ICP-AES<br>ICP-OES | • Inspect torch, peristaltic pump tubing, and nebulizer<br>• Inspect and clean spray chamber<br>• Evaluate profile performance<br>• Check electronics | Metals by SW846 6010C | Check connections, replace worn equipment | Daily or as needed | Acceptable instrument quality control and sensitivity | Inspect system, correct problem, rerun calibration and affected samples | Analyst | L-4, L-9 |
| CVAA | • clean tubing and quartz cell as needed<br>• clean aspirator as necessary<br>• check level of mercury scrubber solution<br>• replace lamps<br>• provide that gas supply is sufficient and delivery pressures are adequate | Mercury by SW846 7471B | Check connections, replace worn equipment | Daily or as needed | Acceptable instrument quality control and sensitivity | Inspect system, correct problem, rerun calibration and affected samples | Analyst | L-5, L-10 |

**Abbreviations:**

CVAA = cold vapor atomic absorption

GC/MS = gas chromatography/mass spectrometry

HPLC = high performance liquid chromatography

HPLC/MS/MS = high performance liquid chromatography with tandem mass spectrometers

ICP-AES = inductively coupled plasma atomic emission spectrometry

ICP-OES = inductively coupled plasma optimcal emission spectrometry

SOP = Standard Operating Procedure

**Note:**

[1]SOP reference numbers correspond to analytical SOPs in QAPP Worksheet #23.

## QAPP Worksheet #26 & 27– Sample Handling, Custody and Disposal

This worksheet is applicable to the MC investigation only.

| | |
|---|---|
| Sampling organization: | PIKA – Pirnie JV |
| Laboratory: | RTI and TestAmerica St. Louis |
| Method of sample delivery (shipper/carrier): | Federal Express |
| Number of days from reporting until sample disposal: | At least 60 days |

| Activity | Organization and title or position of person responsible for the activity | SOP reference |
|---|---|---|
| Sample labeling | Field team leader (TBD)<br>JV | See Worksheet #14/16. |
| Chain of custody form completion | Field team leader (TBD)<br>JV | See MC SOP 5, Worksheet #14/16 and see below. |
| Packaging | Field team leader (TBD)<br>JV | See MC SOP 7, Worksheet #14/16 and see below |
| Shipping coordination | Field team leader (TBD)<br>JV | See MC SOP 5 and Worksheet #14/16. |
| Sample receipt, inspection, and log-in | RTI<br>TestAmerica St Louis | See Worksheet #14/16 and see below |
| Sample custody and storage | RTI<br>RTI to subcontract Dioxins/Furans to Cape Fear Analytical<br>TestAmerica St Louis | See Worksheet #14/16 and see below |
| Sample disposal | RTI<br>TestAmerica St Louis | Samples must be held for 60 days from date of reporting results. Disposal must follow all Federal and State regulations. |

## Sample Handling and Custody

Sample custody procedures ensure the timely, correct, and complete analysis of each sample for all parameters requested. A sample is considered to be in someone's custody if it:

- Is in his/her possession.
- Is in his/her view, after being in his/her possession.
- Is in his/her possession and has been placed in a secure location.
- Is in a designated secure area.

Sample custody documentation provides a written record of sample collection and analysis. The sample custody procedures provide for specific identification of samples associated with an exact location, the recording of pertinent information associated with the sample, including time of sample collection and any preservation techniques, and a chain of custody record that serves as physical evidence of sample custody.

The chain of custody documentation system provides the means to individually identify, track, and monitor each sample from the time of collection through final data reporting. Chain of custody procedures document pertinent sampling data and all transfers of custody until the samples reach the analytical laboratory. All chain of custody forms must be filled out and signed in ink. The following information is typically recorded on manual chain of custody forms.

- Project name and/or project number.
- Signature of Site Superintendent or designee.
- Date and time of sample collection.
- Discrete sample designation.
- Sample matrix.
- Analyses required.
- Preservation technique.
- Signatures and dates for transfer of custody.
- Air express/shipper's bill of lading identification number.

The chain of custody form serves as an official communication to the laboratory detailing the particular analyses required for each sample. The chain of custody record will accompany the samples from the time of sampling through all transfers of custody. It will be kept on file at the laboratory where samples are analyzed and archived. Two copies of the chain of custody form are created: one copy is retained by the Site Superintendent and one is sent to the laboratory. The Site Superintendent or designee completes a chain of custody record to accompany each shipment from the field to the laboratory. The completed chain of custody is put in a zip-lock bag and taped to the inside cover of the sample shipping container. If there is more than one container in a shipment, copies of the chain of custody form will be placed in each container. The container is then sealed with custody seals and custody is transferred to the laboratory. Commercial carriers are not required to sign off on the chain-of-custody form as long as the forms are sealed inside the sample cooler and the custody seals remain intact.

Samples will be packaged for shipment as outlined below:

- Securely affix the sample label to the container with clear packing tape.
- Check the cap on the sample container to confirm that it is properly sealed.
- Wrap the sample container cap with clear packing tape to prevent the label from becoming loose.
- Complete the chain-of-custody form with the required sampling information and confirm that the recorded information matches the sample labels. **Note:** If the designated sampler relinquishes the samples to other sampling or field personnel for packing or other purposes, the sampler will complete the chain-of-custody prior to this transfer. The appropriate personnel will sign and date the chain-of-custody form to document the sample custody transfer.
- Using duct tape, secure the outside drain plug at the bottom of the cooler.
- Wrap sample containers in bubble wrap or other cushioning material.
- Place 1 to 2 inches of cushioning material at the bottom of the cooler.
- Place the sealed sample containers into the cooler.
- Place ice in plastic bags and seal. Place loosely in the cooler.
- Fill the remaining space in the cooler with cushioning material.
- Place chain-of-custody forms in a plastic bag and seal. Tape the forms to the inside of the cooler lid.
- Close the lid of the cooler, lock and secure with duct tape.
- Wrap strapping tape around both ends of the cooler at least twice.

- Mark the cooler on the outside with the shipping address and return address, affix "Fragile" labels and draw (or affix) arrows indicating "this side up." Cover the labels with clear plastic tape.
- Place a signed custody seal over the sample cooler lid.

## Field Procedures

The field sampler is personally responsible for the care and custody of samples until they are transferred to the Site Superintendent or until they are properly dispatched. As few people as possible should handle the samples.

The Site Superintendent, or designee, is responsible for entering the proper information in the field logbook, including all pertinent information such as sample identification number, date and time of sample collection, type of analysis, and description of sample location. The information entered into the field logbook will be used to generate a chain of custody. Field logbooks will provide the means of recording the data collecting activities that are performed. As such, entries will be described in as much detail as possible so that persons going to the site could reconstruct a particular situation without reliance on memory. Entries will be made in ink, with no erasures. If an incorrect entry is made, the information will be crossed out with one strike mark.

All sample containers will be labeled with the project identification, sample number, matrix, analysis required, and preservation used. Sample labels will be completed using waterproof ink. The completed sample labels will be affixed to each sample bottle and covered with clear tape.

The Site Superintendent or designee will review all field activities to determine whether proper custody procedures were followed during the field work and if additional samples are required.

## Transfer of Custody and Shipment

The custody of samples must be maintained from the time of sampling through shipment and relinquishment to the laboratory. Instructions for transferring custody are given below.

All samples are accompanied by a chain of custody. When transferring custody of sample, the individuals relinquishing and receiving will sign, date, and note the time on the chain of custody. This form documents sample custody transfer from the Site Superintendent or designee, through the shipper, to the analytical laboratory. Since a common carrier will usually not accept responsibility for handling chain of custody forms, the name of the carrier is entered under "Received by", the bill-of-lading number is recorded in the comments section, and the chain of custody form is placed in a zip-lock plastic bag and taped to the inside lid of the shipping cooler. Copies of the chain of custody forms will be placed in each cooler included in the shipment. Copies of the COC and bill of lading will be retained by the Site Superintendent and placed into the project files.

Samples will be packaged for shipment and dispatched by the appropriate laboratory via overnight delivery service. Samples will be shipped

within 24 hours of sampling. Shipping containers will be sealed for shipment to the laboratory. Two custody seals will be applied to each cooler to document that the container was properly sealed and to determine if the container was tampered with during shipment. The custody seals will be placed on the coolers in such a manner that the custody seal would be broken if the cooler were opened.

**Laboratory Custody Procedures**

A designated sample custodian accepts custody of the samples and verifies that all information on the sample labels matches that on the COC. The sample custodian will document any discrepancies and will sign and date all appropriate receiving documents. The sample custodian will also document the condition of the samples upon receipt by the laboratory.

Once the samples have been accepted by the laboratory, checked and logged in, they must be maintained in accordance with laboratory custody and security requirements.

To assure traceability of samples while in the possession of the laboratory, a unique laboratory identification number will be assigned to each sample.

The following stages of analysis must be documented by the laboratory:

- Sample extraction/preparation.
- Sample analysis.
- Data reduction.
- Data reporting.

Laboratory personnel are responsible for the custody of the samples until they are returned to the sample custodian.

**Final Evidence Files**

This is the final phase of sample custody. The COC records are archived in the project file. Laboratory custody forms, sample preparation and analysis logbook, and data packages will become part of the laboratory final evidence file. Other relevant documentation including records, reports, correspondence, logs, photographs, and data review reports will be archived by JV personnel.

## QAPP Worksheet #28-1 – Analytical Quality Control and Corrective Action (Semi-volatile Organic Compounds by SW846 8270D)

Matrix: Soil

Concentration Level: Low

Analytical Method: SW846 8270D

Laboratory SOP: L-1 (RTI) / L-6 (TA)

| QC Sample | Frequency/Number | Method/SOP QC Acceptance Limits | Corrective Action | Person(s) Responsible for Corrective Action | DQI | Measurement Performance Criteria |
|---|---|---|---|---|---|---|
| Field duplicate | 1 per 10 field samples | RPD of all analytes ≤ 50% | Qualify the specific analyte(s) in the parent sample and field duplicate. | Data validator | Precision | RPD of all analytes ≤ 50% |
| Method blanks | One per preparatory batch up to 20 samples of the same matrix. | No analytes detected > ½ LOQ | Correct problem. If required, re-prepare and reanalyze method blank and all samples processed with the contaminated blank. | Lab analysts and/or data validator | Accuracy/bias Contamination | No target analytes detected > ½ LOQ |
| LCS | One per preparatory batch up to 20 samples of the same matrix. | %R, See Appendix C, Table 25 DoD QSM V5.0 | Correct problem. If required, re-prepare and reanalyze all samples in the associated preparatory batch for the failed analytes, if sufficient sample material is available. | Laboratory analyst and/or data validator | Accuracy/bias | %R, See Appendix C, Table 25 DoD QSM V5.0 |
| MS | One per preparatory batch up to 20 samples of the same matrix. | %R, See Appendix C, Table 25 DoD QSM V5.0 | Qualify the specific analyte(s) in the parent sample and explain in the case narrative. | Laboratory analyst and/or data validator | Accuracy/bias | %R, See Appendix C, Table 25 DoD QSM V5.0 |
| MSD | One per preparatory batch up to 20 samples of the same matrix. | RPD of all analytes ≤ 20% | Qualify the specific analyte(s) in the parent sample and explain in the case narrative. | Laboratory analyst and/or data validator | Precision | RPD ≤ 20% |
| Surrogates | Add to all field and QC samples | %R, See Appendix C, Table 25 DoD QSM V5.0 | Correct problem, the re-prepare and reanalyze all failed samples for all surrogates in the associated preparatory batch, if sufficient sample material is available. If obvious chromatographic interference with surrogate is present, reanalysis may not be necessary. | Laboratory analyst and/or data validator | Accuracy/bias | %R, See Appendix C, Table 25 DoD QSM V5.0 |

## QAPP Worksheet #28-1 – Analytical Quality Control and Corrective Action (Semi-volatile Organic Compounds by SW846 8270D)

Matrix: Soil

Concentration Level: Low

Analytical Method: SW846 8270D

Laboratory SOP: L-1 (RTI) / L-6 (TA)

| QC Sample | Frequency/Number | Method/SOP QC Acceptance Limits | Corrective Action | Person(s) Responsible for Corrective Action | DQI | Measurement Performance Criteria |
|---|---|---|---|---|---|---|
| Internal standards | Six per sample and QC samples | Area response and retention times, See Table 4 DoD QSM V5.0 | Inspect mass spectrometer and GC for malfunctions and correct problem. Reanalysis of samples analyzed while system was malfunctioning is mandatory. If corrective action fails in field samples, data must be qualified and explained in the case narrative | Laboratory analyst | Precision | Area response and retention times, See Table 4 DoD QSM V5.0 |

## QAPP Worksheet #28-2 – Analytical Quality Control and Corrective Action (Explosives/Nitroaromatics and Nitramines by SW846 8330B)

Matrix: Soil

Concentration Level: Low

Analytical Method: SW846 8330B

Laboratory SOP: L-2 (RTI) / L-7 (TA)

| QC Sample | Frequency/Number | Method/SOP QC Acceptance Limits | Corrective Action | Person(s) Responsible for Corrective Action | DQI | Measurement Performance Criteria |
|---|---|---|---|---|---|---|
| Soil grinding blank | Prior to grinding samples; after every 10 samples; and at the end of the batch. | A grinding blank using clean solid matrix (such as Ottawa sand) must be prepared (e.g., ground and subsampled) and analyzed in the same manner as a field sample. No reported analytes must be detected > ½ LOQ. | Blank results must be reported and the affected samples must be flagged accordingly if blank criteria are not met. | Laboratory analyst and/or data validator | Contamination | No target analytes detected greater than ½ the LOQ |
| Soil sample triplicate | At the subsampling step, one sample per batch. Cannot be performed on any sample identified as a blank. | Three 10 gram subsamples are taken from a sample expected to contain the highest level of explosives within the quantitation range of the method. The RSD for results above the LOQ must not exceed 20%. | Qualify the specific analyte(s) in the parent sample and explain in the case narrative. | Laboratory analyst and/or data validator | Representativeness | RSD <20% for results above the LOQ |
| Field duplicate | 1 per 10 field samples | RPD of all analytes ≤ 50% | Qualify the specific analyte(s) in the parent sample and field duplicate. | Data validator | Precision | RPD ≤ 50% |

## QAPP Worksheet #28-2 – Analytical Quality Control and Corrective Action (Explosives/Nitroaromatics and Nitramines by SW846 8330B)

Matrix: Soil

Concentration Level: Low

Analytical Method: SW846 8330B

Laboratory SOP: L-2 (RTI) / L-7 (TA)

| QC Sample | Frequency/Number | Method/SOP QC Acceptance Limits | Corrective Action | Person(s) Responsible for Corrective Action | DQI | Measurement Performance Criteria |
|---|---|---|---|---|---|---|
| Method blanks | One per preparatory batch up to 20 samples of the same matrix. | No target analytes detected > ½ LOQ | Correct problem. If required, re-prepare and reanalyze method blank and all samples processed with the contaminated blank. | Laboratory analyst and/or data validator | Accuracy/bias Contamination | No target analytes detected > ½ LOQ |
| LCS | One per preparatory batch up to 20 samples of the same matrix. | %R, See Appendix C, Table 37 DoD QSM V5.0 | Correct problem. If required, re-prepare and reanalyze all samples in the associated preparatory batch for the failed analytes, if sufficient sample material is available. | Laboratory analyst and/or data validator | Accuracy/bias | %R, See Appendix C, Table 37 DoD QSM V5.0 |
| MS | One per preparatory batch up to 20 samples of the same matrix. | %R See Appendix C, Table 37 DoD QSM V5.0 | Qualify the specific analyte(s) in the parent sample and explain in the case narrative. | Laboratory analyst and/or data validator | Accuracy/bias | %R See Appendix C, Table 37 DoD QSM V5.0 |
| MSD | One per preparatory batch up to 20 samples of the same matrix. | RPD of all analytes ≤ 20% | Qualify the specific analyte(s) in the parent sample and explain in the case narrative. | Laboratory analyst and/or data validator | Precision | RPD ≤ 20% |

## QAPP Worksheet #28-2 – Analytical Quality Control and Corrective Action (Explosives/Nitroaromatics and Nitramines by SW846 8330B)

Matrix: Soil

Concentration Level: Low

Analytical Method: SW846 8330B

Laboratory SOP: L-2 (RTI) / L-7 (TA)

| QC Sample | Frequency/Number | Method/SOP QC Acceptance Limits | Corrective Action | Person(s) Responsible for Corrective Action | DQI | Measurement Performance Criteria |
|---|---|---|---|---|---|---|
| Surrogates | Add to all field and QC samples | %R, See Appendix C, Table 37 DoD QSM V5.0 | Correct problem, the re-prepare and reanalyze all failed samples for all surrogates in the associated preparatory batch, if sufficient sample material is available. If obvious chromatographic interference with surrogate is present, reanalysis may not be necessary. | Laboratory analyst and/or data validator | Accuracy/bias | %R, See Appendix C, Table 37 DoD QSM V5.0 |
| Confirmation of positive results (second column) | All positive results must be confirmed. | QC criteria are the same for the confirmation analysis as for initial or primary column analysis. Results between primary and second column RPD ≤ 40%. | Qualify the specific analyte(s) in the sample and explain in the case narrative. | Laboratory analyst and/or data validator | Precision | RPD ≤ 40% |

# QAPP Worksheet #28-3 – Analytical Quality Control and Corrective Action (Perchlorate by SW846 6850)

Matrix: Soil

Concentration Level: Low

Analytical Method: SW846 6850

Laboratory SOP: L-3 (RTI) / L-8 (TA)

| QC Sample | Frequency/Number | Method/SOP QC Acceptance Limits | Corrective Action | Person(s) Responsible for Corrective Action | DQI | Measurement Performance Criteria |
|---|---|---|---|---|---|---|
| Isotope ratio $^{35}Cl/^{37}Cl$ | Every sample, batch QC sample, and standard | Monitor for either the parent ion at masses 99/101 or the daughter ion at masses 83/85 depending on which ions are quantitated. Must fall within 2.3 to 3.8. | If criteria are not met, the sample must be rerun. If the sample was not pretreated, the sample must be re-extracted using cleanup procedures. If, after cleanup, the ratio still fails, use alternative techniques to confirm presence of perchlorate, e.g., a post spike sample or dilution to reduce any interference. | Laboratory analyst | Accuracy/bias | Must fall within 2.3 to 3.8 |
| Interference Check Sample | One per preparatory batch up to 20 samples of the same matrix. | Perchlorate concentration within ±20% of its true value. | Correct problem. Reanalyze all samples and QC samples in the batch. If poor recovery from the cleanup filters is suspected, a different lot of filters must be used to re-extract all samples in the batch. If column degradation is suspected, a new column must be calibrated before the samples can be reanalyzed. | Laboratory analyst | Accuracy/bias | Concentration with ±20% of its true value |
| Field duplicate | 1 per 10 field samples | RPD of all analytes ≤ 50% | Qualify the specific analyte(s) in the parent sample and field duplicate. | Data validator | Precision | RPD ≤ 50% |

# QAPP Worksheet #28-3 – Analytical Quality Control and Corrective Action (Perchlorate by SW846 6850)

Matrix: Soil

Concentration Level: Low

Analytical Method: SW846 6850

Laboratory SOP: L-3 (RTI) / L-8 (TA)

| QC Sample | Frequency/Number | Method/SOP QC Acceptance Limits | Corrective Action | Person(s) Responsible for Corrective Action | DQI | Measurement Performance Criteria |
|---|---|---|---|---|---|---|
| Laboratory Reagent Blank | Prior to calibration and at the end of the analytical sequence. | No perchlorate detected > ½ LOQ. | Reanalyze reagent blank (until no carryover is observed) and all samples processed since the contaminated blank. | Laboratory analyst and/or data validator | Accuracy/bias Contamination | No perchlorate detected > ½ LOQ |
| Method blank | One per preparatory batch up to 20 samples of the same matrix. | No perchlorate detected > ½ LOQ. | Correct problem. If required, re-prepare and reanalyze method blank and all samples processed with the contaminated blank. | Laboratory analyst and/or data validator | Accuracy/bias Contamination | No target analytes detected > ½ LOQ |
| LCS | One per preparatory batch up to 20 samples of the same matrix. | %R, See Appendix C, Table 7 DoD QSM V5.0. | Correct problem. If required, re-prepare and reanalyze all samples in the associated preparatory batch for the failed analytes, if sufficient sample material is available. | Laboratory analyst and/or data validator | Accuracy/bias | %R, See Appendix C, Table 7 DoD QSM V5.0. |
| MS | One per preparatory batch up to 20 samples of the same matrix. | %R, See Appendix C, Table 7 DoD QSM V5.0. | Qualify the specific analyte(s) in the parent sample and explain in the case narrative. | Laboratory analyst and/or data validator | Accuracy/bias | %R, See Appendix C, Table 7 DoD QSM V5.0. |
| MSD or matrix duplicate | One per preparatory batch up to 20 samples of the same matrix. | RPD of all analytes ≤ 15% (between MS and MSD or sample and matrix duplicate). | Qualify the specific analyte(s) in the parent sample and explain in the case narrative. | Laboratory analyst and/or data validator | Precision | RPD ≤ 15% |

# QAPP Worksheet #28-3 – Analytical Quality Control and Corrective Action (Perchlorate by SW846 6850)

Matrix: Soil

Concentration Level: Low

Analytical Method: SW846 6850

Laboratory SOP: L-3 (RTI) / L-8 (TA)

| QC Sample | Frequency/Number | Method/SOP QC Acceptance Limits | Corrective Action | Person(s) Responsible for Corrective Action | DQI | Measurement Performance Criteria |
|---|---|---|---|---|---|---|
| Internal Standard | Addition of $^{18}O$-labeled perchlorate to every sample, batch QC sample, standard, instrument blank, and method blank. | Measured $^{18}O$ IS area within ±50% of the value from the average of the IS area counts of the initial calibration. Relative retention time of the perchlorate ion must be 1.0 ±2% (0.98-1.02). | Rerun the samples are increasing dilutions until the ±50% acceptance criteria are met. If criteria cannot be met with dilution, the interference is suspected and the sample must be re-prepared using additional pretreatment steps. | Laboratory analyst | Accuracy/bias | IS area within ±50% and relative retention time 1.0±2% (0.98-1.02) |

# QAPP Worksheet #28-4 – Analytical Quality Control and Corrective Action (Metals[1] by SW846 6010C/7471B)

Matrix: Soil

Concentration Level: Low

Analytical Method: SW846 6010C/7471B

Laboratory SOP: L-4, L-5 (RTI) / L-9, L-10 (TA)

| QC Sample | Frequency/Number | Method/SOP QC Acceptance Limits | Corrective Action | Person(s) Responsible for Corrective Action | DQI | Measurement Performance Criteria |
|---|---|---|---|---|---|---|
| Linear dynamic range or high-level check standard | At initial set up and checked every six months with a high standard at the upper limit of the range. | %R within ±10% of true value. | Dilute samples within the calibration range, or reestablish/verify the linear dynamic range. | Laboratory analyst | Accuracy/bias | %R within ±10% of true value |
| Method blanks | One per preparatory batch up to 20 samples of the same matrix. | No analytes detected > ½ LOQ | Correct problem. If required, re-prepare and reanalyze method blank and all samples processed with the contaminated blank. | Laboratory analyst and/or data validator | Accuracy/bias Contamination | No target analytes detected > ½ LOQ |
| LCS | One per preparatory batch up to 20 samples of the same matrix. | %R, See Appendix C, Table 3 (6010) and Table 11 (7471), DoD QSM V5.0 | Correct problem. If required, re-prepare and reanalyze all samples in the associated preparatory batch for the failed analytes, if sufficient sample material is available. | Laboratory analyst and/or data validator | Precision | %R, See Appendix C, Table 3 (6010) and Table 11 (7471), DoD QSM V5.0 |
| MS | One per preparatory batch up to 20 samples of the same matrix. | %R, Same as LCS | Qualify the specific analyte(s) in the parent sample and explain in the case narrative. | Laboratory analyst and/or data validator | Accuracy/bias | %R, Same as LCS |
| MSD or matrix duplicate | One per preparatory batch up to 20 samples of the same matrix. | RPD of all analytes ≤ 20% (between MS and MSD or sample and matrix duplicate). | Qualify the specific analyte(s) in the parent sample and explain in the case narrative. | Laboratory analyst and/or data validator | Precision | RPD ≤ 20% |

# QAPP Worksheet #28-4 – Analytical Quality Control and Corrective Action (Metals[1] by SW846 6010C/7471B)

Matrix: Soil

Concentration Level: Low

Analytical Method: SW846 6010C/7471B

Laboratory SOP: L-4, L-5 (RTI) / L-9, L-10 (TA)

| QC Sample | Frequency/Number | Method/SOP QC Acceptance Limits | Corrective Action | Person(s) Responsible for Corrective Action | DQI | Measurement Performance Criteria |
|---|---|---|---|---|---|---|
| Serial Dilution test | One per preparatory batch if MS or MSD fails. Only applicable for samples with concentrations > 50x LOQ. Use with MS/MSD and PDS to confirm matrix effects. | Five-fold dilution must agree within ±10% of the original measurement. | Qualify the specific analyte(s) in the parent sample and explain in the case narrative. | Laboratory analyst and/or data validator | Accuracy/bias | %R within ±10% of original measurement |
| Post Digestion Spike | One per preparatory batch if MS or MSD fails (using the same sample as used for the MS/MSD if possible). | %R within 80-120% | Qualify the specific analyte(s) in the parent sample and explain in the case narrative. | Laboratory analyst and/or data validator | Accuracy/bias | %R within 80-120% |
| Field duplicate | 1 per 10 field samples | RPD of all analytes ≤ 50% | Qualify the specific analyte(s) in the parent sample and field duplicate. | Data validator | Precision | RPD of all analytes ≤ 50% |

**Notes:**

1. RCRA metals include: arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver.

## QAPP Worksheet #29 – Project Documents and Records

| Record | Generation | Verification | Storage location/archival |
|---|---|---|---|
| **Sample Collection and Field Records** | | | |
| Field logbook or data collection sheets<br>COC forms<br>Air bills<br>Contractor daily QC reports<br>Deviations<br>Corrective action reports<br>Correspondence<br>Field audit checklists | Dewey Thedford<br>Site Manager<br>JV | Mike Madl, Technical Lead<br>JV | Project file |
| Data verification checklists | Lyndi Mott, Program Chemist<br>JV | Mike Madl, PM<br>JV | Project file |
| Data validation report<br>Data usability assessment report | JV Data Validator, TBD | Lyndi Mott, Program Chemist<br>JV | Project file |
| **Laboratory Records** | | | |
| COC records<br>Sample receipt records<br>Electronic data deliverables<br>Analytical results and supporting data<br>Sample data packages | David Vesey, PM<br>RTI<br><br>Erika Gish, PM<br>TestAmerica St. Louis | Charles O'Bryan, QA Manager<br>RTI<br><br>Marti Ward, QA Manager<br>TestAmerica St. Louis | Project file |
| Records of sample preparation<br>Records of sample analysis<br>Instrument calibration records<br>Raw data files | David Vesey, PM<br>RTI<br><br>Erika Gish, PM<br>TestAmerica St. Louis | Charles O'Bryan, QA Manager<br>RTI<br><br>Marti Ward, QA Manager<br>TestAmerica St. Louis | Project file |

## QAPP Worksheet #31, 32, & 33 – MC Assessments and Corrective Actions

**Assessments:** See Worksheet 14&16 for estimated dates

| Assessment Type | Responsible Party & Organization | Number/Frequency | Estimated Dates | Assessment Deliverable | Deliverable Due Date |
|---|---|---|---|---|---|
| Review of QAPP, SOPs, and daily QC report with field staff | Field Team Leader<br>JV | Prior to sampling start up | Prior to sampling | Contained within daily QC report. | Prior to sampling |
| Daily logbook and field forms | Field Team Leader<br>JV | Daily | During field activities | Contained within written report. | As part of Draft Report |
| Laboratory assessment for appropriate certifications and capacity; QAPP review with laboratory staff | Lyndi Mott, Program Chemist<br>JV | Prior to sampling start up | Prior to sampling | Receipt of copies of certifications. Email traffic concerning laboratory capacity prior to sampling start up. QAPP sign-off sheet received from laboratory. | Prior to sampling |
| Daily tailgate safety meeting | Field Team Leader<br>JV | Daily | During field activities | Verbal debriefing and daily sign off log. If a safety violation occurs, an incident report is completed. | Last deliverable received no later than one week after field activities |
| Field sampling and COC review against QAPP requirements | Field Team Leader<br>JV | Daily | During field activities | Communication in the form of an email. | Last email received no later than 24 hours after last sampling event |
| Laboratory report deliverables and analytical results review against QAPP requirements | Lyndi Mott, Program Chemist<br>JV | Per sample delivery group | Immediately following field sampling | Communication if the form of an email. | Three weeks after receipt of data |
| Data verification | Lyndi Mott, Program Chemist<br>JV | Per sample delivery group | Following analytical report | Communication in the form of an email requesting additional laboratory forms, backup data that may be missing and/ or clarification of the analytical report. | Three weeks after receipt of data |
| Data validation | Lyndi Mott, Program Chemist<br>JV | Per sample delivery group | Following analytical report | Communication in the form of an email requesting additional laboratory forms, backup data that may be missing and/ or clarification of the analytical report. | Three weeks after receipt of data |

## Assessment Response and Corrective Action:

| Assessment Type | Responsibility for Responding to Assessment Findings | Assessment Response Documentation | Timeframe for Response | Responsibility for Implementing Corrective Action | Responsibility for Monitoring Corrective Action Implementation |
|---|---|---|---|---|---|
| Review of QAPP, SOPs, and daily QC report with field staff | Mike Madl, Technical Lead<br>JV | Daily QC report will be amended with corrective action | Within 24 hours | Dewey Thedford, Site Manager<br>JV | Mike Madl, Technical Lead, JV |
| Daily logbook and field forms | Field Team Leader<br>JV | Daily QC report will be amended with corrective action | Within 24 hours | Dewey Thedford, Site Manager<br>JV | Mike Madl, Technical Lead, JV |
| Laboratory assessment for appropriate certifications and capacity; QAPP review with laboratory staff | Charles O'Bryan, QA Manager<br>RTI<br><br>Marti Ward, QA Manager<br>TestAmerica St. Louis | Response to email | Within 48 hours after notification | Charles O'Bryan, QA Manager<br>RTI<br><br>Marti Ward, QA Manager<br>TestAmerica St. Louis | Lyndi Mott, Program Chemist<br>JV |
| Daily tailgate safety meeting | Mike Madl, Technical Lead<br>JV | Included as part of the Incident Report | Within 48 hours after notification | Dewey Thedford, Site Manager<br>JV | Mike Madl, Technical Lead, JV |
| Field sampling and COC review against QAPP requirements | Mike Madl, Technical Lead<br>JV | Response to email | Within 24 hours after sampling | Dewey Thedford, Site Manager<br>JV | Mike Madl, Technical Lead, JV |
| Laboratory report deliverables and analytical results review against QAPP requirements | Charles O'Bryan, QA Manager<br>RTI<br><br>Marti Ward, QA Manager<br>TestAmerica St. Louis | If required, laboratory reports will be amended and corrections noted in the case narrative | Within 72 hours of notification | Charles O'Bryan, QA Manager<br>RTI<br><br>Marti Ward, QA Manager<br>TestAmerica St. Louis | Lyndi Mott, Program Chemist<br>JV |
| Data verification | Charles O'Bryan, QA Manager<br>RTI<br><br>Marti Ward, QA Manager<br>TestAmerica St. Louis | If required, laboratory reports will be amended and corrections noted in the case narrative | Up to 7 days | Charles O'Bryan, QA Manager<br>RTI<br><br>Marti Ward, QA Manager<br>TestAmerica St. Louis | Lyndi Mott, Program Chemist<br>JV |
| Data validation | David Vesey, PM<br>RTI<br><br>Erika Gish, PM<br>TestAmerica St. Louis | If required, laboratory reports will be amended and corrections noted in the case narrative and documented in the validation report | Up to 7 days | David Vesey, PM<br>RTI<br><br>Erika Gish, PM<br>TestAmerica St. Louis | Lyndi Mott, Program Chemist<br>JV |

# QAPP Worksheet #34 – MC Data Verification and Validation Inputs

| Item | Description | Verification (completeness) | Validation (conformance to specifications) |
|---|---|---|---|
| **Planning Documents/Records** | | | |
| 1 | Approved QAPP | X | |
| 2 | Contract | X | |
| 3 | Field SOPs | X | |
| 4 | Laboratory SOPs | X | |
| **Field Records** | | | |
| 5 | Field logbooks | X | |
| 6 | Equipment calibration records | X | |
| 7 | COC forms | X | |
| 8 | Sampling diagrams/surveys | X | |
| 9 | MEC Dig Results | X | |
| 10 | Relevant correspondence | X | |
| 11 | Change orders/deviations | X | |
| 12 | Field audit reports | X | |
| 13 | Field corrective action reports | X | |
| **Analytical Data Package** | | | |
| 14 | Cover sheet (laboratory identifying information) | X | X |
| 15 | Case narrative | X | X |
| 16 | Internal laboratory chain of custody | X | X |
| 17 | Sample receipt records | X | X |
| 18 | Sample chronology (i.e., dates and times of receipt, preparation, and analysis) | X | X |
| 19 | Communication records | X | X |
| 20 | Project-specific proficiency testing sample results | X | X |
| 21 | LOD/LOQ establishment and verification | X | X |
| 22 | Standards traceability | X | X |
| 23 | Instrument calibration records | X | X |
| 24 | Definition of laboratory qualifiers | X | X |
| 25 | Results reporting forms | X | X |
| 26 | QC sample results | X | X |
| 27 | Corrective action reports | X | X |
| 28 | Raw data | X | X |
| 29 | EDD | X | X |

## QAPP Worksheet #35 – MC Data Verification Procedures

| Records Reviewed | Required Documents | Process Description | Responsible Person, Organization |
|---|---|---|---|
| Field logbook (sampling methods and procedures) | UFP-QAPP<br><br>Field SOPs | Establish that required sampling methods were used and documented. Establish that any required field monitoring was performed and results are documented. Verify that the sampling procedures and field measurements met performance criteria and that any deviations were documented in the field logbook. | *Daily* –<br>Dewey Thedford, Site Manager, JV<br><br>*At conclusion of field activities* –<br>Lyndi Mott, Program Chemist, JV |
| Field logbook (documentation) | UFP-QAPP<br><br>Field SOPs | Verify the records are present and complete for each day of field activities. Verify that all planned samples, including field QC samples, were collected and the sample collection locations are documented. Verify that meteorological data were provided for each day of field activities. Verify that changes/exceptions are documented and were reported in accordance with requirements. | *Daily* –<br>Dewey Thedford, Site Manager, JV *At conclusion of field activities* –<br>Lyndi Mott, Program Chemist, JV |
| COC forms | UFP-QAPP<br><br>Field SOPs<br><br>Laboratory SOPs/QA Manual | All samples to be analyzed by the laboratory will be shipped via overnight delivery service under COC. Prior to shipment of the samples to the laboratory, the COC will be checked by the Site Superintendent or representative for completeness and correctness. Upon receipt at the laboratory, the sample custodian will check the COC forms and shipping documentation for verification against the sample coolers they represent, and will sign and data the COC to acknowledge sample receipt. The laboratory is responsible for verifying the integrity of the custody seals and that the sample containers are received in good condition. The Laboratory Information Management System will provide evidence of sample custody from receipt by the laboratory until appropriate disposal. | *Daily* –<br>Dewey Thedford, Site Manager, JV<br><br>*Upon receipt* –<br>Sample Custodian, RTI<br><br>Sample Custodian, TestAmerica St. Louis |

## QAPP Worksheet #35 – MC Data Verification Procedures

| Records Reviewed | Required Documents | Process Description | Responsible Person, Organization |
|---|---|---|---|
| Laboratory corrective action and report procedure | UFP-QAPP<br><br>Laboratory SOPs/QA Manual | Routine corrective actions apply to all analytical quality control parameters and analytical system specification as defined in the laboratory SOPs. Bench analysts have full responsibility and authority for performing routine corrective action, which are documented as part of the analytical record. Defective processes, holding time violations, systematic errors and quality defects that occur are to be reported by the analyst to the laboratory supervisor and a non-conformance record initiated. The Laboratory PM will then notify the JV Program Chemist and PM. All notifications must be made in a timely manner. The non-conformance record should become part of the analytical record. | *Before release* –<br>Charles O'Bryan, QA Manager, RTI<br><br>Marti Ward, QA Manager, TestAmerica St. Louis<br><br>*Upon receipt* –<br>Lyndi Mott, Program Chemist, JV |
| Analytical data package | UFP-QAPP<br><br>Laboratory SOPs/QA Manual | All data produced by the laboratory will be required to undergo several levels of review, which will include two levels of management review at the laboratory. The laboratory will review the data packages internals for completeness and verification that all of the required forms and raw data are included for each data package type. The laboratory QA Manager may also select to review randomly chosen data packages for additional internal audits. Any deviations should be documented in the report narrative. | Charles O'Bryan, QA Manager, RTI<br><br>Marti Ward, QA Manager, TestAmerica St. Louis |
| Analytical data package | UFP-QAPP<br><br>Laboratory SOPs<br><br>DOD QSM, ver 5.0 (July 2013)<br><br>USACE EM 200-1-10, June 2005 | The Program Chemist or Data Validator will verify that data have been received for all samples sent to the laboratory. An evaluation of the data will be performed to determine whether the laboratory met the QC requirements for the analysis as stated in the analytical method, laboratory SOPs, UFP-QAPP, DoD QSM, ver 5.0 (July 2013), and USACE EM 200-1-10 (June 2005).. This verification should include (at a minimum): (1) review of dates of sample preparations and analyses to verify they have been performed within applicable holding times, (2) review of associated blanks for potential contamination, (3) determination that project quantitation limits were achieved, and (4) review of QC sample performance criteria. Any deviations should be documented in the report narrative. | Lyndi Mott, Program Chemist, JV<br><br>Data Validator, JV |

## QAPP Worksheet #35 – MC Data Verification Procedures

| Records Reviewed | Required Documents | Process Description | Responsible Person, Organization |
|---|---|---|---|
| Laboratory EDD | UFP-QAPP<br><br>Automated Data Review (ADR) specifications | The laboratory will provide EDDs in accordance with the Staged Electronic Data Deliverable (SEDD) version 5.2 (or the most recent format). The EDD will be reviewed using ADR software for correctness and completeness with 90% Stage 2b ADR, 10% Stage 3 ADR. | Lyndi Mott, Program Chemist, JV<br><br>Data Validator, JV |

## QAPP Worksheet #36 – MC Data Validation Procedures

| Data Validator: JV | |
|---|---|
| *Analytical group/method:* | SVOCs, Explosives, Perchlorate, RCRA 8 Metals |
| *Data deliverable requirements:* | SEDD Stage 2B XML file |
| *Analytical specifications:* | SVOCs by SW846 8270D<br>Explosives by SW846 8330B<br>Perchlorate by SW846 6850<br>Metals by SW846 6010C/7471B |
| *Measurement performance criteria:* | DoD QSM version 5.0 (see Worksheets #12 and #28) |
| *Percent of data packages to be validated*[1]*:* | 90% Stage 2<br>10% Stage 4 |
| *Percent of raw data reviewed:* | 10% |
| *Percent of results to be recalculated:* | 10% |
| *Validation procedures:* | WP/UFP-QAPP, DoD QSM version 5.0 (July 2013), and USACE EM 200-1-10 Guidance for Evaluating Performance Based Chemical Data (June 2005) |
| *Electronic validation program/version:* | ADR |

**Notes:**
[1] 100% of the data will be reviewed and verified. 100% of the data packages/EDDs will be reviewed using ADR.

## QAPP Worksheet #37 – MC Usability Assessment

The Data Usability Assessment will be performed by JV for data associated with the Parcel 3, Fort Wingate Depot Activity, New Mexico. Data validation will be performed by JV personnel in the information management/data validation group whom are not directly involved in the project, sample/data collection, or analysis in order to keep the data validation independent of the JV project team. Documentation generated during the Data Usability Assessment will consist of data validation report with a summary of overall data usability and a summary table of qualified results, as described by the USACE Guidance, EM 200-1-10. 100% of the data collected will be reviewed and verified at a Stage 2 using ADR to complete the data review. Ten percent of all samples, critical and non-critical, will undergo a full data validation (i.e., Stage 4).

The Data Usability Assessment process involves data verification and validation. Data verification is the process by which laboratory results are checked to provide that the proper QC steps were performed and key items have met QC objectives (both analytical and contractual). Key steps of the data verification include:

- identifying sample collection, handling and analysis procedures
- documenting handling and analysis activities (e.g., QC checklist)
- verifying (internally, at the data generator level) all sampling, handling, on-site analytical laboratory data
- verifying laboratory data (e.g., laboratory-qualified data)
- verifying sampling, on-site analytical laboratory data
- verifying data package deliverable completeness
- reviewing the case narrative
- presenting all analytical results
- summarizing QC sample data
- evaluating applicable raw data

All required data deliverables must be present in the data package in order to proceed to the next step of data validation.

Data validation entails a review of the sample collection, handling, QC data, and the raw data to verify that the laboratory was operating within required limits, analytical results were correctly transcribed from the instrument read-outs and which (if any) environmental samples were related to out-of-control QC samples. The objective of data validation is to identify any questionable or invalid laboratory measurements.

## QAPP Worksheet #37 – MC Usability Assessment

The DQIs used to evaluate conformance with the project DQOs are presented below.

DQIs are generally defined in terms of six parameters:

1. representativeness
2. comparability
3. completeness
4. precision
5. accuracy
6. sensitivity

Each parameter is defined below. Specific objectives for the site actions are presented in other sections of this QAPP, as referenced below.

**Representativeness**

Representativeness is the degree to which sampling data accurately and precisely represent site conditions, and is dependent on sampling and analytical variability and the variability of environmental media at the site. Actions have been designed to assess the presence of chemical constituents at the time of sampling. The QAPP presents the rationale for sample quantities and location. This QAPP presents field sampling and laboratory analytical methodologies. Use of the prescribed field and laboratory analytical methods with associated holding times and preservation requirements are intended to provide representative data.

**Comparability**

Comparability is the degree of confidence with which one data set can be compared to another. Comparability between phases of the actions (if additional phases are required) will be maintained through consistent use of the sampling and analytical methodologies set forth in this QAPP, established QA/QC procedures and use of appropriately trained personnel.

**Completeness**

Completeness is defined as a measure of the amount of valid data obtained from an event and/or investigation compared to the total amount that was obtained. This will be determined upon final assessment of the analytical results. Completeness of a field or laboratory data set will be calculated by comparing the number of valid sample results generated to the total number of results generated.

**QAPP Worksheet #37 – MC Usability Assessment**

$$\text{Completeness} = \frac{\text{Number valid results}}{\text{Total number of results generated}} \times 100$$

As a general guideline, overall project completeness is expected to be at least 90 percent. The assessment of completeness will require professional judgment to determine data usability for intended purposes.

**Precision**

Precision is a measure of the reproducibility of sample results. The goal is to maintain a level of analytical precision consistent with the objectives of the action. To maximize precision, sampling and analytical procedures will be followed. All work for the site actions will adhere to established protocols presented in the QAPP. Checks for analytical precision will include the analysis of matrix spike/matrix spike duplicates, laboratory duplicates and field duplicates. Checks for field measurement precision will include duplicate field measurements.

The precision of data will be measured by calculating the RPD by the following equation:

$$RPD = \frac{(A-B)}{(A+B)/2} \times 100$$

Where:

A = Analytical result from one of two duplicate measurements.

B = Analytical result from the second measurement.

**Accuracy**

Accuracy is a measure of how close a measured result is to the true value. Both field and analytical accuracy will be monitored through initial and continuing calibration of instruments. In addition, reference standards, MSs, blank spikes and surrogate standards will be used to assess the accuracy of the analytical data.

Accuracy will be calculated in terms of percent recovery as follows:

$$\%\ \text{Recovery} = \frac{A-X}{B} \times 100$$

**QAPP Worksheet #37 – MC Usability Assessment**

Where:

A = Value measured in spiked sample or standard.

X = Value measured in original sample.

B = True value of amount added to sample or true value of standard.

**Sensitivity**

Sensitivity is a quantitative measurement to determine if the analytical laboratory's procedures/methodologies and their associated detection limits (DLs) and limit of quantitation (LOQs) can satisfy the project requirements as they relate to the project action limits. DLs are updated annually by the laboratory. The current DLs for the analytical laboratories are presented in QAPP Worksheet #15.

**Data Validation and Usability**

JV will validate data generated using WP/UFP-QAPP, DOD QSM version 5.0 (July 2013) and USACE EM 200-1-10 Guidance for Evaluating Performance Based Chemical Data (June 2005). These procedures and criteria may be modified, as necessary, to address project-specific and method-specific criteria, control limits and procedures. Data validation will consist of data screening, checking, reviewing, editing and interpretation to document analytical data quality and to determine whether the quality is sufficient to meet the DQOs.

The data validator will verify that reduction of laboratory measurements and laboratory reporting of analytical parameters is in accordance with the procedures specified for each analytical method and/or as specified in this QAPP. Any deviations from the analytical method or any special reporting requirements apart from those specified in this QAPP will be detailed on COC forms.

Upon receipt of laboratory data, the following procedures will be executed by the data validator:

- Evaluate completeness of data package.
- Verify that field COC forms were completed and that samples were handled properly.
- Verify that holding times were met for each parameter. Holding time exceedances, should they occur, will be documented. Data for all samples exceeding holding time requirements will be flagged as either estimated or rejected. The decision as to which qualifier is more appropriate will be made on a case-by-case basis.
- Verify that parameters were analyzed according to the methods specified.
- Review QA/QC data (i.e., confirm that duplicates, blanks and spikes were analyzed on the required number of samples, as specified in the

**QAPP Worksheet #37 – MC Usability Assessment**

method and verify that duplicate and MS recoveries are acceptable).

- Investigate anomalies identified during review. When anomalies are identified, they will be discussed with the Project Manager and/or Laboratory Manager, as appropriate.
- If data appear suspect, investigate the specific data of concern. Calculations will be traced back to raw data. If calculations do not agree, the cause will be determined and corrected.

Deficiencies discovered as a result of the data review, as well as the corrective actions implemented in response, will be documented and submitted in the form of a written report addressing the following topics, as applicable to each method:

- assessment of the data package
- description of any protocol deviations
- failures to reconcile reported and/or raw data
- assessment of any compromised data
- overall appraisal of the analytical data
- table of site name, sample quantities, matrix and fractions analyzed

It should be noted that qualified results do not necessarily invalidate data. The goal to produce the best possible data does not necessarily mean that data must be produced without QC qualifiers. Qualified data can provide useful information.

During the review process, laboratory qualified and unqualified data are verified against the supporting documentation. Based on this evaluation, qualifier codes may be added, deleted or modified by the data reviewer. Results will be qualified with the following codes in accordance with the USACE guidance:

U Not detected: Analysis for the analyte was performed, but the analyte was not detected above the level of the associated value. The associated value is the LOD.

J Estimated: The analyte was detected and identified. The associated numerical value is the approximate concentration of the analyte in the sample.

UJ Not detected, LOD is estimated: The analyte was not detected above the reported LOD. The numerical value of the LOD is estimated

**QAPP Worksheet #37 – MC Usability Assessment**

and may be inaccurate.

NJ Tentatively identified, reported concentration is estimated: The analysis indicates the presence of an analyte for which there is presumptive evidence to make a tentative identification and the associated numerical value represents the approximate concentration. For example, analyte not included in the calibration or second column confirmation not performed.

R Rejected: The data are unusable.

X Tentatively rejected. project-specific data quality objectives (e.g., for sensitivity, accuracy, or precision) were not met or were not demonstrated

J+ Estimated (quantitatively) with high bias.

J- Estimated (quantitatively) with low bias.

Two facts will be noted to all data users. First, the "R" flag means that the associated value is unusable. In other words, due to significant QC problems, the analysis is invalid and provides no information as to whether the compound is present or not. Analytes with "R" values should not appear on data tables because they cannot be relied upon for any reason. The second fact is that no compound concentration, even if it has passed all QC tests, is guaranteed to be accurate. Strict QC serves to increase confidence in data, but any value potentially contains error.

Resolution of any issues regarding laboratory performance or deliverables will be handled between the laboratory and the data validator. Suggestions for reanalysis may be made by the Program Chemist at this point.

**Validation Reports**

The data validation reports will identify all deficiencies and the potential impact on the results. The JV Program Chemist (or his designee) will amend qualifiers generated during the validation process to the database. The validation checklists and the database will be the primary location of all applicable data qualifiers. Qualifiers will not be applied to the hard copy analytical reports.

**Field Data Review**

Field data are generated from in-field measurement, which may include a geophysical survey, well development and groundwater sampling. The quality objective for the in-field measurement activities is to obtain accurate measurements of sample characteristics, including aqueous pH, conductivity, temperature, turbidity and dissolved oxygen, using appropriate equipment. Data are recorded in field logbooks or on field sampling sheets and calibration logs. Calibration logs will be reviewed by the JV Site Manager, or designee with other field documentation to identify any potential impacts to data quality and usability. Field logbooks are reviewed as part of the QC inspections.

## QAPP Worksheet #37 – MC Usability Assessment

**Reconciliation with Data Usability Requirements**

Data results will be examined to determine the performance that was achieved for each data usability criterion. The performance will then be compared with the project objectives and DQOs. Deviations from objectives will be noted. Data that has been rejected will not be used. Data that has been qualified but not rejected will be considered useable (i.e., qualified as estimated) and definitive data. If there is an instance where further limitations must be placed on qualified data, the associated data is non-definitive data and should be used for screening purposes only.

Additional action may be warranted when performance does not meet performance objectives for critical data. Options for corrective action relating to incomplete information, questionable results or inconsistent data may include any or all of the following:

- retrieval of missing information
- request for additional explanation or clarification
- reanalysis of sample from extract (when appropriate)
- recalculation or reinterpretation of results by the laboratory

These actions may improve the data quality, reduce uncertainty and eliminate the need to qualify or reject data. If these actions do not improve the data quality to an acceptable level, the following additional actions may be taken:

- extrapolation of missing data from existing data points
- use of historical data
- evaluation of the critical/noncritical nature of the sample

If the data gap cannot be resolved by these actions, the data bias and potential for false negatives and positives can be evaluated. If the resultant uncertainty level is unacceptable, the following action must be taken:

- additional sample collection and analysis

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A JOINT VENTURE

Imagine the result

# MC SOP No. 1

# Incremental Sampling Methodology

Rev. #: 0

Revision Date: January 21, 2015

**Approval Signatures**

Prepared by: _____ Date: 1/21/2015
Rosemarie Potocky, PE

## I. Scope and Application

This Standard Operating Procedure (SOP) describes the general procedures to be employed in obtaining soil samples following Incremental Sampling Methodology (ISM). ISM is a structured composite sampling and processing protocol that reduces data variability and provides a reasonably unbiased estimate of mean contaminant concentrations in a volume of soil targeted for sampling.

ISM provides representative samples of specific soil volumes defined as decision units (DUs) by collecting numerous increments of soil (typically 30–100 increments) that are combined, processed, and subsampled according to specific protocols. The sampling density afforded by collecting many increments, together with the disciplined processing and subsampling of the combined increments, in most cases yields more consistent and reproducible results than those obtained by more traditional (i.e., discrete) sampling approaches. Generally, it would take dozens of discrete samples from any particular area to approach the reliability in an estimate of the mean provided by a well-designed incremental sampling approach (ITRC, 2012).

ISM works to overcome major sources of error in both sampling of soils that have often been apparent with current sampling practices. By design, ISM provides complete spatial coverage within the DU; however, ISM does not provide information on the spatial distribution of contaminants within the DU.

ISM is typically used for testing for energetics/explosives under USEPA SW-846 Method 8330B; however this method can now also be applied to SVOCs, pesticides, PCBs, and metals. ISM can also be applied to VOCs; however, VOC is not covered as part of this SOP.

It is recommended that all ISM sample processing be performed in a controlled laboratory setting to minimize sampling errors. The laboratory processing portion of ISM protocol will be addressed under the selected laboratory's SOP for ISM.

## II. Personnel Qualifications

ARCADIS field sampling personnel will have current health and safety training, including 40-hour HAZWOPER training, Department of Transportation training, site supervisor training, and site-specific training, as needed. In addition, ARCADIS field sampling personnel will be versed in the relevant SOPs and possess the skills and experience necessary to successfully complete the desired field work.

## III. Equipment List

The following equipment and materials will be available, as required:

- Incremental Sampling coring device (e.g. the ISM tool developed by Cold Regions Research and Engineering Laboratory [CRREL], hand augers, core sampling tools, step probes, etc.).[1] Different tools are shown in Figure 1.
- Pin flags, posts, or rope to mark off grid. Spray paint can be used, but it may affect the sample.
- Clean Zip-lock ® bags, 5-gallon plastic containers, or other appropriate large container for placing increments. The size of the container should be adequate to hold the 1-2 kilogram sample.
- Personal protective equipment (as required by the Health and Safety Plan [HASP]).
- Appropriate transport containers and packing, labeling, and shipping materials (coolers) with ice.
- Field notebook.
- Global Positioning System (GPS) device or other survey equipment to document locations of DUs.
- Decontamination supplies.

[1] The sampling tool should obtain cylindrical or core-shaped increments of a constant depth from the presented surface. The diameter of the sampling tool should be a minimum of three times the diameter (d) of the largest particle present in a coarse matrix ($d \geq 3$ mm), and $3d + 10$ mm for a fine material (Pitard, 1993). All samples should have a similar size and weight.

***Figure 1:*** *Examples of coring devices for non-volatile sample collection: Top to bottom: Multi-Incremental Sampling Tool (MIST™), EVC Incremental Sampler, JMC Backsaver Handle, and Soil Tube. (ITRC, 2012)*

## IV. Cautions

The selection of sampling location, equipment, and methodology needs to be made based on the constituents of concern, sampling objectives, and site conditions.

## V. Health and Safety Considerations

Working on or near steep and uneven terrain presents variety of hazards. Please consult the project HASP.

If sampling procedures are to occur in areas where unexploded ordnance (UXO) is known to exist or potentially exists, the area will not be entered until an UXO technician II or higher is available to provide escort and anomaly avoidance.. If, at any time, an unsafe condition is identified, stop work immediately until the unsafe condition is mitigated.

## VI. Procedure

### Defining Decision Units

***Decision Unit***—A DU is a specific area (or volume of soil) about which a decision is to be made.

***Grid Cell***—A grid cell is a sub-division of the DU. DUs are divided into uniform-size grid cells, and one increment is collected from each cell, from the same relative location within each grid cell. The shape of the cells is not specified—the only criterion for cell shape selection is that the cells should be of equal size (they can be triangular, square, rectangular, etc.) so the increments collected from each cell are equally weighted over the DU.

There are various approaches to defining DUs. The approach selected should be consistent with the understanding of the site reflected in the Conceptual Site Model and should support the objectives of the investigation. DUs may be defined in regularly spaced and equal volumes as established by exposure areas, or they may be based on irregular features of the site which define contaminant transport or receptor exposure. Alternatively, DUs may be based on an understanding of the contaminant distributions, for example, in and around source areas.

### Determining Sample Placement

ISM samples are composed of increments collected from specific points throughout the DU. The positioning of the collection points can be set using one of three approaches: simple random sampling (SRS), random sampling within a grid, and systematic random sampling. SRS involves determining random locations across the entire DU. Note that “random” in this context does not mean wherever the sampling team feels like taking a sample and that a formal approach to determining the random increment locations must be used. With random sampling within a grid, the DU is overlain with a sampling grid and soil increments are collected from random locations determined in each grid cell. Systematic random sampling is similar except that only the initial grid cell sampling location is randomly determined and the same relative location is sampled in each of the other grid cells.

SRS yields the most representative (least biased) estimate of the mean. However, it is also the least practical to implement since field staff have to navigate to predetermined locations non-uniformly positioned within the DU. Large portions of a DU may remain unsampled, which may not be acceptable to stakeholders. In practice, systematic random sampling is most often chosen for ease of implementation and to avoid the appearance of over- or underrepresentation of subareas within a DU, as may occur with SRS.

Incremental soil samples are prepared by collecting multiple increments of soil (typically 30 or more) from a specified DU and physically combining these increments into a single sample. As the DU gets significantly larger, the amount of distributional heterogeneity may increase; therefore, it may be necessary to increase the number of increments per DU to 50 or more. In general, a minimum of 30–50 increments is sufficient for most DUs. However, in published reports for solid/particulate-type chemicals of concern (COCs) (e.g., energetics/explosives, particulate metals, etc.) 50–100 increments per DU have been collected. USEPA SW-846 Method 8330B for explosives recommends collecting 30 or more evenly spaced increments to build a sample with a total mass of >1 kilogram. The number of increments per DU will be specified in the Field Sampling Plan.

**Setting The Grid**

A square, rectangular, circular, or other naturally or structurally defined DU (e.g., 5 m perimeter around the exterior of a building) is first subdivided or gridded-off into uniform cells or subareas based on the desired number of increments to be obtained. That is, the number of cells is equivalent to the number of increments. Using the systematic random design, a random position is established for a given cell, and then the same position is repeated in all of the remaining cells in the DU. For the random sampling within grids design, a random position is designated and sampled in each cell. The process is repeated for replicate samples; i.e., a new random position is established for the single collection point to be repeated in all of the cells, or for each cell, depending on the sampling design. A GPS device should be used to delineate the DU. It may or may not be necessary to determine the exact location of each increment depending on the data quality objectives (DQOs) specified during the systematic planning process.

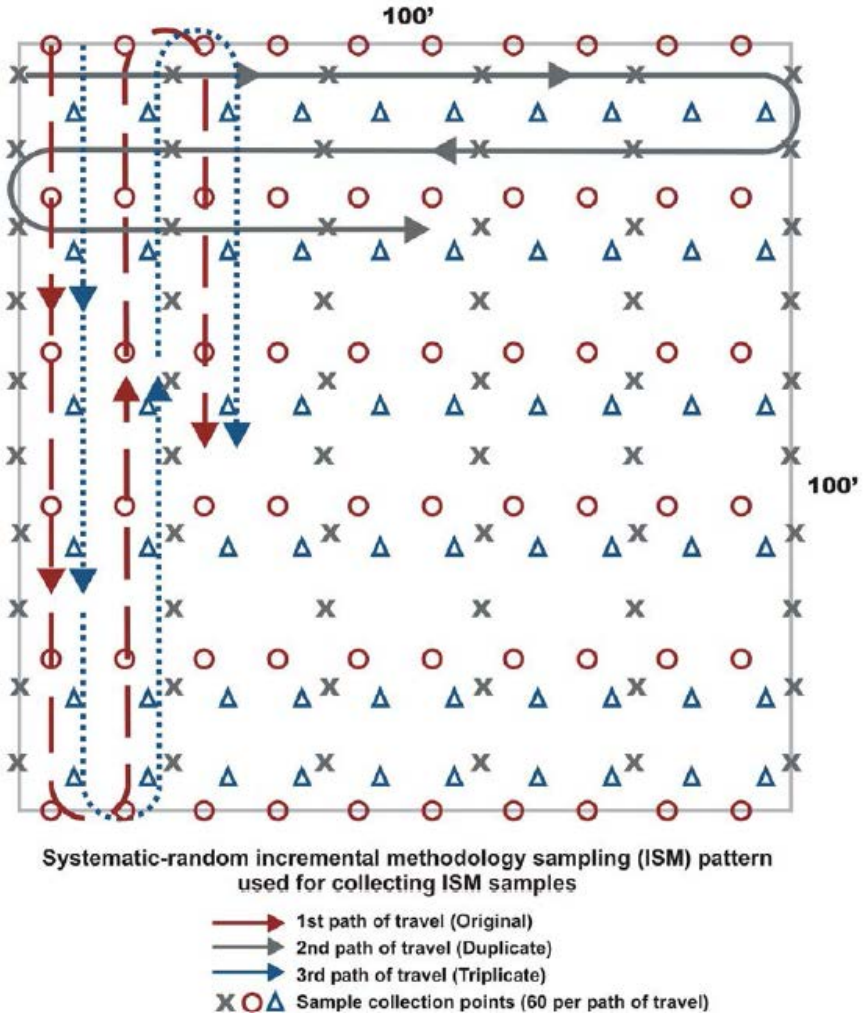
Depending on the size of the DU and terrain features, placement of markers (e.g., pin flags and posts) at the corners and or edges can assist with a visual delineation of the cells or subareas where increments are to be collected. The markers can define lanes, grids, or collection points. Row lengths and increments per row should be constant for regular-shaped DUs (e.g. square or rectangular) but may be modified as needed for odd-shaped DUs. The perimeter should be marked and flags should be prepositioned across the DU in one or more perpendicular lines prior to the start of sampling.

**Sample Collection and Decontamination**

Increments of soil will be collected within each grid cell of the DU. Increments should be approximately of the same size and weight. For surface soil sampling, a coring tool will be used to facilitate the rapid collection of uniform, representative increments from a consistent depth interval. This way, equal volumes are collected for each increment and equal mass is obtained under the assumption that the density of the sampled medium is uniform across the cell of the DU. The size of the coring tool will be selected based on the volume of the increments, which is in turn calculated based on number and depth of the increments and the fact that an adequate total sample mass is typically 1-2 kilograms dry weight (to overcome effects of compositional heterogeneity due to the inherent particulate nature of soil and sediment).

A two-person team is the most efficient method for collecting samples, with one person collecting the increments and the other holding the sample container (e.g., clean polyethylene bag). The second person will also keep track of the number of increments collected at each DU. The ISM sampler starts in one corner or end of the DU and collects an increment at the predetermined positions (described above) using the selected sampling tool. For the systematic random sampling design, the location of the first increment is determined randomly, and subsequent increments are collected in the same relative location within each grid, resulting in a serpentine collection pattern ending at the opposite corner or end of the DU from where sampling was started (see Figure 2).

***Figure 2:*** *Sample collection using SRS (ITRC, 2012)*




To collect an increment, set the tip of the corer at the desired location, step on the footrest to force the tip into the soil, push until progress stops, tip and pull the tool out of the soil, and then push on the plunger to eject the soil plug into the resealable sample bag or bucket. Do not spear the tip into the ground, as this may damage the tip if stones are present. Furthermore, the increment location need not be precisely at a grid point. If a large cobble or root is at the sample point, take the sample increment from a point as near to that point as possible. Repeat this process within each grid cell.

The sampling tool may need to be cleaned with water between increments within the same DU if the soil is very cohesive. Soil and vegetation will sometimes also build up around and behind the disk, causing the depth mechanism to be harder to operate (CRREL, 2009).

Any surface vegetation should be included with the soil sample. In many cases, it is important to include this matter with the sample because many contaminant particles reside on the ground surface and can be lost if moss or other vegetative matter is removed or discarded (CRREL, 2009).

Replicate ISM samples (triplicates or more) should be taken to quantify uncertainty in the estimate of the mean concentration within the DU. The number of replicates and frequency of taking replicate incremental samples should be specified in the Field Sampling Plan and comply with project DQOs. ISM field replicates are made of the same number of increments collected in the initial ISM sample and collected using the same sampling pattern from within the same DU. The replicate samples are prepared and analyzed in the same manner as the initial sample. Three replicate samples (i.e., the initial ISM sample plus two additional samples) should be considered the minimum.

**Decontamination**

Sampling devices can be used within a DU without decontamination but should be decontaminated or disposed of between DUs. If sampling tools will be used for two or more DUs, they should be cleaned of soil particles, decontaminated with the appropriate solutions or solvents, and dried between DUs. Typically, rinse (decontamination) blanks can be used to evaluate the potential effects of cross contamination, if needed.

**Sample Management**

Once ISM increments are collected from all the grid cells in the DU, seal the sample containers. The large re-sealable bag containing the total sample volume will be labeled with indelible ink and then double-bagged. The samples will be bubble-wrapped and taped for shipping and placed into iced coolers at approximately 4 degrees Celsius (°C) (±2°C) for transport under chain-of-custody protocol to the analytical laboratory.

## VII. Waste Management

Disposable personnel protective equipment (such as gloves) and used supplies will be place appropriate disposal containers. Investigation derived waste from sampling tool decontamination will be containerized and properly disposed at the completion of the project.

## VIII. Data Recording and Management

All sample and location measurements and observations will be maintained in a field notebook or log. The following should be documented in the field log:

- Sketch the DU and grid pattern.
- Show the collection locations of all the sample increments on the field notebook sketch.
- Describe and classify the surface soils collected according to Universal Soil Classification System (USCS) nomenclature. At a minimum, do this for the bulk soil sample after all the increments have been collected.
- Additionally, during increment collection, the soil should be described at each significant change in lithology type encountered across the DU.
- Note any observed stains and sampling obstructions. Describe any color or odor for observed stains.
- Document any deviation from the ISM procedure, including sampling of a different grid cell quadrant.

Photographs should be taken of the sampling activities and DU grid to document the sampling locations.

Upon project completion, field notebooks will be forwarded to the Project Manager for storage in the project files. Samplers should keep copies for their files.

## IX. Quality Assurance

Samplers will forward copies of field notes and chains of custody to the Project Manager for quality assurance checks during project implementation daily or at a frequency determined by the Project Manager.

## X. References

CRREL (Cold Regions Research and Engineering Laboratory, 2009). *User's Manual for the CRREL Multi-Increment Sampling Tool.* http://www.itrcweb.org/ism-1/references/umcrrel.pdf

ITRC (Interstate Technology & Regulatory Council). 2012*. Incremental Sampling Methodology*. ISM-1. Washington, D.C.: Interstate Technology & Regulatory Council, Incremental Sampling Methodology Team. www.itrcweb.org.

Pitard, F. 1993. Pierre Gy's Sampling Theory and Sampling Practice: Heterogeneity, Sampling Correctness, and Statistical Process Control, 2nd ed. Boca Raton, Fla.: CRC Press.

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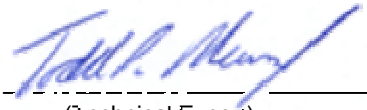
# MC SOP No. 2 - Surface and Subsurface Soil Sampling Using Manual Methods

Rev. #: 1

Rev Date: March 6, 2009

**Approval Signatures**

Prepared by:  Date: 3/6/09

Reviewed by:  Date: 3/6/09
(Technical Expert)

## I. Scope and Application

This document describes procedures for surface and subsurface soil sampling using hand tools.

## II. Personnel Qualifications

ARCADIS personnel directing, supervising, or leading soil sampling activities should have a minimum of 2 years of previous environmental soil sampling experience. ARCADIS personnel providing assistance to soil sample collection and associated activities should have a minimum of 6 months of related experience or an advanced degree in environmental sciences.

## III. Equipment List

The following materials will be available, as required, during soil sampling activities:

- personal protective equipment (PPE), as specified by the site Health and Safety Plan (HASP);
- stainless steel bowls;
- stainless steel spoons;
- stainless steel spades;
- stainless steel hand augers;
- indelible ink pens;
- engineer's ruler or survey rod;
- sealable plastic bags (e.g., Ziploc®);
- equipment decontamination materials
- sample bottles and preservatives appropriate for the parameters to be sampled for laboratory analysis, if any;
- transport container with ice (if sampling for laboratory analysis);
- appropriate sample containers and forms; and

- field notebook and/or personal digital assistant (PDA).

Documentation forms and notebooks to have on hand include: soil sample log forms, chain-of-custody forms, sample labels and seals, field logbook/PDA.

## IV. Cautions / Hazards

Task specific Job Safety Analysis (JSAs) must be developed to identify site hazards associated with the investigation and reviewed by all field crew members prior to the start of work. Safe Performance Self-Assessment (SPSA) to be performed by employees before performing a new task. Underground utilities will be cleared per the ARCADIS Utility Location Policy and Procedure.

## V. Health and Safety Considerations

Soil sample collection will be performed in accordance with a site-specific Health and Safety Plan (HASP) and task specific JSA forms, copies of which will be present on site during such activities.

## VI. Procedure

Soil samples may be collected at intervals from the ground surface to various depths. Sample locations will be identified using stakes, flagging, or other appropriate means, and will be noted in a field logbook, PDA, and/or soil sampling logs. Sample points will be located by surveying, use of a global positioning system (GPS), and/or measurements from other surveyed site features.

1. Equipment that will come in contact with the soil sample should be cleaned in accordance with the appropriate equipment decontamination SOP(s), or else new, disposable equipment should be used. Collect equipment blanks in accordance with the project Project Plan.

2. Clear the ground surface of brush, root mat, grass, leaves, or other debris.

3. Use a spade, spoon, scoop, or hand auger to collect a sample of the required depth interval.

4. Use an engineer's ruler to verify that the sample is collected to the correct depth and record the top and bottom depths from the ground surface.

5. To collect samples below the surface interval, remove the surface interval first; then collect the deeper interval. To prevent the hole from collapsing, it may be

necessary to remove a wider section from the surface or use cut polyvinyl chloride (PVC) tubing or pipe to maintain the opening.

6. Collect samples for volatile organic compounds (VOCs) as discrete samples using Encore® samplers or cut syringes (see Extraction/Preservation of Soil/Sediment Samples for VOCs SOP).

7. Homogenize samples for other analyses across the required interval or mix them with other discrete grab samples to form a composite sample (see Compositing or Homogenizing Samples SOP).

8. Place sample in clean sample container; label with sample identification number, date, and time of collection; and place on ice (if obtained for laboratory analysis). Prepare samples for packaging and shipping to the laboratory in accordance with the Chain-of-Custody Handling, Packing, and Shipping SOP.

9. Backfill sample holes to grade with native material or with clean builder's sand or other suitable material.

## VII. Waste Management

Waste soils will be managed as specified in the FSP or Project Plan, and according to state and /or federal requirements. Personal Protective Equipment (PPE) and decontamination fluids will be contained separately and staged at the project site for appropriate disposal. Waste containers must be a sealed and labeled at the time of generation. Labels will indicate date, sample locations, site name, city, state, and description of the matrix (e.g., soil, PPE).

## VIII. Data Recording and Management

Field documentation such as log book entries and chain-of –custody records will be transmitted to the ARCADIS PM or Task Manager each day unless otherwise directed. The field team leader will retain all site documentation while in the field and add to project files when the field mobilization is complete.

## IX. Quality Assurance

Quality assurance samples (rinse blanks, duplicates, and MS/MSDs) will be collected at the frequency specified in the FSP and/or Project Plan and depending on the project quality objectives. Reusable soil sampling equipment will be cleaned prior to use following equipment cleaning SOP. Field rinse blanks will be used to confirm that decontamination procedures are sufficient and samples are representative of site

conditions. Any deviations from the SOP will be discussed with the project manager prior to changing any field procedures.

**MC SOP No. 3**
**Documenting Sample Locations with a GPS**

I. Introduction

The purpose of this Standard Operating Procedure (SOP) is to provide the protocols for documenting global positioning system (GPS) data collection at field locations for the MC soil sampling program.

II. Materials

a. Field logbook
b. Indelible black pen ink
c. Trimble GeoXT or Trimble GeoXH.

III. General Guidelines

1. Prior to beginning any survey activities, verify all power sources have been properly charged.
2. Once per day, a GPS point feature will be collected at a known survey location to provide control.
3. Quality control will be conducted with all data to ensure confidence that submeter accuracy was achieved for all points.

IV. Operation of the GPS

1. Getting Started

   A. Power up the unit by pressing the green button on the key pad. Start the TerraSync application by selecting the GPS link on the bottom right corner of the screen, or by selecting Terra Sync from the Start Menu.
   B. The GPS receiver will automatically connect to satellites. Verify this by looking at the top of the screen for a picture of a satellite and an adjacent number representing the number of satellites.
   C. Typically when you start the TerraSync software, the Status screen will be the first thing you see. After verifying that the GPS is connecting to satellites, also verify that the slide bar at the bottom of the screen is set in the middle. Sliding to the left will allow GPS positions of lower accuracy than approved for this project.

2. Data Collection

   A. Open the dropdown menu in the upper left hand corner, and select Data. Make sure that the dropdown menu located just below this is set to “New” and the Dictionary Name is set to "(Your Project Name)” or the default data dictionary. All other settings can remain the same. Note that the default file name is set according to date. To create a new file, click on the “Create” button.

*Note: It is recommended that a new data file be created for each day of data collection. If you wish to reopen an existing file at anytime, open the drop down menu near the upper right corner and change from "New" to "Existing". A list of existing files will appear, then select the file name you wish to add data to.*

B. A dialogue box will appear asking to confirm antenna height. Enter height of the antenna as measured from the ground surface. Unless you plan to use an external antenna, this height should represent how high you will hold the handheld unit when collecting data. When finished, click "OK".

C. Now data collection can begin. You will see the two drop down menus on the upper left hand corner of the screen. The top menu will be set to *Data*, and the menu just below it will be set to *Collect* (see below). If not, use the dropdown menus to adjust. A list of features will be provided on the screen. Highlight the name of the feature you will collect GPS data for, then click "Create".

D. After clicking Create, enter attribute data in the spaces provided. If a keyboard does not automatically appear, click on the small keyboard icon located at the bottom of the screen.

E. A number will appear in the top of the screen to the right hand side of the battery indicator. This number represents the number of GPS positions recorded for the current point feature. The number will increase as a new GPS position is recorded every 5 seconds. After 20 positions are collected, click "OK" The point feature is then stored and you'll return to the feature list.

*Notes:*

*If the picture and number of satellites start blinking, no positions can be collected. This indicates that satellites are too few, or PDOP is too high. It will resume as soon as the conditions improve.*

*The number just above the positions in smaller font represents the predicted postprocessed accuracy of your point. You will periodically receive a message if the carrier lock is lost. This is important because subfoot accuracy requires a carrier lock for at least two minutes.*

*Also notice the Pause button. Toggle this button on or off if to start or stop the collection of GPS positions.*

2. Close the File. When finished collecting point features, click on the "Close" button. Close the TerraSync program by clicking the X in the upper right corner of the screen. Use the power button to turn off the unit.

*Note: If the GPS unit is idle for a period of time, it will go into Suspend mode. Press the green power button at any time to toggle the suspend mode on or off.*

3. Using an external antenna (Optional)

   A. The GPS unit contains an internal antenna. An external antenna (Hurricane Antenna) can be used. Its benefits include a higher powered antenna that would likely increase satellite reception under tree canopy, but make little or no difference if there is an clear view of the sky. The external antenna is mounted on a pole which also helps place the antenna above the user's head, which sometime improves the view of the sky and subsequent number of satellite signals received.

   B. To use the external antenna, assemble the range pole, bracket, antenna, and cabling. Select "Setup" from the drop down menu in the upper right hand corner of the screen. Click on the button next to Antenna Height, select Hurricane Antenna from the list, and assign the antenna height of 2 meters (or 6.56 feet) which corresponds to the height of the range pole. It is recommended that the external antenna is connected while the handheld is turned off, or while the TerraSync field software is up and running. Do not attempt to connect the antenna while TerraSync is not running or is not currently the display screen. It is also recommended that the Antenna setting be changed back to internal antenna if you suspect the next operator will not be using an external antenna. The next operator may not know that the handheld unit is set for an external antenna and may encounter confusion while waiting for satellite reception.

4. Setting the Coordinate System

   A. The coordinate system can be set by selecting "Setup" from the pull down menu in the upper right hand corner of the screen, then select "Coordinate System". Units are also set from the Setup screen. This is important if you wish to view coordinate values in the field, or calculate distances in the Map screen. It is also critical if you are using a background file such as an aerial photo because your position on the aerial photo would only display correctly if the GPS coordinate system matches the aerial photo coordinate system.

   It should be noted that if you plan to collect data in the field and manage the data later in other software (*i.e.*, Pathfinder Office or ArcGIS), the coordinate system and units can be established at that time. The coordinate system set on the GPS unit will only affect display properties because the GPS collects raw data that is projected in the desired coordinate system after download.

## V. Quality Control

Quality control will involve a review of each point using Trimble Pathfinder Office software. Data review will include the following checks:

1. Confirm that each point was real-time corrected, Differential correction by post-processing will be conducted if real time corrections were not attained during data collection.

2. Confirm that the standard deviation does not exceed one meter. If standard deviation is greater than one meter, the GPS data will be re-collected.

3. Control points will be verified to ensure they are within one meter of their true location.

VI. Transferring Files from the Datalogger to the PC.

1. Plug the yellow "D" 9- pin connector into the Comm port on the PC
2. Plug the yellow "D" 9-pin connector, other end, into "Data i/o on the GPS battery charger
3. Plug in the charger (this will preserve the battery in the GPS)
4. Plug round pin connector from the battery charger into the round pin connector to the bottom port on the Trimble TSC1 hand-held unit
5. Turn on GPS TSC1
6. On the GPS, from the main menu, highlight and enter "**File Ma**nager"
7. Highlight and enter "**File Transfer**"
8. On the PC go to the PATHFINDER OFFICE program on the computer by double clicking on the PATHFINDER OFFICE icon from the Windows desktop.
9. Select the correct Project Name "(Project Name)" for the data to be transferred into (This should have already been set up)
10. Set Pathfinder Office display by selecting "View" dropdown and "Map", also select "Data" dropdown and "Feature Properties" and Position Properties"
11. Under the "Utilities" dropdown select Data Transfer
    a. "wait to connect", and "Connected to Asset Surveyor" should appear
    b. At "Press ADD to select file", press "Add – data file"
    c. Select Files from "Open", click OK
    d. Click on "Transfer All"
    e. After files transfer and are converted (automatically), close the transfer dialog box. The files are now located on the PC in C:\pfdata\
    f. Open the files one at a time (or else they will be combined into one view)
    g. Using "File", "open", (Select a file) open the file
    h. View Map showing the path of the surface rate scan, just to confirm that you have the data.

VII. Performing the Differential Correction (post-Processing) of the GPS Data

In Pathfinder Office do the following:

1. Select "(Project Name)"
2. "File", "Open" (This should be an .ssf file)
3. Open "Utilities" dropdown
    a. Select "Differential Correction"
    b. Verify that file is listed under "Selected Files"
    c. Check "Base File" – click on "Internet Search"

d. Click “Yes” to “Do you want to download latest?”
e. Click “Yes” (Important the first time, but not later. Do once a month.)
f. Select the closest CORS location
g. Click “OK”
h. “Provider Properties” check OK
i. “Base file loads” – Click OK

## VIII. Exporting the Data

1) Initially on the computer, set the attributes prior to exporting data:
   i) “Utility” dropdown
   ii) Select “Export”
   iii) Click “New”
   iv) Set up name “(Project Name)”
   v) “Create”:
      (1) “New Setup”
      (2) Select “MS Access MDB” or “ESRI Shapefile”
      (3) Click “OK”
   vi) “Properties” dropdown
      (1) Data tab
         (a) Features
            (i) Export All
            (ii) Check “Include…”
            (iii)Check “Sensor…”
      (2) Attributes tab
         (a) Check “PDOP”
         (b) Check “Corr Status”
         (c) Check “Date”
         (d) Check “Time”
      (3) Point Features Tab
         (a) Check “Horizontal Precision”
      (4) All checked default boxes, leave as is.
   vii) Click “OK” – the setup has been saved and no longer has to be done on this computer.

2) Exporting the Differentially Corrected Data
   i) Open the Differentially Corrected File .COR
   ii) “Utilities” dropdown
   iii) Select “Export”
      (1) Check that the selected file is a .COR and is the correct file
      (2) Note: If the project is listed then the following **bold** should already be set up:
         (a) Output
            (i) Check that it is C:\pfdata\”Project Name”\export
         (b) Export Setup
            (i) Check that it is Sample MS Access MDB Setup or Sample ESRI Shapefile Setup
         (c) Properties
            (i) Verify:

1. Data Tabs (as above)
2. Attributes (as above)
3. Point Features (as above)
4. Line Features (as above)

(3) Click “OK”
(4) Verify on Export Screen
(5) Click OK

**Note**: After the EXPORT has been performed an .MDB file is created and placed in: C:\pfdata\”Project Name”\export.

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# MC SOP 4 -

# Field Log Book Entries

Rev. #: 0

Rev Date: 11 August 2009

**Approval Signatures**

Prepared by: Andrew Kamik Date: 8/11/09

Reviewed by: Michael J. Hefferon Date: 8/11/09
(Technical Expert)

## I. Scope and Application

This ARCADIS Standard Operating Procedure covers the entries needed in a field log book for environmental investigations.

This SOP does not address all of the entries that may be needed for a specific project, and does not address health and safety, equipment decontamination, field parameter measurements, sample preservation, chain-of-custody, or laboratory analysis. For direction on requirements in these areas, refer to other ARCADIS SOPs, the Project Plans including the quality assurance project plan, sampling plan, and health and safety plan, as appropriate.

## II. Personnel Qualifications

ARCADIS personnel participating in fieldwork and making entries into the field log book should have a minimum of one (1) year of field experience (or be under the supervision and accompanied in the field by someone who does) and current health and safety training including 40-hour HAZWOPER training, site supervisor training, site-specific training, first aid, and CPR, as needed. Field personnel will also be compliant with client-specific training requirements. In addition, ARCADIS field sampling personnel will be versed in the relevant SOPs and posses the required skills and experience necessary to successfully complete the desired field work.

## III. Equipment List

Field Log Book

Ball point (medium point) pen with blue or black ink (black preferred). A fine point Sharpie pen may be used if the ink does not bleed through the page and become visible on back side of the page. If weather conditions prevent the use of a pen, indicate so in the log and use an alternate writing instrument .

Zip-lock baggie or other weather-proof container to protect the field log book from the elements.

## IV. Cautions

All entries in the field log must be legible and archivable. Do not leave the field log book exposed to the elements or other conditions that might moisten the pages and smear/dissolve the entries. When not in the field, the log book should be stored in a location that is easily accessible to field crews.

## V. Health and Safety Considerations

ARCADIS field personnel will be familiar and compliant with Client-specific health and safety requirements.

## VI. Procedure

Print legibly. Do not use cursive writing.

The name of the project, project number and project location should be written in indelible ink on the outside of the field log book.

On the inside of the front cover, write “If Found, Please Return to ARCADIS” and include the appropriate address and phone number, the name of the person to which the book is assigned, and the name of the project manager.

Reserve the first page of the book for a Table of Contents.

Reserve the last five (5) pages of the book for important contacts, notes, reminders, etc.

Each day of field work, the following should be recorded in the field log book as applicable:

a) Project Name

b) Date and time arrived

c) Work Site Location

d) Names of people on-site related to the project including ARCADIS employees, visitors, subcontractor employees, agency personnel, client representative, etc.

e) Describe the work to be performed briefly, and list the equipment on-site

f) Indicate the health and safety (H&S) level to be used

g) Record instrument calibrations and checks

h) Record time and general content of H&S briefing

i) Describe the weather conditions, including temperature, precipitation, and wind speed and direction

j) List periodic time entries in the far left hand column of each page

k) Minimize unused space on each page

The tailgate meeting must be recorded in the log book and the tailgate form completed. If H&S monitoring is performed, record the time and results of initial and followup monitoring.

Note factual observations including collection of QA/QC samples, delays, well damage, accidents, Project Plan deviations, instrument problems, and problem resolutions.

Describe work performed and how documented such as photographs, sample core logs, water sampling logs, etc.

Describe bases for field decisions including pertinent conversations with visitors, regulators, or project personnel.

Note final instrument calibrations and checks.

Sign the log book at the end of each day at a minimum. Draw a line to the end of the page to indicate no further entries on that page. Sign the bottom of each page if possible.

If an entry to the log book is changed, strike out the deleted text or item with a single line such that the entry remains legible, and initial and date the change. Such changes should only be made by the same person that made the initial entry.

Field log book entries must be made in the field at the site, not at a later time at a different location. Supplemental entries to the log book may be made at a later date. The supplemental entry must be clearly identified as such and the entry must be signed and dated as described in this SOP.

Problems noted in the field log book must be brought to the attention of the project manager and task manager in a timely fashion. Problems may be reported in person, on the telephone, or in a written daily log form. If daily logs are prepared and you will not be able to personally give the daily log to the project manager, send the daily log via FAX or overnight courier to the project manager and task manager.

## VII. Waste Management

Investigation-derived waste will be managed as described in the Investigation-Derived Waste Handling and Storage SOP. A drum/waste inventory should be maintained on a pre-designated page in the field log book.

## VIII. Data Recording and Management

Each page of the field log book should be scanned for electronic/digital archiving at periodic intervals. This will ensure that copies of the field notes are available in the event the field book is lost or damaged, and that field data can be easily disseminated to others without the risk of physically sending the field log book. Field log books that are full should be archived with the project files, and readily retrievable.

## IX. Quality Assurance

Be mindful that the field log book may be produced in court. All entries should be legible (as discussed above). Entries should also be in English, unless working in a country where English is not the predominant language or you are directed otherwise by the project manager.

## X. References

Not Applicable

ARCADIS

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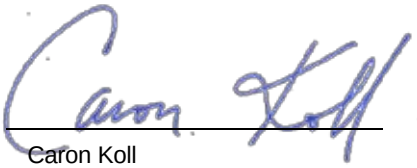
# MC SOP 5 –

# Chain-of-Custody, Handling, Packing and Shipping

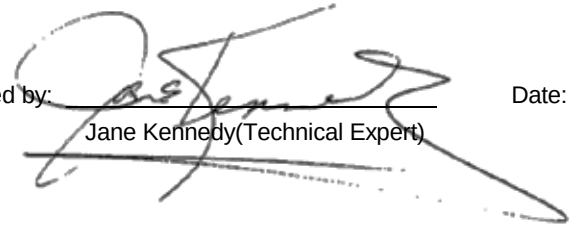
Rev. #: 3

Rev Date: September 30, 2010

**Approval Signatures**

Prepared by:  Date: 3/6/09

Caron Koll

Reviewed by:  Date: 3/6/09

Jane Kennedy(Technical Expert)

## I. Scope and Application

This Standard Operating Procedure (SOP) describes the chain-of-custody, handling, packing, and shipping procedures for the management of samples to decrease the potential for cross-contamination, tampering, mis-identification, and breakage, and to insure that samples are maintained in a controlled environment from the time of collection until receipt by the analytical laboratory.

## II. Personnel Qualifications

ARCADIS field sampling personnel will have current health and safety training, including 40-hour HAZWOPER training, Department of Transportation (DOT) training, site supervisor training, and site-specific training, as needed. In addition, ARCADIS field sampling personnel will be versed in the relevant SOPs and possess the skills and experience necessary to successfully complete the desired field work.

## III. Equipment List

The following list provides materials that may be required for each project. Project documents and sample collection requirements should be reviewed prior to initiating field operations:

- indelible ink pens (black or blue);
- polyethylene bags (resealable-type);
- clear packing tape, strapping tape, duct tape;
- chain of custody
- DOT shipping forms, as applicable
- custody seals or tape;
- appropriate sample containers and labels,;
- insulated coolers of adequate size for samples and sufficient ice to maintain 4°C during collection and transfer of samples;
- wet ice;
- cushioning and absorbent material (i.e., bubble wrap or bags);

- temperature blank
- sample return shipping papers and addresses; and
- field notebook.

## IV. Cautions

Review project requirements and select appropriate supplies prior to field mobilization.

Insure that appropriate sample containers with applicable preservatives, coolers, and packing material have been supplied by the laboratory.

Understand the offsite transfer requirements for the facility at which samples are collected.

If overnight courier service is required schedule pick-up or know where the drop-off service center is located and the hours of operation. Prior to using air transportation, confirm air shipment is acceptable under DOT and International Air Transport Association (IATA) regulation

Schedule pick-up time for laboratory courier or know location of laboratory/service center and hours of operation.

Understand DOT and IATA shipping requirements and evaluate dangerous goods shipping regulations relative to the samples being collected (i.e. complete an ARCADIS shipping determination). Review the ARCADIS SOPs for shipping, packaging and labeling of dangerous goods. Potential samples requiring compliance with this DOT regulation include:

- Methanol preservation for Volatile Organic Compounds in soil samples
- Non-aqueous phase liquids (NAPL)

## V. Health and Safety Considerations

Follow health and safety procedures outlined in the project/site Health and Safety Plan (HASP).

Use caution and appropriate cut resistant gloves when tightening lids to 40 mL vials. These vials can break while tightening and can lacerate hand. Amber vials (thinner glass) are more prone to breakage.

Some sample containers contain preservatives.

- The preservatives must be retained in the sample container and should in no instance be rinsed out.
- Preservatives may be corrosive and standard care should be exercised to reduce potential contact to personnel skin or clothing. Follow project safety procedures if spillage is observed.
- If sample container caps are broken discard the bottle. Do not use for sample collection.

## VI. Procedure

### Chain-of-Custody Procedures

1. Prior to collecting samples, complete the chain-of-custody record header information by filling in the project number, project name, and the name(s) of the sampling technician(s) and other relevant project information. Attachment 1 provides an example chain-of-custody record.

2. Chain-of-custody information MUST be printed legibly using indelible ink (black or blue).

3. After sample collection, enter the individual sample information on the chain-of-custody:

    a. Sample Identification indicates the well number or soil location that the sample was collected from. Appropriate values for this field include well locations, grid points, or soil boring identification numbers (e.g., MW-3, X-20, SB-30). When the depth interval is included, the complete sample ID would be “SB-30 (0.5-1.0) where the depth interval is in feet. Please note it is very important that the use of hyphens in sample names and depth units (i.e., feet or inches) remain consistent for all samples entered on the chain-of-custody form. DO NOT use the apostrophe or quotes in the sample ID. Sample names may also use the abbreviations “FB,” “TB,” and “DUP” as prefixes or suffixes to indicate that the sample is a field blank, trip blank, or field duplicate, respectively. NOTE: The sample nomenclature may be dictated by the project database and require

unique identification for each sample collected for the project. Consult the project data management plan for additional information regarding sample identification.

b. List the date of sample collection. The date format to be followed should be mm/dd/yy (e.g., 03/07/09) or mm/dd/yyyy (e.g. 03/07/2009).

c. List the time that the sample was collected. The time value should be presented using military format. For example, 3:15 P.M. should be entered as 15:15.

d. The composite field should be checked if the sample is a composite over a period of time or from several different locations and mixed prior to placing in sample containers.

e. The “Grab”. field should be marked with an “X” if the sample was collected as an individual grab sample. (e.g. monitoring well sample or soil interval).

f. Any sample preservation should be noted.

g. The analytical parameters that the samples are being analyzed for should be written legibly on the diagonal lines. As much detail as possible should be presented to allow the analytical laboratory to properly analyze the samples. For example, polychlorinated biphenyl (PCB) analyses may be represented by entering “PCBs” or “Method 8082.” Multiple methods and/or analytical parameters may be combined for each column (e.g., PCBs/VOCs/SVOCs or 8082/8260/8270). These columns should also be used to present project-specific parameter lists (e.g., Appendix IX+3 target analyte list. Each sample that requires a particular parameter analysis will be identified by placing the number of containers in the appropriate analytical parameter column. For metals in particular, indicate which metals are required.

h. Number of containers for each method requested. This information may be included under the parameter or as a total for the sample based on the chain of custody form used.

i. Note which samples should be used for site specific matrix spikes.

j. Indicate any special project requirements.

k. Indicate turnaround time required.

l. Provide contact name and phone number in the event that problems are encountered when samples are received at the laboratory.

m. If available, attach the Laboratory Task Order or Work Authorization forms.

n. The remarks field should be used to communicate special analytical requirements to the laboratory. These requirements may be on a per sample basis such as “extract and hold sample until notified,” or may be used to inform the laboratory of special reporting requirements for the entire sample delivery group (SDG). Reporting requirements that should be specified in the remarks column include: 1) turnaround time; 2) contact and address where data reports should be sent; 3) name of laboratory project manager; and 4) type of sample preservation used.

o. The “Relinquished By” field should contain the signature of the sampling technician who relinquished custody of the samples to the shipping courier or the analytical laboratory.

p. The “Date” field following the signature block indicates the date the samples were relinquished. The date format should be mm/dd/yyyy (e.g., 03/07/2005).

q. The “Time” field following the signature block indicates the time that the samples were relinquished. The time value should be presented using military format. For example, 3:15 P.M. should be entered as 15:15.

r. The “Received By” section is signed by sample courier or laboratory representative who received the samples from the sampling technician or it is signed upon laboratory receipt from the overnight courier service.

3. Complete as many chain-of-custody forms as necessary to properly document the collection and transfer of the samples to the analytical laboratory.

4. Upon completing the chain-of-custody forms, forward two copies to the analytical laboratory and retain one copy for the field records.

5. If electronic chain-of-custody forms are utilized, sign the form and make 1 copy for ARCADIS internal records and forward the original with the samples to the laboratory.

**Handling Procedures**

1. After completing the sample collection procedures, record the following information in the field notebook with indelible ink:

   - project number and site name;
   - sample identification code and other sample identification information, if appropriate;
   - sampling method;
   - date;
   - name of sampler(s);
   - time;
   - location (project reference);
   - location of field duplicates and both sample identifications;
   - locations that field QC samples were collected including equipment blanks, field blanks and additional sample volume for matrix spikes; and
   - any comments.

2. Complete the sample label with the following information in indelible ink:

   - sample type (e.g., surface water);
   - sample identification code and other sample identification information, if applicable;
   - analysis required;
   - date;
   - time sampled;
   - initials of sampling personnel;
   - sample matrix; and

- preservative added, if applicable.

3. Cover the label with clear packing tape to secure the label onto the container and to protect the label from liquid.

4. Confirm that all caps on the sample containers are secure and tightly closed.

5. In some instances it may be necessary to wrap the sample container cap with clear packing tape to prevent it from becoming loose.

6. For some projects individual custody seals may be required. Custody seal evidence tape may be placed on the shipping container or they may be placed on each sample container such that the cooler or cap cannot be opened without breaking the custody seal. The custody seal should be initialed and dated prior to relinquishing the samples.

**Packing Procedures**

Following collection, samples must be placed on wet ice to initiate cooling to less than or equal to 6 °C without freezing the sample(s). Retain samples on ice until ready to pack for shipment to the laboratory.

1. Secure the outside and inside of the drain plug at the bottom of the cooler being used for sample transport with “Duct” tape.

2. Place a new large heavy duty plastic garbage bag inside each cooler

3. Place each sample bottle wrapped in bubble wrap inside the garbage bag. VOC vials may be grouped by sample in individual resealable plastic bags). If a cooler temperature blank is supplied by the laboratory, it should be packaged following the same procedures as the samples. If the laboratory did not include a temperature blank, do not add one. Place 1 to 2 inches of cushioning material (i.e., vermiculite) at the bottom of the cooler.

4. Place the sealed sample containers upright in the cooler.

5. Package ice in large resealable plastic bags and place inside the large garbage bag in the cooler. Samples placed on ice will be cooled to and maintained at a temperature of less than or equal to 6 °C without freezing the sample(s).

6. Fill the remaining space in the cooler with cushioning material such as bubble wrap. The cooler must be securely packed and cushioned in an upright position and be surrounded (Note: to comply with 49 CFR 173.4, filled cooler must not

exceed 64 pounds).

7. Place the completed chain-of-custody record(s) in a large resealable bag and tape the bag to the inside of the cooler lid.

8. Close the lid of the cooler and fasten with packing tape.

9. Wrap strapping tape around both ends of the cooler.

10. Mark the cooler on the outside with the following information: shipping address, return address, “Fragile, Handle with Care” labels on the top and on one side, and arrows indicating “This Side Up” on two adjacent sides.

11. Place custody seal evidence tape over front right and back left of the cooler lid, initial and date, then cover with clear plastic tape.

**Note**: Procedure numbers 2, 3, 5, and 6 may be modified in cases where laboratories provide customized shipping coolers. These cooler types are designed so the sample bottles and ice packs fit snugly within preformed styrofoam cushioning and insulating packing material.

**Shipping Procedures**

1. All samples will be delivered by an express carrier within 48 hours of sample collection. Alternatively, samples may be delivered directly to the laboratory or laboratory service center or a laboratory courier may be used for sample pickup.

2. If parameters with short holding times are required (e.g., VOCs [EnCore™ Sampler], nitrate, nitrite, ortho-phosphate and BOD), sampling personnel will take precautions to ship or deliver samples to the laboratory so that the holding times will not be exceeded.

3. Samples must be maintained at less than or equal to 6 °C without freezing the sample(s) until receipt at the laboratory.

4. All shipments must be in accordance with DOT regulations and ARCADIS dangerous goods shipping SOPs.

5. When the samples are received by the laboratory, laboratory personnel will complete the chain-of-custody by recording the date and time of receipt of samples, measuring and recording the internal temperature of the shipping

container, and checking the sample identification numbers on the containers to ensure they correspond with the chain-of-custody forms.

Any deviations between the chain-of-custody and the sample containers, broken containers, or temperature excursions will be communicated to ARCADIS immediately by the laboratory.

## VII. Waste Management

Not applicable

## VIII. Data Recording and Management

Chain-of-custody records will be transmitted to the ARCADIS PM or designee at the end of each day unless otherwise directed by the ARCADIS PM. The sampling team leader retains copies of the chain-of-custody forms for filing in the project file. Record retention shall be in accordance with project requirements.

## IX. Quality Assurance

Chain-of-custody forms will be legibly completed in accordance with the applicable project documents such as Sampling and Analysis Plan (SAP), Project Plan, or other project guidance documents. A copy of the completed chain-of-custody form will be sent to the ARCADIS Project Manager or designee for review.

## X. References

Not Applicable

**Attachment 1**

ARCADIS
Infrastructure, environment, facilities

ID#:

# CHAIN OF CUSTODY & LABORATORY ANALYSIS REQUEST FORM

Page ___ of ___

Lab Work Order #

Send Results to:
Contact & Company Name:
Telephone:
Address:
Fax:
City State Zip
E-mail Address:

Project Name/Location (City, State):
Project #:
Sampler's Printed Name:
Sampler's Signature:

| Sample ID | Collection Date | Collection Time | Type (✓) Comp | Type (✓) Grab | Matrix |
|---|---|---|---|---|---|
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Preservative
Filtered (✓)
# of Containers
Container Information

PARAMETER ANALYSIS & METHOD

Keys

Preservation Key:
A. $H_2SO_4$
B. HCL
C. $HNO_3$
D. NaOH
E. None
F. Other: _____
G. Other: _____
H. Other: _____

Container Information Key:
1. 40 ml Vial
2. 1 L Amber
3. 250 ml Plastic
4. 500 ml Plastic
5. Encore
6. 2 oz. Glass
7. 4 oz. Glass
8. 8 oz. Glass
9. Other: _____
10. Other: _____

Matrix Key:
SO - Soil
W - Water
T - Tissue
SE - Sediment
SL - Sludge
A - Air
NL - NAPL/Oil
SW - Sample Wipe
Other: _____

REMARKS

Special Instructions/Comments:

☐ Special QA/QC Instructions(✓):

| Laboratory Information and Receipt | | Relinquished By | Received By | Relinquished By | Laboratory Received By |
|---|---|---|---|---|---|
| Lab Name: | Cooler Custody Seal (✓) | Printed Name: | Printed Name: | Printed Name: | Printed Name: |
| ☐ Cooler packed with ice (✓) | ☐ Intact ☐ Not Intact | Signature: | Signature: | Signature: | Signature: |
| Specify Turnaround Requirements: | Sample Receipt: | Firm: | Firm/Courier: | Firm/Courier: | Firm: |
| Shipping Tracking #: | Condition/Cooler Temp: _____ | Date/Time: | Date/Time: | Date/Time: | Date/Time: |

20720826 DoD AR Form 01.12.2007

Distribution: WHITE – Laboratory returns with results YELLOW – Lab copy PINK – Retained by BBL

ARCADIS

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# MC SOP 6 - Investigation-Derived Waste Handling and Storage

Rev. #: 2

Rev Date: March 6, 2009

**Approval Signatures**

Prepared by: Andrew Kanik Date: 3/6/09

Reviewed by: Liz Marsh Date: 3/6/09
(Technical Expert)

## I. Scope and Application

The objective of this Standard Operating Procedure (SOP) is to describe the procedures to manage investigation-derived wastes (IDW), both hazardous and non-hazardous, generated during site activities, which may include, but are not limited to - drilling, trenching/excavation, construction, demolition, monitoring well sampling, soil sampling, decontamination and remediation. Please note that this SOP is intended for materials that have been deemed a solid waste as defined by 40 CFR § 261.2 (which may include liquids, solids, and sludges). In some cases, field determinations will be made based on field screening or previous data that materials are not considered a solid waste. IDW may include soil, groundwater, drilling fluids, decontamination liquids, personal protective equipment (PPE), sorbent materials, construction and demolition debris, and disposable sampling materials that may have come in contact with potentially impacted materials. IDW will be collected and staged at the point of generation. Quantities small enough to be containerized in 55-gallon drums will be taken to a designated temporary storage area (discussed in further detail under Drum Storage) onsite pending characterization and disposal. Waste materials will be analyzed for constituents of concern to evaluate proper disposal methods. PPE and disposable sampling equipment will be placed in DOT-approved drums prior to disposal and typically does not require laboratory analysis. This SOP describes the necessary equipment, field procedures, materials, regulatory references, and documentation procedures necessary for proper handling and storage of IDW up to the time it is properly disposed. The procedures for handling IDW are based on the United States Environmental Protection Agency's Guide to Management of Investigation Derived Wastes (USEPA, 1992). IDW is assumed to be contaminated with the site constituents of concern (COCs) until analytical evidence indicates otherwise. IDW will be managed to ensure the protection of human health and the environment and will comply with all applicable or relevant and appropriate requirements (ARAR). The following Laws and Regulations on Hazardous Waste Management are potential ARAR for this site.

**State Laws and Regulations**

To Be Determined Based on Location of Site and Location of Treatment, Storage, and/or Disposal Facility (TSDF) to be utilized

**Federal Laws and Regulations**

Resource Conservation and Recovery Act (RCRA) 42 USC § 6901-6987

Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) 42 USC § 9601-9675

Superfund Amendments and Reauthorization Act (SARA)

Department of Transportation (DOT) Hazardous Materials Transportation

Pending characterization, IDW will be stored appropriately within each area of contamination (AOC). Under RCRA, “storage” is defined as the holding of hazardous waste for a temporary period, at the end of which the hazardous waste is treated, disposed of, or stored elsewhere” (40 CFR § 260.10). The onsite waste staging area will be in a secure and controlled area. Waste characterization can either be based on generator knowledge, such as using materials safety data sheets (MSDS’), or can be based upon analytical results. The laboratory used for waste characterization analysis must have the appropriate state and federal certifications and be approved by ARCADIS and Client. IDW will be classified as RCRA hazardous or non-regulated under RCRA based on the waste characterization.

If IDW is characterized as RCRA hazardous waste, RCRA and DOT requirements must be followed for packaging, labeling, transporting, storing, and record keeping as described in 40 CFR § 262 and 49 CFR § 171-178. Wastes judged to potentially meet the criteria for hazardous wastes shall be stored in DOT approved packaging. Waste material classified as RCRA non-hazardous may be handled and disposed of as an industrial waste.

Liquid wastes judged to potentially meet the criteria for hazardous wastes shall be stored in DOT approved 55 gallon drums or other approved containers that are compatible with the type of material stored therein. Solid materials deemed to potentially meet hazardous criteria will be drummed where practicable. Large quantities of potentially hazardous solid materials must be containerized (such as in a roll-off box) for up to a maximum of 90 or 180 days as described in the Excavated Solids Section. Waste material classified as non-hazardous may be handled and disposed of as an industrial waste and is not subject to the 90-day or 180-day on-site storage limitation.

This is a standard (i.e., typically applicable) operating procedure which may be varied or changed as required, dependent upon site conditions, equipment limitations, or limitations imposed by the procedure. The ultimate procedure employed will be documented in the Project Plans or reports. If changes to the sampling procedures are required due to unanticipated field conditions, the changes will be discussed with the Project Manager and Client as soon as practicable and documented in the report.

## II. Personnel Qualifications

ARCADIS field sampling personnel will have current health and safety training including 40-hour HAZWOPER training, site supervisor training, site-specific training, first aid, and CPR, as needed. ARCADIS personnel may sign manifests on a case-to-case basis for clients, provided the appropriate agreement is in place between ARCADIS and the client documenting that ARCADIS is not the generator, but is acting as authorized representative for the generator. ARCADIS personnel who sign hazardous waste manifests will have the current DOT hazardous materials transportation training according to 49 CFR § 172.704. ARCADIS field personnel will also comply with client-specific training such as LPS. In addition, ARCADIS field sampling personnel will be versed in the relevant SOPs and possess the required skills and experience necessary to successfully complete the desired field work.

## III. Equipment List

The following materials, as required, shall be available for IDW handling and storage:

Appropriate personal protective equipment as specified in the Site Health and Safety Plan

55-gallon steel drums, DOT 1A2 or equivalent

¾ -inch socket wrench

Hammer

Leather gloves

Drum dolly

Appropriate drum labels (outdoor waterproof self adhesive)

Polyethylene storage tank

Frac Tank

Appropriate labeling, packing, chain-of-custody forms, and shipping materials as specified in the *Chain-of-Custody* SOP and *Field Sampling Handling, Packing, and Shipping* SOP.

Indelible ink and/or permanent marking pens

Plastic sheeting

Appropriate sample containers, labels, and forms

Stainless-steel bucket auger

Stainless steel spatula or knife

Stainless steel hand spade

Stainless steel scoop Disposable

Bailer

Digital camera

Field logbook.

## IV. Cautions

Filled drums can be very heavy, always use appropriate moving techniques and equipment.

Similar media will be stored in the same drums to aid in sample analysis and disposal.

Drum lids must be secured to prevent rainwater from entering the drums.

Drums containing solid material may not contain any free liquids.

Waste containers stored for extended periods of time may be subject to deterioration. Drum over packs may be used as secondary containment.

All drums must be in good condition to prevent potential leakage and facilitate subsequent disposal. Inspect the drums for dents and rust, and verify the drum has a secure lid prior to use.

## V. Health and Safety Considerations

Appropriate personal protective equipment must be worn by all field personnel within the designated work area.

Air monitoring may be required during certain field activities as required in the Site Health and Safety Plan.

If excavating in potentially hazardous areas is possible, contingency plans should be developed to address the potential for encountering gross contamination or non-aqueous phase liquids.

ARCADIS field personnel will be familiar and compliant with Client-specific health and safety requirements such as Chevron's hand safety policy including the prohibition of fixed and/or folding blade knives.

## VI. Procedure

Waste storage and handling procedures to be used depend upon the type of generated waste. For this reason, IDW should be stored in a secure location onsite in separate 55-gallon storage drums, solids can be stockpiled onsite (if non-hazardous), and purge water may be stored in polyethylene tanks. Waste materials such as broken sample bottles or equipment containers and wrappings will be stored in 55-gallon drums unless they were not in contact with sample media.

### Management of IDW

Minimization of IDW should be considered by the Project Manager during all phases of the project. Site managers may want to consider techniques such as replacing solvent-based cleaners with aqueous-based cleaners for decontamination of equipment, reuse of equipment (where it can be decontaminated), limitation of traffic between exclusion and support zones, and drilling methods and sampling techniques that generate little waste. Alternative drilling and subsurface sampling methods may include the use of small diameter boreholes, as well as borehole testing methods such as a core penetrometer or direct push technique instead of coring (EPA, 1993).

### Drum Storage

Drums containing hazardous waste shall be stored in accordance with the requirements of 40 CFR 265 Subpart I (for containers) and 265 Subpart DD (for containment buildings). All 55-gallon drums will be stored at a secure, centralized on-site location that is readily accessible for vehicular pick-up. Drums confirmed as, or believed to contain hazardous waste will be stored over an impervious surface provided with secondary containment. The storage location will, for drums containing liquid, have a containment system that can contain at least the larger of 10% of the aggregate volume of staged materials or 100% of the volume of the largest container. Drums will be closed during storage and be in good condition in accordance with the Guide to Management of Investigation-Derived Wastes (USEPA, 1992).

**Hazardous Waste Determination**

Waste material must be characterized to determine if it meets any of the federal definitions of hazardous waste as required by 40 CFR § 262.11. If the waste does not meet any of the federal definitions, it must then be established if any state-specific hazardous waste criteria exist/apply.

**Generator Status**

Once hazardous waste determination has been made, the generator status will be determined. Large quantity generators (LQG) are generators who generate more than 1,000 kilograms of hazardous waste in a calendar month. Small quantity generators (SQG) of hazardous waste are generators who generate greater than 100 kilograms but less than 1,000 kilograms of hazardous waste in a calendar month. Conditionally exempt small quantity generators (CESQG) are generators who generate less than 100 kilograms of hazardous waste per month. Please note that a generator status may change from month to month and that a notice of this change is usually required by the generator's state agency.

**Accumulation Time for Hazardous Waste**

A LQG may accumulate hazardous waste on site for 90 days or less without a permit and without having interim status provided that such accumulation is in compliance with specifications in 40 CFR § 262.34. A SQG may accumulate hazardous waste on site for 180 days or less without a permit or without having interim status subject to the requirements of 40 CFR § 262.34(d). CESQG requirements are found in 40 CFR § 261.5. **NOTE**: The CESQG and SQG provisions of 40 CFR § 261.5, 262.20(e), 262.42(b) and 262.44 may not be recognized by some states (e.g. Rhode Island). **State-specific regulations must be reviewed and understood prior to the generation of hazardous waste.**

Satellite Accumulation of Hazardous Waste

Satellite accumulation (SAA) shall mean the accumulation of as much as fifty-five (55) gallons of hazardous waste, or the accumulation of as much as one quart of acutely hazardous waste, in containers at or near any point of generation where the waste initially accumulates, which is under the control of the operator of the process generating the waste, without a permit or interim status and without complying with the requirements of 40 CFR § 262.34(a) and without any storage time limit, provided that the generator complies with 40 CFR § 262.34(c)(1)(i).

Once more than 55 gallons of hazardous waste accumulates in SAA, the generator has three days to move this waste into storage.

Storage recommendations for hazardous waste include:

Ignitable Hazardous wastes must be >50 feet from the property line per 40 CFR § 265.176 (LQG generators only).

Hazardous waste must be stored on a concrete slab (asphalt is acceptable if there are no free liquids in the waste) per 40 CFR § 265.176.

Drainage must be directed away from the accumulation area.

Area must be properly vented.

Area must be secure.

**Drum/Container Labeling**

Drums will be labeled on both the side and lid of the drum using a permanent marking pen. Old drum labels must be removed to the extent possible, descriptions crossed out should any information remain, and new labels affixed on top of the old labels. Other containers used to store various types of waste (polyethylene tanks, roll-off boxes, end-dump trailers, etc.) will be labeled with an appropriate "Waste Container" or “Testing in Progress” label pending characterization. Drums and containers will be labeled as follows:

Appropriate waste characterization label (Testing In Progress, Hazardous, or Non-Hazardous)

Waste generator's name (e.g., client name)

Project name

Name and telephone number of ARCADIS project manager

Composition of contents (e.g., used oil, acetone 40%, toluene 60%)

Media (e.g., solid, liquid)

Accumulation start date

Drum number of total drums as reconciled with the Drum Inventory maintained in the field log book.

IDW containers will remain closed except when adding or removing waste. Immediately upon beginning to place waste into the drum/container, a “Waste Container” or “Testing in Progress” label will be filled out to include the information specified above, and affixed to the container. Once the contents of the container are identified as either non-hazardous or hazardous, the following additional labels will be applied. Containers with waste determined to be non-hazardous will be labeled with a green and white "Non-Hazardous Waste" label over the "Waste Container" label. Containers with waste determined to be hazardous will be stored in an onsite storage area and will be labeled with the "Hazardous Waste" label and affixed over the "Waste Container" label. The ACCUMULATION DATE for the hazardous waste is the date the waste is first placed in the container and is the same date as the date on the "Waste Container" label. DOT hazardous class labels must be applied to all hazardous waste containers for shipment offsite to an approved disposal or recycling facility. In addition a DOT proper shipping name shall be included on the hazardous waste label. The transporter should be equipped with the appropriate DOT placards. However, placarding or offering placards to the initial transporter is the responsibility of the generator per 40 CFR § 262.33.

**Inspections and Documentation**

All IDW will be documented as generated on a Drum Inventory Log maintained in the field log book. The Drum Inventory will record the generation date, type, quantity, matrix and origin (e.g. Boring-1, Test Pit 3, etc.) of materials in every drum, as well as a unique identification number for each drum. The drum inventory will be used during drum pickup to assist with labeling of drums. The drum storage area and any other areas of temporarily staged waste, such as soil/debris piles, will be inspected weekly. The weekly inspections will be recorded in the field notebook or on a Weekly Inspection Log. Digital photographs will be taken upon the initial generation and drumming/staging of waste, and final labeling after characterization to document compliance with labeling and storage protocols, and condition of the container. Evidence of damage, tampering or other discrepancy should be documented photographically.

**Emergency Response and Notifications**

Specific procedures for responding to site emergencies will be detailed in the HASP. If the generator is designated as a LQG, a Contingency Plan will need to be prepared to include emergency response and notification procedures per 40 CFR § 265 Subpart D. In the event of a fire, explosion, or other release which could threaten human health

outside of the site or when Client or ARCADIS has knowledge of a spill that has reached surface water, Client or ARCADIS must immediately notify the National Response Center (800-424-8802) in accordance with 40 CFR § 262.34. Other notifications to state agencies may also be necessary.

**Drilling Soil Cuttings and Muds**

Soil cuttings are solid to semi-solid soils generated during trenching activities, subsurface soil sampling, or installation of monitoring wells. Depending on the drilling method, drilling fluids known as "muds" may be used to remove soil cuttings. Drilling fluids flushed from the borehole must be directed into a settling section of a mud pit. This allows reuse of the decanted fluids after removal of the settled sediments. Soil cuttings will be labeled and stored in 55-gallon drums with bolt-sealed lids.

**Excavated Solids**

Excavated solids may include, but are not limited to soil, fill and construction and demolition debris. Excavated solids may be temporarily stockpiled onsite as long as the material is a RCRA non-hazardous waste and the solids will be treated onsite pursuant to a certified, authorized, or permitted treatment method, or properly disposed off-site. Stockpiled materials characterized as hazardous must be immediately containerized and removed from the site within 90 days of generation (except for soils using satellite accumulation). Excavated solids should be stockpiled and maintained in a secure area onsite. At a minimum, the floor of the stockpile area will be covered with a 20-mil high density polyethylene liner that is supported by a foundation or at least a 60-mil high density polyethylene liner that is not supported by a foundation. The excavated material will not contain free liquids. The owner/operator will provide controls for windblown dispersion, run-on control, and precipitation runoff. The run-on control system will prevent flow onto the active portion of the pile during peak discharge from at least a 25-year storm and the run-off management system will collect and control at least the water volume resulting from a 24-hour, 25-year storm (EPA, 1992). Additionally, the stockpile area will be inspected on a weekly basis and after storm events. Individual states may require that the stockpile be inspected/certified by a licensed professional engineer. Stockpiled material will be covered with a 6-mil polyvinyl chloride (PVC) liner. The stockpile cover will be secured in place with appropriate material (concrete blocks, weights, etc.) to prevent the movement of the cover. Excavated solids may also be placed in roll off containers and covered with a 6- mil PVC liner pending results for waste characterization.

**Decontamination Solutions**

Decontamination solutions are generated during the decontamination of personal protective equipment and sampling equipment. Decontamination solutions may range from detergents, organic solvents and acids used to decontaminate small field sampling equipment to steam cleaning rinsate used to wash heavy field equipment. These solutions are to be labeled and stored in 55-gallon drums with bolt-sealed lids.

**Disposable Equipment**

Disposable equipment includes personal protective equipment (tyvek coveralls, gloves, booties and APR cartridges) and disposable sampling equipment such as trowels or disposable bailers. If the media sampled exhibits hazardous characteristics per results of waste characterization sampling, disposable equipment will also be disposed of as a hazardous waste. These materials will be stored onsite in labeled 55- gallon drums pending analytical results for waste characterization.

**Purge Water**

Purge water includes groundwater generated during well development, groundwater sampling, or aquifer testing. The volume of groundwater generated will dictate the appropriate storage procedure. Monitoring well development and groundwater sampling may generate three well volumes of groundwater or more. This volume will be stored in labeled 55-gallon drums. Aquifer tests may generate significantly greater volumes of groundwater depending on the well yield and the duration of the test. Therefore, large-volume portable polyethylene tanks will be considered for temporary storage pending groundwater-waste characterization.

**Purged Water Storage Tank Decontamination and Removal**

The following procedures will be used for inspection, cleaning, and offsite removal of storage tanks used for temporary storage of purge water. These procedures are intended to be used for rented portable tanks such as Baker Tanks or Rain for Rent containers. Storage tanks will be made of inert polyethylene materials.

The major steps for preparing a rented tank for return to a vendor include characterizing the purge water, disposing of the purge water, decontaminating the tank, final tank inspection, and mobilization. Decontamination and inspection procedures are describe in further detail below.

Tank Cleaning: Most vendors require that tanks be free of any sediment and water before returning, a professional cleaning service may be required. Each

specific vendor should be consulted concerning specific requirements for returning tanks.

Tank Inspection: After emptying the tank, purged water storage tanks should be inspected for debris, chemical staining, and physical damage. The vendors require that tanks be returned in the original condition (i.e., free of sediment, staining and no physical damage).

## VII. Waste Characterization Sampling and Shipping

### Soil/Solids Characterization

Waste characterization will be conducted in accordance with waste hauler, waste handling facility, and state/federal requirements. In general, RCRA hazardous wastes are those solid wastes determined by a Toxicity Characteristic Leaching Procedure (TCLP) test or to contain levels of certain toxic metals, pesticides, or other organic chemicals above specific federally regulated thresholds. If the one or more of 40 toxic compounds listed in Table I of 40 CFR § 261.24 are detected in the sample at levels above the maximum unregulated concentrations, the waste must be characterized as a toxic hazardous waste. Wastes can also be considered “listed” hazardous waste depending on site-specific processes.

Composite soil samples will be collected at a frequency of one sample per 10 cubic yard basis for stockpiled soil or one per 55-gallon drum for containerized. A four point composite sample will be collected per 10 cubic yards of stockpiled material and for each drum. Sample and composite frequencies may be adjusted in accordance with the waste handling facility’s requirements. Waste characterization samples may be analyzed for the TCLP volatile organic compounds (VOCs), TCLP semi-volatile organic compounds (SVOCs), TCLP RCRA metals, and polychlorinated biphenyls, as well as corrosivity (pH), reactivity and flammability (flashpoint). Additional samples may be collected and analyzed by the laboratory on a contingency basis.

### Wastewater Characterization

Waste characterization will be conducted in accordance with the requirements of the waste hauler, waste handling facility, and state/federal governments. In general, purge water should be analyzed by methods appropriate for the known contaminants, if any, that have been historically detected in the monitoring wells. Samples will be collected and analyzed in accordance with the requirements of the waste disposal facility. Disposable bailers will be used to collect a representative grab wastewater sample from the wastewater container. The bailer should be slowly lowered into the wastewater container to at least the mid-point of the container. The bailer should be retrieved

slowly, and the water collected directly into the sample bottles. Repeat this procedure until the required volume of wastewater has been collected.

Wastewater characterization samples may be analyzed for TCLP volatile organic compounds (VOCs), TCLP semi-volatile organic compounds (SVOCs), TCLP RCRA metals, and polychlorinated biphenyls, as well as corrosivity (pH), reactivity and flammability (flashpoint), as required. Additional samples may be collected and analyzed by the laboratory on a contingency basis.

**Sample Handling and Shipping**

All samples will be appropriately labeled, packed, and shipped, and the chain-of-custody will be filled out in accordance with the Chain-of-Custody SOP and Field Sampling Handling, Packing, and Shipping SOP and Hazardous Materials Packaging and Shipping SOP.

It should be noted that additional training is required for packaging and shipping of hazardous and/or dangerous materials. Please reference the following ARCADIS intranet team page for more information: http://team/sites/hazmat/default.aspx.

**Preparing Waste Shipment Documentation (Hazardous and Non-Hazardous)**

Waste profiles will be prepared by the ARCADIS PM and forwarded, along with laboratory analytical data to the Client PM for approval/signature. The Client PM will then return the profile to ARCADIS who will then forward to the waste removal contractor for preparation of a manifest. The manifest will be reviewed by ARCADIS prior to forwarding to the Client PM for approval. Upon approval of the manifest, the Client PM will return the original signed manifest directly to the waste contractor or to the ARCADIS PM for forwarding to the waste contractor.

Final drum labeling and pickup will be supervised by an ARCADIS representative who is experienced with waste labeling procedures. The ARCADIS representative will have a copy of the drum inventory maintained in the field book and will reconcile the drum inventory with the profile numbers on the labels and on the manifest. Different profile numbers will be generated for different matrices or materials in the drums. For example, the profile number for drill cuttings will be different than the profile number for purge water. **When there are multiple profiles it is critical that the proper label, with the profile number appropriate to a specific material be affixed to the proper drums.** A copy of the ARCADIS drum inventory will be provided to the waste transporter during drum pickup and to the facility receiving the waste.

## VIII. Data Recording and Management

Waste characterization sample handling, packing, and shipping procedures will be documented in accordance with the *Quality Assurance Project Plan*, if one exists. Copies of the chains-of-custody forms will be maintained in the project file.

Following waste characterization, IDW containers will be re-labeled with the appropriate waste hazardous or non-hazardous waste labels and the client will initiate disposal at the appropriate waste disposal facility.

## IX. Quality Assurance

The chain-of-custody and sample labels for waste characterization samples will be filled out in accordance with the *Quality Assurance Project Plan*.

## X. References

United States Environmental Protection Agency (USEPA). 1992. Guide to Management of Investigation-Derived Wastes. Office of Remedial and Emergency Response. Hazardous Site Control Division. January 1992.

USEPA. 1991. *Guide to Discharging CERCLA Aqueous Wastes to Publicly Owned Treatment Works (POTWs)*. Office of Remedial and Emergency Response. Hazardous Site Control Division 0S-220W. March 1991.

# SAMPLE HANDLING, PACKAGING AND SHIPPING

## STANDARD OPERATING PROCEDURE

## 1.0 Purpose

This Standard Operating Procedure (SOP) outlines the methods and responsibilities for field personnel to use in the packaging and shipping of environmental samples for chemical and physical analysis. This SOP only applies to the packaging and shipping of limited quantity, low concentration environmental samples. This procedure does not apply to those samples considered hazardous materials, hazardous waste, mixed waste, radioactive waste, and/or dangerous goods. Those requirements are specified in the Department of Transportation (DOT) 49 CFR 114-327 and the International Air Transport Association (IATA) procedures. The details within this SOP are only applicable to the general requirements for sample packaging and shipping and should only be used as a guide for developing more job-specific work plans.

## 2.0 References

2.1 EPA, September 1987, Compendium of Superfund Field Operations Methods, EPA 540/P-87/001a, OSWER 9355.0-14.

2.2 EPA, August 1988, EPA Guidelines for Conducting Remedial Investigation and Feasibility Studies under CERCLA, Interim Final OSWER Directive 9355.3-01.

2.3 Code of Federal Regulations, DOT 49 CFR parts 100 to 177, Revised October 1, 1992.

2.4 Dangerous Goods Regulations, IATA, January 1, 1994.

2.5 ARCADIS, 2004, Site Wide Quality Assurance Project Plan (QAPP), Lake City Army Ammunition Plant.

2.6 ARCADIS, 2004, Site Wide Field Sampling Plan (FSP), Lake City Army Ammunition Plant.

# 3.0 Definitions

## 3.1 Environmental Sample

A limited quantity, low concentration sample that does not require DOT or IATA hazardous waste labeling as a hazardous waste or material.

## 3.2 Hazardous Waste Sample

Medium or high concentration sample requiring either DOT or IATA labeling as a hazardous waste or material.

## 3.3 Hazardous Waste

Any substance listed in 40 CFR Subpart D (260.30 et seq.) or otherwise characterized as ignitable, corrosive, reactive, or toxic as specified in Subpart C (261.20 et seq.) that would be subject to manifest and packaging requirements specified in 40 CFR 262. Hazardous waste is defined and regulated by the U.S. Environmental Protection Agency (USEPA).

## 3.4 Hazardous Material

A substance or material in a quantity or form which may pose an unreasonable risk to health, safety, and/or property when transported in commerce. Hazardous material is defined and regulated by DOT (49 CFR 173.2 and 172.101) and IATA (Section 4.2).

## 3.5 Sample

Physical evidence collected from a facility or the environment which is representative of conditions at the point and time at which the sample is collected.

# 4.0 Procedure

## 4.1 Responsibilities

4.1.1 Compliance with this procedure is the responsibility of project management, site management, health and safety, and field personnel.

4.1.2 Project Manager - is responsible for the development and review of site-specific work plans which address the specific sample handling, packaging, and shipping requirements for the project. Review the project specific documentation forms to ensure they are appropriate for the field activities. The Project Manager is also responsible for

seeing that field personnel receive proper training and maintain quality assurance/quality control (QA/QC).

4.1.3 Field Operation Leader – is responsible for observing field activities and the periodic review of documentation generated during sample handling, packaging, and shipping and the periodic review and audit of field personnel as they perform the work.

If problems arise, the Field Operation Leader is also responsible for swift implementation of corrective action (i.e., retraining personnel, additional review of work plans and SOPs, variances to requirements, issuing nonconformances).

### *4.2 Sample Handling*

4.2.1 Inspect the sampling containers (obtained from the analytical laboratory prior to the sampling event) to ensure that they are appropriate for the samples being collected, correctly preserved, and undamaged.

4.2.2 When collecting a sample always use approved/site specific personal protective equipment (e.g., gloves, etc.) to prevent cross-contamination from sample to sample but also as a health and safety requirement.

### *4.3 Field Packaging*

4.3.1 Collect the samples in accordance with the site-specific work plans and applicable SOPs.

4.3.2 As soon as possible after sample collection, tightly seal the container, and place a piece of custody tape over or around the cap. The custody tape should be placed over the cap so that any attempt to remove the cap will cause the tape to be broken. Do not place custody tape over a volatile organic analysis (VOA) vial septum.

4.3.3 Place all containers in separate, appropriately sized, airtight, seam sealing polyethylene bags (e.g., Ziploc™). Seal the bag, removing any excess air.

4.3.4 Place the bagged container inside an insulating shipping container, "cooler." This cooler should have frozen blue ice inside to assure samples remain cool, "4°," during transit

from field to the packaging location.

4.3.5 Because blue ice does not maintain the 4°C standard required for sample shipping, it should only be used while in the field collecting samples.

4.3.6 Maintain the samples under chain of custody (COC) (Form 1) in accordance with the site-specific work plans and appropriate SOPs.

### *4.4 Sample Packaging*

4.4.1 Inspect the integrity of the shipping container. The container is generally a "cooler" constructed of heavy plastic or metal with appropriate insulating properties so that variations in temperature during shipping are minimized. Also make sure that the drain plug has been sealed with nylon reinforced strapping tape or mailing tape.

4.4.2 Place two to four inches of absorbent packaging material (e.g., bubble wrap) in the bottom of the shipping container.

4.4.3 Carefully check the COC record against the collected sample labels and containers to ensure that the sample numbers, sample description, date and time of collection, container type and volume, preservative, and the required analytical methods are correct and in agreement.

4.4.4 Place the samples in the shipping container, allowing sufficient room between the samples to place ice and/or packing material.

4.4.5 Double bag and seal crushed or cubed ice in heavy-duty polyethylene bags. Place these bags of ice on top of and between samples. Blue ice should not be used for sample shipping; it does not maintain the 4°C temperature necessary for regulatory compliance. Include a VOA vial of tap water clearly labeled "temperature check" so that the laboratory can verify the temperature of the samples upon receipt. The remaining space will be filled with packing material.

4.4.6 All samples requiring temperature preservation stated at 4°C will be acceptable "as in" within the range of 2°C to 6°C. The laboratory should record the temperature of receipt

upon the COC. For all samples received above 6°C to 10°C, the sample(s) and temperature (in 1°C increments) will be noted on the COC and then analyzed. For samples with temperatures greater than 10°C, the samples will be rejected by the laboratory for analysis and immediately reported to the Project Chemist. For VOA samples below 0°C, the samples will be indicated as such to the project chemist or their designee and analyzed and also reported.

### *4.5 Sample Shipping*

4.5.1 The person in charge of sample custody will time, date, and sign over relinquishment of custody on the COC. When a common carrier is to be used for sample shipment, also record the air bill number (tracking number) and the name of the carrier on the COC record. Place the original copy of the COC record in a sealed, clear plastic envelop or bag and tape the COC record envelope to the inside lid of the shipping container. Retain a copy of the COC record for tracking purposes.

4.5.2 Using nylon reinforced strapping tape or mailing tape, seal the shipping container.

4.5.3 Place custody tape over opposite ends of the lid.

4.5.4 Mark the container "THIS END UP," or apply arrow labels that indicate the proper position to be maintained during shipping.

4.5.5 Apply a label stating the name and address of the shipper and the receiving laboratory on the outside of the cooler.

4.5.6 Turn the sample over to the courier or carrier for delivery to the laboratory. All samples should be shipped by the fastest available method to the laboratory as soon as possible after sample collection.

NOTE: The courier or carrier is not responsible for sample custody and is not required to sign the COC.

4.5.7 Contact the appropriate laboratory personnel to advise them of the sample shipment.

4.5.8 Review the COC and sample collection forms for completeness and turn them over to site or project management.

## 5.0 Records

5.1 Records generated as a result of implementation of this SOP will be controlled and maintained in the project record files and in accordance with Section 1.0 of the Site Wide QAPP for Lake City Army Ammunition Plant.

## 6.0 Figures / Forms

6.1 Analysis Request and Chain of Custody Record (Attachment A-2 of the Site Wide FSP).

RTI Laboratories, Inc.
31628 Glendale St.
Livonia, Michigan 48150

# STANDARD OPERATING PROCEDURE

# ANALYSIS OF SEMI-VOLATILE ORGANIC COMPOUNDS

| | |
|---|---|
| **Analyte:** | **Base Neutral & Acid Extractable (BNA's)**<br>**Semi Volatile Organics** |
| **SOP #:** | **8270D_110713_R13** |
| **Method Reference:** | **EPA SW-846 8270D, EPA 625** |
| **Issue Date:** | **June 1, 1996** |
| **Revision No.:** | **13** |
| **Revision Date:** | **November 7, 2013** |

**Reviewed and Approved: November 7, 2013**

Director, Quality Management: Charles O'Bryan

Director, Environmental Services: Yemane Yohannes

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**ANALYSIS OF SEMI-VOLATILE ORGANIC COMPOUNDS**

**SOP#: 8270D_110713_R13**

**TABLE OF CONTENTS**

# 1.0 Scope and Application

## 1.1 Introduction

RTI Lab, Inc, has prepared this document to detail the Standard Operating Procedure (SOP) for the analysis of water and soil samples for semi-volatile compounds by gas chromatography/mass spectrometry. Method 8270D can be used to quantify most neutral, acidic, and basic semi - volatile organic compounds that are soluble in methylene chloride and capable of being eluted, without requiring formation of derivatives, as sharp peaks from a GC fused-silica cap column coated with a slightly polar silicone. Such compounds include PNA's, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters and pesticides, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, phenols and nitrophenols. Specific compound lists are contained in the test codes resident in the Omega LIMS.

A detailed description of the instrumentation, calibration, run parameters and quality control procedures where applicable is included in this SOP. This SOP is to be used in conjunction with the RTI QAP quality control procedures. Please review the QAP to fully implement this SOP. For definition of terms not specifically defined in this document refer to RTI QAP Section 16.

## 1.2 Summary of Method

The samples are prepared for analysis using either liquid: liquid extraction (aqueous) or sonication (solids/soils). Sample cleanup procedures are employed when necessary (See 3550B and 3510C SOPs for cleanup procedures). The semi - volatile compounds are introduced into the GC/MS by injecting an aliquot of the sample extract. The GC column is temperature programmed to separate the analytes, which are then detected with a mass spectrometer (MS). Identification of the target analytes is accomplished by comparing their mass spectra with the electron impact spectra of standard compounds. Quantification is accomplished by comparing the response of the primary quant ion relative to an internal standard using at least a five-point calibration curve.

# 2.0 Safety Precautions

2.1 Compounds applicable to this method are known or suspected carcinogens. Standard preparation is conducted in fume hoods designated for organic use.

2.2 Extraction solvents are flammable and/or toxic and must be handled with caution. All extractions are performed in a manner designed to minimize exposure to these chemicals using appropriate hoods and personal protection.

## 3.0 Sample Requirements and Sample Handling Procedures

3.1 Samples are received in accordance with the RTI Lab Standard Operating Procedure for Sample Receipt and Custody (SRC001-A). Appropriate U. S. Environmental Protection Agency (EPA) sample handling procedures and sample preservation recommendations are followed. Water samples are collected in 1L amber bottles with Teflon lined screw caps. Soil samples are received in wide mouth jars with Teflon lined lids ranging from 2 oz. to 9 oz. in size. Refer to Sample Receipt and Custody SOP (SRC001-A) and QAP section 5 for sample preservation requirements and checks.

3.2 The holding time for water samples is 7 days from collection to extraction and 40 days from extraction to analysis.

3.3 The holding time for solid samples is 14 days from collection to extraction and 40 days from extraction to analysis.

3.4 All samples are stored at 4$^{o}$ C. Extracts are stored in a designated freezer at <0$^{o}$ C

## 4.0 MDL, Linear Range, Accuracy and Precision

4.1 The method detection limit (MDL) is statistically defined at the 99% confidence level according to 40 CFR Part 136 App. B. Seven replicates containing all of the analytes of interest at a concentration level of 1-5 times the estimated D.L. are analyzed and the standard deviation is calculated. The Student's T Value for the 7 replicates (3.143) is multiplied by the standard deviation of the analyte to calculate the MDL. MDLs are updated annually (or as needed) and are kept on file in the Laboratory. MDLs and reporting limits are incorporated into the applicable test code in the Omega LIMS.

4.2 The LOD (limit of detection) is determined by spiking reagent water at 1-4 times the MDL and prepared using the same procedure as samples. Analytes must be present at levels 3 times or greater than the blank response (greater than 3 times the signal to noise ratio). The concentration used is the LOD for that analyte. LOD determinations must be performed quarterly.

4.3 The LOQ (limit of quantification) is determined by spiking reagent water at the reporting limit (RL/CRQL) and prepared in the same manner as samples. Analyte recovery must be within 20% of the expected concentration. The concentration used and successfully recovered is the LOQ for that analyte. LOQ determinations must be performed quarterly.

4.4 Initially accuracy and precision at the LOQ is determined by spiking 4 aliquots of reagent water at the reporting limit (RL/CRQL) and prepared using the same procedure used for samples. The average recovery must be within 50-130% of the expected value or LCS control limits. The %RSD must be less than 15%. This procedure is performed annually.

4.5 LOD/LOQ determinations that do not meet the specifications above require repeat analysis, adjustment to the spiking levels and/or reporting limits, repeating the MDL determination at adjusted concentrations if required and repeat LOD/LOQ determinations.

4.6 The accuracy and precision for this method are determined by analyzing four aliquots from a Laboratory Control Sample containing the element(s) of interest at the mid-level of the calculated range (diluted if above this range). Percent recovery, standard deviation, and the relative standard deviation are calculated for each analyte and documents are kept on file in the laboratory.

4.7 The analytical range used by RTI Lab, Inc is from 1.0 µg/L to 50 µg/L for most of the compounds determined by this method. If an analyte concentration is beyond its established calibration range, a dilution of that sample is required. Quantification of all reportable analytes must originate from a response within the established linear range.

4.8 Preparation of initial LOD, LOQ and MDL:

4.81. An LOD/LOD/MDL of various concentrations is prepared according to the table below in a 25 ml volumetric flask and diluting to volume with pesticide grade acetone. Spike 1mL of this standard for every LOQ/MDL sample. Spike 0.5mL of full list spike and 0.75 ml of the PNA spike for every LOD sample.

Table 1 - Full list LOD/LOQ/MDL Spike

| Standard | Volume (µl) | Final Concentration (µg/ml) |
|---|---|---|
| Hydrocarbon Std 2-comp (n-Decane/N-Octadecane), 2000 ug/ml, Absolute, 94376 | 62.5 | 5 |
| Pyridine 1000µg/ml, Absolute Standards, 79091 | 125 | 5 |
| Benzoic Acid 2000µg/ml, Restek, 31879 | 250 | 20 |
| Benzidine Mix 2000µg/ml, Restek, 31834 | 250 | 20 |
| 1,4-Dioxane, 2000 ug/ml, Restek | 62.5 | 5 |
| 8270 SVOA 64-comp, AccuStandard, M-8270-AG01-ASL | 125 | 5 |
| 8270 SVOA 39-comp, AccuStandard, M-8270-AG02-ASL | 125 | 5 |

| | | |
|---|---|---|
| 4-Nitrophenol 1000µg/ml, Absolute Standards, 70231 | 375 | 15 |
| Hexachlorocyclopentadiene 1000µg/ml, Absolute Standards, 70198 | 375 | 15 |
| 2,4-Dinitrophenol 1000µg/ml, Absolute Standards, 70159 | 375 | 15 |
| 2,3,4,6-Tetrachlorophenol 1000µg/ml, Absolute Standards, 70477 | 375 | 15 |
| Biphenyl, 2000 ug/ml, Absolute, 90495 | 12.5 | 1 |
| Additions Std (Benaldehyde/Caprolactam/Atrazine), 1000 ug/ml each, Restek, 31902 | 375 | 15 |
| 1-Methylnaphthalene, 1000 µg/ml, Ultra, EPA-1225 | 125 | 5 |

Table 2 - PNA LOD/LOQ/MDL Spike

| Standard | Volume (µl) | Final Concentration (µg/ml) |
|---|---|---|
| 8270 SVOA 64-comp, AccuStandard, M-8270-AG01-ASL | 2 | 0.2 |
| 1-Methylnaphthalene, 1000 µg/ml, Ultra, EPA-1225 | 2 | 0.2 |

## 5.0 Interferences

5.1 Interferences can arise from carryover due to high sample concentrations or contamination from reagents and/or glassware. Blanks are injected to ensure system cleanliness in both instances. All glassware must be scrupulously cleaned before use. Phthalates are notorious lab contaminants and will leach from any soft plastic material used during sampling or sample preparation.

5.2 Samples containing high concentrations of non-target analytes or extremely high levels of select target analytes can result in elevated detection limits for other target analytes. Dilution of the extract may improve the resolution and quantification of some analytes but will generally cause an elevation in the RDL. Interferences from high molecular weight organics such as oils will cause an elevated baseline. If this background is at a high concentration it will interfere with analyte identification as well as quantification. While RTI does not currently employ this method of clean up, GPC clean up (refer to GPC reference method for specifics) is a method available to reduce high molecular weight interference.

5.3 Benzidine may be subject of oxidative loss during solvent concentration and exhibits poor chromatographic behavior.

5.4 Hexachlorocyclopentadiene will thermally decompose in the GC inlet, chemically react in acetone solutions and is subject to photochemical decomposition.

5.5 N-Nitrosodimethylamine does not separate well from the solvent.

5.6 N-Nitrosodiphenylamine decomposes in the GC inlet and cannot be distinguished from diphenylamine. These compounds are reported as a combined concentration.

5.7 1,2-Diphenylhydrazine is unstable even at room temperature and converts to Azobenzene. These compounds are reported as a combined concentration.

5.8 Pentachlorophenol, 2,4-Dinitrophenol, 4-Nitrophenol, Benzoic acid, 4,6-Dinitro-2-methylphenol, 4-Chloro-3-methylphenol, Nitroanilines and Benzyl alcohol are subject to erratic chromatographic behavior especially if the GC system becomes contaminated with oils or other high boiling point materials.

5.9 Pyridine performs poorly with the injection temperature used for analysis. If this compound is critical to the program objectives a separate analysis may be required.

## 6.0 Apparatus and Materials

6.1 Glass Funnels or HDPE if glass is unavailable

6.2 pH indicator paper

6.3 Graduated cylinders. 1000ml and 100ml

6.4 Glass beakers, 250 ml size.

6.5 Microliter syringes, 10ul, 25 ul, 50ul, 100µl, 500µl, and 1000µl.

6.6 Volumetric glassware, class A

6.7 Glass vials – 2ml with Teflon lined crimp caps.

6.8 Pyrex glass wool

6.9 Pasteur pipettes

6.10 HP6890 GC/5973 MS with 7673 auto sampler – SVOC 5, Chemstation version B.

6.11 HP7890A GC/5975C MS with 7693 auto sampler – SVOC 7, Chemstation version E.

6.12 HP6890N GC/5973 MS with 7693 auto sampler – SVOC 8, Chemstation version E.

6.13 GC column – RXI-5 Sil MS 20m x 0.18mmID, 0.36 film thickness.

6.14 Restek Gooseneck Splitless Liner IP Deact., SV Wool 4mm ID (Restek #20799-231.5)

6.15 2ml amber autosampler vials

6.16 250µl vial inserts

6.17 11mm aluminum auto sampler caps with Teflon lined septa

6.18 11mm crimper tool

6.19 Pasteur pipettes.

6.20 1/16”x0.5mm ID Compact Vespel/Graphite Inlet Ferrules (Restek 20248).

6.21 1/16”x0.4mm ID Vespel/Graphite GC/MS Interface Ferrules (Restek 20211).

6.22 Gold-plated Inlet Seals, 0.8mm ID (Restek 21241).

6.23 PC with Microsoft Windows, Agilent EnviroQuant Chemstation-G1701BA Ver. B.01.00, E.02.02 and Omega LIMS.

## ~~7.0 Reagents~~

7.1 Anhydrous Sodium sulfate, muffled at 450° C for 4 hours

7.2 Methylene chloride – pesticide grade

7.3 Acetone – pesticide grade

7.4 8270 LCS Spike, 200µg/mL (Cerriliant ERS-077)- Add 100µL to each LCS, MS, and MSD samples (20ug/extract).

7.5 Working surrogate solution 250 ppm: prepared by adding 1.56mL of 6 Component BNA Surrogate Standard (Absolute Standards, catalog # 25015) to a 25ml class A volumetric flask and dilute to the mark with pesticide grade acetone. Add 100µl to each sample, method blank, MS/MSD and LCS (25ug/extract).

7.6 Internal standard mix – 4000 µg/mL (10009 from Absolute Standards), add 10 ul per 1 ml extract (40 ug/extract).

7.7 Internal standard solutions are prepared, stored and handled in a manner designed to minimize the deviation in response from the time a vial is opened until the next new vial is opened for use. Changes to the internal standard solution may occur due to evaporation of solvent into the headspace of the vial storing the solution. The repeated opening and closing of this solution over a period of several days could lead to a concentrating of the compounds with a concomitant change in response.

7.7.1 Transfer internal standard solution into a 2ml amber autosampler vial.

7.7.2 Store the vials at room temperature protected from exposure to light.

7.8 Sulfuric acid – 1:1 in DI water

7.9 ASTM Type II DI water

7.10 Helium – UHP

7.11 Tune Standard – DFTPP Tuning Standard, 500 ug/mL, Absolute, 43030

7.12 Internal Standard – CLP Semi-VOC Internal Standard, 4000 ug/mL, Absolute, 10009

7.13 LCS/MS Spike Standard - 8270 LCS Spike, 200µg/mL, Cerilliant, ERS-077

7.14 Calibration standards –

7.14.1 8270 SVOA 64-comp, AccuStandard, M-8270-AG01-ASL
7.14.2 1,4-Dioxane, 2000ppm, Restek, 31853
7.14.3 Benzidine Mix, 2000ppm, Restek, 31834
7.14.4 Hydrocarbon 2 components, 2000ppm, Absolute, 94376
7.14.5 Benzoic Acid, 2000ppm, Restek, 31879
7.14.6 8270 BNA working Surrogates, 4000ppm, Absolute, 25015
7.14.7 1,4-Dioxane-d8, 2000ppm, Restek, 30614
7.14.8 8270 SVOA 35-comp, Ultra, SVM8271-1
7.14.9 1-Methylnaphthalene, 1000ppm, Ultra, EPA-1225
7.14.10 4-Nitrophenol, Absolute, 70231, 1000ppm
7.14.11 2,4-Dinitrophenol, Absolute, 70159, 1000ppm
7.14.12 Pyridine, Absolute,1000ppm, 79091

7.15 Calibration check standard –

7.15.1 Benzidine Mix, 2000ug/mL, Cerilliant, ERS-018
7.15.2 8270 BNA surrogate, 4000 ug/ml, AccuStandard, M-8270-SS
7.15.3 1,4-Dioxane-d8, 1000 ug/ml, Absolute, 79305
7.15.4 8270 Custom Mix, 1000ug/mL, AccuStandard, S-24053

7.15.5 Mega Mix, 1000ppm, Restek, 31850
7.15.6 Pentachloronitrobenzene, 5000ppm, PPS-133-1
7.15.7 N-Nitrosodiethylamine, 2000ppm, AccuStandard, APP-0-148-20X
7.15.8 2,6-Dichlorophenol, ABSOLUTE, 1000ppm, 70143
7.15.9 Pentachlorobenzene, absolute, 1000ppm, 70321
7.15.10 1,2,4,5-Tetrachlorobenzene, absolute, 2000ppm, 93004
7.15.11 p-Cresol (4-methylphenol), Absolute, 1000ppm, 70216
7.15.12 m-Cresol (3-methylphenol), absolute, 1000ppm, 70215

7.16 Standards are stored according to the manufacturer's recommendations.

7.17 All reagents and standards prepared must be logged in the appropriate standards/reagents log labeled with a minimum:

7.17.1 Identity of the material.
7.17.2 Concentration of the solution.
7.17.3 Date prepared.
7.17.4 Initials of analyst preparing the solution.
7.17.5 Expiration date.

## 8.0 Preparation of Standards and Calibration Procedure

8.1 Storage conditions of standards are found with the manufacturer instructions and must be followed. The expiration date of all prepared standards and spikes in this method is 6 months or the shortest expiration date of any stock standard used that is less than 6 months.

8.2 Tune check standard 50ng/µl- Prepare by adding 1000µl of the Tuning Standard (Sec. 7.8) to a 10ml class A volumetric flask and diluting to the mark with pesticide grade methylene chloride.

8.3 Tune verification – A solution containing 50 ng of DFTPP, DDT, benzidine, and pentachlorophenol is injected into the GC/MS and evaluated against the criteria specified in Method 8270D. These parameters are incorporated into the data system and appear on the tune report. The tune verification must be performed prior to analyzing samples and every 12 hours of continuous instrument run time. See section 13 of this document for more information.

8.4 A pentachlorophenol, benzidine peak tailing check is performed along with the tune check on a daily basis. Peak tailing factors must be <2. DDT degradation must not exceed 20%. If results exceed the criteria, injection port maintenance must be performed. This check must be done using Enviroquant. See section 13 for more information. Peak tailing factors and DDT degradation results are captured as PDF files and stored in the data folder for the each individual sequence.

8.5 RLVS Preparation: The RLVS is prepared according to Table 1 below.

**Table 3**
**RLVS Preparation - Full List RLVS**

| Standard | Volume (µl) | Final Concentration (µg/ml) |
|---|---|---|
| Hydrocarbon Std 2-comp (n-Decane/N-Octadecane), 2000 ug/ml, Absolute, 94376 | 62.5 | 5 |
| Pyridine 1000µg/mL, Absolute Standards, 79091 | 125 | 5 |
| Benzoic Acid 2000µg/mL, Restek | 250 | 20 |
| Benzidine Mix 2000µg/mL, Restek, 31834 | 250 | 20 |
| Base/Neutral and Acid Surrogate, 4000 ug/ml, Absolute, 25015 | 156 | 25 |
| 1,4-Dioxane, 2000 ug/ml, Restek | 62.5 | 5 |
| 1,4-Dioxane-d8, 2000 ug/ml, Restek, 30614 | 312.5 | 25 |
| 8270 SVOA 64-comp, AccuStandard, M-8270-AG01-ASL | 125 | 5 |
| 8270 SVOA 39-comp, AccuStandard, M-8270-AG02-ASL | 125 | 5 |
| 4-Nitrophenol 1000µg/mL, Absolute Standards, 70231 | 375 | 15 |
| 2,4-Dinitrophenol 1000µg/mL, Absolute Standards, 70159 | 375 | 15 |
| Biphenyl, 2000 ug/ml, Absolute, 90495 | 62.5 | 5 |
| Additions Std (Benaldehyde/Caprolactam/Atrazine), 1000 ug/ml each, Restek, 31902 | 125 | 5 |
| 2,3,4,6-Tetrachlorophenol 1000µg/mL, Absolute Standards, 70477 | 125 | 5 |

**Table 4 - PNA RLVS**

| Standard | Volume (µl) | Final Concentration (µg/ml) |
|---|---|---|
| 8270 SVOA 64-comp, AccuStandard, M-8270-AG01-ASL | 5 | 0.2 |
| 1-Methylnaphthalene, 1000ppm, Ultra, | 5 | 0.2 |

8.6 Initial Calibration Stock Standard Preparation: The ICAL Stock Standard is prepared at 50 ug/mL according to Table 1 below.

**Table 5**
**Initial Calibration Stock Standard Preparation**

| Standard | Volume (µL) |
|---|---|
| 8270 SVOA 64-comp, AccuStandard, M-8270-AG01-ASL | 250 |
| 8270 SVOA 35-comp, Ultra, SVM8271-1 | 250 |
| Benzoic Acid, Restek, 2000ppm, 31879 | 125 |
| 4-Nitrophenol, Absolute, 70231, 1000ppm | 250 |
| Benzidine Mix, 2000 ug/ml, Restek, 31834 | 125 |
| 2,4-Dinitrophenol, Absolute, 70159, 1000ppm | 250 |
| 1-Methylnaphthalene, Absolute, 2000ppm | 125 |
| 1,4-Dioxane, Restek, 2000ppm, 31853 | 125 |
| Hydrocarbon Standard, Absolute, 2000ppm, 94376 | 125 |
| Pyridine, Absolute, 1000ppm, 79091 | 250 |
| 8270 BNA working Surrogates, 4000ppm, Absolute, 25015 | 62.5 |

8.6.1 The calibration curve is made through a series of dilutions of the 50 µg/ml calibration standard (Sec 8.6) to encompass the range from 1.0 – 50 ug/mL. The levels of calibration are designed to incorporate the linear range of all compounds of interest. However, all levels may not actually be used to calibrate all compounds. The lowest level used for each analyte is a reflection of the lowest limit that will allow adequate identification of all compounds ions above the instrument noise level. Therefore, some compounds may have linear ranges that include 5-6 of

the most concentrated standards. Some compounds become non-linear at the higher concentration range and 5-6 of the least concentrated standards may be used as the linear range. Standards chosen for the calibration will be continuous. Standards are prepared according to the table below.

**Table 6**
**Calibration Standard Preparation**

| Level Concentration (µg/ml) | Volume (ml) of 50µg/mL | Volume (ml) Internal Standard | Volume (ml) Methylene Chloride |
|---|---|---|---|
| 1 | 20 | 10 | 980 |
| 2.5 | 50 | 10 | 950 |
| 5 | 100 | 10 | 900 |
| 10 | 200 | 10 | 800 |
| 15 | 300 | 10 | 700 |
| 20 | 400 | 10 | 600 |
| 25 | 500 | 10 | 500 |
| 50 | 1000 | 10 | 0 |

8.7 Calibration Check Standard (CCV) Preparation: The CCV is prepared according to Table 1 below.

**Table 7**
**CCV Preparation**

| Standard | Volume (µl) |
|---|---|
| Benzidine Mix, 2000ug/mL, Cerilliant, ERS-018 | 62.5 |
| 8270 BNA surrogate, 4000 ug/ml, AccuStandard, M-8270-SS | 31.25 |
| 1,4-Dioxane-d8, 1000 ug/ml, Absolute, 79305 | 125 |
| 8270 Custom Mix, 1000ug/ml, AccuStandard, S-24053 | 125 |
| Mega Mix, 1000ppm, Restek, 31850 | 125 |
| Pentachloronitrobenzene, 5000ppm, PPS-133-1 | 25 |
| N-Nitrosodiethylamine, 2000ppm, AccuStandard, APP-0-148-20X | 62.5 |

| | |
|---|---|
| 2,6-Dichlorophenol, ABSOLUTE, 1000ppm, 70143 | 125 |
| Pentachlorobenzene, absolute,, 1000ppm, 70321 | 125 |
| 1,2,4,5-Tetrachlorobenzene, absolute, 2000ppm, 93004 | 62.5 |
| p-Cresol (4-methylphenol), Absolute, 1000ppm, 70216 | 62.5 |
| m-Cresol (3-methylphenol), absolute, 1000ppm, 70215 | 62.5 |

8.8 All ICAL compounds must pass using one of three types of criteria: <20% RSD of the RRF, a linear regression model, which must include at least 5 data points, where the correlation coefficient is >0.99, or a non-linear (quadratic) regression, which must include at least 6 data points and have a correlation coefficient >0.99. For compounds that exceed the 20% RSD the linear or non-linear regression function of the data system will be used for analyte quantification provided the correlation coefficient is greater than 0.99. The equations for these regressions can be found in the HP Chemstation software. The average RRF for each compound will be evaluated and must be greater than the minimum RRF for the SPCC compounds included in Sec. 8.9.3.1. The RRF for the standard corresponding to the LOQ for each compound must meet the minimum RRF criteria. If necessary the RRF for each compound in each ICAL standard may be evaluated to ensure compounds are responding as expected.

8.8.1 The method of linear regression analysis has the potential for a significant bias to the lower portion of a calibration curve, while the relative percent difference and quadratic methods of calibration do not have this potential bias. When calculating the calibration curves using the linear regression model, a minimum quantification check on the viability of the lowest calibration point should be performed by re-fitting the response from the low concentration calibration standard back into the curve (see Method 8000 for additional details). It is not necessary to re-analyze a low concentration standard rather the data system can recalculate the concentrations as if it were an unknown sample. The recalculated concentration of the low calibration point should be within ± 30% of the standard's true concentration. Other recovery criteria may be applicable depending on the project data quality objectives and for those situations the minimum quantification check criteria should be outlined in a laboratory standard operating procedure, or a project-specific Quality Assurance Project Plan. Analytes that do not meet the minimum quantification calibration re-fitting criteria should be considered out of control and corrective action such as redefining the lower limit of quantification and/or reporting those out of control target analytes as estimated when the concentration is at or near the lowest calibration point may be appropriate.

8.8.2 Quantification of results at or slightly above the lowest standard may be more accurate when using the force through zero option of the data system. Since the data system does not include zero in the calculation of the regression equation and merely pivots the line through zero, this procedure is consistent with the guidelines in Method 8000C.

8.8.3 In situations where a sample is analyzed on an initial calibration where one or more compounds could not be calibrated to these specifications, then both non-detections and detections must be qualified as estimated if the sample cannot be re-analyzed.

8.8.4 Immediately following initial calibration a second source standard (Sec. 7.10) must be analyzed. The concentration of all compounds must be within 20% of the expected value and compound must meet the minimum RRF values in Sec. 8.9.3.1. This standard is prepared at 25 μg/L corresponding to the mid point of the calibration range.

8.9 Twelve (12) hour continuing calibration verification (CCV with evaluation of the SPCC compounds) standards. SPCC – system performance check compounds. See section 13 for more information.

8.9.1 The SPCC must be evaluated every 12 hours whenever samples are being analyzed or on failure of a SPCC.

8.9.2 The CCV is prepared by making a midpoint calibration standard, 25ug/ml according to the table in Sec. 87 from the second source standards.

8.9.3 SPCC criteria – minimum RRF

8.9.3.1 SPCC Compounds:

| SPCC Compound | Minimum RFF |
|---|---|
| Phenol | 0.800 |
| bis(2-Chloroethyl)ether | 0.700 |
| 2-Chlorophenol | 0.800 |
| 2-Methylphenol | 0.700 |
| 2,2'-Oxybis-(1-chloropropane) | 0.010 |
| Acetophenone | 0.010 |
| 4-Methylphenol | 0.600 |
| N-Nitroso-di-n-propylamine | 0.500 |
| Hexachloroethane | 0.300 |
| Nitrobenzene | 0.200 |
| Isophorone | 0.400 |
| 2-Nitrophenol | 0.100 |

| SPCC Compound | Minimum RFF |
|---|---|
| 2,4-Dimethylphenol | 0.200 |
| bis(2-Chloroethoxy)methane | 0.300 |
| 2,4-Dichlorophenol | 0.200 |
| Naphthalene | 0.700 |
| 4-Chloroaniline | 0.010 |
| Hexachlorobutadiene | 0.010 |
| 4-Chloro-3-methylphenol | 0.200 |
| 2-Methylnaphthalene | 0.400 |
| Hexachlorocyclopentadiene | 0.050 |
| 2,4,6-Trichlorophenol | 0.200 |
| 2,4,5-Trichlorophenol | 0.200 |
| 2-Chloronaphthalene | 0.800 |
| 2-Nitroaniline | 0.010 |
| Dimethyl phthalate | 0.010 |
| 2,6-Dinitrotoluene | 0.200 |
| Acenaphthylene | 0.900 |
| 3-Nitroaniline | 0.010 |
| Acenaphthene | 0.900 |
| 2,4-Dinitrophenol | 0.010 |
| 4-Nitrophenol | 0.010 |
| Dibenzofuran | 0.800 |
| 2,4-Dinitrotoluene | 0.200 |
| Diethyl phthalate | 0.010 |
| 1,2,4,5-Tetrachlorobenzene | 0.010 |
| 4-Chlorophenyl-phenyl ether | 0.400 |
| Fluorene | 0.900 |
| 4-Nitroaniline | 0.010 |
| 4,6-Dinitro-2-methylphenol | 0.010 |
| 4-Bromophenyl-phenyl ether | 0.100 |
| N-Nitrosodiphenylamine | 0.010 |
| Hexachlorobenzene | 0.100 |
| Pentachlorophenol | 0.050 |
| Phenanthrene | 0.700 |
| Anthracene | 0.700 |
| Carbazole | 0.010 |
| Di-n-butyl phthalate | 0.010 |
| Fluoranthene | 0.600 |
| Pyrene | 0.600 |
| Butyl benzyl phthalate | 0.010 |

| SPCC Compound | Minimum RFF |
|---|---|
| 3,3'-Dichlorobenzidine | 0.010 |
| Benzo(a)anthracene | 0.800 |
| Chrysene | 0.700 |
| Bis-(2-Ethylhexyl)phthalate | 0.010 |
| Di-n-octyl phthalate | 0.010 |
| Benzo(b)fluoranthene | 0.700 |
| Benzo(k)fluoranthene | 0.700 |
| Benzo(a)pyrene | 0.700 |
| Indeno (1,2,3-cd) pyrene | 0.500 |
| Dibenzo (a,h)anthracene | 0.400 |
| Benzo (g,h,i)perylene | 0.500 |
| 2,3,4,6-Tetrachlorophenol | 0.010 |
| Benzaldehyde | 0.010 |
| Acetophenone | 0.010 |
| Caprolactam | 0.010 |
| 1,1'-Biphenyl | 0.010 |
| Atrazine | 0.010 |

8.9.4 Target compounds calibrated using relative response factors must exhibit less than 20% difference and those calibrated using linear or quadratic models must exhibit less than 20% drift. 80% of all compounds must meet the criteria above for analysis to proceed. If more than 20% of the compounds exceed the criteria corrective action must be taken prior to analysis.

8.9.5 Compounds present in samples that exceed the 20% criteria are noted in the case narrative or flagged as estimated.

8.10 An ending CCV must be analyzed following sample analysis within the 12-hour analytical sequence for samples requiring adherence to DoD QSM 5.0 protocol. The percent drift or percent difference must be within 50% of the expected value for all target compounds.

## 9.0 Sample Preparation

9.1 Allow samples to warm to ambient temperature and prepare according to SOPs 3510C and 3550B. Oily, viscous or samples suspected of containing high concentrations of matrix interference are diluted with methylene chloride prior to instrument introduction. Clean up procedures, other than dilution, are not currently performed.

## 10.0 Diagram/Table

10.1 Reserved.

## 11.0 Analytical Procedure

11.1 Set up run sequence according to the data system software protocol using the following template after a successful tune check (Note: the below list is a guide and samples and QC samples may be loaded in any sequence within the 12 hour time frame). Run sequence follows successful ICAL and ICV results.

11.1.1 CCV
11.1.2 RLVS
11.1.3 Method Blank or Reagent Blank
11.1.4 LCS
11.1.5 QC sample and MS/MSD
11.1.6 Continue with sample analyses up to 12 hours from time of initial CCV
11.1.7 Ending CCB within the 12-hour analytical sequence
11.1.8 Repeat tune check and CCV at 12 hours and proceed from 11.1.2

11.2 Set GC conditions according to the table below.

| **Typical GCMS Parameters:** | **Settings: Instrument SVOC 7** | **Settings: Instruments SVOC 5 and 8** |
|---|---|---|
| Flow/Initial column temperature | Flow UHP Helium – 1.6 ml/min Splitless, constant flow EPC injection at 35 degrees C | Flow UHP Helium – 1.0 ml/min Splitless, constant flow EPC injection at 50 degrees C |
| Initial hold time | 1.0 minutes | 1.0 minutes |
| 1st ramp rate/temp. | 15 degrees/min to 110 degrees C. | 15 degrees/min to 110 degrees C. |
| Hold time – temp 1 | 0 minutes | 0 minutes |
| 2nd ramp rate/temp | 25 degrees/min to 330 degrees C. | 30 degrees/min to 280 degrees C. |
| Hold time – temp 2 | 2 minutes | 0 minutes |
| 3nd ramp rate/temp | NA | 15 degrees/min to 330 degrees C. |
| Hold time – temp 3 | NA | 2.5 minutes |
| Injector Temperature | 280 degrees C. | 280 degrees C. |
| Detector Temperature | 280 degrees C. | 280 degrees C. |

| Typical GCMS Parameters: | Settings: Instrument SVOC 7 | Settings: Instruments SVOC 5 and 8 |
|---|---|---|
| MS Quad Temperature | 150 degrees C. | 150 degrees C. |
| MS Source Temperature | 230 degrees C. | 230 degrees C. |

11.3 Set transfer line to 280 degrees C, and filament delay to a setting after the solvent peak has been identified.

11.4 Data interpretation, qualitative identifications and MS software specific protocol are addressed in method 8270D of SW-846, the HP GC/MS operator's and Enviroquant manual. Qualitative identifications must meet the method criteria before positive identification can be made.

11.5 Compound identification and quantification

11.5.1 Compound identification is based on retention time and characteristic mass spectrum.

11.5.2 Initial identification is a compound that elutes with the compound specified retention time (RT) window (0.25 min. for most compounds) or within a relative retention time of +/- 0.06 RRT units of the RRT of the standard compound. A minimum retention time deviation is programmed into the data system method for each compound.

11.5.3 The mass spectrum of compounds within the RRT range is compared to the spectrum of the standard compound. Relative intensities of the characteristic ions should be within 30% of the expected relative intensities for the reference spectrum.

11.5.4 Co-eluting structural isomers whose resolution is less than 50% of the average peak heights and that have similar mass spectra are to be reported as the sum of the isomers (i.e. m,p-cresols).

11.5.5 Analyst experience in evaluating mass spectra and identifying compounds in the presence of interfering components is important in final compound identification.

11.5.6 Identified compounds are quantified from the average response factor of the initial calibration or other calibration models employed when required.

11.5.7 Compounds exhibiting concentrations above the upper calibration level are diluted into the calibration range. If insufficient sample is available for dilution the concentration is flagged as estimated ("E"). Data from all dilutions are evaluated and compound results will be reported from the lowest dilution that exhibits lack of interference.

11.5.8 Compound concentrations that are below the laboratory reporting limit or lowest calibration point but positively identified above the MDL are flagged as estimated ("J").

11.6 Manual integration guidelines and procedures

11.6.1 Situations may arise whereby the quantification provided by the data system is inappropriate. This can occur due to co-elution, baseline noise or matrix interference.

11.6.2 When manual integration of a compound is necessary the following guidelines must be followed.

11.6.2.1 Manual quantification is performed by integrating the area of the quant ion for the compound.

11.6.2.2 The integration will only include the area attributable to the compound of interest.

11.6.2.3 The area integrated shall not include baseline background noise.

11.6.2.4 The area integrated shall not extend beyond the point where the sides of the peak intersect with the baseline.

11.6.2.5 Manual integration must not be used solely to meet quality control criteria.

11.6.2.6 Manual integration must not be used as a substitute for corrective action on the GC/MS system.

11.6.2.7 Instances of manual integration are flagged with a "m" by the data system. Cases of manual integrations require review and approval by the Laboratory Manager or QA Director and are documented in the corresponding instrument Excel file or in the LIMS analytical sequence Linked Files.

11.7 SIM Analysis.

11.7.1 Set up run sequence according to the data system software protocol using the following template after a successful tune check (Note: the below list is a guide and samples and QC samples may be loaded in any sequence within the 12 hour time frame):

11.7.1.1 CCV

11.7.1.2 RLVS

11.7.1.3 Method Blank

11.7.1.4 LCS

11.7.1.5 QC sample and MS/MSD

11.7.1.6 Continue with sample analyses up to 12 hours from time of initial CCV.

11.7.1.7 CCV

11.7.1.8 Repeat tune check and CCV at 12 hours and proceed from

11.7.2 Set GC conditions according to the table below.

| **Typical GC Parameters:** | **Settings: Instrument** |
|---|---|
| Flow/Initial column temperature | Flow UHP Helium – 1.0 ml/min Splitless, constant flow EPC injection at 50 degrees C |
| Initial hold time | 1.0 minutes |
| 1st ramp rate/temp. | 15 degrees/min to 110 degrees C. |
| Hold time – temp 1 | 0 minutes |
| 2nd ramp rate/temp | 30 degrees/min to 280 degrees C. |
| Hold time – temp 2 | 0 minutes |
| 3nd ramp rate/temp | 15 degrees/min to 330 degrees C. |
| Hold time – temp 3 | 3 minutes |
| Injector Temperature | 280 degrees C. |
| Detector Temperature | 280 degrees C. |

11.7.3 Data interpretation, qualitative identifications and MS software specific protocol are addressed in method 8270D of SW-846, the HP GC/MS operator's and Enviroquant manual. Qualitative identifications must meet the method criteria before positive identification can be made.

11.7.4 For SIM analysis, internal standard calibration is used.

11.7.5 A SIM method containing the analytes of interest is created. The retention time of each analyte is determined by running the standard in the full scan mode. The primary (Quantification), secondary and tertiary ions from section 13.12 are used to create an ion-monitoring window that incorporates the retention time of the analyte of interest.

11.7.6 The resolution is set to high and the dwell time to 50ms.

11.7.7 Sections 11.5 and 11.6 of this document are used for data analysis.

## 12.0 Details of Calibration and Calculations

12.1 Response Factor:

$$RF = \frac{(A_x)(C_{is})}{(A_{is})(C_x)}$$

Where: $A_x$ = Area of the characteristic ion for the compound being measured.
$A_{is}$ = Area of the characteristic ion for the specific internal standard.
$C_{is}$ = Amount of the specific internal standard (ng).
$C_x$ = Concentration amount of the compound being measured (ng).

12.2 Concentration:

$$\frac{ug}{l} or \frac{ug}{Kg} = \frac{(A_x)(IS)}{(A_{is})(RF)(V_o)} DF$$

Where: $A_x$ = Area of characteristic ion for compound being measured.
IS = Amount of internal standard injected (ng).
$A_{is}$ = Area of characteristic ion for the internal standard.
RF = Response factor for compound being measured.
DF = Dilution factor (where applicable)
$V_o$ = Sample volume in gm or ml.

12.2 Percent Relative Standard Deviation:

$$\%RSD = \frac{s}{x} 100$$

Where: RSD = Relative Standard Deviation.
X = Mean of the 3-5 initial R.F for a compound.
$\sigma$ = Standard Deviation of average R.F for a compound.

12.4 Percent Difference:

$$\%Dif = \frac{|RF - RFc|}{RF} 100$$

Where: RF = Average response factor from initial calibration.
RFc = Response factor from current verification check standard.

12.5 Percent Drift:

$$\%Drift = \frac{C_m}{C_e}100$$

Where: $C_m$ = Concentration measured
$C_e$ = Concentration expected

12.6 Tailing Factor :

$$TailingFactor = \frac{AC}{AB}$$

Where: AC = distance from the point at peak midpoint to the trailing edge (measured at 10% of peak height)
AB = distance from the leading edge of of peak to the midpoint (measured at 10% of peak height)

12.5 Linear Regression:

$$y = ax + b$$

Where: y = Instrument response (peak area)
a = Slope of the line
x = Concentration of the calibration standard
b = The intercept

12.6 Quadratic Regression: $y = ax^2 + bx + c$

$$y = ax^2 + bx + c$$

Where: y = Instrument response (peak area)
a = Slope of the line
x = Concentration of the calibration standard
b = The intercept

## 13.0 Quality Assurance/Quality Control (QA/QC) Requirements

13.1 Initial tune verification – 50 ng of tuning standard is injected into the GC/MS and evaluated against the criteria specified in Method 8270D. These parameters are incorporated into the data system and appear on the tune report.

13.1.1 The DFTPP tune evaluation must be performed prior to analyzing samples and every 12 hours of continuous instrument run time. Tune parameters must be within established limits.

13.1.1.1 Possible Corrective Actions

13.1.1.1.1 Retune the instrument.

13.1.1.1.2 Adjust the target values for the tuning procedure, retune and re-inject the tune solution.

13.1.1.1.3 Clean source.

13.1.2 Evaluate pentachlorophenol and benzidine tailing factors. If factors exceed 2 investigate and perform any necessary corrective actions.

13.1.2.1 Possible Corrective Actions.

13.1.2.1.1 Replace injection port liner.

13.1.2.1.2 Trim or replace guard column.

13.1.2.1.3 Trim or replace analytical column.

13.1.3 Evaluate DDT breakdown. Breakdown must be less than 20%. If breakdown exceeds 20% corrective actions must be performed.

13.1.3.1 Possible Corrective Actions.

13.1.3.1.1 Replace injection port liner.

13.1.3.1.2 Trim or replace guard column.

13.1.3.1.3 Trim or replace analytical column.

13.2 Refer to Section 8.6 for initial calibration evaluation criteria.

13.3 Following successful tuning, and valid initial calibration, the CCV/SPCC sample must be analyzed and must pass the method criteria (Section 8.7). This sample must be analyzed every 12 hours of continuous instrument run time.

13.3.1 Possible Corrective Action

13.3.1.1 Repeat CCV/SPCC sample.

13.3.1.2 Re-prepare the CCV standard and repeat.

13.3.1.3 Replace injection port liner.

13.3.1.4 Trim or replace guard column.

13.3.1.5 Trim or replace analytical column.

13.3.1.6 Clean the source.

13.3.1.7 Once the problem has been identified and corrected, repeat the initial calibration procedure.

13.3.1.8 Check to be sure that there are no errors in integration of internal standards and SPCC and CCC compounds. Examine chromatograms for interfering peaks and integrated peak areas. If errors are found, recalculate the data accordingly.

13.3.1.9 Make sure certified solutions and calibration standards are not expired. Expired solutions and standards may exhibit analyte degradation. Replace all expired standards and remake all calibration standards. Recalibrate the instrument.

13.3.1.10 High variability of phenol compounds may indicate a system leak or reactive sites on the column. Leaks are noted if base line levels are high and atmospheric masses are predominant in the tune (18, 28,32, and 44). Check connections for leaks. A column that has developed active sites may need to be replaced. Typical column life expectancy is 6 months or less.

13.3.2 The CCV is further evaluated for all target analytes in the batch. Percent recovery for each should be within 80 – 120 %. Refer to Sec. 8.7.4 and 8.7.5.

13.4 For each 12-hour or less analytical event a Method Blank or CCB is analyzed prior to analysis of samples to ensure the system is free of contamination that may impact sample results. Prepare the method blank for each matrix for each batch of twenty or less samples using DI water for aqueous samples and cleaned sand (or reagents only if necessary) for solid samples.

13.4.1 Acceptance Criteria: All analytes <1/2 RL

13.4.2 Corrective Action: Clean system and check for sources of contamination.

13.5 For each batch of samples a Laboratory Control Sample (LCS) at 20 ug/ml (aqueous, 666.67 ug/Kg solid concentration) is evaluated. Prepare the laboratory control sample (LCS) for each matrix for each batch of twenty or less samples by adding 0.1 ml of the spike mix (section 7.4) to one liter of DI water for aqueous samples or 30 gm of cleaned sand (or reagents only if necessary) for solid samples.

13.5.1 Acceptance Criteria: Control limits as specified in the DoD QSM. If not listed default limits of 50 – 130 % recovery or statistically derived control limits.

13.5.2 Corrective Action: Repeat LCS, re-prepare solution and repeat LSC and repeat calibration procedure if necessary.

13.6 For each matrix batch of 20 or less samples a MS/MSD is included that contains all of the components of interest. Prepare a matrix spike (MS) for each matrix for each batch of twenty or less samples by adding 0.1 ml of the spike mix (section 7.4) to a representative sample. Prepare a matrix spike duplicate (MSD) for each batch of twenty or less samples by adding 0.1 ml of the spike mix (section 7.4) to the same sample used for the MS. MS/MSD for aqueous sample require additional material to be supplied by the client.

13.6.1 Acceptance Criteria: Set to LCS control limits. MSD RDP not to exceed 25%. Spike concentration is 20 ug/ml (aqueous (based on a 1000ml sample size and a 1ml extract final volume), 666.67 ug/Kg solid concentration (based on a 30g sample size and a 1ml extract final volume)).

13.6.2 Corrective Action – Evaluate the sample spiked for matrix interference and flag the data as necessary.

13.7 Surrogate Control Limits

13.7.1 Surrogate control limits are set to the values listed in the DoD QSM. If required surrogate limits may be calculated for a sample matrix using at least 20 data points and the Mean recovery +/- 3 times the standard deviation.

13.7.2 For samples (including QC samples) in which the surrogate recovery falls outside the established control limits check the following:

13.7.2.1 Check integrations for errors.

13.7.2.2 Check calculations for errors.

13.7.2.3 Check instrument performance.

13.7.2.4 Re-extract and re-analyzed the samples if the above show no problems or flag the data if sample matrix interference is present.

13.8 Internal standard responses.

13.8.1 The response for each internal standard in the CCV must be within –50% to +100% of the mid-level calibration standard.

13.8.2 Failure to achieve the above criteria requires inspection of system operation and any necessary corrective actions. Any sample associated with the CCV having internal standard failures must be re-analyzed.

13.9 The retention times of the internal standards in the calibration verification standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the that in the mid-point standard level of the most recent initial calibration sequence, then the chromatographic system must be inspected for malfunctions and corrections must be made, as required. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

13.10 Initial demonstrations of proficiency are performed by all analysts for all instruments and methods. IDP records are kept on file in the laboratory and referenced in analyst training files. Demonstrations of proficiency are re-performed in instances of new staff or major changes in methodology or equipment. Continuing demonstration of proficiency is performed annually in conjunction with Sec. 4.4.

13.11 Refer also to the RTI QAP sections 3.0, 8.0, 9.0, 12.0 and 13.0.

13.12 Table of analytes (internal standards, surrogates and target compounds), including primary (quantification), and confirmation ions.

| Type | Compound | Primary Ion | Secondary Ion | Tertiary Ion | Quaternary Ion | Internal Standard Use |
|---|---|---|---|---|---|---|
| Internal | 1,4-Dichlorobenzene-$d_4$ | 152 | 150 | 115 | 78 | 1,4-Dichlorobenzene-d |
| Target | *N*-Nitrosodimethylamine | 74 | 42 | 43 | 59 | 1,4-Dichlorobenzene-d |
| Target | Pyridine | 79 | 52 | 51 | 50 | 1,4-Dichlorobenzene-d |
| Surrogate | 2-Fluorophenol | 112 | 64 | 92 | 57 | 1,4-Dichlorobenzene-d |
| Target | *N*-Nitrosodiethylamine | 102 | 56 | 42 | 71 | 1,4-Dichlorobenzene-d |
| Surrogate | Phenol-$d_5$ | 99 | 71 | 100 | 42 | 1,4-Dichlorobenzene-d |
| Target | Acetophenone | 105 | 77 | 120 | | 1,4-Dichlorobenzene-d |
| Target | Phenol | 94 | 66 | 65 | 55 | 1,4-Dichlorobenzene-d |
| Target | Benzaldehyde | 77 | 106 | 51 | | 1,4-Dichlorobenzene-d |
| Target | Aniline | 93 | 66 | 65 | | 1,4-Dichlorobenzene-d |
| Target | bis(2-Chloroethyl) ether | 93 | 63 | 95 | | 1,4-Dichlorobenzene-d |
| Target | n-Decane | 57 | 43 | 71 | 142 | 1,4-Dichlorobenzene-d |
| Target | 2-Chlorophenol | 128 | 64 | 130 | 92 | 1,4-Dichlorobenzene-d |
| Target | 1,3-Dichlorobenzene | 146 | 148 | 111 | | 1,4-Dichlorobenzene-d |

| | | | | | | |
|---|---|---|---|---|---|---|
| Target | 1,4-Dichlorobenzene | 146 | 148 | 111 | | 1,4-Dichlorobenzene-d |
| Target | Benzyl alcohol | 108 | 79 | 77 | 51 | 1,4-Dichlorobenzene-d |
| Target | 1,2-Dichlorobenzene | 146 | 148 | 111 | | 1,4-Dichlorobenzene-d |
| Target | 2-Methylphenol | 107 | 108 | 79 | 90 | 1,4-Dichlorobenzene-d |
| Target | *bis*(2-Chloroisopropyl) ether | 45 | 77 | 121 | | 1,4-Dichlorobenzene-d |
| Target | 4-Methylphenol | 108 | 107 | 79 | 90 | 1,4-Dichlorobenzene-d |
| Target | *N*-Nitrosodipropylamine | 70 | 42 | 130 | 101 | 1,4-Dichlorobenzene-d |
| Target | o-Toluidine | 106 | 107 | 79 | 77 | 1,4-Dichlorobenzene-d |
| Target | Hexachloroethane | 117 | 201 | 199 | 166 | 1,4-Dichlorobenzene-d |
| Internal | Naphthalene-$d_8$ | 136 | 68 | 108 | 54 | Naphthalene-$d_8$ |
| Surrogate | Nitrobenzene-$d_5$ | 82 | 54 | 128 | | Naphthalene-$d_8$ |
| Target | Nitrobenzene | 77 | 123 | 65 | 51 | Naphthalene-$d_8$ |
| Target | Isophorone | 82 | 138 | 95 | 54 | Naphthalene-$d_8$ |
| Target | 2-Nitrophenol | 139 | 109 | 65 | 81 | Naphthalene-$d_8$ |
| Target | 2,4-Dimethylphenol | 122 | 107 | 121 | 77 | Naphthalene-$d_8$ |
| Target | Benzoic acid | 122 | 105 | 77 | 51 | Naphthalene-$d_8$ |
| Target | *bis*(2-Chloroethoxy)methane | 93 | 95 | 123 | | Naphthalene-$d_8$ |
| Target | 2,4-Dichlorophenol | 162 | 164 | 98 | 63 | Naphthalene-$d_8$ |
| Target | 1,2,4-Trichlorobenzene | 180 | 182 | 145 | 109 | Naphthalene-$d_8$ |
| Target | 4-Chlorophenol | 128 | 130 | 65 | 73 | Naphthalene-$d_8$ |
| Target | Naphthalene | 128 | 129 | 127 | 63 | Naphthalene-$d_8$ |
| Target | 4-Chloroaniline | 127 | 129 | 65 | 92 | Naphthalene-$d_8$ |
| Target | 2,6-Dichlorophenol | 162 | 164 | 98 | 63 | Naphthalene-$d_8$ |
| Target | Hexachlorobutadiene | 225 | 223 | 227 | 118 | Naphthalene-$d_8$ |
| Target | Caprolactam | 55 | 113 | 85 | | Naphthalene-$d_8$ |
| Target | 4-Chloro-3-methylphenol | 107 | 142 | 144 | | Naphthalene-$d_8$ |
| Target | 2-Methylnaphthalene | 142 | 141 | 115 | 71 | Naphthalene-$d_8$ |
| Internal | Acenaphthene-$d_{10}$ | 164 | 162 | 160 | | Acenaphthene-$d_{10}$ |
| Target | Hexachlorocyclopentadiene | 237 | 95 | 272 | 235 | Acenaphthene-$d_{10}$ |
| Target | 1,2,4,5-Tetrachlorobenzene | 216 | 108 | 214 | 179 | Acenaphthene-$d_{10}$ |
| Target | 2,4,6-Trichlorophenol | 196 | 198 | 97 | 200 | Acenaphthene-$d_{10}$ |
| Target | 2,4,5-Trichlorophenol | 196 | 198 | 97 | 132 | Acenaphthene-$d_{10}$ |
| Surrogate | 2-Fluorobiphenyl | 172 | 85 | 75 | 171 | Acenaphthene-$d_{10}$ |
| Target | Biphenyl | 154 | 153 | 152 | | Acenaphthene-$d_{10}$ |
| Target | 2-Chloronaphthalene | 162 | 164 | 127 | 63 | Acenaphthene-$d_{10}$ |

| | | | | | | |
|---|---|---|---|---|---|---|
| Target | 1-Chloronaphthalene | 162 | 164 | 127 | 63 | Acenaphthene-$d_{10}$ |
| Target | 2-Nitroaniline | 138 | 65 | 92 | 77 | Acenaphthene-$d_{10}$ |
| Target | Dimethyl phthalate | 163 | 77 | 194 | 164 | Acenaphthene-$d_{10}$ |
| Target | 2,6-Dinitrotoluene | 165 | 89 | 63 | 121 | Acenaphthene-$d_{10}$ |
| Target | Acenaphthylene | 152 | 151 | 76 | 153 | Acenaphthene-$d_{10}$ |
| Target | 3-Nitroaniline | 65 | 138 | 92 | | Acenaphthene-$d_{10}$ |
| Target | Acenaphthene | 153 | 154 | 76 | 152 | Acenaphthene-$d_{10}$ |
| Target | 2,4-Dinitrophenol | 184 | 107 | 63 | 154 | Acenaphthene-$d_{10}$ |
| Target | 4-Nitrophenol | 65 | 109 | 81 | 139 | Acenaphthene-$d_{10}$ |
| Target | Pentachlorobenzene | 250 | 215 | 143 | 129 | Acenaphthene-$d_{10}$ |
| Target | 2,4-Dinitrotoluene | 165 | 63 | 89 | 182 | Acenaphthene-$d_{10}$ |
| Target | Dibenzofuran | 168 | 139 | 169 | 84 | Acenaphthene-$d_{10}$ |
| Target | 2,3,4,6-Tetrachlorophenol | 232 | 131 | 166 | 230 | Acenaphthene-$d_{10}$ |
| Target | Diethyl phthalate | 149 | 177 | 105 | 150 | Acenaphthene-$d_{10}$ |
| Target | 4-Chlorophenyl phenyl ether | 204 | 141 | 206 | | Acenaphthene-$d_{10}$ |
| Target | Fluorene | 166 | 165 | 167 | 139 | Acenaphthene-$d_{10}$ |
| Target | 4-Nitroaniline | 138 | 65 | 92 | 108 | Acenaphthene-$d_{10}$ |
| Surrogate | 2,4,6-Tribromophenol | 330 | 332 | 61 | 141 | Acenaphthene-$d_{10}$ |
| Internal | Phenanthrene-$d_{10}$ | 188 | 80 | 94 | | Phenanthrene-$d_{10}$ |
| Target | 4,6-Dinitro-2-methylphenol | 198 | 105 | 121 | 51 | Phenanthrene-$d_{10}$ |
| Target | *N*-Nitrosodiphenylamine | 169 | 168 | 167 | | Phenanthrene-$d_{10}$ |
| Target | Azobenzene | 77 | 182 | 105 | 152 | Phenanthrene-$d_{10}$ |
| Target | 4-Bromophenyl phenyl ether | 248 | 250 | 141 | | Phenanthrene-$d_{10}$ |
| Target | Hexachlorobenzene | 284 | 142 | 249 | | Phenanthrene-$d_{10}$ |
| Target | Atrazine | 200 | 215 | 58 | 43 | Phenanthrene-$d_{10}$ |
| Target | Pentachlorophenol | 266 | 165 | 264 | 268 | Phenanthrene-$d_{10}$ |
| Target | Pentachloronitrobenzene | 237 | 297 | 179 | 265 | Phenanthrene-$d_{10}$ |
| Target | n-Octadecane | 57 | 71 | 85 | 254 | Phenanthrene-$d_{10}$ |
| Target | Phenanthrene | 178 | 152 | 179 | 176 | Phenanthrene-$d_{10}$ |
| Target | Anthracene | 178 | 76 | 176 | 179 | Phenanthrene-$d_{10}$ |
| Target | Carbazole | 167 | 139 | 84 | 166 | Phenanthrene-$d_{10}$ |
| Target | Di-n-butyl phthalate | 149 | 150 | 104 | 278 | Phenanthrene-$d_{10}$ |
| Target | Fluoranthene | 202 | 101 | 203 | 88 | Phenanthrene-$d_{10}$ |
| Target | Benzidine | 184 | 92 | 185 | 156 | Phenanthrene-$d_{10}$ |
| Internal | Chrysene-$d_{12}$ | 240 | 236 | 120 | | Chrysene-$d_{12}$ |

| | | | | | | |
|---|---|---|---|---|---|---|
| Target | Pyrene | 202 | 200 | 203 | 101 | Chrysene-$d_{12}$ |
| Internal | Terphenyl-$d_{14}$ | 244 | 122 | 245 | 212 | Chrysene-$d_{12}$ |
| Target | Butyl benzyl phthalate | 149 | 91 | 206 | 312 | Chrysene-$d_{12}$ |
| Target | 3,3'-Dichlorobenzidine | 252 | 154 | 126 | 254 | Chrysene-$d_{12}$ |
| Target | *bis*(2-Ethylhexyl) phthalate | 149 | 167 | 279 | 113 | Chrysene-$d_{12}$ |
| Target | Benz(a)anthracene | 228 | 226 | 114 | 229 | Chrysene-$d_{12}$ |
| Target | Chrysene | 228 | 226 | 114 | 229 | Chrysene-$d_{12}$ |
| Target | Di-n-octyl phthalate | 149 | 167 | 43 | 279 | Chrysene-$d_{12}$ |
| Internal | Perylene-$d_{12}$ | 264 | 132 | 260 | 265 | Perylene-$d_{12}$ |
| Target | Benzo(b)fluoranthene | 252 | 253 | 126 | 125 | Perylene-$d_{12}$ |
| Target | Benzo(k)fluoranthene | 252 | 253 | 126 | 125 | Perylene-$d_{12}$ |
| Target | Benzo(a)pyrene | 252 | 126 | 113 | 125 | Perylene-$d_{12}$ |
| Target | Indeno(1,2,3-cd)pyrene | 276 | 138 | 124 | 277 | Perylene-$d_{12}$ |
| Target | Dibenz(a,h)anthracene | 278 | 139 | 125 | 279 | Perylene-$d_{12}$ |
| Target | Benzo(g,h,i)perylene | 276 | 138 | 124 | 277 | Perylene-$d_{12}$ |

## 14.0 Data Reporting Requirements

14.1 If any compound is found in a sample at a concentration greater than that of the highest standard the sample must be re-analyzed after dilution. The sample should be diluted until all compounds of interest are within the working range of the standard curve. Data from all dilutions are evaluated and compound results will be reported from the lowest dilution that exhibits lack of interference. The LIMS is capable on accepting multiple dilutions on a sample and reporting only the applicable compounds for each dilution. The surrogate recoveries must fall within the statistical ranges (section 13.4).

14.2 Blank results are not to be subtracted from sample values.

14.3 Sample concentrations are reported in ug/ml from the Enviroquant data system.

14.4 Raw results are entered into Omega. Prep factors are automatically imported from sample prep logs. Dilutions are entered in the analytical sequence.

14.5 Sample results are reported as ug/L for water and ug/kg for soil as dry weight.

14.6 Raw instruments results are entered directly into the Omega LIMS system using excel spreadsheets, direct instrument interface or manually. All calculations to derive final result (including dry weight conversions) are performed automatically by the LIMS. Sample preparation information and percent moisture results are entered into the appropriate section of the LIMS prior to instrument data and are automatically factored into the final results.

14.7 Confirm that there are no QC flags or qualifiers in this sequence. If present, investigate and repeat or reanalyze as necessary. See section 9.2 of the QAP for more detail on qualifiers.

## 15.0 Preventative Maintenance and Routine Cleaning

15.1 Daily: Perform air and water check, tune check, monitor tank pressures, check for RT shifts by monitoring compound RTs, and perform injection port maintenance.

15.2 Annual: Change pump oil.

15.3 All maintenance is recorded in the Omega LIMS for the applicable instrument.

## 16.0 Waste Management and Pollution Prevention

16.1 Pollution Prevention

16.1.1 Reagents are purchased and quantities used to reflect anticipated usage and minimize disposal of expired or unused chemicals.

16.1.2 Chemicals are handled in a manner, which minimizes the potential for release or spill of the material.

16.2 Waste Management

16.2.1 Organic solvents are treated as hazardous waste and placed in the appropriate waste drum for disposal.

16.2.2 Soil samples are composited in a drum designated for incineration.

16.2.3 Disposal of materials is addressed in the laboratory QAP (Section 5.6).

## 17.0 References

17.1 EPA Test Methods for Evaluating Solid Waste. Laboratory Manual Physical/Chemical Methods, Method 8270D Revision 4, 3550C, 3545A, and 3510C.

17.2 RTI Lab SOPs 3510C and 3550B.

17.3 RTI Laboratories, Inc. Quality Assurance Plan.

17.4 RTI Laboratories, Inc. Chemical Hygiene Plan.

17.5 RTI Laboratories, Inc. SOP: SRC001-A, Sample Receipt and Custody SOP.

17.6 RTI Laboratories, Inc. Employee Handbook.

RTI Laboratories, Inc.
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# STANDARD OPERATING PROCEDURE

# SONICATION EXTRACTION PROCEDURE FOR SEMI – VOLATILE ORGANICS

| | |
|---|---|
| **Analyte:** | **Semi-volatile organic compounds** |
| **SOP #:** | **3550C_022814_R8** |
| **Method Reference:** | **EPA SW-846 3550C** |
| **Issue Date:** | **December 2, 2005** |
| **Revision No.:** | **8** |
| **Revision Date:** | **February 28, 2014** |

**Reviewed and Approved February 28, 2014 by:**

Director Quality Management: Charles O'Bryan

Director, Environmental Services: Yemane Yohannes

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**SONICATION EXTRACTION PROCEDURE FOR**
**SEMI – VOLATILE ORGANICS**

**SOP#: 3550C_022814_R8**

**TABLE OF CONTENTS**

## 1.0 Scope and Application

1.1 Introduction

RTI Laboratories, Inc, has prepared this document to detail the Standard Operating Procedure (SOP) for the preparation of the preparation of solid samples for analysis of semi-volatile compounds by gas chromatography/mass spectrometry, pesticides and PCB's by GC/ECD, PNAs by HPLC and DRO by GC/FID. This SOP contains the procedures for sonication extraction (Method 3550B) for solid samples. Wipe samples (particularly for PCB's) are prepared using this procedure.

A detailed description of the instrumentation, calibration, run parameters and quality control procedures used for analysis are not included in this SOP. For definition of terms not specifically defined in this document refer to RTI QAP Section 16.

1.2 Summary of Method

1.2.1 A 25 to 30 g aliquot of sample is weighed and dried with anhydrous sodium sulfate. The solvent appropriate to the analysis, surrogates and spikes (where applicable) are added to the solid sample or wipe and extracted by sonication for 3 minutes at full power. The solvent extract is removed and filtered through anhydrous sodium sulfate. The procedure is repeated three times and the final extract is concentrated to the desired volume. This method has been modified to use 50ml aliquots instead of 100ml aliquots of extraction solvent.

## 2.0 Safety Precautions

2.1 Compounds applicable to this method are known or suspected carcinogens. Standard preparation is conducted in fume hoods designated for organic use.

2.2 Extraction solvents are flammable and/or toxic and must be handled with caution. All extractions are performed in a manner designed to minimize exposure to these chemicals using appropriate hoods and personal protection (such as, gloves, lab coat, and safety glasses.

## 3.0 Sample Requirements and Sample Handling Procedures

3.1 Samples are received in accordance with the RTI Standard Operating Procedure for Sample Receipt and Custody (SRC001-A). Appropriate U. S. Environmental Protection Agency (EPA) sample handling procedures and sample preservation recommendations are followed. Soil samples are collected in 2 to 9 oz. pre-cleaned wide mouth jars with Teflon lined lids.

3.2 For PCB samples the holding time is 1 year from collection to extraction and 1 year from extraction to analysis. For all other analytes covered in this SOP, the holding time for soil samples is 14 days from collection to extraction and 40 days from extraction to analysis.

3.3 All samples are stored at $4^{o}$ C in the walk-in cooler.

3.4 Minimum sample size – 30 g.

## 4.0 MDL, Linear Range, Accuracy and Precision

4.1 Not applicable to this SOP. See the appropriate analytical SOP for details

## 5.0 Interferences

5.1 Interferences can arise from carry over due to high sample concentrations or contamination from reagents and/or glassware. Method blanks are prepared to ensure system cleanliness in both instances. All glassware must be scrupulously cleaned before use. Phthalates are common lab contaminants and will leach from any soft plastic material used during sampling or during prep.

5.2 Samples containing high concentrations of non-target analytes or extremely high levels of select target analytes can result in elevated detection limits for some or all compounds. Dilution of the extract may improve the resolution and quantification of some analytes but will generally cause an elevation in the RDL. Interferences from high molecular weight organics such as oils will cause an elevated baseline. If this background is at a high concentration it will interfere with analyte identification as well as quantification.

5.3 Sample extract interferences can be cleaned up using techniques described in the SOP for sample extract cleanup (florisil cleanup, acid cleanup, sulfur cleanup or dilution (3610B, 3611A, 3620B, 3630C, 3650B, 3660B)). Dilution of the extract can also be used to minimize interferences.

## 6.0 Apparatus and Materials

6.1 Analytical Balance capable of weighing to 0.1 gm.

6.2 Glass Funnels

6.3 Glass beakers, 250 ml size.

6.4 Sonicators

6.5 Class A Micro liter syringes, 50µl, 10µl, 25µl, 1000µl and 5000µl.

6.6 Volumetric glassware

6.7 Glass vials – 2ml amber crimp top auto sampler or 8 ml clear with screw cap

6.8 Glass wool

6.9 Pasteur pipettes

6.10 TurboVap II evaporator

6.11 200ml concentrators tubes with a 1.0ml graduated tip

6.12 4" x 4" gauze pads – for wipe collection.

6.13 PC with Balance Link software, Microsoft Excel and Omega.

## ~~7.0 Reagents~~

7.1 Anhydrous Sodium sulfate- clean in a muffle furnace for 4 hours at 400 degrees C

7.2 Methylene chloride – pesticide grade

7.3 Hexane – pesticide grade

7.4 Acetone – pesticide grade

7.5 ASTM Type II Deionized water.

7.6 Ottawa sand for Method Blank and LCS, heated in a muffle furnace for 4 hours at 400 degrees C.

7.7 Dry Nitrogen – for TurboVap.

7.8 Stock Standards

7.8.1 Base/Neutral & acid surrogate standard, Absolute, part# 25015, 4000ppm
7.8.2 1,4-Dioxane-d8, 2000ppm Restek
7.8.3 8270 SVOA 64-comp, AccuStandard, M-8270-AG01-ASL
7.8.4 8270 SVOA 35-comp, ultra, svm8271-1
7.8.5 Benzoic Acid, Restek, 2000ppm, 31879
7.8.6 4-Nitrophenol, absolute, 70231
7.8.7 Benzidine Mix, 2000 ug/ml, Restek, 31834
7.8.8 2,4-Dinitrophenol, absolute, 70159, 1000ppm
7.8.9 1-Methylnaphthalene, 2000ppm, absolute, 90494
7.8.10 1,4-Dioxane, Restek 2000ppm 31853
7.8.11 Hydrocarbon standard, absolute, 2000ppm 94376
7.8.12 Pyridine, absolute, 1000ppm, 79091

7.8.13 Pesticide Mix 2000ug/mL, AccuStandard Z-014C-R
7.8.14 TCMX/DCB Surrogate 200ug/mL, Ultra, Part No. ISM-320
7.8.15 PCB 1016/1260 1000ug/mL, Ultra, Part No. PPM-8082

7.9 SVOC working standards. All solutions have a 6-month expiration date.

7.9.1 BNA Surrogate spiking solution - 25 ppm.

7.9.1.1 Working surrogate solution 25 ppm: prepared by adding 625 µl of Base/Neutral & acid surrogate standard (7.13.1) and 1.25 ml of 1,4-Dioxane d-8 to a 100 ml class A volumetric flask and dilute to the mark with pesticide grade acetone. Add 1.0mL to each sample (25µg/extract).

7.9.2 BNA MS/MSD/LCS spike mix - 20 ppm –

7.9.2.1 Full BNA spike mix –20 ppm- prepared by adding 1 ml of 8270 SVOA 64-comp, 1ml of 8270 SVOA 35-comp, 0.5 ml of Benzoic Acid, 1.5 ml of 4-Nitrophenol, 0.5 ml of Benzidine Mix, 1.5 of 2,4-Dinitrophenol, 0.5 ml of 1-Methylnapthalene, 0.5 ml of 1,4-Dioxane, 0.5ml of Hydrocarbon Standard and 1 ml of Pyridine to a 50 ml volumetric flask and dilute to the mark with pesticide grade acetone. Add 1.0mL to each LCS, MS, and MSD samples (20 µg/extract). The final volume of prepared standard made may vary but the proportions will be consistent.

7.10 PCB/Pesticide standards:

7.10.1 Pesticide Mix 2000ug/mL, AccuStandard Z-014C-R
7.10.2 TCMX/DCB Surrogate 200ug/mL, Ultra, Part No. ISM-320
7.10.3 PCB 1016/1260 1000ug/mL, Ultra, Part No. PPM-8082
7.10.4 Pesticide ICV/CCV Intermediate standard 10ppm - prepared by adding 50µl of AccuStandard-z-014c-r(7.12.1) to a 10ml class A volumetric flask and dilute to 10ml with pest grade Hexane
7.10.5 Working TCMX/DCB Surrogate 0.25ug/mL – prepared by adding 125µl TCMX/DCB Surrogate 200ug/mL(7.12.2) to a 100ml Class A volumetric flask and diluting to mark with pesticide grade acetone.
7.10.6 PCB MS/MSD/LCS spike mix 5ug/mL - prepared by adding 125µl of the PCB 1016/1260 1000ug/mL(7.12.3) to a 25ml Class A volumetric flask and diluting to mark with pesticide grade acetone. Add 1.0ml per MS/MSD/LCS.
7.10.7 Pesticide MS/MSD/LCS Working Spike 0.25ug/mL - prepared by adding 625µl of Pesticide ICV/CCV standard 10ppm (7.12.4) to a 25ml Class A volumetric flask and diluting to mark with pesticide grade acetone. Add 1.0ml per MS/MSD/LCS

7.10.8 Technical Chlordane and Toxaphene are not routinely part of the pesticide spike mixes.

7.10.9 Spike Mixes supplied by GC department.

7.11 DRO/ORO.

7.11.1 DRO/ORO Surrogate Intermediate 5000ug/mL – weigh 0.05g of n-Eicosane (7.10.6) in a 10mL volumetric flask and dilute to the mark with pesticide grade methylene chloride.

7.11.2 DRO/ORO Working Surrogate 150ug/mL – prepare by adding 300uL of the DRO/ORO Surrogate Intermediate (7.14.1) to a 10mL volumetric flask and dilute to the mark with pesticide grade acetone. Add 100uL to each sample.

7.11.3 DRO/ORO MS/MSD/LCS Spike Mix 5000/10000ug/mL - add 500 ul SAE 30W Motor Oil (7.10.7) and 250uL Diesel #2 Fuel Oil (7.10.7) to a final volume of 1mL with pesticide grade acetone. Add 10uL to each MS/MSD/LCS.

7.12 All reagents and standards prepared must be labeled with a minimum:

7.12.1 Identity of the material
7.12.2 Concentration of the solution
7.12.3 Date prepared
7.12.4 Initials of analyst preparing the solution
7.12.5 Expiration date.

## 8.0 Preparation of Standards and Calibration Procedure

8.1 Branson Sonicator 250 – Tune according to manufacturer instructions.

8.2 Ultra sonic processor tuning procedure – Branson Sonifier 550. Tune each use.

8.2.1 The probe should not be in contact with or immersed in liquid during tuning.

8.2.2 Turn AMPLITUDE CONTROL KNOB counter-clockwise to zero

8.2.3 Press POWER SWITCH to ON (up) position. The switch will illuminate

8.2.4 When the prompt appears, press the TUNE key. The screen will read: (TUNING ---PROBE ACTIVE).

8.2.5 Turn the Amplitude Control Knob to a setting of 3.

8.2.5.1 Note the position of the Bar Graph on the LCD display as you turn the knob. DO NOT allow the reading to exceed 50%. STOP if the reading reaches 50%.

8.2.5.2 Rotate the tuning knob clockwise or counter-clockwise until a minimum reading is obtained (usually less than 10%). DO NOT force the tuning knob past where it stops.

8.2.6 Turn the Amplitude Control Knob to a setting of 6 (Note: if using a Microtip or an extender, tune at a setting of 5 only!!!)

8.2.6.1 Note the position of the Bar Graph and DO NOT exceed a reading of 50%.

8.2.6.2 Rotate the tuning knob to obtain a minimum meter reading (less than 10%).

8.2.7 Repeat 8.3.6 at a setting of 10 (DO NOT do this step if using a Microtip or an extender!!!) and minimize the meter reading one last time.

8.2.8 Press the STOP key and turn the Amplitude Control Knob back to Zero.

## 9.0 Sample Preparation

9.1 Allow samples to warm to ambient temperature.

9.2 With each batch of samples prepare a method blank, LCS, MS and MSD by adding spiking solution specified for analytical request (Section 7).

9.3 Verify the calibration of the balance used and record the calibration in the logbook daily.

9.4 Measure 30 gm of well-mixed soil eliminating foreign objects such as sticks, rocks, etc. and capture the weight into the “SampAmt” column of the Omega Prep Batch using the BalanceLink software. If the sample is a wipe, place the entire wipe sample into a 250 ml beaker.

9.4 Add minimum amount of sodium sulfate and mix until the sample is free flowing like sand. If needed for a wet sample, add additional sodium sulfate. If sample is dry, less sodium sulfate may be used.

9.5 Add 1.0ml of the appropriate surrogate mix (section 7.9 through 7.11) then immediately add 50 ml of Methylene chloride or Hexane for PCB\Pesticides samples.

9.6 Place the cleaned sonicator horn approximately 3-8 mm below the surface of the solvent but not in contact with the soil and sonicate for 3 min at full power with the pulse duty set to 50%.

9.7 Decant the extracts through a funnel containing glass wool and approximately ½ inch of sodium sulfate and collect in a 200 ml TurboVap vessel. Be careful not to fill the TurboVap vessel more than 2/3 full, too much solvent in the vessel will spray out the top. After the solvent drains into the tube rinse the sodium sulfate with the appropriate solvent.

9.8 Add 50ml Methylene chloride or Hexane for PCB/Pesticides samples to the beaker and repeat 9.6 and 9.7 two additional times combining the extracts.

9.9 Transfer the container to the TurboVap concentrator. Set the TurboVap according to the manufacturer's instructions (use the manual setting and tank pressure at 12psi). Concentrate to <1.0 ml at 44 degrees C.

9.10 Remove TurboVap container and bring to volume as below.

9.10.1 BNA samples: Use a syringe filled with Methylene chloride to adjust the final volume to the 1 ml line on the TurboVap container. Transfer the extract to a 2 ml auto sampler vial with a Pasteur pipette.

9.10.2 Pesticide/PCB samples: Use a syringe filled with Hexane to adjust the final volume to the 1 ml line on the TurboVap container. Using a graduated cylinder add 4 ml of Hexane (5 ml final volume) and transfer to a 8 ml vial.

9.10.3 In cases where the sample will not concentrate to <1 ml transfer and measure the remaining volume in a graduated cylinder and adjust with the appropriate solvent to a 5 or 10 ml final volume.

9.10.4 Note any non-routine characteristics of the extract in the comments section of the sample preparation table. These would included:

9.10.4.1 Discoloration.
9.10.4.2 Viscosity
9.10.4.3 Odor
9.10.4.4 Oily or other unusual appearance

9.10.5 The analyst will decide what cleanup technique, if any will be required.

9.11 In the sample preparation log in the LIMS enter initial the sample volume in g or Kg based on the test code units requirement, final extract volume in ml and sample matrix. Additionally enter the amount of surrogate and spike solutions added in ml.

9.12 The preparation analyst must also enter the date and time of start and completion, the name of the analyst and the test code designation.

9.13 Enter all applicable Reagents/Chemicals and Spikes/Standard information in the preparation form.

## 10.0 Diagram/Table

10.1 Reserved

## 11.0 Analytical Procedure

11.1 This section is not applicable to this SOP.

## 12.0 Details of Calibration and Calculations

12.1 This section is not applicable to this SOP.

## 13.0 Quality Assurance/Quality Control (QA/QC) Requirements

13.1 Prepare a method blank for each batch of twenty or less samples by extracting cleaned sand.

13.2 Prepare a laboratory control sample (LCS) for each batch of twenty or less samples per matrix, by adding the appropriate amount of the spike mix to 30 g of cleaned sand.

13.3 Prepare a matrix spike (MS) and matrix spike duplicate (MSD) for each batch of twenty or less samples per matrix, if sufficient volume is available by adding the appropriate amount of the spike mix to a representative sample.

13.4 Corrective action procedures are specified in the applicable SOP's.

## 14.0 Data Reporting Requirements

14.1 Refer to applicable analytical SOP.

## 15.0 Preventative Maintenance and Routine Cleaning

15.1 The sonicators are tuned according to the manufacturers instructions daily or with each use. Record tuning in the maintenance log.

15.2 At the end of the work shift, the glassware is to be cleaned and put away. The counters are to be cleaned and wiped down.

15.3 Daily: Balance must be checked prior to use with the certified weights and recorded.

15.4 TurboVap: Ensure that the water bath reservoir is filled to at least above the bottom of the cutout circle on the vertical portion of the interior wall. Check to make sure that the N2 tank is not empty and that the nitrogen is flowing to the sample tube at the proper pressures..

15.5 Check the TurboVap displayed temperature with a calibrated thermometer on each day of use.

## 16.0 Pollution Prevention and Waste Management

16.1 Pollution Prevention

16.1.1 Reagents are purchased and quantities used to reflect anticipated usage and minimize disposal of expired or unused chemicals.

16.1.2 Chemicals are handled in a manner, which minimizes the potential for release or spill of the material.

16.2 Waste Management

16.2.1 Organic solvents are treated as hazardous waste and placed in the appropriate waste drum for disposal.

16.2.2 Disposal of materials is addressed in the laboratory QAP (Section 5).

## 17.0 References

17.1 EPA Test Methods for Evaluating Solid Waste. Laboratory Manual Physical/Chemical Methods, Nov, 1986, Revision 1 Sept, 1994. Method 3550C.

17.2 RTI Laboratories, Inc. Quality Assurance Plan.

17.3 RTI Laboratories, Inc. SOP SRC001-A, Sample Receipt and Custody.

17.4 RTI Laboratories, Inc. Chemical Hygiene Plan.

17.5 RTI Laboratories, Inc. Employee Handbook.

**RTI Laboratories, Inc.**
**31628 Glendale**
**Livonia, Michigan 48150**

# STANDARD OPERATING PROCEDURE

# ANALYSIS OF EXPLOSIVES BY HPLC

| | |
|---|---|
| **Analyte:** | **Explosives** |
| **SOP#:** | **8330B_022114_R4.1** |
| **Method Reference:** | **SW-8330B** |
| **Issue Date:** | **March 9, 2009** |
| **Revision No.:** | **4.1** |
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**Reviewed and Approved: March 6, 2014**

Director, Quality Management: Charles O'Bryan

Director, Environmental Services: Yemane Yohannes

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**STANDARD OPERATING PROCEDURE**

**ANALYSIS OF EXPLOSIVES**

**SOP#: 8330B_022114_R4.1**

**TABLE OF CONTENTS**

## 1.0 Scope and Application:

1.1 Introduction

RTI Laboratories, Inc. has prepared this document to detail the Standard Operating Procedure (SOP) for the analysis of explosives in aqueous and solid samples. Compounds applicable to the method are listed in Table 3. Soil extraction procedures according to method versions 8330B and 8330A are included in this SOP.

A detailed description of the instrumentation, calibration, run parameters and quality control procedures is included in this SOP. For definition of terms not specifically defined in this document refer to RTI QAP Section 16.

1.2 Summary of Method

1.2.1 To determine content of various explosives, an extract is injected into an HPLC system and separated on a determinative column. The separated components are analyzed via UV detection. Compounds are identified by comparison of the peak retention time (RT) to the RT standards. Quantification is performed by comparison of the compound response to an established calibration curve

## 2.0 Safety Precautions

2.1 Waste materials submitted for analyses may contain hazardous components. Uncharacterized waste samples should be handled in a manner that minimizes exposure and personal contact.

2.2 Chemicals used should be regarded as a potential health risk. Sample preparation and analysis is performed in a manner designed to minimize exposure using routine good laboratory practices.

2.3 Acetonitrile may be fatal if swallowed, inhaled or absorbed through the skin. Affects the cardiovascular system, central nervous system, liver and kidneys. Flammable liquid and vapor. May cause irritation to skin, eyes and respiratory tract.

## 3.0 Sample Requirements and Sample Handling Procedures

3.1 Samples are received in accordance with RTI Laboratories, Inc. Standard Operating Procedure for Sample Receipt and Custody (SRC001-A). Appropriate U. S. Environmental Protection Agency (EPA) sample handling procedures and sample preservation recommendations are followed.

3.1.1 Aqueous samples are collected in clean 1L amber bottles and maintained on ice at 4 degrees C following collection. Holding time is 7 days from the time of collection.

3.1.2 Soil, sludge and solid samples are collected in pre cleaned wide mouth glass jars and stored at 4 degree C. Holding time is 14 days from the time of collection.

3.1.3 Sample volume minimum requirements: 800 mL, aqueous – 40 g, solids.

3.1.4 All samples and sample extracts are stored at 4 degrees C in the dark.

3.1.5 Extracts have a holding time of 40 days from preparation.

## 4.0 MDL, Linear Range, Accuracy and Precision

4.1 The method detection limit (MDL) is statistically defined at the 99% confidence level according to 40 CFR Part 136 App. B. Seven replicates containing all of the analytes of interest at a concentration level of 1-5 times the estimated D.L. are analyzed and the standard deviation is calculated. The Student's T Value for the 7 replicates (3.143) is multiplied by the standard deviation of the analyte to calculate the MDL. MDLs are updated on major instrument changes and are kept on file in the Laboratory. MDLs and reporting limits are incorporated into the applicable test code in the Omega LIMS.

4.2 The LOD (limit of detection) is determined by spiking reagent water at 1-4 times the MDL and prepared using the same procedure as samples. Analytes must be present at levels 3 times or greater than the blank response (greater than 3 times the signal to noise ratio). The concentration used is the LOD for that analyte. LOD determinations must be performed quarterly.

4.3 The LOQ (limit of quantification) is determined by spiking reagent water at the reporting limit (RL/CRQL) and prepared in the same manner as samples. Analyte recovery must be within 20% of the expected concentration. The concentration used and successfully recovered is the LOQ for that analyte. LOQ determinations must be performed quarterly.

4.4 Initially accuracy and precision at the LOQ is determined by spiking 4 aliquots of reagent water at the reporting limit (RL/CRQL) and prepared using the same procedure used for samples. The average recovery must be within 20% of the expected value and the %RSD must be less than 15%.

4.5 LOD/LOQ determinations that do not meet the specifications above require repeat analysis, adjustment to the spiking levels and/or reporting limits, repeating the MDL determination at adjusted concentrations if required and repeat LOD/LOQ determinations.

4.6 The accuracy and precision for this method are determined by analyzing four laboratory control samples (LCS). The average percent recovery, standard deviation, and the relative standard deviation are calculated for each analyte. Quality control limits, mean recovery values and RPD results are incorporated in the Omega LIMS.

## 5.0 Interferences

5.1 Tetryl decomposes rapidly in water/methanol solutions and with heat.

5.2 Interferences can arise from carry over due to high sample concentrations or contamination from reagents and/or glassware. Blanks are analyzed to ensure system cleanliness in both instances. All glassware must be scrupulously cleaned before use. Glassware-cleaning procedures are specified in the QAP. Glassware should be heated in a muffle furnace at 400 degrees C for 15 to 30 minutes, or solvent rinsed prior to use. High purity solvents are used for preparation and analysis.

## 6.0 Apparatus and Materials

6.1 HPLC system (LC-5): Agilent 1100 Series Degasser G1322A, Agilent 1100 Series ALS G1311A, Agilent 1100 Series Column Compartment G1316A, Agilent 1100 Series DAD G1315A, PC with Chemstation for LC 3D Rev.B.01.03, Windows XP Professional and Omega LIMS.

6.2 HPLC system (LC-6): Agilent 1100 Series BinPump G1312A, Agilent 1100 Series ALS G1313A, Agilent 1100 Series Column Compartment G1316A, Agilent 1100 Series DAD G1315A, PC with Chemstation for LC 3D Rev.B.01.03, Windows XP Professional and Omega LIMS.

6.3 HPLC system (LC-7): Waters Acquity uPLC with a TUV Detector, Sample Manager Auto Sampler and Binary Solvent Manager pump, PC with Empower Rev. 5.00, Windows 2000, Chromeleon 6.80 Build 2212

6.4 Volumetric Flasks, 5mL; 10mL; 25mL; and 1 Liter – Class A.

6.5 Column 1: Waters Acquity uPLC BEH C18 1.7u, 2.1 x 100mm (part #186002352) with guard cartridge. This is a primary column.

6.6 Column 2: Dionex Acclaim E2 Explosives Column (part # 064309) with guard cartridge. This is a secondary column to Column 1 (Sec. 6.5) or a primary to column 3.

6.7 Column 3: Dionex Acclaim E1 Explosive Column (Part # 064305) with guard cartridge. This is a secondary column to Column 2 (Sec. 6.6).

6.8 Micro syringes – 10uL, 50uL, 100uL, 500uL, 1000uL

6.9 Balance capable of weight +/-0.0001g

6.10 Vortex mixer

6.11 8 ml amber vials with Teflon lined caps

6.12 PTFE magnetic stir bars

6.13 Disposable 0.45µm PTFE cartridge filters

6.14 Pasteur pipettes

6.15 2mL amber auto sampler vials

6.16 11mm Teflon/Silicon aluminum crimp seal caps

6.17 250 ml amber bottles

6.18 40 ml vials with PTFE-lined cap

6.19 10 and 200 mesh sieves

6.20 Graduated cylinders – 10 ml, 25 ml and 1L

6.21 Ultrasonic water bath.

6.22 2oz. wide-mouthed jars.

6.23 5 - 10 ml disposable syringes.

6.24 Centrifuge.

6.25 10 mesh sieves.

6.26 Puck and ring grinder. - Essa

6.27 Top-loading balance.

6.28 Platform shaker

## 7.0 Reagents and Standards

7.1 Acetonitrile, HPLC-grade

7.2 Methanol, HPLC-grade

7.3 Organic-free reagent water

7.4 Formic acid 88%, ACS Reagent grade

7.5 Ottawa sand.

7.6 LCS – Solid reference material obtained from Absolute Standards - 100 g.

7.7 1% Formic Acid Solution – Prepare by adding 10 ml of Formic Acid, 88% to a 100 ml volumetric containing approximately 80 ml of deionized water. The solution is brought to a final volume of 100 ml with deionized water.

7.8 NaCl, either delivered in glass bottles or muffled at 400 C for an hour and stored in a glass bottle.

7.9 All standards, surrogates and spikes are stored in the dark at 4 degrees C.

7.10 Primary Standards:

- 7.10.1 Method 8330 Explosives Mix, 1.0 mg/ml (AccuStandard: M-8330-R)
- 7.10.2 PETN, 1.0 mg/ml (Absolute: 79250)
- 7.10.3 Nitroglycerine, 1.0 mg/l (AccuStandard: M-8330-ADD-1-10X)

7.11 Secondary Standards:

- 7.11.1 Method 8330 Explosives Mix, 1.0 mg/ml (Ultra Scientific: NAIM-833E)
- 7.11.2 PETN, 0.1 mg/ml (AccuStandard: M-8330-ADD-2)
- 7.11.3 Nitroglycerin, 1000 µg/ml (Restek: 31498)

7.12 Surrogate Standard:

- 7.12.1 4-Nitroaniline, 1000 µg/ml (Absolute Standards: 70227)

7.13 All reagents and standards prepared must be logged in the appropriate standards/reagents log labeled with a minimum:

- 7.13.1 Identity of the material
- 7.13.2 Concentration of the solution
- 7.13.3 Date prepared
- 7.13.4 Initials of analyst preparing the solution
- 7.13.5 Expiration date.

## 8.0 Preparation of Standards and Spikes

8.1 Instrument Blank Intermediate Preparation - 4-Nitroaniline (0.2 µg/ml) - Dilute 2 µl 4-nitroaniline (7.11.1) to 10ml with acetonitrile. Store at 4 degrees C in the dark.

8.2 Working Instrument Blank Preparation - Dilute 0.5 ml of Instrument Blank Intermediate with 0.5 ml 1% Formic Acid Solution (Sec. 7.7).

8.3 Initial Calibration Stock Intermediate Standard – Store at 4 degrees C in the dark.

| Standard | Volume added | Final volume | Concentration |
|---|---|---|---|
| Nitroglycerin 1000 mg/l (Section 7.9.3) (AccuStandard: M-8330-ADD-1-10X) | 40µl | 10mL with acetonitrile | 4.0 µg/ml |
| PETN 1000 µg/ml(Section 7.9.2) (Absolute: 79250) | 100µl | | 10 µg/ml |
| 8330 Mix 1.0 mg/ml (Section 7.9.1) (AccuStandard: M-8330-R) | 20µl | | 2.0 µg/ml |
| 4-Nitroaniline 1000 ug/ml (Section 7.11.1) (Absolute Standards: 70227) | 20µl | | 2.0 µg/ml |

8.4 Initial Calibration Standards– Store at 4 degrees C in the dark.

| Standard Conc. | Initial Cal Stock (Section 8.2) (µl) | Acetonitrile (µl | 1% Formic Acid Solution (Section 7.7) (µl) |
|---|---|---|---|
| 0.020µg/ml | 10 | 490 | 500 |
| 0.050µg/ml | 25 | 475 | 500 |
| 0.100µg/ml | 50 | 450 | 500 |
| 0.500µg/ml | 250 | 250 | 500 |
| 1.0µg/ml | 500 | 0 | 500 |

8.5 Initial Calibration Verification/Continuing Calibration Verification Intermediate Standard – Store at 4 degrees C in the dark.

| Standard | Volume added (µl) | Final Volume (ml) | Concentration (µg/ml) |
|---|---|---|---|
| Nitroglycerin 1000 ug/ml (Section 7.10.3) (Restek: 31498) | 10 | 10 ml with acetonitrile | 1.0 |
| PETN 0.1 mg/ml (Section 7.10.2) (AccuStandard: M-8330-ADD-2) | 100 | | 1.0 |
| 8330 Mix 1.0 mg/ml (Section 7.10.1) (Ultra Scientific: NAIM-833E) | 10 | | 1.0 |
| 4-Nitroaniline 1000 ug/ml (Section 7.11.1) (Absolute Standards: 70227) | 10 | | 1.0 |

8.6 Initial Calibration Verification/Continuing Calibration Verification Working Standard-ICV/CCV standards are prepared fresh before use.

| Standard Conc. | ICV/CCV Intermediate (Section 8.4) (µl) | Acetonitrile (µl) | 1% Formic Acid Solution (Section 7.7) (µl) |
|---|---|---|---|
| 0.5 µg/ml | 500 | 0 | 500 |

8.7 Matrix Spike Solution for Aqueous Samples – Store at 4 degrees C in the dark.

| Standard | Volume added (µl) | Final Volume (ml) | Concentration (µg/ml) |
|---|---|---|---|
| Nitroglycerin 1000 ug/ml (Section 7.10.3) (Restek: 31498) | 100 | 50 ml with acetonitrile | 2.0 |
| PETN 1000 µg/ml(Section 7.9.2) (Absolute: 79250) | 100 | | 2.0 |
| 8330 Mix 1.0 mg/ml (Section 7.10.1) (Ultra Scientific: NAIM-833E) | 100 | | 2.0 |

8.8 Matrix Spike Solution for Solid Samples – Store at 4 degrees C in the dark.

| Standard | Volume added (µl) | Final Volume (ml) | Concentration (µg/ml) |
|---|---|---|---|
| Nitroglycerin 1000 ug/ml (Section 7.10.3) (Restek: 31498) | 200 | 25 ml with acetonitrile | 8.0 |
| PETN 1000 µg/ml(Section 7.9.2) (Absolute: 79250) | 100 | | 4.0 |
| 8330 Mix 1.0 mg/ml (Section 7.10.1) (Ultra Scientific: NAIM-833E) | 200 | | 8.0 |

8.9 Surrogate Spiking Solution for Aqueous Samples (2.0µg/ml) - Dilute 200µLl4-nitroaniline (7.11.1) to 100mL with acetonitrile. Store at 4 degrees C in the dark.

8.10 Surrogate Spiking Solution for Solid Samples (8.0µg/ml) - Dilute 800µl 4-nitroaniline (7.11.1) to 100mL with acetonitrile. Store at 4 degrees C in the dark.

8.11 LOD/LOD Spike Solution for Aqueous Samples

| Standard | Volume added (µl) | Final Volume (ml) |
|---|---|---|
| Nitroglycerin 1000 ug/ml (Section 7.10.3) (Restek: 31498) | 4 | 10 ml with acetonitrile |
| PETN 0.1 mg/ml (Section 7.10.2) (AccuStandard: M-8330-ADD-2) | 100 | |
| 8330 Mix 1.0 mg/ml (Section 7.10.1) (Ultra Scientific: NAIM-833E) | 2 | |

8.12 LOD/LOQ Spike Solution for Soil Samples

| Standard | Volume added (µl) | Final Volume (ml) |
|---|---|---|
| Nitroglycerin 1000 ug/ml (Section 7.10.3) (Restek: 31498) | 16 | 10 ml with acetonitrile |
| PETN 0.1 mg/ml (Section 7.10.2) (AccuStandard: M-8330-ADD-2) | 400 | |
| 8330 Mix 1.0 mg/ml (Section 7.10.1) (Ultra Scientific: NAIM-833E) | 8 | |

8.13 The correlation coefficient of the calibration curve (at least 5 points) must be >0.995 for each compound to continue with the analysis of samples. If this criterion is not met the calibration standards must be re-analyzed or new standards prepared and analyzed until an acceptable cc is obtained.

8.14 Initial calibration verification standard must be run immediately after calibration. The standard is prepared from a different source than the calibration standards at a concentration corresponding to the mid-point of the curve. The ICV standard must be within ±20% of the expected concentration.

8.15 Continuing calibration verification standards are analyzed at the mid-point of the calibration at the beginning of each analytical sequence, after every 10 samples and at the end of the analytical sequence. The measured concentration of each compound in the standard must be within ±20% of the expected value.

## 9.0 Sample Preparation

9.1 Preparation of solid samples – Prior to processing samples the grinding procedure must be evaluated to ensure that particle size is being reduced to <75um by passing representative portions of a ground sample through a 200 mesh sieve.

9.1.1 Place entire solid sample on a tray, spread and air dry at room temperature (<25 degrees C). Do not expose the samples to direct sunlight.

9.1.1.1 Allow samples to dry 1-3 days depending on matrix – sand samples will dry in 1 day while clay samples will take up to 3 days to dry.

9.1.1.2 Record date time and ambient temperature daily while samples are drying.

9.1.1.3 When sample appears dry place tray on scale and record weight.

9.1.1.4 Re-weigh samples after 1 hour. If weight change is less than 4% samples are considered at constant weight.

9.1.1.5 If weight change exceeds 4% allow sample to dry overnight and re-weigh.

9.1.1.6 Repeat steps 9.1.1.4 and 9.1.1.5 until constant weight is obtained (<4% change).

9.1.1.7 Dried samples can be stored at room temperature (<25 degrees C)

9.1.2 The entire dried sample less large pebbles, rocks and sticks must be sieved through a 10-mesh sieve. Agglomerates (especially clay) must be broken up with a gloved hand or forced through the sieve by pressing the material on the sieve with a gloved hand. Vegetation is physically shredded while sieving.

9.1.3 Pulverize the entire sieved sample in quantities of 200 – 500g for 60 seconds in the ring puck mill (Sec. 6.24). NOTE: For NC based propellant based residues five 60-second grinding intervals are required with two minute cool down periods between grind cycles.

9.1.4 For samples requiring 8330B - Spread the entire sample out onto a clean pan so that it is 1-2cm thick. Randomly chose 30 increments from the entire depth to obtain a 10 g sub sample. Place the 10g sample into a pre-cleaned 40 ml VOA vial.

9.1.5 For Samples requiring 8330A – Place a 2 g sub sample in a pre-cleaned 40 ml VOA vial.

9.1.6 Grinding blank prep - Between each sample grinding, process a grinding blank using Ottawa Sand according to the procedure in Sec. 9.1.3. Each Grinding Blank must be collected separately and cataloged. A composite is made from all the grinding blanks by adding equal parts of each blank to make a 10 g sample.

9.1.7 Grinding LCS – Process a grinding LCS using the nitroaromatic reference material (Sec. 7.6) with each batch of samples according to the procedure in Sec. 9.1.3 - 9.1.5.

9.1.8 MS/MSD prep - Process a MS/MSD (if sufficient sample is available) with each batch of samples according to the procedure in Sec. 9.1.1 – 9.1.5.

9.1.9 DUP and DUP-DUP sample prep – Process one sample in triplicate according to the procedure in Sec 9.1.1 – 9.1.5.

9.1.10 Extraction LCS/LCSD – DO NOT GRIND! Prepare a LCS/LCSD by adding 10 g (8330B) or 2 g (8330A) of Ottawa Sand (Sec. 7.5) into a pre-cleaned 40 ml VOA vial. An LCSD is only required if sufficient sample is not available for a MS/MSD.

9.1.11 Extraction Method Blank – **DO NOT GRIND**! Prepare an Extraction Method Blank by adding 10 g (8330B) or 2 g (8330A) of Ottawa Sand (Sec. 7.5) into a pre-cleaned 40 ml VOA vial.

9.1.12 LOD/LOQ prep – DO NOT GRIND! Prepare a LOD and LOQ by adding 10g of Ottawa Sand (Sec. 7.5) into a pre-cleaned 40 ml VOA vial.

9.1.13 Add surrogate (Sec. 8.10), spike (Sec 8.8) and acetonitrile according to Table 1 below.

**Table 1**
**Surrogate and Spike Procedure**

| Sample Type | Surrogate (ml) | Spike (ml) | LOD/LOQ Spike (ml) | 8330B ACN (ml) | 8330A ACN (ml) |
|---|---|---|---|---|---|
| Sample | 1 | 0 | 0 | 19 | 9 |
| MS/MSD | 1 | 1 | 0 | 18 | 8 |
| DUP/DUPDUP | 1 | 0 | 0 | 19 | 9 |
| Grinding Blank | 1 | 0 | 0 | 19 | 9 |
| Grinding LCS | 1 | 0 | 0 | 19 | 9 |
| Extraction Blank | 1 | 0 | 0 | 19 | 9 |
| Extraction LCS/LCSD | 1 | 1 | 0 | 18 | 8 |
| LOD | 1 | 0 | 0.5 | 18.5 | 8.5 |
| LOQ | 1 | 0 | 1 | 18 | 8 |

9.1.14 For Samples that require 8330B, place sample on a on a platform shaker for 18 hours. For samples that require 8330A, place samples in a cooled ultrasonic bath for 18 hours.

9.1.15 After the sample has extracted, settle for 30 minutes.

9.1.16 Transfer 6 ml of the supernatant liquid to a disposable syringe equipped with a 0.45 µm syringe filter. Pass the extract through the filter, discarding the first milliliter.

9.1.17 Prior to analysis all sample and QC extracts are diluted 1:1 by adding 0.5 ml of 1% Formic Acid Solution (Sec. 7.7) to 0.5 ml extract in a 2 ml amber auto sampler vials.

## 10.0 Diagram/Table

10.1 Reserved.

## 11.0 Analytical Procedure

11.1 Method, run, and integration parameters are stored in the respective instrumentation according to manufacturers procedures.

11.2 A new sample list is created for each batch of samples.

11.3 Data interpretation, qualitative identification is made when sample peak falls within the established RT window. Qualitative identifications must meet the method criteria before positive identification can be realized. These identifications are drawn from USEPA SW-846 Method 8000 – eluting within 0.05min of RT of the standard compound.

11.4 All compound identification must be confirmed by the results for the second column. The compound must be within the RT window on both compounds for positive identification.

11.5 Positive sample results are reported from both columns. The results are qualified (P-flagged) if the RPD result from values obtained on each column exceeds 40% in the absence of overlapping peaks causing an erroneously high result on one column. The disparity is noted in the comments field in the LIMS analytical sequence table for inclusion on the report case narrative.

11.6 A typical analytical sequence should proceed as below.

11.6.1 ICB
11.6.2 Initial calibration *
11.6.3 CCV (±20%)or ICV (±20%)
11.6.4 CRQL
11.6.5 LCS
11.6.6 Method Blank
11.6.7 10 samples
11.6.8 CCV
11.6.9 10 samples
11.6.10 MS and MSD
11.6.11 Reagent Blank (CCB)
11.6.12 CCV

*NOTE: Initial calibration is required on method initiation and subsequently on failure of the CCV acceptance criteria.

11.7 Set instrument parameters according to the Tables below.

**TABLE 1**
**Liquid Chromatograph Parameters Primary Column**

| **Typical LC-7Parameters:** | **Settings:** |
|---|---|
| Flow Rate (Injection Loop) | 0.5 ml/min (5 µl) |
| UV wavelength | 254 nm and 210 nm, BW 4, peak width >0.05 min (0.5s) |
| Gradient: A: 5%/95% v/v Methanol/Water; B: 100% Methanol @ 55.4°C | Primary Column: Waters BEH-C18 (section6.5) |

**TABLE 2**
**Liquid Chromatograph Parameters Confirmation Column**

| **Typical LC-5 Parameters:** | **Settings:** |
|---|---|
| Flow Rate(Injection Loop) | 1.0 ml/min (100 µl) |
| UV wavelength | 254 nm and 210 nm, BW 4, peak width >0.05 min (1s), Slit width 4nm |
| Isocratic 45%/55% v/v Methanol/Water @ 25-35°C | Secondary Column: Acclaim Explosives E2 (section6.6) |

**TABLE 3**
**Liquid Chromatograph Parameters Confirmation Column**

| **Typical LC-6 Parameters:** | **Settings:** |
|---|---|
| Flow Rate(Injection Loop) | 1.0 ml/min(100 μl) |
| UV wavelength | 254 nm and 210 nm, BW 4, peak width >0.05 min (1s), Slit width 4nm |
| Isocratic 37%/63% v/v Methanol/Water @ 10-40°C | Secondary Column: Acclaim Explosives E1 (section6.7) |

11.8 Compound identification and quantification

11.8.1 Compound identification must be confirmed by the results for the second column. The compound must be within the RT window on both columns for positive identification. Batch QC must also be analyzed on the secondary column as below.

11.8.1.1 Batch Method Blank (Grinding and/or Extracted) must be analyzed.
11.8.1.2 Batch LCS.
11.8.1.3 Include the parent, MS and MSD if the parent sample requires confirmation analysis.
11.8.1.4 Omit the parent, MS and MSD if the parent sample is non-detect for all compounds on the primary column.

11.8.2 Positive sample results are reported from both columns. The results are qualified (P-flagged) if the RPD result from values obtained on each column exceeds 40% in the absence of overlapping peaks causing an erroneously high result on one column. The disparity is noted in the comments field in the LIMS analytical sequence table for inclusion on the report case narrative.

11.8.3 Compound identification is based on the retention time (RT) of the eluting peak in comparison to calibration standard.

11.8.4 Initial identification is a compound that elutes within 0.05 min. of the RT of the standard compound. The 0.05 criteria is programmed into the data system method.

11.8.5 All compound identification must be confirmed by the results for the second column. The compound must be within the RT window on both compounds for positive identification.

11.8.6 Co-eluting compounds must be resolved on one of the columns.

11.8.7 Analyst experience in evaluating chromatographic data and identifying compounds in the presence of interfering components is important in final compound identification.

11.8.8 Identified compounds are quantified from the linear regression curve generated by the data system during initial calibration.

11.8.9 Compounds exhibiting concentrations above the upper calibration level are diluted into the calibration range. If insufficient sample is available for dilution (i.e. both water sample vials already used) the concentration is flagged as estimated ("E").

11.8.10 Compound concentrations that are below the laboratory reporting limit or lowest calibration point but positively identified above the MDL are flagged as estimated ("J").

11.9 Manual integration guidelines and procedures

11.9.1 Situations may arise whereby the quantification provided by the data system is inappropriate. This can occur due to co-elution, baseline noise or matrix interference.

11.9.2 When manual integration of a compound is necessary the following guidelines must be followed.

11.9.2.1 Manual quantification is performed by integrating the area of the peak for the compound.

11.9.2.2 The integration will only include the area attributable to the compound of interest.

11.9.2.3 The area integrated shall not include baseline background noise.

11.9.2.4 The area integrated shall not extend beyond the point where the sides of the peak intersect with the baseline.

11.9.2.5 Manual integration must not be used solely to meet quality control criteria.

11.9.2.6 Manual integration must not be used as a substitute for corrective action on the HPLC system.

11.9.3 Instances of manual integration are flagged with an "M" by the data system. Manual integrations require reason and initials of the analyst performing the manual integration and are documented in the corresponding Excel file and incorporated in the LIMS analytical sequence.

## 12.0 Details of Calibration and Calculations

12.1 Final results are calculated as specified in section 14.

12.2 The CCV must be analyzed at the frequency specified in Section 13 and the concentration must be within 20% of the known value for confirmation of instrument calibration.

12.3 Linear Regression: y = ax + b

Where: y = Instrument response (peak area)
a = Slope of the line
x = Concentration of the calibration standard
b = The intercept

12.4 % RSD

$$\overline{Rf} = \frac{\sum_{i=1}^{n} Rf_i}{n}$$

$$s = \sqrt{\frac{\sum_{i=1}^{n} (Rf_i - \overline{Rf})^2}{n-1}}$$

$$\%RSD = \frac{s}{\overline{Rf}} 100$$

12.5 Percent Drift

$$\% \text{ Drift} = \frac{Ce - Cf}{Ce} \times 100$$

Where: Ce = Expected concentration
Cf = Concentration found

12.6 Relative Percent Difference (RPD)

RPD = (| R1 – R2 | / ((R1 + R2)/2)) * 100

Where: R1 = First result, R2 = Second result

## 13.0 Quality Assurance/Quality Control (QA/QC) Requirements

13.1 Aqueous Samples - Prepare a method blank for each batch of samples using DI water.

13.1.1 Acceptance Criteria: < ½ **LOQ (RL)**

13.1.2 Corrective Action: Determine the source and eliminate (see interferences) - re-analyze samples as necessary.

13.2 Aqueous Samples - Prepare a laboratory control sample (LCS) and LCS duplicate (LCSD – when insufficient volume is supplied for MS/MSD analyses) for each batch of twenty or less samples by adding 1.0 ml of the Matrix Spiking Solution to 1L of DI water in a 1L amber bottle for each.

13.2.1 Acceptance Criteria: **QSM 5.0 percent recovery limits. LCSD PRD <20%**

13.2.2 Corrective Action: For results outside of acceptance limits determine source of the problem. Re-analyze LCS and samples if sufficient volume is supplied. Flag and narrate data if re-analysis is not possible.

13.3 Aqueous Samples - Prepare a matrix spike (MS) and matrix spike duplicate (MSD) for each batch of twenty or less samples by adding 1.0 ml of the Matrix Spiking Solution to the QC sample bottle when sufficient sample volume is supplied.

13.3.1 Acceptance Criteria: **Percent recovery acceptance ranges are set to LCS limits. MSD RPD <20%**

13.3.2 Corrective Action: For results outside of lab established control limits attempt to determine source of the problem (matrix interferences/poor injection/instrument problems). Re-analyze and/or flag data.

13.4 Aqueous Samples - Duplicate Sample (DUP) – Prepared if sufficient volume is supplied with each batch of samples. Not required if MSD is prepared.

13.4.1 Acceptance Criteria (RPD) **<20 %** or within laboratory established statistical control limits.

13.4.2 Corrective Action: Evaluate sample homogeneity and flag data if necessary.

13.5 Soil Samples – A grinding blank is processed through the grinding and sub-sampling steps using clean Ottawa sand (Sec. 7.5). Batch grinding blanks are prepared prior to analysis, after every 10 samples and at the end of the batch. The grinding blanks in each batch may be composited.

13.5.1 Acceptance Criteria: **< ½ LOQ (RL)**

13.5.2 Corrective Action: If the acceptance criteria is exceeded all samples in the batch are flagged with a B qualifier..

13.6 Soil Samples, Extraction blank – A method extraction blank is processed through the sample extraction procedure using clean Ottawa sand (Sec. 7.5).

13.6.1 Acceptance Criteria: **< ½ LOQ (RL)**

13.6.2 Corrective Action: If the acceptance criteria is exceeded all samples in the batch are flagged with a B qualifier..

13.7 Soil Samples -A grinding LCS from the standard reference material (Sec. 7.6) is processed through the entire grinding and sub-sampling procedure for each batch of samples.

13.7.1 Acceptance Criteria: **Within Specified Control Limits**

13.7.2 Corrective Action: Investigate and correct problem and flag data. Repeat instrument analysis if appropriate.

13.8 Soil Samples –An extraction LCS is prepared by spiking clean Ottawa sand and process through the extraction procedure for each batch of samples.

13.8.1 Acceptance Criteria: **QSM 5.0 percent recovery limits.**

13.8.2 Corrective Action: Investigate and correct problem and flag data. Repeat instrument analysis if appropriate.

13.9 Soil Samples - A MS and MSD is prepared by spiking a sample post grinding for each batch of samples.

13.9.1 Acceptance Criteria: **Percent recovery acceptance ranges are set to LCS limits. MSD RPD <20%**

13.9.2 Corrective Action: Evaluate, investigate and flag data. Repeat instrument analysis if appropriate.

13.10 Soil Samples – Sample Triplicate: From a sample expected to contain the highest concentrations of analytes three 10g aliquots are taken from the ground sample and analyzed individually.

13.10.1 Acceptance Criteria: **%RSD <20% for results >RL.**

13.10.2 Corrective Action: Investigate the grinding process to ensure sufficient sample particle size reduction is occurring. Flag and Narrate data.

13.11 Retention Time Windows

13.11.1 Retention time windows will be established and maintained for all components.

13.11.2 RT windows are determined by analyzing three control samples over a 72-hour time frame.

13.11.3 The average and standard deviation of the three determinations are calculated and the window is defined as the Mean (average) +/- 3 times the standard deviation.

13.11.4 The retention time windows are re-calculated whenever a new column is installed.

13.11.5 The GC data system does not allow for compound specific RT windows. The widest window (0.05 min.) is programmed into the applicable method and applied to all compounds.

13.12 Surrogate Control Limits

13.12.1 Acceptance Criteria: **70 – 130%**

13.12.2 For samples and QC samples in which the surrogate recovery falls outside the established control limits, the following is required.

13.12.3 Check calculations for errors.

13.12.4 Check instrument performance

13.12.5 Re-analyze extract- if acceptable no other actions are required.

13.12.6 Re-extract and re-analyze the samples or flag the data as estimated concentration if sample cannot be re-analyzed or if matrix interferences are obvious and cannot be cleaned up using the methods defined in the appropriate cleanup SOP's.

13.13 Recovery limits for compounds not included in the QSM tables for LCS, LCSD, MS and MSD samples will be set at 70-130%.

## 14.0 Data Reporting Requirements

14.1 Sample results are reported as µg/L (aqueous samples) and µg/kg (solid samples).

14.2 Sample results are reported as µg/L for water and µg/kg for soil as dry weight.

µg/kg dry wt. = µg/kg wet wt.*100/percent solids

14.3 Raw instruments results are entered directly into the Omega LIMS system using excel spreadsheets, direct instrument interface or manually. All calculations to derive final result (including dry weight conversions) are performed automatically by the LIMS. Sample preparation information and percent moisture results are entered into the appropriate section of the LIMS prior to instrument data and are automatically factored into the final results.

14.4 Confirm that there are no QC flags or qualifiers in this sequence. If present, investigate and repeat or reanalyze as necessary. See section 9.2 of the QAP for more detail on qualifiers.

## 15.0 Preventative Maintenance and Routine Cleaning

15.1 At the beginning of each instrument start up monitor the system for large fluctuations in pressure. Pressure should be 900 – 1600 psi. The system is checked for leaks if low pressures are observed. High pressure situations require back flushing the system with methanol for 1 hour.

15.2 All maintenance is recorded in the Omega LIMS for the applicable instrument.

## 16.0 Waste Management and Pollution Prevention

16.1 Pollution Prevention

16.1.1 Reagents are purchased and quantities used to reflect anticipated usage and minimize disposal of expired or unused chemicals.

16.1.2 Chemicals are handled in a manner that minimizes the potential for release or spill of the material.

16.2 Waste Management

16.2.1 Acidic materials (pH<2) are treated as hazardous waste and placed in the appropriate waste drum for disposal.

16.2.2 Disposal of materials is addressed in the laboratory QAP (Section 5.6).

## 17.0 References

17.1 EPA Test Methods for Evaluating Solid Waste. Laboratory Manual Physical/Chemical Methods, Method 8330B, Revision 2 October 2006.

17.2 RTI Laboratories, Inc. Quality Assurance Plan.

17.3 RTI Laboratories, Inc. SOP SRC001-A, Sample Receipt and Custody.

17.4 RTI Laboratories, Inc. Chemical Hygiene Plan.

17.5 RTI Laboratories, Inc. Employee Handbook.

## 18.0 Target Analyte List With Example Retention Times

| Analyte | Retention Time (min.) on Column E1 | Retention Time (min.) on Column E2 | Retention Time (min.) on Column BEH-C18 | Quantification Range (µg/L) |
|---|---|---|---|---|
| HMX | 5.75 | 8.060 | 1.633 | 20 – 1000 |
| 4-Nitroaniline | 8.78 | 10.396 | 2.292 | 20 – 1000 |
| RDX | 9.60 | 13.089 | 2.625 | 20 – 1000 |
| 1,3,5-Trinitrobenzene | 13.13 | 13.519 | 3.983 | 20 – 1000 |
| 1,3-Dinotrobenzene | 17.37 | 17.290 | 5.033 | 20 – 1000 |
| Nitrobenzene | 19.39 | 18.940 | 5.883 | 20 – 1000 |
| Nitroglycerine | 20.21 | 25.451 | 6.733 | 40 – 2000 |
| Tetryl | 21.79 | 25.811 | 6.917 | 20 – 1000 |
| 2,4,6-Trinitrobenzene | 24.05 | 24.012 | 7.067 | 20 – 1000 |
| 4-Amino-2,6-dinitrotoluene | 28.38 | 42.670 | 7.367 | 20 – 1000 |
| 2-Amino-4,6-dinitrotoluene | 29.56 | 44.868 | 7.225 | 20 – 1000 |
| 2,6-Dinitrotoluene | 30.69 | 28.942 | 7.625 | 20 – 1000 |
| 2,4-Dinitrotoluene | 31.76 | 30.068 | 7.525 | 20 – 1000 |
| 2-Nitrotoluene | 37.57 | 33.429 | 8.208 | 20 – 1000 |
| 3-Nitrotoluene | 45.51 | 39.327 | 8.575 | 20 – 1000 |
| 4-Nitrotoluene | 42.08 | 36.579 | 8.358 | 20 – 1000 |
| PETN | 43.97 | 55.838 | 9.292 | 100 – 5000 |

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# STANDARD OPERATING PROCEDURE

# ANALYSIS OF PERCHLORATE BY HPLC/MS/MS

| | |
|---|---|
| **Analyte:** | **Perchlorate, $ClO_4^-$** |
| **SOP#:** | **6850_071513_R0.1** |
| **Method Reference:** | **EPA SW-6850** |
| **Issue Date:** | **July 1, 2013** |
| **Revision No.:** | **0.1** |
| **Revision Date:** | |

**Reviewed and Approved: July 15, 2013**

Director, Quality Management: Charles O'Bryan

Director, Environmental Services: Yemane Yohannes

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# STANDARD OPERATING PROCEDURE

# ANALYSIS OF PERCHLORATE

# SOP#: 6850_070113_R0

## TABLE OF CONTENTS

## 1.0 Scope and Application:

1.1 Introduction

RTI Laboratories, Inc. has prepared this document to detail the Standard Operating Procedure (SOP) for the analysis of Perchlorate (CAS No. 14797-73-0) in aqueous and solid samples.

A detailed description of the instrumentation, calibration, run parameters and quality control procedures is included in this SOP. For definition of terms not specifically defined in this document refer to RTI QAP Section 16.

1.2 Summary of Method

1.2.1 An aliquot of a sample or extract is introduced into an HPLC system. Perchlorate is separated on a determinative column, and analyzed via tandem mass spectrometry (MS/MS). Resulting fragments with mass-to-charge ratios of 83 ($ClO_3^-$), 85($^{37}ClO_3^-$) and 86 ($Cl^{18}O_3^-$) are detected and quantified by comparison of the compound response to an established calibration curve.

## 2.0 Safety Precautions

2.1 Waste materials submitted for analyses may contain hazardous components. Uncharacterized waste samples should be handled in a manner that minimizes exposure and personal contact.

2.2 Chemicals used should be regarded as a potential health risk. Sample preparation and analysis is performed in a manner designed to minimize exposure using routine good laboratory practices.

2.3 Acetonitrile may be fatal if swallowed, inhaled or absorbed through the skin and affects the cardiovascular system, central nervous system, liver and kidneys. Liquid and vapor are flammable. May cause irritation to skin, eyes and respiratory tract.

## 3.0 Sample Requirements and Sample Handling Procedures

3.1 Samples are received in accordance with RTI Laboratories, Inc. Standard Operating Procedure for Sample Receipt and Custody (SRC001-A). Appropriate U.S. Environmental Protection Agency (EPA) sample handling procedures and sample preservation recommendations are followed.

3.1.1 Aqueous samples are collected in clean 125mL polyethylene bottles. Holding time is 28 days from the time of collection.

3.1.2 Whenever possible aqueous samples should be sterilely filtered in the field at the time of collection using 0.2um PTFE membrane filters in order to remove potential perchlorate degrading microbial organisms.

3.1.3 Soil, sludge and solid samples are collected in clean 4oz amber glass bottles. Solid sample must be extracted within 28 days from the time of collection - extracts must be analyzed within 28 days from preparation.

3.1.4 Care should be taken to avoid temperature extremes during shipment and storage. Samples should be shipped on ice at 4 degrees C (+/-2).

3.1.5 Sample volume minimum requirements: 10mL, aqueous – 1g, solids.

3.1.6 Samples and extracts should be stored at 4 degrees C (+/-2) with headspace to reduce potential anaerobic biodegradation.

## 4.0 MDL, Linear Range, Accuracy and Precision

4.1 The method detection limit (MDL) is statistically defined at the 99% confidence level according to 40 CFR Part 136 App. B. Seven replicates containing all of the analytes of interest at a concentration level of 1-5 times the estimated D.L. are analyzed and the standard deviation is calculated. The Student's T Value for the 7 replicates (3.143) is multiplied by the standard deviation of the analyte to calculate the MDL. MDLs are updated on major instrument changes and are kept on file in the Laboratory. MDLs and reporting limits are incorporated into the applicable test code in the Omega LIMS.

4.2 The LOD (limit of detection) is determined by spiking reagent water at 1-4 times the MDL and prepared using the same procedure as samples. Analytes must be present at levels 3 times or greater than the blank response (greater than 3 times the signal to noise ratio). The concentration used is the LOD for that analyte. LOD determinations must be performed quarterly.

4.3 The LOQ (limit of quantification) is determined by spiking reagent water at the reporting limit (RL/CRQL) and prepared in the same manner as samples. Analyte recovery must be within 20% of the expected concentration. The concentration used and successfully recovered is the LOQ for that analyte. LOQ determinations must be performed quarterly.

4.4 Initially accuracy and precision at the LOQ is determined by spiking 4 aliquots of reagent water at the reporting limit (RL/CRQL) and prepared using the same procedure used for samples. The average recovery must be within 20% of the expected value and the %RSD must be less than 15%.

4.5 LOD/LOQ determinations that do not meet the specifications above require repeat analysis, adjustment to the spiking levels and/or reporting limits, repeating the MDL determination at adjusted concentrations if required and repeat LOD/LOQ determinations.

4.6 The accuracy and precision for this method are determined by analyzing four laboratory control samples (LCS). The average percent recovery, standard deviation, and the relative standard deviation are calculated for each analyte. Quality control limits, mean recovery values and RPD results are incorporated in the Omega LIMS.

## 5.0 Interferences.

5.1 Interferences can arise from carry over due to high sample concentrations or contamination from reagents and/or glassware. Blanks are analyzed to ensure system cleanliness in both instances. All glassware must be scrupulously cleaned before use. Glassware-cleaning procedures are specified in the QAP. Glassware should be heated in a muffle furnace at 400 degrees C for 15 to 30 minutes, or solvent rinsed prior to use. High purity solvents are used for preparation and analysis.

5.2 Ionization suppression may arise when analyzing samples containing high levels of total dissolved solids (TDS). Including oxygen-18 labeled perchlorate internal standard monitors this matrix effect. Samples producing internal standard recoveries below 50% are reanalyzed and in some cases diluted to reduce the matrix interferences.

5.3 Particulates can potentially cause instrument damage. All samples, extracts, QC samples and reagent solutions should be filtered through a 0.45 um membrane filter.

## 6.0 Apparatus and Materials

6.1 HPLC system (LC-4): Agilent 1100 Series QuatPump G1311A, Agilent 1100 Series ALS G1313A, 3200 QTRAP MS/MS/MS System, PC with AB Sciex Analyst 1.6, Microsoft Windows XP and Omega LIMS.

6.2 Volumetric Flasks, 5mL; 10mL; 25mL; 100mL; and 1 Liter – Class A.

6.3 Column: Waters IC-Pak Anion HR column (4.6x75mm) or column capable of providing adequate separation

6.4 Disposable pipettes

6.5 Disposable 6mL plastic syringes

6.6 Disposable 0.45um PTFE syringe filters

6.7 Plastic centrifuge tubes (15, 50mL)

6.8 Graduated cylinders – 10mL, 25mL and 1L

6.9 Branson 5510 Ultrasonic water bath or equivalent

6.10 8mL amber vials with Teflon caps

6.11 Analytical balance, +/- 0.0001g accuracy

6.12 Centrifuge

## 7.0 Reagents and Standards

7.1 Acetonitrile (ACN) HPLC grade

7.2 Organic-free reagent water

7.3 Silica sand or sodium sulfate

7.4 Ammonium Acetate

7.5 Nitrogen gas, 99+%

7.6 Mass Calibration Solutions – Standards chemical kit with high/low concentrations of PPG (poly propylene glycol), AB Sciex, P/N 4406127

7.7 Mobile Phase: Add 7.708 grams of ammonium acetate to 500mL water. Add 500mL of acetonitrile and mix well. Degas solution by sonication or vacuum.

7.8 Primary Standards:

7.8.1 Perchlorate, 1mg/mL (Absolute: 57001)

7.9 Secondary Standards:

7.9.1 Perchlorate, 1mg/mL (AccuStandard: IC-PER-10X-1)

7.10 Internal Standard

7.10.1 Sodium Perchlorate ($^{18}O_4$): 1ug/mL (Absolute: 54022)

7.11 All standards, surrogates and spikes are stored in the dark at 4 degrees C.

7.12 All reagents and standards prepared must be logged in the appropriate standards/reagents log labeled with a minimum:

7.12.1 Identity of the material
7.12.2 Concentration of the solution
7.12.3 Date prepared
7.12.4 Initials of analyst preparing the solution
7.12.5 Expiration date.

## 8.0 Preparation of Standards and Spikes

8.1 Mass Calibration: Instrument mass calibration is performed according to the manufacturer's instructions on instrument set up and on an as-needed basis due to inability to meet QC criteria, following major instrumentation maintenance or instrumentation relocation. Mass calibration must meet the manufacturer's specifications.

8.2 Tuning: Following any mass calibration or prior to each initial calibration the instrument tuning is verified by introducing the standard perchlorate solution with internal standard directly into the 3200 QTRAP. Masses 83, 85 and 89 are monitored and must be within ± 0.3 m/z.

8.3 Initial Calibration Stock Standard (1ug/mL) Add 100uL of the primary standard solution (7.8) to a 100mL volumetric flask. Bring to volume with reagent water. Standard expires either 1 year from the date made or when the primary standard expires, whichever is first.

8.4 Initial Calibration Standards

| Standard ID | uL Stock Standard (8.1) | uL internal standard (7.10) | Final Volume | Std. Concentration (ppb) |
|---|---|---|---|---|
| Ical1 | 2 | 50 | 10 | 0.2 |
| Ical2 | 5 | 50 | 10 | 0.5 |
| Ical3 | 10 | 50 | 10 | 1 |
| Ical4 | 50 | 50 | 10 | 5 |
| Ical5 | 100 | 50 | 10 | 10 |
| Ical6 | 500 | 50 | 10 | 50 |

8.5 Initial Calibration Verification/Continuing Calibration Verification Stock Standard (1ug/mL) Add 100uL of the secondary standard solution (7.9) to a 100mL volumetric flask. Bring to volume with reagent water. Standard expires either 1 year from the date made or when the primary standard expires, whichever is first.

8.6 Initial Calibration Verification/Continuing Calibration Verification Working Standard- (5ng/mL) Add 50uL of the ICV/CCV stock standard (8.3) and 50uL of the internal standard solution (7.10) to a 10mL volumetric flask. Bring to volume with reagent water.

8.7 Spike Solution – (100ng/mL) Add 1mL of the ICV/CCV stock standard (8.3) to a 10mL volumetric flask. Bring to volume with reagent water.

8.8 Interference Threshold/Interference Check Sample (ICS) – The ICS is prepared by adding approximately 0.0824 g NaCl, 0.1108 g $Na_2SO_4$, and 0.0884 g $Na_2CO_3$ and 50uL of the primary standard solution (7.6) and 500uL Sodium Perchlorate ($^{18}O_4$) (7.10) in 100 ml reagent water. This solution gives a conductivity reading of approximately 10,000 uS/cm and a perchlorate concentration of 0.2ug/L (reporting limit concentration).

8.9 Limit of Detection Verification (LODV) Standard 0.1ug/L – Add 1uL of the Initial Calibration Stock Standard (8.1) and 50uL of the Sodium Perchlorate ($^{18}O_4$) internal standard to a 10mL volumetric flask. Bring to volume with reagent water.

8.10 Generate an internal standard calibration curve using the response of the 83 ion and internal standard response (89 ion). For first-order linear regression calibration curves, the correlation coefficient must be 0.995 or higher and the absolute value of the Y intercept must not be greater than or equal to the established LOD.

8.11 Initial calibration verification standard must be run immediately after calibration. The standard is prepared from a different source than the calibration standards at a concentration corresponding to the mid-point of the curve. The ICV standard must be within 15% of the expected concentration.

8.12 Continuing calibration verification (CCV) standards are analyzed, at a concentration equivalent to the mid-point of the calibration curve, at the beginning of each analytical sequence, after every 10 samples and at the end of the analytical sequence. The measured concentration of each compound in the standard must be within 15% of the expected value.

## 9.0 Sample Preparation

9.1 Aqueous Sample Preparation

9.1.1 Sample Preparation: Measure 10mL of sample into a 15mL disposable centrifuge tube. Add 50uL of Internal Standard solution and shake well. Filter solution using a 0.45um syringe filter and plastic syringe into an auto sampler vial

9.1.2 Method Blank Preparation – DI Water, see 9.1.1

9.1.3 Instrument Blank – DI Water

9.1.4 LCS/LCSD Preparation – Spike 20uL of the Spike Solution (Sec 8.5) and 50uL of Internal Standard solution per 10mL of DI water. Filter solution using a 0.45um syringe filter and plastic syringe into an auto sampler vial

9.1.5 MS/MSD Preparation – Spike 20uL of the Spike Solution (Sec 8.5) and 50uL of Internal Standard solution per 10mL of sample. Filter solution using a 0.45um syringe filter and plastic syringe into an auto sampler vial

9.1.6 LOD/LOQ Preparation – To 10 ml of DI water add 10uL (LOD) or 20uL (LOQ) of the Spike Solution (Sec 8.5). Add 50uL of Internal Standard solution. . Filter solution using a 0.45um syringe filter and plastic syringe into an auto sampler vial

9.2 Soil Sample Preparation

9.2.1 Sample Preparation – Weigh 1g of solid sample recording the weight to 0.01g. Transfer to a 15mL centrifuge tube. Bring to 10mL mark with DI water. Add 50uL of Internal Standard solution. Vortex

mixture, then sonicate for 10 minutes, then vortex the samples again. Centrifuge samples for 5 minutes to separate the solids from the extract solution if necessary. Filter the solution using a 0.45um PTFE syringe filter and plastic syringe into an auto sampler vial. C18 cartridge columns can be used to clean up the samples if needed (supernatant is not relatively clear or is highly colored).

9.2.2 Method Blank Preparation - Weigh 1g of silica sand and follow the procedure outlined in section 9.2.1

9.2.3 Instrument Blank Preparation – DI Water

9.2.4 LCS/LCSD Preparation – Spike 20uL of the Spike Solution (Sec 8.5) and 50uL of Internal Standard solution per 1g of silica sand. Follow the procedure outlined in section 9.2.1

9.2.5 MS/MSD Preparation - Spike 20uL of Spike Solution (Sec 8.5)) and 50uL of Internal Standard solution per 1g of sample. Follow the procedure outlined in section 9.2.1.

9.2.6 LOD/LOQ Preparation – To 1g of silica sand add 10uL (LOD) or 20uL (LOQ) of the Spike Solution (Sec 8.5). Add 50uL of Internal Standard solution. Follow the procedure outlined in section 9.2.1

## 10.0 Diagram/Table

10.1 Reserved.

## 11.0 Analytical Procedure

11.1 Method, run, and integration parameters are stored in the respective instrumentation according to manufacturers procedures.

11.2 A new sample list is created for each batch of samples.

11.3 Data interpretation, qualitative identification is made when sample peak falls within the established RT window. Qualitative identifications must meet the method criteria before positive identification can be realized. These identifications are drawn from USEPA SW-846 Method 6850

11.4 A typical analytical sequence should proceed as below.

11.4.1 ICB (reagent blank)

11.4.2 Initial calibration *

11.4.3 CCV or ICV

11.4.4 LODV

11.4.5 INF

11.4.6 Method Blank

11.4.7 LCS/MS/MSD

11.4.8 10 samples

11.4.9 LODV

11.4.10 CCV

11.4.11 Reagent blank

*NOTE: Initial calibration is required on method initiation and subsequently on failure of the CCV acceptance criteria.

11.5 Instrument Parameters:

Flow rate: 1mL/min
Run time: 12.0 min
Column temp. 30 °C
Injection vol.: 40uL
Column: Waters IC-Pak Anion HR column (4.6x75mm)
Mobile Phase: 50% 200mM Ammonium Acetate, 50% acetonitrile

11.5.1 Mass spectrometer.

Ionization mode: Electrospray
Polarity: Negative

| | | | |
|---|---|---|---|
| Gas Temp | 500 C | Declustering Potential | -50 |
| Curtain Gas | 30 L/min | Entrance Potential | -10 |
| Ion Spray Voltage | -4500V | Collision Energy | -35 |
| Ion Source Gas 1 | 60 | Collision Cell Exit Potential | -1 |
| Ion Source Gas 2 | 60 | | |
| Collision Gas | High | | |
| | | | |

11.5.2 MRM parameters (shall vary according to instrument conditions)

| Q1 Mass | Q2 Mass | Time (msec) |
|---|---|---|
| 101 | 85 | 500 |
| 98.9 | 82.9 | 500 |
| 107 | 89 | 500 |

11.6 Compound identification and quantification

11.6.1 Initial identification of perchlorate is based on comparison of the RT to that of the internal standard. The relative retention time (RRT) should be within 1.0 +/- 2% (0.98 – 1.02).

11.6.2 Perchlorate is identified by retention time and the detection of the 99 to 83m/z and the 101 to 85m/z transitions. Oxygen-18 labeled perchlorate is identified by retention time and the detection of the 107 to 89 m/z transition

11.6.3 The isotope ratio is to be monitored for every sample, batch QC sample and standard. Measure the ratio of the perchlorate daughter ion 83 m/z to the daughter ion 85 m/z. The expected ratio is 3.08 and the measured ratio must fall within 2.3 and 3.8. If criteria are not met, the sample must be rerun. Sample quantification is performed by comparing the response of the 83/89 ions to the calibration curve.

11.6.4 Measure the area of the internal standard in every sample, batch QC sample, standard, and instrument blank. The measured area must be within +/-50% of the value from the average of the IS area counts of the ICAL. If criteria are not met, rerun the samples at increasing dilutions until the +/-50% acceptance criteria are met.

11.6.5 Analyst experience in evaluating chromatographic data and identifying compounds in the presence of interfering components is important in final compound identification.

11.6.6 Identified compounds are quantified from the curve generated by the data system during initial calibration.

11.6.7 Compounds exhibiting concentrations above the upper calibration level are diluted into the calibration range. If insufficient sample is available for dilution the concentration is flagged as estimated (“E”).

11.6.8 Compound concentrations that are below the laboratory reporting limit or lowest calibration point but positively identified above the MDL are flagged as estimated (“J”).

11.7 Manual integration guidelines and procedures

11.7.1 Situation may arise whereby the quantification provided by the data system is inappropriate. This can occur due to co-elution, baseline noise or matrix interference.

11.7.2 When manual integration of a compound is necessary the following guidelines must be followed.

11.7.2.1 Manual quantification is performed by integrating the area of the peak for the compound.

11.7.2.2 The integration will only include the area attributable to the compound of interest.

11.7.2.3 The area integrated shall not include baseline background noise.

11.7.2.4 The area integrated shall not extend beyond the point where the sides of the peak intersect with the baseline.

11.7.2.5 Manual integration must not be used solely to meet quality control criteria.

11.7.2.6 Manual integration must not be used as a substitute for corrective action on the HPLC system.

11.7.3 Instances of manual integration are flagged with an “M” by the data system. Manual integrations require reason and initials of the analyst performing the manual integration and are documented in the corresponding Excel file and incorporated in the LIMS analytical sequence.

## 12.0 Details of Calibration and Calculations

12.1 Final results are calculated as specified in section 14.

12.2 The CCV must be analyzed at the frequency specified in Section 13 and the concentration must be within 15% of the known value for confirmation of instrument calibration.

12.3 Linear Regression: $y = ax + b$
Where: y = Instrument response (peak area)
a = Slope of the line
x = Concentration of the calibration standard
b = The intercept

12.4 % RSD

Average Rf = (Rf1+Rf2+Rf3+Rf4+Rf5)/5

Std. Dev. = SQRT [(sumx2 - sum(x)2/n)/(n-1)]

%RSD = Std. Dev./Average Rf x 100

12.5 Percent Recovery

$$\% \text{ Rec.} = \frac{C_e - C_f}{C_e} \times 100$$

Where: Ce = Expected concentration
Cf = Concentration found

12.6 Relative Percent Difference (RPD)

RPD = (| R1 – R2 | / ((R1 + R2)/2)) * 100

1.2.1.1.1 Where: R1 = First result, R2 = Second result

## 13.0 Quality Assurance/Quality Control (QA/QC) Requirements

13.1 Mass calibration must be performed on instrument set up and as required due to inability to adequately meet QC requirements or on major instrumentation maintenance or relocation.

13.1.1 Acceptance criteria: Meets manufacturer's specifications

13.2 Instrument tuning is performed following mass calibrations and prior to each initial calibration according to Section 8.2.

13.2.1 Acceptance criteria: Perchlorate ions 83, 85 and 89 within ± 0.3 m/z.

13.3 Conductivity Limit/Interference Threshold Study (ICS – Section 8.6) must be performed following instrument set up and prior to initial sample analysis.

13.3.1 Acceptance criteria: Perchlorate recovery within 85 – 115%.

13.4 Initial demonstration of capability must be performed prior to initial sample analysis, on change in instrument type, change of personnel or major instrument maintenance by the analysis of 4 prepared LCS samples for each matrix.

13.4.1 Acceptance criteria – percent recovery: 80 – 120%
13.4.2 Acceptance criteria - %RSD: <15%

13.5 Sample analysis cannot commence until procedures and criteria in Sections 13.1 – 13.4 have been successfully performed.

13.6 Initial calibration is performed prior to initial sample analysis and when ICV/CCV criteria cannot be achieved by the analysis of a minimum of 5 calibration standards to establish linearity.

13.6.1 Acceptance criteria are $r \geq 0.995$ or $RSD \leq 20\%$. No samples may be analyzed until ICAL criteria have been verified.

13.7 ICV/CCV - An ICV is analyzed immediately following initial calibration. CCV sample are analyzed at the beginning of an analytical sequence if an ICAL is not required, after every ten samples and at the end of the analytical sequence.

13.7.1 Acceptance Criteria: 85-115%.

13.7.2 Corrective Action: Repeat or re-prepare CCV. Re-calibrate.

13.8 Laboratory reagent blank must be analyzed prior to calibration or the start of an analytical sequence (prior to CCV) and at the end of each analytical sequence or when a sample perchlorate concentration is over range.

13.8.1 Acceptance criteria: Result <1/2 the LOQ.

13.8.2 Corrective action: Re-analyze blank until result is acceptable, clean system. Re-analyze any affected samples. All sample results reported must be associated with acceptable laboratory reagent blanks.

13.9 Limit of Detection Verification (LODV) – Prior to sample analysis and at the end of the analytical sequence.

13.9.1 Acceptance Criteria: Within +/-30% of true value

13.9.2 Corrective Action: Rerun LODV and all samples analyzed since last successful LODV. If a sample with perchlorate concentration at or between the LOD and RL is bracketed by a failing LODV, it must be reanalyzed. A sample with a concentration above the RL can be reported.

13.10 Interference Check Sample (ICS) – One ICS is prepared with every batch of 20 samples or less and undergoes the same preparatory steps.

13.10.1 Acceptance Criteria: Within +/-30% of true value.

13.10.2 Corrective Action: Correct problem and reanalyze all samples in that batch

13.11 Method Blank - For each batch of 20 or less samples a method blank (Sec 9.2.3) is prepared and analyzed through the entire method.

13.11.1 Acceptance Criteria: < ½ RL

13.11.2 Corrective Action: If the target analyte or interfering non target compounds are found in the blank at levels greater than the reporting limits, then the source of contamination must be identified and corrective action taken before sample analysis can proceed. Corrective actions include reanalysis of the method blank, analysis of reagent blanks, cleaning systems components (column, detector) and checks on sample preparation procedure. Contamination that does not interfere with target compounds may be ignored.

13.12 LCS/LCSD (prepare if insufficient sample volume for MS/MSD) - Prepare a laboratory control sample (LCS) (Sec. 9.2.4) for each batch of twenty or less samples.

13.12.1 Acceptance Criteria: 80 - 120 % recovery, RPD <15% (LCSD).

13.12.2 Corrective Action: For results outside of acceptance limits determine source of the problem. Re-analyze LCS/LCSD and samples if required. Flag and narrate data if re-analysis is not possible.

13.13 MS/MSD - Prepare a matrix spike (MS) and matrix spike duplicate (MSD) (Sec. 9.2.5) for each batch of twenty or less sample.

13.13.1 Acceptance Criteria: 80 – 120% recovery, <15% RPD (acceptance ranges are set to LCS limits).

13.13.2 Corrective Action: For results outside of acceptance limits determine source of the problem. Re-analyze MS/MSD and samples if required. Flag and narrate data if re-analysis is not possible.

13.14 Isotope ratio $^{35}Cl/^{37}CL$: For every sample, QC sample or standard the ion masses at 82 and 85 are monitored. The ratio must be within 2.3 – 3.8 (theoretical ration ~3.06). If the ration exceeds the range the sample must be re-analyzed. In cases where an acceptable ratio cannot be achieve documentation of the data is required in the case narrative.

13.15 Internal standard is added to all samples, QC samples and standards. The area response of the internal standard must be within ±50% of the value of the average of the internal standard responses for the associated ICAL. If any response exceeds the criteria the affected sample must be re-analyzed at increasing dilutions until the criteria is met. In cases where dilution does not resolve the problem interference is suspected and documentation in the case narrative is required.

## 14.0 Data Reporting Requirements

14.1 Sample results are reported as µg/L (aqueous samples) and µg/kg (solid samples corrected on a dry weight basis).

14.1.1 µg/kg dry wt. = µg/kg wet wt.*100/percent solids

14.2 Raw instruments results are entered directly into the Omega LIMS system using excel spreadsheets, direct instrument interface or manually. All calculations to derive final result (including dry weight conversions) are performed automatically by the LIMS. Sample preparation information and percent moisture results are entered into the appropriate section of the LIMS prior to instrument data and are automatically factored into the final results.

14.3 Confirm that there are no QC flags or qualifiers in this sequence. If present, investigate and repeat or reanalyze as necessary. See section 9.2 of the QAP for more detail on qualifiers.

14.4 Narrate all cases as required in Section 13.

## 15.0 Preventative Maintenance and Routine Cleaning

15.1 At the beginning of each instrument start up monitor the system for large fluctuations in pressure. Pressure should be 900 – 1600 psi. The system is checked for leaks if low pressures are observed. High-pressure situations require back flushing the system with methanol for 1 hour.

15.2 All maintenance is recorded in the Omega LIMS for the applicable instrument.

## 16.0 Waste Management and Pollution Prevention

16.1 Pollution Prevention

16.1.1 Reagents are purchased and quantities used to reflect anticipated usage and minimize disposal of expired or unused chemicals.

16.1.2 Chemicals are handled in a manner that minimizes the potential for release or spill of the material.

16.2 Waste Management

16.2.1 Acidic materials (pH<2) are treated as hazardous waste and placed in the appropriate waste drum for disposal.

16.2.2 Disposal of materials is addressed in the laboratory QAP (Section 5.6).

## 17.0 References

17.1 Perchlorate in Water, Soils and Solid Wastes. Laboratory Manual Physical/Chemical Methods, Jan 2007, Revision 0. Method 6850.

17.2 RTI Laboratories, Inc. Quality Assurance Plan.

17.3 RTI Laboratories, Inc. SOP SRC001-A, Sample Receipt and Custody.

17.4 RTI Laboratories, Inc. Chemical Hygiene Plan.

17.5 RTI Laboratories, Inc. Employee Handbook.

RTI Laboratories, Inc.
31628 Glendale
Livonia, Michigan 48150

# STANDARD OPERATING PROCEDURE

# ANALYSIS OF ELEMENTS BY INDUCTIVELY COUPLED PLASMA - OPTICAL EMISSION SPECTROMETRY (ICP-OES)

| | |
|---|---|
| **Analyte:** | **Elements** |
| **SOP#:** | **6010C_100713_R3.2** |
| **Method Reference:** | **SW 6010C, EPA 200.7** |
| **Issue Date:** | **November 8, 2012** |
| **Revision:** | **3.2** |
| **Revision Date:** | **August 11, 2014** |

**Reviewed and Approved: August 11, 2014**

Director, Quality Management: Charles O'Bryan

Director, Environmental Services: Yemane Yohannes

**ANALYSIS OF ELEMENTS BY INDUCTIVELY COUPLED PLASMA-OPTICAL EMISSION SPECTROMETRY (ICP-OES)**

**SOP#: 6010C_100713_R3.2**

## TABLE OF CONTENTS

# 1.0 Scope and Application

## 1.1 Introduction

1.1.1 This Standard Operating Procedure details the analysis of samples according to the U. S. EPA Methods 6010 and 200.7 for the elements listed in the associated Omega LIMS test code using inductively coupled plasma (ICP/OES).

1.1.2 This method applies to aqueous samples, soil/solid samples, industrial wastes and extracts.

1.1.3 Acid digestion and filtration are required prior to analysis of these samples. Analyses for dissolved metals may only require filtration.

1.1.4 Maintenance for the ICP-OES instruments can be found in the ICP-OES Optima 8300 Hardware Manuals provided with the instrument.

1.1.5 Detailed instructions on the ICP – WinLab32 software can be found in the instrument Software Manuals.

1.1.6 For definition of terms not specifically defined in this document refer to RTI QAP Section 16.

## 1.2 Summary of Method

1.2.1. The analysis described in this method involves multi-elemental determinations by ICP-OES using sequential or simultaneous optical systems and axial or radial viewing of the plasma. The instrument measures characteristic emission spectra by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element specific emission spectra are produced by radio frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the line spectra are monitored at specific wavelengths by a photosensitive device. Photocurrents from the photosensitive device are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of the analytes. Background must be measured adjacent to the analyte wavelength during analysis. Various interferences must be considered and addressed appropriately.

1.2.2. Samples are prepared according to the matrix by applicable preparation procedures according to the associated SOP. Samples for dissolved metals do not require additional sample preparation procedures prior to analysis.

## 2.0 Safety Precautions

2.1 Acids used in the digestion procedure are corrosive. All digestions are performed in a fume hood designated for use with mineral acids. Proper safety equipment (gloves, lab coats, etc.) is worn when handling concentrated acids. Many elements are toxic and should be handled with care.

2.2 Good laboratory technique and safety practices should be used at all times to reduce the risks associated with chemicals and potential hazards.

2.3 The ICP/OES instrument is fully interlocked for safety purposes. Never attempt to disable these interlocks.

2.4 Spilled samples must be cleaned up immediately when they come in contact with the instrument. Neutralize all acid spills with sodium bicarbonate.

## 3.0 Sample Requirements and Sample Handling Procedures

3.1 Samples are received in accordance with RTI Laboratory's Standard Operating Procedure for Sample Log-in (SOP: SRC001-A). Appropriate U. S. Environmental Protection Agency (EPA) sample handling procedures and sample preservation recommendations are followed.

3.1.1 Soil, sludge and solid samples are collected in pre cleaned wide mouth glass jars.

3.1.2 Aqueous samples are collected in pre cleaned plastic bottles preserved with approximately 2.0 ml of 1:1 high purity nitric acid:DI water. The pH of the sample is checked on receipt and prior to sample preparation for the presence of adequate preservative. The pH of preserved samples should be < 2. Preserved samples received at pH>2 or at sample preparation are at pH>2 are adjusted to pH<2 with additional acid and held for a minimum of 16 hours until verified to be pH<2.

3.1.3 Maximum sample holding time is six (6) months.

3.1.4 Samples received for filtration in the laboratory or samples that have been filtered prior to receipt must be preserved and held for 24 hours prior to commencing the sample preparation procedure. Laboratory filtration is performed by filtering a portion of the sample sufficient for analysis through a 0.45-µm filter. The pH is checked prior to analysis and if required the procedure in Sec. 3.1.2 is followed.

## 4.0 MDL, LOD, LOQ, Linear Range, Accuracy and Precision

4.1 The method detection limit (MDL) is statistically defined at the 99% confidence level according to 40 CFR Part 136 App. B. Seven replicates containing all of the analytes of interest at a concentration level of 1-5 times the estimated D.L. are analyzed and the standard deviation is calculated. The Student's T Value for the 7 replicates (3.143) is multiplied by the standard deviation of the analyte to calculate the MDL. MDLs are performed on instrument set up and following significant changes to the instrument, method or personnel. MDLs are kept on file in the Laboratory. MDLs and reporting limits are incorporated into the applicable test code in the Omega LIMS.

4.2 The LOD (limit of detection) is determined by spiking reagent water at 1-4 times the MDL and prepared using the same procedure as samples. Analytes must be present at levels 3 times or greater than the blank response (greater than 3 times the signal to noise ratio). The concentration used is the LOD for that analyte. LOD determinations must be performed quarterly.

4.3 The LOQ (limit of quantification) is determined by spiking reagent water at the reporting limit (RL/CRQL) and prepared in the same manner as samples. Analyte recovery must be within 20% of the expected concentration. The concentration used and successfully recovered is the LOQ for that analyte. LOQ determinations must be performed quarterly.

4.4 Initially accuracy and precision at the LOQ is determined by spiking 4 aliquots of reagent water at the reporting limit (RL/CRQL) and prepared using the same procedure used for samples. The average recovery must be within 20% of the expected value and the %RSD must be less than 15%.

4.5 LOD/LOQ determinations that do not meet the specifications above require repeat analysis, adjustment to the spiking levels and/or reporting limits, repeating the MDL determination at adjusted concentrations if required and repeat LOD/LOQ determinations.

4.6 The linear range for this method is element specific. Linear ranges are addressed in Section 13. If a sample falls above the linear range or highest calibration standard dilutions of the sample digestate must be made until the concentration falls within the established calibration range.

4.7 The accuracy and precision for this method are determined by analyzing four aliquots from a Laboratory Control Sample containing the element(s) of interest at the mid-level of the calibration range. Percent recovery, standard deviation, and the relative standard deviation are calculated for each analyte. Quality control limits, mean recovery values and RPD results are incorporated in the Omega LIMS.

## 5.0 Interferences

5.1. Spectral interferences encountered in ICP-OES falls into four different categories, each with its own causes and remedies:

5.1.1 A shift in background that is essentially constant over a given range. The background may shift either up or down. This can be caused by a high concentration of an interfering analyte that may emit a continuum radiation in the given wavelength range. There are two remedies: set a background correction point somewhere near, but not falling on, the profile of the analyte being measured, or select a different wavelength that is not affected by the interference. Background correction is accomplished through programmed one or two point stops around each wavelength. Under normal operations, these background filters are not adjusted. The analyst may adjust these filters in samples by overlaying the samples and standards and manually adjusting the plus, minus or both wavelength filters for samples that exhibit conflicting spectra. Any adjustments to the standard background correction will be noted for QA review.

5.1.2 A shift that occurs on only one side of the given wavelength range. This can be caused by: i) an overlapping of an analyte line by one wing of another severely broadened line nearby, or ii) a molecular emission bands that are sometimes present in the ICP discharge, especially when the plasma is not shielded from the ambient atmosphere. Since the slope of the interference is constant on either side of the peak, set two background correction points, one on either side of the peak of the analyte being measured.

5.1.3 Ideally no interfering emission line can fall directly on the analyte emission line; however, because spectral lines have a finite width and measurement systems are imperfect, direct spectral overlap does occur. Two lines may appear to be overlapped when they cannot be resolved by the spectrometer. There are two remedies: use an alternate wavelength for the analyte being measured, if available, or use the Interelement Correction (IEC) technique (refer to Sec. 13).

5.1.4 Complex Background Shift is represented by a shift in background intensity that varies significantly on either side of the analyte line. This interference is usually caused by the occurrence of a number of intense, closely spaced emission lines nearby, and perhaps directly overlapping, the analyte wavelength. There are two remedies: use an alternate wavelength for the analyte being measured, if available, or use the Multispectral component Fitting (MSF) technique.

5.2 Reagents, glassware and other sample preparation equipment may contain artifacts that will interfere with the analysis. Method blanks are routinely analyzed to demonstrate that materials are free from contamination. Sample bottles and reagents are assayed prior to use for suitability. Glass containers cannot be used for analyses requiring determination of Boron or Silicon.

5.3 Carryover can occur when a high concentration sample is analyzed. Additional rinse time may be required when encountering an elevated concentration sample to eliminate potential memory affects.

5.4 Physical interferences associated with dissolved solids content or matrix viscosity can cause suppression or enhancement of the signal. Dilution of the sample will usually eliminate the physical interference problem

## 6.0 Apparatus and Materials

6.1 ICPOES - Perkin-Elmer ICPOES Optima 8300, Cetac ASX-520 auto sampler with HP computer system (Windows 7) and WinLab 32 software – Version 5.2.0.0612.

6.2 ICPOES: Peristaltic pump tubing black/black - 0.76mm id, yellow/orange – 0.51 mm id, red/red – 1.14mm id.

6.3 Calibrated mechanical pipettes with metal free plastic pipette tips 10 – 100 µl, 100 – 1000 µl, 500 – 5000 µl, 1 – 10 ml.

6.4 50 ml plastic auto sample tubes with plastic caps and auto sample cultures plastic tubes for samples.

6.5 Beakers – various sizes.

6.6 Volumetric flasks, Class A – various volumes.

6.7 Filter Mate Filtration Devices from Environmental Express.

## 7.0 Reagents

7.1 High purity reagents, acid and water must be used at all times. Trace metals grade acids are required for this method.

7.2 5% (vol/vol) hydrochloric acid + 2% (vol/vol) nitric acid. Prepared by adding 1L of hydrochloric acid + 400 mL nitric acid to a 20 L container. Expiration date for this solution is 3 month.

7.3 Single element standards - ICP grade, 1000 ug/mL: Stock Calibration Standards Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Pb, Li, Mg, Mn, Mo, Ni, K, Na, Sb, Se, Si, Sn, Sr, Ti, Tl, V, Zn.

7.4 Second Source Standard – Multi-element, Absolute Standards: 50 ug/ml Ag, As, Be, Cd, Co, Li, Mo, Sb, Se, Sn, Sr, Ti, Tl, V and B – 250 ug/ml Al, Ba, Cr, Cu, Pb, Mn, Ni, Zn – 2500 ug/ml Ca, Fe, Mg, K, Na in 5% Nitric acid/2% Hydrochloric acid.

7.5 Calibration Intermediary Stock Standards:

7.5.1 1 ppm for Ag, Be, Cd, Co, Li, Mo, Sb, Ti, V - 50 ul of 1000 ug/mL in 50 mL 5% hydrochloric acid/2% nitric acid.
7.5.2 10 ppm for As, Tl, Se, Si, Sn, Sr - 500 ul of 1000 ug/mL in 50 mL 5% hydrochloric acid/2% nitric acid.
7.5.3 20 ppm for Ba, Cr, Cu, Pb, Mn, Ni, Zn - 1mL of 1000 ug/mL in 50 mL 5% hydrochloric acid/2% nitric acid.
7.5.4 100 ppm for Al, B, Ca, Fe, Mg, K, Na - 5mL of 1000 ug/mL in 50 mL 5% hydrochloric acid/2% nitric acid.

7.6 Calibration Standards: Prepare fresh daily.

7.6.1 Calibration Standard 1/CRQL:

Made from Calibration Intermediary Stock Standard (7.5)

Dilute in 5% hydrochloric acid/ 2% nitric acid to the mark in a Class “A” 50 mL volumetric flask:

| Analyte | Std Conc. (µg/mL) | Add this amount (µL) | Final Vol. (mL) | STD1/ CRQL | Units |
|---|---|---|---|---|---|
| Aluminum | 100 | 50 | 50 | 100 | µg/L |
| Antimony | 1 | 1000 | 50 | 20 | µg/L |
| Arsenic | 10 | 200 | 50 | 40 | µg/L |
| Barium | 20 | 500 | 50 | 200 | µg/L |
| Beryllium | 1 | 250 | 50 | 5 | µg/L |
| Boron | 100 | 125 | 50 | 250 | µg/L |
| Cadmium | 1 | 250 | 50 | 5 | µg/L |
| Calcium | 100 | 500 | 50 | 1000 | µg/L |
| Chromium | 20 | 25 | 50 | 10 | µg/L |
| Cobalt | 1 | 1000 | 50 | 20 | µg/L |
| Copper | 20 | 250 | 50 | 100 | µg/L |
| Iron | 100 | 150 | 50 | 300 | µg/L |
| Lead | 20 | 250 | 50 | 100 | µg/L |
| Lithium | 1 | 500 | 50 | 10 | µg/L |
| Magnesium | 100 | 500 | 50 | 1000 | µg/L |
| Manganese | 20 | 50 | 50 | 20 | µg/L |
| Molybdenum | 1 | 500 | 50 | 10 | µg/L |
| Nickel | 20 | 250 | 50 | 100 | µg/L |

| | | | | | |
|---|---|---|---|---|---|
| Potassium | 100 | 200 | 50 | 400 | µg/L |
| Selenium | 10 | 200 | 50 | 40 | µg/L |
| Silicon | 10 | 200 | 50 | 40 | µg/L |
| Silver | 1 | 1000 | 50 | 20 | µg/L |
| Sodium | 100 | 500 | 50 | 1000 | µg/L |
| Strontium | 10 | 500 | 50 | 100 | µg/L |
| Thallium | 10 | 200 | 50 | 40 | µg/L |
| Tin | 10 | 200 | 50 | 40 | µg/L |
| Titanium | 1 | 500 | 50 | 10 | µg/L |
| Vanadium | 1 | 2500 | 50 | 50 | µg/L |
| Zinc | 20 | 250 | 50 | 100 | µg/L |

7.6.2 Calibration Standard 4: Prepared from single analyte standards (7.3). Dilute the following in 5% hydrochloric acid/ 2% nitric acid to the mark in a Class "A" 100 mL volumetric flask:

| Analyte | Std Conc. (µg/mL) | Add this amount (µL) | Final vol (mL) | STD4 | Units |
|---|---|---|---|---|---|
| Aluminum | 1000 | 500 | 100 | 5000 | µg/L |
| Antimony | 1000 | 100 | 100 | 1000 | µg/L |
| Arsenic | 1000 | 100 | 100 | 1000 | µg/L |
| Barium | 1000 | 500 | 100 | 5000 | µg/L |
| Beryllium | 1000 | 100 | 100 | 1000 | µg/L |
| Boron | 1000 | 100 | 100 | 1000 | µg/L |
| Cadmium | 1000 | 100 | 100 | 1000 | µg/L |
| Calcium | 1000 | 5000 | 100 | 50000 | µg/L |
| Chromium | 1000 | 500 | 100 | 5000 | µg/L |
| Cobalt | 1000 | 100 | 100 | 1000 | µg/L |
| Copper | 1000 | 500 | 100 | 5000 | µg/L |
| Iron | 1000 | 5000 | 100 | 50000 | µg/L |
| Lead | 1000 | 500 | 100 | 5000 | µg/L |
| Lithium | 1000 | 100 | 100 | 1000 | µg/L |
| Magnesium | 1000 | 5000 | 100 | 50000 | µg/L |
| Manganese | 1000 | 500 | 100 | 5000 | µg/L |
| Molybdenum | 1000 | 100 | 100 | 1000 | µg/L |
| Nickel | 1000 | 500 | 100 | 5000 | µg/L |
| Potassium | 1000 | 5000 | 100 | 50000 | µg/L |
| Selenium | 1000 | 100 | 100 | 1000 | µg/L |
| Silicon | 1000 | 100 | 100 | 1000 | µg/L |
| Silver | 1000 | 100 | 100 | 1000 | µg/L |
| Sodium | 1000 | 5000 | 100 | 50000 | µg/L |
| Strontium | 1000 | 100 | 100 | 1000 | µg/L |
| Thallium | 1000 | 100 | 100 | 1000 | µg/L |
| Tin | 1000 | 100 | 100 | 1000 | µg/L |
| Titanium | 1000 | 100 | 100 | 1000 | µg/L |
| Vanadium | 1000 | 100 | 100 | 1000 | µg/L |
| Zinc | 1000 | 500 | 100 | 5000 | µg/L |

7.6.3 Calibration Standard 3: Prepared from Standard 4 (7.6.2). Add 25mL to a 50 mL volumetric flask and dilute to the mark with 5% hydrochloric acid/ 2% nitric acid:

| Analyte | STD3 | Units | Analyte | STD3 | Units |
|---|---|---|---|---|---|
| Aluminum | 2500 | µg/L | Manganese | 2500 | µg/L |
| Antimony | 500 | µg/L | Molybdenum | 500 | µg/L |
| Arsenic | 500 | µg/L | Nickel | 2500 | µg/L |
| Barium | 2500 | µg/L | Potassium | 25000 | µg/L |
| Beryllium | 500 | µg/L | Selenium | 500 | µg/L |
| Boron | 2500 | µg/L | Silicon | 500 | µg/L |
| Cadmium | 500 | µg/L | Silver | 500 | µg/L |
| Calcium | 25000 | µg/L | Sodium | 25000 | µg/L |
| Chromium | 2500 | µg/L | Strontium | 500 | µg/L |
| Cobalt | 500 | µg/L | Thallium | 500 | µg/L |
| Copper | 2500 | µg/L | Tin | 500 | µg/L |
| Iron | 25000 | µg/L | Titanium | 500 | µg/L |
| Lead | 2500 | µg/L | Vanadium | 500 | µg/L |
| Lithium | 500 | µg/L | Zinc | 2500 | µg/L |
| Magnesium | 25000 | µg/L | | | |

7.6.4 Calibration Standard 2: Prepared from Standard 4 (7.6.2). Add 6.25mL to a 50 mL volumetric flask and dilute to the mark with 5% hydrochloric acid/ 2% nitric acid:

| Analyte | STD2 | Units | Analyte | STD2 | Units |
|---|---|---|---|---|---|
| Aluminum | 625 | µg/L | Manganese | 625 | µg/L |
| Antimony | 125 | µg/L | Molybdenum | 125 | µg/L |
| Arsenic | 125 | µg/L | Nickel | 625 | µg/L |
| Barium | 625 | µg/L | Potassium | 6250 | µg/L |
| Beryllium | 125 | µg/L | Selenium | 125 | µg/L |
| Boron | 625 | µg/L | Silicon | 125 | µg/L |
| Cadmium | 125 | µg/L | Silver | 125 | µg/L |
| Calcium | 6250 | µg/L | Sodium | 6250 | µg/L |
| Chromium | 625 | µg/L | Strontium | 125 | µg/L |
| Cobalt | 125 | µg/L | Thallium | 125 | µg/L |
| Copper | 625 | µg/L | Tin | 125 | µg/L |
| Iron | 6250 | µg/L | Titanium | 125 | µg/L |
| Lead | 625 | µg/L | Vanadium | 125 | µg/L |
| Lithium | 125 | µg/L | Zinc | 625 | µg/L |
| Magnesium | 6250 | µg/L | | | |

7.6.5 Calibration Blank: 5% hydrochloric acid/2% nitric acid in a 50 ml auto sampler tube.

7.7 Independent Calibration Verification (ICV) - This solution must be from a different source, different vendor than the calibration standards. ICV Standard must be prepared fresh daily.

7.7.1 Add 100 uL of the second source standard (Sec. 7.4)to a final volume of 100 ml in 5% hydrochloric acid+2% nitric acid in a Class “A” volumetric flask.

| Analyte | ICV | Units |
|---|---|---|
| Aluminum | 500 | µg/L |
| Antimony | 500 | µg/L |
| Arsenic | 500 | µg/L |
| Barium | 500 | µg/L |
| Beryllium | 500 | µg/L |
| Boron | 500 | µg/L |
| Cadmium | 500 | µg/L |
| Calcium | 500 | µg/L |
| Chromium | 500 | µg/L |
| Cobalt | 500 | µg/L |
| Copper | 500 | µg/L |
| Iron | 500 | µg/L |
| Lead | 500 | µg/L |
| Lithium | 500 | µg/L |
| Magnesium | 500 | µg/L |
| Manganese | 500 | µg/L |
| Molybdenum | 500 | µg/L |
| Nickel | 500 | µg/L |
| Potassium | 500 | µg/L |
| Selenium | 500 | µg/L |
| Silicon | 500 | µg/L |
| Silver | 500 | µg/L |
| Sodium | 500 | µg/L |
| Strontium | 500 | µg/L |
| Thallium | 500 | µg/L |
| Tin | 500 | µg/L |
| Titanium | 500 | µg/L |
| Vanadium | 500 | µg/L |
| Zinc | 500 | µg/L |

7.8 Continuing Calibration Standard - Prepared fresh daily.

Continuing Calibration Verification (CCV) standard: Prepared from single analyte standards (7.3). Dilute the following in 5% hydrochloric acid/ 2% nitric acid to the mark in a Class “A” 50 mL volumetric flask:

| Analyte | Std Conc. (µg/mL) | Add this amount (µL) | Final vol (mL) | CCV | Units |
|---|---|---|---|---|---|
| Aluminum | 1000 | 50 | 50 | 1000 | µg/L |
| Antimony | 1000 | 12.5 | 50 | 250 | µg/L |
| Arsenic | 1000 | 12.5 | 50 | 250 | µg/L |
| Barium | 1000 | 25 | 50 | 500 | µg/L |
| Beryllium | 1000 | 12.5 | 50 | 250 | µg/L |
| Boron | 1000 | 25 | 50 | 500 | µg/L |
| Cadmium | 1000 | 12.5 | 50 | 250 | µg/L |

| | | | | | |
|---|---|---|---|---|---|
| Calcium | 1000 | 100 | 50 | 2000 | µg/L |
| Chromium | 1000 | 12.5 | 50 | 250 | µg/L |
| Cobalt | 1000 | 12.5 | 50 | 250 | µg/L |
| Copper | 1000 | 12.5 | 50 | 250 | µg/L |
| Iron | 1000 | 50 | 50 | 1000 | µg/L |
| Lead | 1000 | 25 | 50 | 500 | µg/L |
| Lithium | 1000 | 12.5 | 50 | 250 | µg/L |
| Magnesium | 1000 | 100 | 50 | 2000 | µg/L |
| Manganese | 1000 | 12.5 | 50 | 250 | µg/L |
| Molybdenum | 1000 | 12.5 | 50 | 250 | µg/L |
| Nickel | 1000 | 12.5 | 50 | 250 | µg/L |
| Potassium | 1000 | 50 | 50 | 1000 | µg/L |
| Selenium | 1000 | 12.5 | 50 | 250 | µg/L |
| Silicon | 1000 | 12.5 | 50 | 250 | µg/L |
| Silver | 1000 | 12.5 | 50 | 250 | µg/L |
| Sodium | 1000 | 100 | 50 | 2000 | µg/L |
| Strontium | 1000 | 25 | 50 | 500 | µg/L |
| Thallium | 1000 | 12.5 | 50 | 250 | µg/L |
| Tin | 1000 | 12.5 | 50 | 250 | µg/L |
| Titanium | 1000 | 12.5 | 50 | 250 | µg/L |
| Vanadium | 1000 | 12.5 | 50 | 250 | µg/L |
| Zinc | 1000 | 12.5 | 50 | 250 | µg/L |

7.8 Interference check solutions (ICSA and ICSAB):

7.8.1 ICSA - Interference elements 50 ug/ml Al, Ca, Mg, Cr, Cu, Mn, Ni, Ti and V and 20 ug/ml Fe.

7.8.2 ICSAB – Elements in ICSA at same concentration (Sec. 7.9.1) - 0.5 ug/ml Sb, As, Be, B, Cd, Co, Mo, Se, Ag, Sr, Tl, Sn and Li - 1ug/ml Zn – 2.5 ug/ml Ba and Pb - 25 ug/ml K and Na.

7.9 Spiking Standards

7.9.1 AAC-STD-2: Custom standard from Inorganic Ventures, 1000µg/mL Ag, B, Se, Ti, Sb, Mo, Si, As and Sn.
7.9.2 AAC-STD-3A: Custom standard from Inorganic Ventures, 10,000µg/mL Ca, Fe, K, Mg and Na.
7.9.3 AAC-STD-4A: Custom standard from Inorganic Ventures, 1000µg/mL Ag, Ba, Be, Bi, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sr, Th, Tl, V and Zn.

For each LCS soil sample, 25 µL of 7.9.1, 7.9.2 and 7.9.3 is used, with a final volume of 50 ml.

Each MS/MSD soil sample is spiked with 25 or 100 µL of each standard, with a final volume of 50 ml. 25 µL is used for samples that will not be diluted, and 100 µL is used for samples that will be diluted by a factor of 4.

For each LCS water sample, 12.5 µL of 7.9.1, 7.9.2 and 7.9.3, with a final volume of 25 ml.

Each MS/MSD water sample is spiked with 12.5 µL of each standard, with a final volume of 25 ml.

## 8.0 Preparation of Standards and Calibration Procedure

8.1 The ICP-OES must be calibrated before analysis with a blank and at least 1 standard. Sample concentrations above the highest standard require dilution until the result is within the calibration range or a high-level check standard is analyzed with concentrations exceeding the sample concentration. Percent recovery for the check standard must be within 10% of the expected value.

8.2 Standards are prepared as specified in section 7.

8.2.1 Multipoint initial calibration is performed daily:

| Analyte | STD1 | STD2 | STD3 | STD4 | STD5 | Units |
|---|---|---|---|---|---|---|
| Aluminum | 100 | 1000 | 5000 | | 10000 | µg/L |
| Antimony | 20 | 250 | 1000 | | | µg/L |
| Arsenic | 40 | 250 | 1000 | | | µg/L |
| Barium | 200 | 500 | 1000 | 5000 | 10000 | µg/L |
| Beryllium | 5 | 250 | 1000 | | | µg/L |
| Boron | 250 | 500 | 1000 | | | µg/L |
| Cadmium | 5 | 250 | 1000 | | | µg/L |
| Calcium | 1000 | 2000 | 5000 | 50000 | 100000 | µg/L |
| Chromium | 10 | 250 | 1000 | 5000 | 10000 | µg/L |
| Cobalt | 20 | 250 | 1000 | | | µg/L |
| Copper | 100 | 250 | 1000 | 5000 | 10000 | µg/L |
| Iron | 300 | 1000 | 5000 | 50000 | 100000 | µg/L |
| Lead | 100 | 500 | 1000 | 5000 | 10000 | µg/L |
| Lithium | 10 | 250 | 1000 | | | µg/L |
| Magnesium | 1000 | 2000 | 5000 | 50000 | 100000 | µg/L |
| Manganese | 20 | 250 | 1000 | 5000 | 10000 | µg/L |
| Molybdenum | 10 | 250 | 1000 | | | µg/L |
| Nickel | 100 | 250 | 1000 | 5000 | 10000 | µg/L |
| Potassium | 400 | 1000 | 5000 | 50000 | 100000 | µg/L |
| Selenium | 40 | 250 | 1000 | | | µg/L |
| Silicon | 40 | 250 | 1000 | | | µg/L |
| Silver | 20 | 250 | 1000 | | | µg/L |
| Sodium | 1000 | 2000 | 5000 | 50000 | 100000 | µg/L |
| Strontium | 100 | 500 | 1000 | | | µg/L |
| Thallium | 40 | 250 | 1000 | | | µg/L |
| Tin | 40 | 250 | 1000 | | | µg/L |
| Titanium | 10 | 250 | 1000 | | | µg/L |
| Vanadium | 50 | 250 | 1000 | | | µg/L |
| Zinc | 100 | 250 | 1000 | 5000 | 10000 | µg/L |

8.3 The correlation coefficient of the calibration standards must be >0.998 for each element. Sample data cannot be reported for elements that do not meet the minimum criteria.

8.4 Calibration is verified with a second source standard (ICV) prepared at the concentrations listed in Sec 7.9. Element concentrations must be within 5% of the expected value for analyses reported by Method 200.7 or 10% for analyses reported by Method 6010.

8.5 Calibration blanks are analyzed following initial calibration and after every 10 samples. Results must be less that the LOD.

8.6 A continuing calibration standard (CCV, Sec. 7.8) is analyzed following initial calibration and after every 10 samples. Element concentrations must be within 10% of the expected value. Sample must be bracketed by acceptable CCV results. Re-analysis of associated samples is required when CCV results exceed 10%.

8.7 A reporting limit verification sample (CRQL, Calibration Standard 1) is analyzed following initial calibration and prior to sample analysis and at the end of each analytical sequence. The results of the CRQL must be within 20% of the expected concentration.

8.8 Interference check solutions (ICSA and ICSAB) must be analyzed at the beginning of each analytical sequence following the ICV. The ICSAB must analyzed immediately following ICSA. The ICSA solution contains interferences and the ICSAB contains analytes plus interferences. The absolute value of analyte elements in the ICSA must be <LOD. If any element concentration is greater than the LOD results for that element cannot be reported. Analyte concentrations in the ICSAB must be within 20% of the true value. If any element concentration exceeds this limit the problem must be corrected and the element reanalyzed.

Acceptance Criteria
ICSA

| Element | Control Limits (ppb) | True Value (ppb) |
|---|---|---|
| Aluminum | 400000 – 600000 | 500000 |
| Calcium | 400000 – 600000 | 500000 |
| Iron | 400000 – 600000 | 500000 |
| Magnesium | 400000 – 600000 | 500000 |
| Chromium | 4000 – 60000 | 5000 |
| Copper | 4000 – 60000 | 5000 |
| Manganese | 4000 – 60000 | 5000 |
| Nickel | 4000 – 60000 | 5000 |
| Titanium | 800 – 1200 | 1000 |
| Vanadium | 800 – 1200 | 1000 |

Acceptance Criteria
ICSAB

| Element | Control Limits (ppb) | True Value (ppb) |
|---|---|---|
| Aluminum | 400000 – 600000 | 500000 |
| Calcium | 400000 – 600000 | 500000 |
| Iron | 400000 – 600000 | 500000 |
| Magnesium | 400000 – 600000 | 500000 |
| Antimony | 800 – 1200 | 1000 |
| Arsenic | 800 – 1200 | 1000 |
| Barium | 4000 – 6000 | 5000 |
| Beryllium | 800 – 1200 | 1000 |
| Boron | 800 – 1200 | 1000 |
| Cadmium | 800 – 1200 | 1000 |
| Chromium | 4000 – 6000 | 5000 |
| Cobalt | 800 – 1200 | 1000 |
| Copper | 4000 – 6000 | 5000 |
| Lead | 4000 – 6000 | 5000 |
| Manganese | 4000 – 6000 | 5000 |
| Molybdenum | 800 – 1200 | 1000 |
| Nickel | 4000 – 6000 | 5000 |
| Potassium | 40000 – 60000 | 50000 |
| Selenium | 800 – 1200 | 1000 |
| Silver | 800 – 1200 | 1000 |
| Sodium | 40000 – 60000 | 50000 |
| Strontium | 800 – 1200 | 1000 |
| Thallium | 800 – 1200 | 1000 |
| Tin | 800 – 1200 | 1000 |
| Titanium | 800 – 1200 | 1000 |
| Vanadium | 800 – 1200 | 1000 |
| Zinc | 4000 – 6000 | 5000 |
| Lithium | 800 – 1200 | 1000 |

## 9.0 Sample Preparation

9.1 Allow samples to warm to ambient temperature prior to analyzing.

9.2 Check the pH of aqueous samples prior to beginning digestion.

9.3 Prepare samples according to the appropriate SOP for the particular matrix.

## 10.0 Diagram/Table

10.1 Reserved.

## 11.0 Analytical Procedure

11.1 Open WinLab32 software. Open the workspace Plasma Startup. Initiate the plasma (click the plasma switch to ON). Carefully note the characteristics of the plasma. A stable plasma will be situated just above the inner quartz tube in the torch and will have a bright discharge of the shape An unstable plasma has an irregular shape and may have an air gap underneath. If the plasma is stable, wait one hour before running samples.

11.2 Open the workspace 1-200.7.

11.3 Open Mn method and perform Optimization using Continuous Graphic. Check gas flows and RF power using 1mg/L Mn.

11.4 Perform View X and X/Y Alignment using 1mg/L Mn for Axial view and 10 mg/L Mn for Radial view.

11.5 Insert all QC samples in their proper location. Start the run.

11.6 For instances of sample matrix interference the Method of Standard Additions (Internal Calibration Quantification) may be required for sample quantification.

11.8.1 Four identical aliquots of the extract are taken.

11.8.2 Three of the aliquots are spiked with calibration standard solution at various concentrations that would approximate 50%, 100% and 150% of the expected analyte concentration.

11.8.3 The four aliquots are analyzed and the instrument signal is plotted versus the added concentration. This may be performed directly by the instrument or by using a linear regression plot (i.e. Excel spreadsheet). The y-intercept is determined which corresponds to the concentration of the analyte in the sample.

## 12.0 Details of Calibration and Calculations

12.1 The instrument will note if excessive curvature of the calibration curve occurs. A Correlation Coefficient of 0.998 is programmed into the software for multi-standard calibration protocols when used. Deviations from this will result in the run being stopped until a successful calibration is achieved.

12.2 Continuing calibration standards are evaluated by:

$$\% \text{ Recovery} = \text{actual conc.}/\text{expected conc.} * 100$$

12.3 Percent recovery - matrix spikes, post digestion spikes and LCS

$$\% \text{ Recovery} = \text{conc. recovered-sample conc. (MS/PDS)}/\text{conc. expected} * 100$$

12.4 Relative Percent Difference

RPD = [result 1 - result 2]/average result1..result2) * 100

12.5 Serial Dilutions

% D = (original result - Dilution result)/original result * 100

12.6 Calculation for Hardness

mg/L CaCO3 = ug/L (instrument reading) x Final vol. (L) x CF/Initial vol. (ml)

CF=Conversion factor (Section 14.5)

## 13.0 Quality Assurance/Quality Control (QA/QC) Requirements

13.1 On initial instrument set-up and as required due to major maintenance the following must be performed and documented.

13.1.1 Determination of background correction points (Sec. 5.1).

13.1.2 Verification of the linear range – on instrument set-up and every 6 months: Perform an initial calibration, prepare a standard at the highest calibration concentration and analyze the standard. Results for this standard must be within 10% of the expected concentration. If results exceed 10% adjust the upper calibration range and repeat the verification procedure.

13.1.3 Analysis of second source standard. Verification of calibration standards is performed by determining the mean concentrations from three analyses of the second source calibration verification standard (ICV). The mean recovery must be with 5% of the known concentration.

13.1.4 Instrument Detection Limits (IDL) must be performed initially and after significant changes to instrumentation, personnel, test method or sample matrix by the analysis of 10 calibration blanks on three non-consecutive days.

13.1.5 Establish interelement corrections (IEC): Analyze interference solutions and establish corrections using the IEC model in the instrument software. Store IEC in the method to be used for sample analysis and verify daily with the ICSA/ICSAB solutions. Repeat procedure on unacceptable results for the interference check solutions.

13.2 An initial demonstration of proficiency must be performed on instrument set-up, by all analysts performing the method or engaged in sample preparation or whenever substantial changes are made to the instrument or procedure. This is accomplished by preparing and analyzing four laboratory control samples. The average recovery must be within 20% of the expected concentration and the %RSD must be less than15%.

13.3 Method Detection Limit studies (MDL) are performed initially, on failure to achieve successful LOD/LOQ results, after significant changes to instrumentation, personnel, and test method or sample matrix.

13.4 LOD/LOQ determinations are performed quarterly as specified in Sec. 4.

13.5 ICV- must be run after a calibration. The results must be +/- 5%(Method 200.7) or +/- 10% (Method 6010) of the stated value. If the ICV is not within limits the analysis must be terminated for the elements exceeding +/- 5% or 10%.

13.6 CCV - continuing calibration verifications. This standard must be run after every 10 samples. The limits are +/- 10% of the true value. If this standard fails the problem must be corrected and the previous samples repeated.

13.7 CRQL – reporting limit verification standard, prepared at the reporting limit concentration and analyzed prior to and at the end of each analytical sample sequence. Results must be within 20% of the expected concentration. If the CRQL standard exhibits results beyond the acceptance limits sample results cannot be reported. Investigate, correct and recalibrate if necessary until acceptable CRQL results are obtained.

13.8 ICB- Initial calibration blank analyzed following calibration. The result must be less than the LOD for each element. If this standard fails, correct the problem and reanalyze the samples affected.

13.9 CCB- continuing calibration blank analyzed following calibration and every 10 samples. The result must be less than the LOD for each element. If this standard fails, correct the problem and reanalyze the samples affected.

13.10 A serial dilution (1:5) must be preformed for each batch and evaluated for elements >50 times the CRQL (LOQ). The serial dilution must agree within +/- 10% of the original reading. A post digestion spike must be analyzed for elements when the serial dilution results exceed 10%.

13.11 A post digestion spike must be prepared when the serial dilution results exceed 10%, when analyte concentrations in all samples are <50 times the LOD or when MS/MSD results exceed control limits and the sample result is less than 10 times the CRQL. The recovery should be within 80 – 120 % of the spiked value. If the PDS and SD do not produce acceptable results the affected elements are flagged as estimated.

13.11 LCS- laboratory control sample. One LCS is required per batch. The LCS must be 80-120 % of the known value. If the LCS results exceed control limits all batch associated samples must be re-analyzed and if results are not with control limits the batch must be re-digested.

13.12 Matrix Spike (MS) at a frequency of 5% - Matrix Spike Duplicate (MSD) at a frequency of 5%. For each batch of samples a MS and MSD and a second MS are prepared. The recovery and relative percent difference (RPD) are determined.

13.19.1 Acceptance Criteria Recovery **80 - 120 %**

13.19.2 Acceptance Criteria RPD **<20 %**

13.13 A Method Blank is prepared for each batch of sample. The results for each analyte must be < ½ the RL. If unacceptable results are obtained re-analyze method blank once and if unacceptable results persist terminate the analysis and correct the problem. Re-prepare sample batch if necessary.

13.14 Optional - One duplicate sample may be run per every 20 samples. A control limit of 20 % RPD should not be exceeded.

## 14.0 Data Reporting Requirements

14.1 Sample results are reported as ug/L (aqueous samples) and ug/kg (solid samples).

**NOTE:** TCLP extracts may require analysis by the method of Standard Additions and are processed according to the instrument protocol for analysis by Standard Addition (Refer to Sec. 11.8).

14.2 Raw results are entered into Omega. Prep factors are automatically imported from sample prep logs. Dilutions are entered in the analytical sequence.

14.3 Sample results are reported as ug/L for water and ug/kg for soil as dry weight.

14.4 Raw instruments results are entered directly into the Omega LIMS direct instrument interface. All calculations to derive final result (including dry weight conversions) are performed automatically by the LIMS. Sample preparation information and percent moisture results are entered into the appropriate section of the LIMS prior to instrument data and are automatically factored into the final results.

14.5 Reporting Hardness results by Standard Methods 2340B:

14.5.1 Import Calcium and Magnesium data using Omega test code EPA_200.7-HARD. Calculations are performed automatically by the LIMS using the factors 2.497 (Ca) and 4.118 (Mg) to convert instrument results to mg/L CaCO3. Converted Ca and Mg results are automatically summed by the LIMS for reporting Total Hardness (as CaCO3).

14.6 Observe and evaluate QC flags or qualifiers in the sequence. If present, investigate and repeat or reanalyze as necessary.

**Quality Control Criteria**

| CONTROL ITEM | FREQUENCY | CRITERIA | CORRECTIVE ACTION |
|---|---|---|---|
| Initial Calibration Verification (ICV) | Daily immediately following calibration | 90 – 110 % | Repeat Calibration |
| ICB | After ICV | < LOD | Stop, repeat -determine cause and correct |
| ICSA/ICSAB | After ICB | Non interfering analytes <LOD in ICSA, +/- 20% of expected in ICSAB | Stop, repeat -determine cause and correct |
| CCV | After ICSAB and every 10 samples | 90 – 110 % of True Value | Repeat CCV and all samples preceding a CCV failure – recalibrate if problem persists |
| CCB | After CCV and every10 samples | <LOD | Stop, repeat -determine cause and correct |
| CRQL | After CCB and at the end of the sample set | 80 – 120 % | Investigate, determine cause and correct. Repeat samples analyzed prior to unacceptable CRQL |
| Method Blank | 1 per batch. | <1/2RL | 1) Repeat once and if unacceptable terminate analysis, correct problem and repeat.<br>2) evaluate system<br>3)repeat batch digestion if necessary |
| LCS | 1 per batch | 80 – 120 % | Analytes with unacceptable results cannot be reported. Investigate, repeat batch as necessary. |
| MS/MSD | 5% - 1 per batch | 80 – 120 % | 1) Flag Data |
| Duplicate Samples | 5% - 1 per batch | RPD < 20% | Investigate and repeat as necessary |

## 15.0 Preventative Maintenance and Routine Cleaning

15.1 Sample waste container must be checked daily.

15.2 Visually check the torch condition and measure for alignment daily.

15.3 Visually check for acceptable roller pressure and condition of the sample introduction tubing. Correct pump rotation and the condition of the drain tubing daily.

15.4 Visually check for torch, radial and axial lens. Clean them as needed.

15.5 Check and replace filters as needed or monthly at a minimum.

15.6 Check and replace Cu string as needed.

15.7 Check argon pressure daily.

15.8 Once in a year change chiller fluid.

## 16.0 Waste Management and Pollution Prevention

16.1 Pollution Prevention

16.1.1 Reagents are purchased and quantities used to reflect anticipated usage and minimize disposal of expired or unused chemicals.

16.1.2 Chemicals are handled in a manner that minimizes the potential for release or spill of the material.

16.2 Waste Management

16.2.1 Acidic materials (pH<2) are treated as hazardous waste and placed in the appropriate waste drum for disposal.

16.2.2 Soil samples are composited in a drum designated for incineration.

16.2.3 Disposal of materials is addressed in the laboratory QAP (Section 5.6).

## 17.0 References

17.1 EPA Test Methods for Evaluating Solid Waste. Laboratory Manual Physical/Chemical Methods, Method 6010C, Revision 3, February 2007.

17.2 EPA Methods for Chemical Analysis of Water and Wastewater. Method 200.7, Revision 4.4 (1994).

17.3 RTI Laboratories, Inc. SOP 3020A – Acid Digestion of Aqueous Samples.

17.4 RTI Laboratories, Inc. SOP 3050A – Acid Digestion of Solid Sample.

17.5 RTI Laboratories, Inc. Quality Assurance Plan.

17.6 RTI Laboratories, Inc. SOP SRC001-A_R3, Sample Receipt and Custody.

17.7 RTI Laboratories, Inc. Chemical Hygiene Plan.

17.8 RTI Laboratories, Inc. Employee Handbook.

# Appendix A – Interelement Corrections

| | Al 500 ppm | Ca 500 ppm | Cr 100 ppm | Cu 100 ppm | Fe 200 ppm | Mg 500 ppm | Mn 100 ppm | Ni 100 ppm | Ti 100 ppm | V 100 p |
|---|---|---|---|---|---|---|---|---|---|---|
| 338.289 | 0 | 0 | 18.839615 | 0 | 0 | 0 | 0 | 0 | 3.757833 | 0 |
| 396.153 | N/A | 0.34923 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 188.979 | 0 | 0 | 4.535307 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 08.889 | 0.177821 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 493.408 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 234.861 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 317.933 | 0 | N/A | 0 | 0 | 0 | 0.288293 | 0 | 0 | 0 | 0.6514 |
| 226.502 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 230.786 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 205.560 | 0 | 0 | N/A | 3.443005 | 0 | 0 | 0 | 0.896605 | 0 | 0 |
| 327.393 | 0.165735 | 0 | 0 | N/A | 0 | 0 | 0 | 0 | 0 | 0 |
| 259.939 | 0 | 0 | 0 | 0 | N/A | 0 | 0 | 0 | 0 | 0 |
| 66.490 | 0 | 0 | 0 | 0 | 0 | 0.336132 | 0 | 0 | 0 | 0 |
| 370.784 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 285.213 | 0 | 0 | 0 | 0 | 0.598408 | N/A | 0 | 0 | 0 | 0 |
| 259.372 | 0 | 0 | 0 | 0 | 1.37359 | 0 | N/A | 0 | 0 | 0 |
| 259.372 | 0 | 0 | 0 | 0 | 0.310125 | 0 | 0 | 0 | 0 | 0 |
| 589.592 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 341.476 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | N/A | 1.024119 | 0.8618 |
| 220.353 | 0 | 0 | 0 | 0.629282 | 0 | 0 | 0 | 0 | 0.772611 | 0 |
| 231.146 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 196.026 | 0 | 0 | 0 | 0 | 0.281397 | 0 | 0 | 0 | 0 | 0 |
| 251.611 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 7.43461 | 0 |
| 189.927 | 0 | 0.260685 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 407.771 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 334.940 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | N/A | 0 |
| 190.801 | 0 | 0 | 0 | 0 | 0 | 0 | 5.615419 | 0 | 4.071975 | 0.9064 |
| 92.402 | 0 | 0 | 2.344744 | 0 | 0 | 0 | 0 | 0 | 0.885925 | N/A |
| 202.548 | 0 | 0 | 1.505368 | 8.481186 | 0 | 1.051813 | 0 | 0 | 0 | 0 |

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Livonia, Michigan 48150

# STANDARD OPERATING PROCEDURE

# ACID DIGESTION OF SOLID SAMPLES FOR THE ANALYSIS OF TOTAL METALS

| | |
|---|---|
| **Analyte:** | **Metals** |
| **SOP #:** | **3050_110512_R11** |
| **Method Reference:** | **EPA SW846/3050B** |
| **Issue Date:** | **March 11, 1998** |
| **Revision No.:** | **11** |
| **Revision Date:** | **November 5, 2012** |

**Reviewed and Approved: February 19, 2014**

Director, Quality Management: Charles O'Bryan

Director, Environmental Services: Yemane Yohannes

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**ACID DIGESTION OF SOLID SAMPLES**
**FOR THE ANALYSIS OF TOTAL METALS**

**SOP#: 3050_110512_R11**

**TABLE OF CONTENTS**

# 1.0 Scope and Application

## 1.1 Introduction

1.1.1 This SOP details the sample preparation procedures for the acid digestion of solid/soil samples for total metals analysis. This SOP applies to all metals except mercury. Following digestion the samples can be analyzed for elements by ICP/MS or ICP/OES. For definition of terms not specifically defined in this document refer to RTI QAP Section 16.

## 1.2 Method Summary

1.2.1 A representative 1-2 g aliquot of sample is digested with repeated addition of nitric acid and hydrogen peroxide. Hydrochloric acid is added to samples requiring analysis by ICP/OES or for ICP/MS analysis of antimony and/or silver. The digestate is reduced in volume while heating, diluted to volume with DI water and filtered.

1.2.2 Analytical procedures follow the appropriate SOP for the particular element(s) of interest. A procedure for preparing samples for the analysis of lead in fine and coarse fractions is detailed in Section 9.

# 2.0 Safety Precautions

2.1 Concentrated acids are corrosive. All digestions are performed in a fume hood designated for use with mineral acids. Proper safety equipment is worn when handling concentrated acids. Some metals are toxic and should be handled with care.

# 3.0 Sample Requirements and Sample Handling Procedures

3.1 Samples are received in accordance with RTI Laboratories' Standard Operating Procedure for Sample Log-in. Appropriate U.S. Environmental Protection Agency (EPA) sample handling procedures and sample preservation recommendations are followed.

3.1.1 Solid samples are collected in pre cleaned 4-8 oz. wide mouth glass jars.

3.1.2 Samples are refrigerated until ready for analysis.

3.1.3 Holding time for samples is 180 days from collection.

3.1.4 Minimum sample volume – 50 g.

## 4.0 MDL, Linear Range, Accuracy and Precision

4.1 Not applicable. See SOP corresponding to the analytical method of interest.

## 5.0 Interferences

5.1 Diverse matrix types can pose an analytical challenge. Spiked samples should be processed to aid in determining whether this digestion procedure is applicable to the samples.

5.2 All glassware and apparatus should be scrupulously cleaned before use to avoid possible source of contamination.

5.3 Further information concerning potential interference's can be found in the SOP for the particular element(s) of interest.

## 6.0 Apparatus and Materials

6.1 Apparatus

6.1.1 Drying oven

6.1.2 Thermometer

6.1.3 Hot Plates

6.1.4 Filter paper - Whatman #41 or equivalent

6.1.5 Funnels

6.1.6 Oxford/Eppendorf Pipettes

6.1.7 Graduated Cylinders – Class A

6.1.8 Hot Block

6.1.9 Plastic disposable digestion vessels - 50 ml (manufacturer certified volume)

6.1.10 Plastic watch glasses

6.1.11 Aluminum weighing dishes.

6.1.12 Glass beakers.

6.1.13 Sieves (stainless steel) 10 mesh (2 mm) and 60 mesh (250 micron)

6.1.14 Mortar and pestle

6.1.15 Analytical balance - capable of weighing to 0.1 mg with computer interface.

6.1.16 PC with Balancelink software, Microsoft Excel and Omega LIMS.

## 7.0 Reagents

7.1 Deionized Water – Crossbow DI Express, mixed bed. – Type II

7.2 High purity concentrated $HNO_3$. 1:1 solutions are prepared by adding equal volumes of the concentrated acid to DI water.

7.3 High purity concentrated HCL. 1:1 solutions are prepared by adding equal volumes of the concentrated acid to DI water.

7.4 Hydrogen peroxide ($H_2O_2$) 30%, reagent grade.

7.5 1000 ppm Stock Metal Concentrates plasma pure grade.

7.6 All reagents and standards prepared must be labeled with a minimum:

7.6.1 Identity of the material
7.6.2 Concentration of the solution
7.6.3 Date prepared
7.6.4 Initials of analyst preparing the solution
7.6.5 Expiration date.

## 8.0 Calibration Procedure

8.1 Pipette calibration procedure - All pipettes are calibrated monthly.

8.1.1 Weigh a weighing boat and record the weight.

8.1.2 Note temperature of the water at time of weighing and enter on the Pipette Calibration Check log.

8.1.3 Draw up the desired volume of water into the pipette.

8.1.4 Deliver the $H_2O$ to the tarred weighing boat.

8.1.5 Weigh the weighing boat containing the water.

8.1.6 Repeat this procedure 10 times for the maximum pipette volume and 5 times for a volume at the mid to low range of the pipette.

8.1.7 Enter result in the log.

8.1.8 Calculation: Volume = mass/density.

8.1.9 The mean of the 10 measurements at the maximum pipette volume must be within 2% of the volume setting. The mean of the 5 measurements at the mid to low range must be within 3% of the pipette setting.

8.2 All spiking solutions for preparation of LCS, MS, MSD are maintained and prepared by the instrumentation analysts. Composition and preparation of spiking solutions is specified in the applicable analytical SOP.

## 9.0 Sample Preparation

9.1 Hot Block Digestion for ICP/MS analysis - For elements except silver and antimony (Refer to Section 9.2 for the preparation for Ag and Sb)

9.1.1 Turn on power

9.1.2 Set temperature to 95 +/- 5$^{o}$C. Check temperature with calibrated thermometer placed in a digestion vessel containing DI water.

9.1.3 Mix sample thoroughly to achieve homogeneity and sieve if necessary through a #10 sieve.

9.1.3.1 Transfer the entire contents of the sample container to a glass beaker.

9.1.3.2 Mix sample thoroughly with a wooded tongue depressor.

9.1.3.3 If materials such as sticks, leaves, rocks, etc. are present sieve the sample with a #10 sieve.

9.1.4 Transfer 1-2 g of the as received sample weighed to 0.01 g into a digestion vessel and capture the weight into the “SampAmt” column of the Omega Prep Batch using the BalanceLink software. For samples requiring analysis on dried basis prepare according to the SOP for Sub_Sampling, take a 1g aliquot and proceed with Sec 9.1.5.

9.1.5 Add 10 ml of 1:1 $HNO_{3,}$ mix and cover with a ribbed watch glass.

9.1.6 Place sample in the hot block and heat at 95 +/- 5 $^{o}$C for 10-15 minutes without boiling.

9.1.6.1 Allow the sample to cool and add 5 ml concentrated nitric acid.

9.1.6.2 Replace the cover and reflux for 30 minutes concentrating the sample to approximately 5 ml. If brown fume are generated repeat the addition of 5 ml concentrated nitric acid over and over until no brown fumes are observed

9.1.6.3 Continue heating at 95±5 degrees C for two hours or until the volume is reduced to approximately 5 ml. Do not allow to boil and maintain a covering of solution over the bottom of the vessel at all times.

9.1.6.4 Allow the sample to cool and add 2 ml DI water and 3 ml 30% hydrogen peroxide.

9.1.6.5 Cover and heat (the peroxide reaction will commence and be evident by effervescence).

9.1.6.6 Continue to add $H_2O_2$ in 1 ml aliquots until the effervescence is minimal to a maximum of 10 ml added to the sample.

9.1.6.7 Cover and continue heating without boiling at 95±5 degrees C until the volume has been reduced to approximately 5 ml or two hours. Maintain a covering of solution on the bottom of the digestion tube at all times.

9.1.7 Allow sample to cool.

9.1.8 Wash the walls of the beaker with a small amount of DI water

9.1.9 Bring sample to a final volume of 50 ml in a digestion vessel (accuracy 50 ml +/- 0.2ml – 0.4%) with DI water and mix.

9.1.10 If solution is turbid or solids are present allow to settle overnight or centrifuge if samples will be analyzed sooner.

9.1.10 All digestates (samples and QC samples) are filtered through Whatman filter (6.1.6)

9.2 Hot Block Digestion for ICP/OES analysis and for ICP/MS analysis of samples requiring the analysis of silver and antimony.

9.2.1 Turn on power

9.2.2 Set temperature to 95 +/- 5°C

9.2.3 Prepare samples according to Sec. 9.1.3 and 9.1.4 above.

9.2.4 Add 10 ml of concentrated HCl and 2.5 ml of concentrated $HNO_3$, mix and cover with a ribbed watch glass.

9.2.5 Place sample in the hot block and heat at 95 +/- 5 °C for 10-15 minutes without boiling. Temperature must be verified using a calibrated thermometer.

9.2.5.1 Reflux for 30 minutes concentrating the sample to approximately 5 ml.

9.2.5.2 Remove from hot block and allow the sample to cool.

9.2.6 Wash the walls of the beaker with a small amount of DI water

9.2.7 Bring sample to a final volume of 50 ml with DI water using the graduated hot block digestion vessels (manufacturer certified volume) and mix.

9.2.8 Allow to settle overnight or centrifuge if samples will be analyzed sooner.

9.2.9 All digestates (samples and QC samples) are filtered through Whatman filter (6.1.6)

9.3 Procedure for the preparation of samples for Fine and Coarse Lead.

9.3.1 Remove large objects such as rocks, twigs, vegetation, etc.

9.3.2 Mix samples and sieve through a No 10 mesh (2 mm) sieve.

9.3.3 Homogenize the sample by mixing with a spatula (manually break up large soil clumps if necessary).

9.3.4 Weigh and record the weight of a numbered aluminum weighing dish.

9.3.5 Transfer approximately 20 g of the well mixed sample (50-100 g if high moisture content - >35%) to a clean, tared, labeled weighing dish.

9.3.6 Weigh and record the weight of the dish containing the sample.

9.3.7 Dry the sample at 105 degrees C +/-2 in a drying oven for 24 hours +/- 2.

9.3.8 Remove from the oven and place in a desiccator to cool for at least 1 hour.

9.3.9 Weigh and record the weight of the dish containing the dried sample.

9.3.10 Sieve the sample through a 60 mesh (250 micron) sieve using a mechanical shaker for 10 minutes.

9.3.11 Weigh and record the sieved portion of the sample.

9.3.12 Grind the sample with a mortar and pestle and place in a labeled plastic container. This portion of the sample represents the Fine Soil Fraction.

9.3.13 Weigh and record the portion of the sample that did not pass through the sieve.

9.3.14 Grind the sample with a mortar and pestle and place in a labeled plastic container. This portion of the sample represents the Coarse Soil Fraction.

9.3.15 Digest samples according to procedure specified in Section 9.1 above.

## 10.0 Diagram/Table

10.1 Reserved

## 11.0 Analytical Procedure

11.1 See SOP corresponding to the analytical method of interest.

## 12.0 Details of Calibration and Calculations

12.1 Calculate the percent solids as

% Total Solids = DWt/WWt x 100

DWt = weight of sample after drying at 105 deg. C
WWt = weight of sample prior to drying.

12.2 Calculation of Total Lead.

Total Lead (ug/Kg) = ((FF x WtF) + (CF x WtC)) / (WtF + WtC)

FF = Lead concentration (ug/Kg) in Fine Fraction
CF = Lead concentration (ug/Kg) in Coarse Fraction
WtF = Weight of Fine Fraction (Sec 9.3.12)
WtC = Weight of Coarse Fraction (Sec 9.3.14)

## 13.0 Quality Assurance/Quality Control (QA/QC) Requirements

13.1 The following quality control samples are prepared with each batch of samples.

13.1.1 Method Blank

13.1.2 Matrix Spike – prepared at a frequency of not less than 5% (1 per batch of 20 samples) by spiking a solid samples chosen from the batch of samples.

13.1.3 Matrix Spike Duplicate – prepared at a 5% frequency (1 per batch of 20 samples) .by again spiking the sample chosen above.

13.1.4 Duplicate Sample – prepared if specified in project quality assurance plan, at the frequency required.

13.1.5 Laboratory control sample prepared by spiking DI water.

13.1.6 SRM – Standard Reference Material. Required for analysis of Fine/Coarse lead.

13.2 Consult with appropriate SOP for spike concentration for the individual elements.

13.3 Preparation batch information is entered into the Omega LIMS including digestion temperature and spike ID information.

## 14.0 Data Reporting Requirements

14.1 Samples are reported on a dry weight basis. A percent moisture determination is performed and entered into the LIMS. Data calculations for dry weight reporting of the sample results are performed by the LIMS following analytical data entry. Refer to the analytical SOP for calculations and reporting specifications.

## 15.0 Preventative Maintenance and Routine Cleaning

15.1 Inspect all glassware for cracks or abrasions. Discard damaged glassware.

15.2 Clean preparation area daily.

15.3 Keep surfaces clean.

15.4 Monitor fume hood for proper face velocity quarterly and record.

## 16.0 Pollution Prevention and Waste Management

16.1 Pollution Prevention

16.1.1 Reagents are purchased and quantities used to reflect anticipated usage and minimize disposal of expired or unused chemicals.

16.1.2 Chemicals are handled in a manner that minimizes the potential for release or spill of the material.

16.2 Waste Management

16.2.1 Acidic materials (pH<2) are treated as hazardous waste and placed in the appropriate waste drum for disposal.

16.2.2 Soil samples are composited in a drum designated for incineration.

16.2.3 Disposal of materials is addressed in the laboratory QAP (Section 5.6).

## 17.0 References

17.1 EPA Test Method for Evaluating Solid Waste. Laboratory Manual Physical/Chemical Methods. Method 3050B Revision 2. Dec. 1996.

17.2 RTI Laboratories, Inc. Quality Assurance Plan.

17.3 RTI Laboratories, Inc. SOP SRC001-A, Sample Receipt and Custody.

17.4 RTI Laboratories, Inc. Chemical Hygiene Plan.

17.5 RTI Laboratories, Inc. Employee Handbook.

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# STANDARD OPERATING PROCEDURE

# ANALYSIS FOR MERCURY

| | |
|---|---|
| **Analyte:** | **Mercury** |
| **SOP #:** | **7470A_ 7471B_022014_R7** |
| **Method Reference:** | **SW-846 7470A, 7471B** |
| **Issue Date:** | **January 22, 2006** |
| **Revision No.:** | **7** |
| **Revision Date:** | **February 20, 2014** |
| **Reviewed Date:** | **February 20, 2014** |

Reviewed and Approved: **February 20, 2014**

Director, Quality Management: Charles O'Bryan

Director, Environmental Services: Yemane Yohannes

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**ANALYSIS FOR MERCURY**
**SOP#: 7470A_ 7471B_022014_R7**

## TABLE OF CONTENTS

## 1.0 Scope and Application

1.1 Introduction

RTI Laboratories, Inc, has prepared this document to detail the Standard Operating Procedure (SOP) for the analysis of drinking, surface, and saline waters, domestic and industrial wastes and solid materials. In addition to inorganic forms of mercury, organic mercurials may be present. These compounds do not respond to the cold vapor atomic absorption technique unless they are first broken down and converted to mercuric ions. Potassium permanganate oxidizes many of these compounds, Potassium persulfate has been found to give approximately 100% recovery when used as the oxidant with these compounds.

1.2 Summary of Method

The flameless AA procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrometer. Absorbance (peak height) is measured as a function of mercury concentration and recorded. For definition of terms not specifically defined in this document refer to RTI QAP Section 16.

## 2.0 Safety Precautions

2.1 This method involves working with hazardous substances. Some of the toxicological properties of these substances are not known. Always wear gloves, eye protection and clothing protection.

2.2 Potassium permanganate is a strong oxidizer. Contact with other materials may cause fire. Exposure to potassium permanganate may cause severe eye, skin, and respiratory and digestive tract irritation. May cause kidney damage.

2.3 Hydroxylamine sulfate is corrosive. May cause burns to any area of contact. Harmful if swallowed or inhaled. Affects the blood and is a powerful reducing agent.

2.4 Sodium persulfate causes severe irritation. Harmful if swallowed or inhaled. Strong oxidizer. Contact with other materials may cause fire.

2.5 Stannous chloride is corrosive. May cause severe skin and eye irritation. May cause liver damage, severe respiratory tract irritation and digestive tract irritation with nausea, vomiting and diarrhea

## 3.0 Sample Requirements and Sample Handling Procedures

3.1 Samples are received in accordance with RTI's Standard Operating Procedure for Sample Receipt and Custody (SRC001-A). Appropriate U.S. Environmental Protection Agency (EPA) sample handling procedures and sample preservation recommendations are followed.

3.1.1 Soil, sludge and solid samples are collected in pre cleaned wide mouth glass jars.

3.1.2 Samples can be collected in glass or plastic bottles. Aqueous samples should be preserved with nitric acid to a pH of less than 2 and refrigerated at 4°C. Aqueous samples should have zero headspace and the bottle should not be opened until mercury is ready to be analyzed.

3.1.3 Sample volume minimum requirements: solids - 10 grams, aqueous - 100 ml.

3.1.4 Maximum sample holding time is 28 days.

## 4.0 MDL, Linear Range, Accuracy and Precision

4.1 The method detection limit (MDL) is statistically defined at the 99% confidence level according to 40 CFR Part 136 App. B. Seven replicates containing all of the analytes of interest at a concentration level of 1-5 times the estimated D.L. are analyzed and the standard deviation is calculated. The Student's T Value for the 7 replicates (3.143) is multiplied by the standard deviation of the analyte to calculate the MDL. MDLs are updated annually (or as needed) and are kept on file in the Laboratory. MDLs and reporting limits are incorporated into the applicable test code in the Omega LIMS.

4.2 The LOD (limit of detection) is determined by spiking reagent water at 1-4 times the MDL and prepared using the same procedure as samples. Analytes must be present at levels 3 times or greater than the blank response (greater than 3 times the signal to noise ratio). The concentration used is the LOD for that analyte. LOD determinations must be performed quarterly.

4.3 The LOQ (limit of quantification) is determined by spiking reagent water at the reporting limit (RL/CRQL) and prepared in the same manner as samples. Analyte recovery must be within 20% of the expected concentration. The concentration used and successfully recovered is the LOQ for that analyte. LOQ determinations must be performed quarterly.

4.4 Initially accuracy and precision at the LOQ is determined by spiking 4 aliquots of reagent water at the reporting limit (RL/CRQL) and prepared using the same procedure used for samples. The average recovery must be within 20% of the expected value and the %RSD must be less than 15%.

4.5 LOD/LOQ determinations that do not meet the specifications above require repeat analysis, adjustment to the spiking levels and/or reporting limits, repeating the MDL determination at adjusted concentrations if required and repeat LOD/LOQ determinations.

4.6 The accuracy and precision for this method are determined by analyzing four aliquots from a Laboratory Control Sample containing the element(s) of interest at the mid-level of the calculated range (diluted if above this range). Percent recovery, standard deviation, and the relative standard deviation are calculated for each analyte and documents are kept on file in the laboratory.

## 5.0 Interferences

5.1 Possible interference from sulfide is eliminated by addition of potassium permanganate. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from distilled waster.

5.2 Sea waters, Brines and industrial effluents high in chlorides require additional permanganate (as much as 25 mL) Care must be taken to assure that free chlorine is absent before the mercury is reduced and swept into the cell. Adding excess of hydroxylamine sulfate (25 mL) can eliminate this interference.

5.3 Copper is a reported interference. However copper concentrations up to 10 mg/L have shown no affect on recovery of mercury from spiked samples.

5.4 Volatile organic compounds that absorb at the wavelength used may interfere.

## 6.0 Apparatus and Materials

6.1 Mercury Analyzer: Cetac Quick Trace M6100 with ASX-260 Auto sampler.

6.2 Digestion cups – plastic cups for digesting the samples with marking at 10, 25 and 50ml from Environmental Express

6.3 Water bath, capable of maintaining 95 °C

6.4 Compressed Nitrogen 99.9999%.

6.5 Volumetric glassware - Class A

6.6 Variable volume pipettes – calibrated

6.7 PC with Microsoft Windows XP, Quick Trace Software and Omega LIMS.

## 7.0 Reagents

7.1 Hydrochloric acid concentrated, trace metals grade: JT Baker.

7.2 10% Stannous chloride, reagent grade: Dissolve 10g of stannous chloride in 100ml of 7% HCL. Store at room temperature for up to 5 days.

7.3 Sodium chloride - hydroxylamine hydrochloride, reagent grade: Dissolve 120 g of sodium chloride and 120 g of hydroxylamine hydrochloride in distilled water and dilute to 1000 ml with DI water. Stored at room temperature. Expiration date – 6 mos.

7.4 5% Potassium Permanganate (Alfa Aesar) (%w/v): Dissolve 5 g of potassium permanganate in 100 ml distilled water. Stored at room temperature. Expiration date – 6 mos. Stored at room temperature. Expiration date – 6 mos.

7.5 5% Potassium persulfate (JT Baker) (%w/v): Dissolve 5 g of potassium persulfate in 100 ml of distilled water. Stored at room temperature. Expiration date – 6 mos.

7.6 Primary stock mercury standard 1000mg/L - Absolute. Store at room temperature until manufacturer's expiration date.

7.7 Secondary stock mercury 1000mg/L – Inorganic Ventures. Store at room temperature until manufacturer's expiration date.

7.8 Concentrated Sulfuric acid. – Trace metals grade

7.9 Concentrated nitric acid – Trace metals grade

7.10 Aqua regia – Combine 300 ml concentrated hydrochloric acid with 100 ml of nitric acid. Prepare for each use.

7.11 Reagent Water - Deionized Water – Crossbow DI Express, mixed bed. – Type II

7.12 All reagents and standards prepared must be logged in the appropriate standards/reagents log labeled with a minimum:

7.12.1 Identity of the material.
7.12.2 Concentration of the solution.
7.12.3 Date prepared.
7.12.4 Initials of analyst preparing the solution.
7.12.5 Expiration date.

## 8.0 Preparation of Standards and Calibration Procedure

8.1 Working Mercury Solution: 1 mg/L - prepared fresh daily. Acidity of the working standard should be maintained at 0.15% HCL. Measure 100 µL of 1000 mg/L stock standard (6) and dilute to 100 ml in a volumetric flask containing 1.5 ml nitric acid.

8.1.1 Intermediate standard for soil calibration – Volumetrically dilute 5 ml of the working standard to 50 ml DI water in a volumetric flask. Solution concentration is 100 ug/L.

8.2 Calibration standards are prepared as described below in the same manner as the samples according to Section 9.0. The correlation coefficient of the calibration curve must be >0.995 to continue with the analysis of samples. If this criterion is not met the calibration standards must be re-analyzed or new standards prepared and analyzed until an acceptable correlation coefficient is obtained.

8.2.1 1.0 ppb: (µg/L): Pipette 100 µL of 1 ppm (8.1) working standard into a 100ml volumetric flask that is half full of DI water and 1.5ml of concentrated $HNO_3$ and dilute to mark.

8.2.2 2.0 ppb: (µg/L): Pipette 200 µL of 1ppm(8.1) working standard into a 100ml volumetric flask that is half full of DI water and 1.5ml of concentrated $HNO_3$ and dilute to mark. For reference purposes, the absorbance should be 8000 – 12000 for this standard.

8.2.3 5.0 ppb: (µg/L): Pipette 500 µL of 1ppm(8.1) working standard into a 100ml volumetric flask that is half full of DI water and 1.5ml of concentrated $HNO_3$ and dilute to mark.

8.2.4 10.0 ppb: (µg/L): Pipette 1000 µL of 1ppm (8.1) working standard into a 100ml volumetric flask that is half full of DI water and 1.5ml of concentrated $HNO_3$ and dilute to mark.

8.2.5 0.2 ppb: (µg/L): Pipette 10 ml of 2 ppb (8.2.2) calibration standard into a 100ml volumetric flask that is half full of DI water and 1.5ml of concentrated $HNO_3$ and dilute to mark.

8.2.6 0.5 ppb: (µg/L): Pipette 10 ml of 5 ppb (8.2.2) calibration standard into a 100ml volumetric flask that is half full of DI water and 1.5ml of concentrated $HNO_3$ and dilute to mark

8.3 A calibration blank is prepared using 25 ml of DI water and is processed according to the procedure in Section 9.0.

8.4 An intermediate calibration verification standard is prepared from the second source by diluting 100 μl of the 1000 μg/ml standard to a final volume 100 ml DI water containing 1.5 ml of $HNO_3$. Prepare fresh each use.

8.4.1 The daily working CCV is prepared by dilution 200 μl of the intermediate standard (section 8.4) to 100 ml final volume DI water containing 1.5 ml $HNO_3$.

8.5 LCS and Matrix spikes are prepared from the intermediate second source standard (section 8.4).

8.5.1 The LCS is prepared by adding 25 μof the standard to 25 ml DI water. The final concentration of this standard 1 μg/L..

8.5.2 MS/MSD samples are prepared by adding 25 μL of standard to 25 ml of a sample. The final concentration of the MS/MSD are 100 μg/Kg.

8.6 Soil calibration standards are prepared as below in the same manner as the samples according to Section 9.0. The correlation coefficient of the calibration curve must be >0.995 to continue with the analysis of samples. If this criterion is not met the calibration standards must be re-analyzed or new standards prepared and analyzed until an acceptable cc is obtained.

8.6.1 1.0 ppb: (μg/L): Pipette 30 μL of 1 ppm (8.1) working standard into a digestion cup containing 5 ml of reagent water and 5 ml of aqua regia and proceed with Sec. 9.3.3.

8.6.2 2.0 ppb: (μg/L): Pipette 60 μL of 1 ppm (8.1) working standard into a digestion cup containing 5 ml of reagent water and 5 ml of aqua regia and proceed with Sec. 9.3.3.

8.6.3 5.0 ppb: (μg/L): Pipette 150 μL of 1 ppm (8.1) working standard into a digestion cup containing 5 ml of reagent water and 5 ml of aqua regia and proceed with Sec. 9.3.3.

8.6.4 8.0 ppb: (μg/L): Pipette 240 μL of 1 ppm (8.1) working standard into a digestion cup containing 5 ml of reagent water and 5 ml of aqua regia and proceed with Sec. 9.3.3.

8.6.5 0.2 ppb: (μg/L): Pipette 60 μL of 100 ppb (8.1.1) intermediate standard into a digestion cup containing 5 ml of reagent water and 5 ml of aqua regia and proceed with Sec. 9.3.3.

8.6.6 0.5 ppb: (μg/L): Pipette 150 μL of 100 ppb (8.1.1) intermediate standard into a digestion cup containing 5 ml of reagent water and 5 ml of aqua regia and proceed with Sec. 9.3.3.

8.7 A calibration blank is prepared using 5 ml of DI water and 5 ml of aqua regia and is processed according to the procedure in Section 9.0.

8.8 An intermediate calibration verification standard is prepared from the second source by diluting 100 µl of the 1000 µg/ml standard to a final volume 100 ml DI water containing 1.5 ml of $HNO_3$. Prepare fresh each use.

8.8.1 The daily working CCV is prepared by dilution 60 µl of the intermediate standard (section 8.8) to a digestion cup containing 5 ml DI water and 5 ml aqua regia and continue with section 9.3.3.

8.9 LCS and Matrix spikes are prepared from the intermediate second source standard (section 8.8).

8.9.1 The LCS is prepared by adding 30 µL of the standard (Sec 8.8) to 5 ml DI water and 5ml aqua regia. The final concentration of this standard is 50 µg/Kg.

8.9.2 MS/MSD samples are prepared by adding 30 µL of the standard to 0.6 g of a sample. The final concentrations of the MS/MSD are 50 µg/Kg.

## 9.0 Sample Preparation

9.1 Allow samples to warm to ambient temperature.

9.2. Method 7470 sample preparation

9.2.1 Transfer 25ml of sample or an aliquot diluted to 25ml in the 50ml digestion cups.

9.2.2 Add 0.75 ml of concentrated $HNO_3$ and 1.25 ml concentrated sulfuric acid to each sample, standard and QC samples.

9.2.3 Add 3.75 ml of potassium permanganate solution (see 7.4) to each bottle and mix. Alternatively add enough crystals of potassium permanganate for the sample to turn purple and hold color for at least 15 minutes

Note: For sewage samples, additional permanganate may be required. Add potassium permanganate crystals until the purple color persists for 15 minutes.

9.2.4 Add 2.0 ml of potassium persulfate (see 7.5) to each bottle.

9.2.5 Heat for 2 hours in a water bath at 95°C.

9.2.6 Add 2.0ml hydroxylamine hydrochloride (see 7.3) to the cups.

9.3 Method 7471 sample preparation.

9.3.1 Transfer 0.5 – 0.6g of solid sample taken as ~0.2g portions from the container.

9.3.2 Add 5 ml of reagent water and 5 ml aqua regia to each sample.

9.3.3 Heat for 2 minutes at 95 +/- 3 degrees C in a water bath.

9.3.4 Allow to cool: then add 25 ml of reagent water and 7.5 ml of potassium permanganate solution.

9.3.5 Mix thoroughly and place in the water bath at 95 degrees C for 30 minutes.

9.3.6 Cool and add 2.0ml hydroxylamine hydrochloride (see 7.3).

## 10.0 Diagram/Table

10.1 Reserved.

## 11.0 Analytical Procedure

11.1 Prepared samples are analyzed within 48 hours of sample preparation.

11.2 Turn the instrument on. (Let it warm up for at least 1 hour)

11.3 Turn the mercury lamp on (Let it warm for 10 minutes)

11.4 Connect the tensioners on the auto sampler over the rinse tubes (located behind the left corner of the auto sampler.

11.5 Connect the tubes on the peristaltic pump and engage the tensioner (also turn pump ~30° so that sample line doesn't get tangled).

11.6 Align the tensioner fingers over the tubing.

11.7 Fill reagent bottle (10% $SnCl_2$). Fill rinse bottle (2%$HNO_3$).

11.8 Reagent bottle: in a 1L plastic add 100g Stannous Chloride dehydrate. Add about 200ml DIW. Shake. Add 70ml conc. HCL. Shake to dissolve completely. Fill up to the 1L mark with DIW. Shake. Solution is ready for use. Solution can be stored in refrigerator for up to 5 days.

11.9 Rinse solution: 2.0% Nitric acid (20ml conc. $HNO_3$ diluted to 1000ml)

11.10 Check waste container and empty if needed.

11.11 Turn peristaltic pump on.

11.12 Wet the GLS (gas liquid separator) as in the following steps

11.13 Pinch the drain tubing (coming out of the GLS) to fill the GLS with liquid (DIW or rinse solution) without allowing the liquid to reach the dryer (Nafion).

11.14 Turn on the rinse pump and put the auto sampler tube down using the software controls (go to Auto Sampler, click “Down” for sample probe to go down to rinse).

11.15 Turn the Gas flow on from the tank. (N2, valve is behind peristaltic pump and set at 40 PSI).

11.16 Set up Worksheet for mercury analysis.

11.17 Load a new Worksheet from a template

11.18 Make label file (date, analyst, comment, sample type-QC std., QC blk., Sample ID-MB, LCS, etc.)

11.19 Final sample preparation steps immediately before analysis.

11.20 Add 1.5 ml of hydroxylamine hydrochloride to 10ml of sample (1.5ml/ 10ml)

11.21 Decant the clear portion of the sample into the culture tubes.

11.22 Filter samples through Whatman #41 filter paper if samples contain significant particulates, these will clog the sampling tube, so must be removed.

11.23 Then place the culture tubes in the sample rack.

11.24 Zero the instrument.

11.25 Calibrate the instrument following manufacturer’s manual and instructions. Place calibration standards, QC check std. and QC check blank in the calibration rack (be sure to remove the caps).

11.26 After the calibration is done, make sure correlation coefficient is 0.995 or greater. The calibration must be based on at least five data points.

11.27 Run samples that are in the worksheet.
(Note: SnCl2 is added on line)

11.28 After all analyses are complete put instrument into standby mode.

11.29 Use a bottle of DI water to rinse all lines starting with the reagent lines.

11.30 Remove the tubing from the reagent bottle and put it in the DIW bottle, and allow the pump to run for several minutes, and then turn off the pump.

11.31 Remove the two tubes from the Rinse bottle and allow DI water to pump for several minutes, and then use the software to raise the auto sampler sipper up and stop the auto sampler pump. Then release the tension on the auto sampler rinse lines.

## 12.0 Details of Calibration and Calculations

12.1 Final results are calculated as specified in section 14.

12.2 The CCV must be analyzed at the frequency specified in Section 13 and the concentration must be within 10% of the known value for confirmation of instrument calibration.

12.3 Continuing calibration standards are evaluated by:

% Recovery = actual conc./expected conc. * 100

12.4 Percent recovery - LCS

% Recovery = conc. recovered/conc. expected * 100

12.5 Relative Percent Difference – Duplicate samples

RPD = [result 1 - result 2]/average result1.result2) * 100

12.6 Initial Calibration Equation.

y = mx + b
y = sample absorbance
m = slope
x = sample concentration
b = intercept

## 13.0 Quality Assurance/Quality Control (QA/QC) Requirements

13.1 A calibration verification standard (CCV) is analyzed following initial instrument calibration, after every 10 samples and at the end of the analytical sequence.

13.1.1 Acceptance Criteria **90 - 110 %**

13.1.2 Corrective Action: Repeat CCV and all samples preceding a CCV failure. Recalibrate if the problem persists.

13.2 A calibration verification blank (CCB) is analyzed following initial instrument calibration, after every 10 samples and at the end of the analytical sequence.

13.2.1 Acceptance Criteria **< LOD**

13.2.2 Corrective Action: Repeat CCB and all samples preceding a CCB failure. Evaluate system for sources of contamination and correct the problem before proceeding with sample analysis.

13.3 A Method Blank is processed with each batch of samples.

13.3.1 Acceptance Criteria **< ½ LOQ (RL)**

13.3.2 Corrective Action: Repeat analysis. Evaluate the systems for contamination sources and repeat the batch as necessary.

13.4 Laboratory Control Sample (LCS) – Prepared according to Section 8.5.

13.4.1 A LCS is processed with each batch of samples

13.4.2 Acceptance Criteria **80 – 120 %**

13.4.3 Corrective Action: Repeat LCS and sample batch as necessary.

13.5 Matrix Spike (MS) - Matrix Spike Duplicate (MSD) – Prepare as in Section 8.5.

13.5.1 For each batch of samples a MS/MSD is prepared. The recovery and relative percent difference (RPD) are determined. Statistical control limits are calculated in the LIMS.

13.5.2 Acceptance Criteria (% recovery) **80 - 120 %** or within laboratory established statistical control limits.

13.5.3 Corrective Action: Dilute and re-spike/re-analyze to determine if interferences can be overcome by sample dilution. If unsuccessful or if sample volume precludes re-analysis, flag data as possible matrix interference.

13.5.4 Acceptance Criteria (RPD) **<20 %** or within laboratory established statistical control limits.

13.5.5 Corrective Action: Evaluate sample homogeneity and flag data if necessary.

13.6 Duplicate Sample (DUP) prepared with each of samples

13.6.1 Acceptance Criteria (RPD) **<20%** or within laboratory established statistical control limits.

13.6.2 Corrective Action: Evaluate sample homogeneity and flag data if necessary.

13.7 One serial dilution must be preformed for every batch of samples prepared provided one of the samples has a concentration of >25 times the MDL .The dilution test is performed by making a five fold dilution of the sample. The result of the serial dilution must agree within +/- 10% of the original reading.

13.8 One post digestion spike (PDS) must be preformed for every batch of samples prepared that exhibits MS/MSD results exceeding control limits, provided one of the samples has a concentration of <25 times the MDL. The digestion solution is spiked at a concentration of 1 ug/L. The recovery of the PSD must be within 80 - 120%.

13.9 Reporting limit verification is assessed by analyzing the 0,2 calibration standard at the end of the analytical sequence. Recovery of this standard must be within 70 – 130 %. If the recovery falls outside of this range the analytical sequence must be repeated.

13.10 Method of Standard Additions (Internal Calibration Quantification) – performed for cases of matrix interference.

13.10.1 Four identical aliquots of the sample are taken.

13.10.2 Three of the aliquots are spiked with calibration standard solution at various concentrations that would approximate 50%, 100% and 150% of the expected analyte concentration.

13.10.3 The four aliquots are analyzed and the instrument signal is plotted versus the added concentration. This may be performed directly by the instrument or by using a linear regression plot (i.e. Excel spreadsheet). The y-intercept is determined which corresponds to the concentration of the analyte in the sample.

## 14.0 Data Reporting Requirements

14.1 Sample results are reported as μg/L (aqueous samples) and μg/kg (solid samples).

14.2 Raw results are entered into Omega. Prep factors are automatically imported from sample prep logs. Dilutions are entered in the analytical sequence.

14.3 Sample results are reported as ug/L for water and ug/kg for soil as dry weight.

μg/kg dry wt. = μg/kg wet wt.*100/percent solids

14.4 Raw instruments results are entered directly into the Omega LIMS system using excel spreadsheets, direct instrument interface or manually. All calculations to derive final result (including dry weight conversions) are performed automatically by the LIMS. Sample preparation information and percent moisture results are entered into the appropriate section of the LIMS prior to instrument data and are automatically factored into the final results.

14.5 Confirm that there is no QC flags or qualifiers in this sequence. If present, investigate and repeat or reanalyze as necessary. See section 9.2 of the QAP for more detail on qualifiers.

## 15.0 Preventative Maintenance and Routine Cleaning

15.1 Examine all tubing and replace as needed.

15.2 Clean GLS as needed.

15.3 Replace Nafion drying cartridge as needed.

## 16.0 Pollution Prevention and Waste Management

16.1 Pollution Prevention

16.1.1 All hazardous waste produced by this method is stored in a waste drum until that drum can be processed and disposed of properly by a professional waste management company

.

16.1.2 All samples are processed with the minimum quantity of reagents possible. This is to reduce the amount of waste generated by the test method, and, consequently, the amount of pollution generated by RTI.

16.2 Waste Management

16.2.1 Acidic materials (pH<2) are treated as hazardous waste and placed in the appropriate waste drum for disposal.

16.2.2 Disposal of materials is addressed in the laboratory QAP.

## 17.0 References

17.1 EPA Test Methods for Evaluating Solid Waste. Laboratory Manual Physical/Chemical Methods, Method 7471B (Update IVA).

17.2 EPA Test Methods for Evaluating Solid Waste. Laboratory Manual Physical/Chemical Methods, November 1986, Revision 1 September 1994 Method 7470A.

17.3 Standard Methods for the Examination of Water and Wastewater, 20th Edition, Method 3112 B.

17.4 USEPA Methods for Chemical Analysis of Water and Wastewater, 600/4/70/200 (Rev.3/1983), Method 245.1.

17.5 RTI Laboratories, Inc. Quality Assurance Plan.

17.6 RTI Laboratories, Inc. SOP SRC001-A, Sample Receipt and Custody.

17.7 RTI Laboratories, Inc. Chemical Hygiene Plan.

17.8 RTI Laboratories, Inc. Employee Handbook.

# Title: GC/MS SEMIVOLATILES ANALYSIS [SW-846 8270D; EPA 625]

**Approvals (Signature/Date):**

Jeff Winkler 9-16-14
Jeff Winkler Date
Extractable Dept. Supervisor

Mike Ridenhower 9/16/14
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**This SOP was previously identified as SOP No. ST-MS-0001 Rev. 16**



**Facility Distribution No.:** 0 **Distributed To:** See Electronic Distribution Sheet

## 1.0 SCOPE AND APPLICATION

1.1 This SOP is applicable to the determination of the concentration of semivolatile organic compounds in extracts prepared from solid and aqueous matrices.

1.2 This SOP is based on SW-846 Method 8000B, 8000C and 8270D and EPA method 625.

1.3 The following compounds are documented in the method as problematic:

1.3.1 Benzidine can be subject to oxidative losses during solvent concentration and exhibits poor chromatography. Neutral extraction should be performed if this compound is expected.

1.3.2 Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition.

1.3.3 Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, benzoic acid, 2-nitroaniline, 3-nitroaniline, 4-chloroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.

1.3.4 Hexachlorophene may not be amenable to analysis by this method.

1.4 N-Nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be distinguished from Diphenylamine.

1.5 3-Methylphenol cannot be separated from 4-Methylphenol by the conditions specified in this method.

1.6 Phthalic acid decomposes in the gas chromatographic inlet and cannot be distinguished from Phthalic anhydride.

1.7 Azobenzene is formed by decomposition of 1,2-diphenlyhydrazine. If 1,2-diphenylhydrazine is requested, it will be reported as Azobenzene.

1.8 The laboratory target analytes supported by this method, the reporting limits, method detection limits and QC limits are maintained in the Laboratory Information Management System (LIMS).

1.8.1 Additional compounds may be amendable to this method. The minimum requirement for non-standard analytes is that the reporting limit be set at the lowest required concentration that can actually be detected by the instrument, and when an MDL study can not be conducted, the MDL be set equal to the reporting limit.

## 2.0 SUMMARY OF METHOD

2.1 Aqueous samples are extracted with methylene chloride using a separatory funnel. Solid samples are extracted with methylene chloride / acetone using sonication. Waste dilution is used for organic or unusual matrix samples. The sample extract is concentrated to a volume of 1 mL, 5 mL or 10 mL, and analyzed by GC/MS. Qualitative identification of the parameters in the extract is performed using the retention time and the relative abundance of characteristic ions. Quantitative analysis is performed using the internal standard technique with a single characteristic ion.

2.2 The use of selected ion monitoring (SIM) is acceptable for applications requiring quantitation limits below the normal range of electro impact mass spectrometry. However, SIM may provide a lesser degree of confidence in the compound identification, since less mass spectral information is available. Instead of scanning everything in a retention time range, SIM looks for specific ions (qualitative and quantitative) that are placed in retention time groups. The ions used for qualitative and quantitative purposes are the same for scan and SIM analysis.

## 3.0 DEFINITIONS

3.1 See the TestAmerica St. Louis Quality Assurance Manual (QAM) for a glossary of common laboratory terms and data reporting qualifiers.
3.2 SIM –Selected Ion Monitoring

## 4.0 INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. If an interference is detected it is necessary to determine if the source of interference is in the preparation and/or cleanup of the samples; then take corrective action to eliminate the problem.

4.2 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature of the sample.

4.3 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed with solvent between samples. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross contamination.

4.4 Phthalate contamination is commonly observed in this analysis and its occurrence should be carefully evaluated as an indicator of a contamination problem in the sample preparation step of the analysis.

## 5.0 SAFETY

5.1 Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), Radiation Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.2 **SPECIFIC SAFETY CONCERNS OR REQUIREMENTS**

5.2.1 Latex and vinyl gloves provide no protection against the organic solvents used in this method. Nitrile, Silver Shield, or similar gloves must be used.

5.2.2 The gas chromatograph and mass spectrometer contain zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

5.2.3 The mass spectrometer is under deep vacuum. The mass spectrometer must be brought to atmospheric pressure prior to working on the source.

5.2.4 There are areas of high voltage in both the gas chromatograph and the mass spectrometer. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

5.3 PRIMARY MATERIALS USED

5.3.1 The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

| Material | Hazards | Exposure Limit (2) | Signs and symptoms of exposure |
|---|---|---|---|
| Methylene Chloride | Carcinogen Irritant | 25 ppm (TWA)<br><br>125 ppm (STEL) | Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin. |
| 1 – Always add acid to water to prevent violent reactions. | | | |
| 2 – Exposure limit refers to the OSHA regulatory exposure limit. | | | |
| TWA – Time Weighted Average | | | |
| STEL – Short Term Exposure Limit | | | |

## 6.0 EQUIPMENT AND SUPPLIES

6.1 Gas Chromatograph/Mass Spectrometer System: HP 6890/5973 - An analytical system complete with a temperature-programmable gas chromatograph suitable for split/splitless injection and all required accessories, including syringes, analytical columns, and gases. The capillary column should be directly coupled to the source. Capable of scanning from 35 to 500 AMU every one second or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for decafluorotriphenylphosphine (DFTPP) which meets all of the criteria in Table 1 when 50 ng of the GC/MS tuning standard is injected through the GC.

6.2 Data System:

6.2.1 ChemStation software system that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the length of the chromatographic program.

6.2.2 Target software system allows the searching of any GC/MS data file for ions of a specified mass and plots such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). The software allows integrating the abundances in any EICP for a specified time or scan-number limit. Also, for the non-target compounds with a mass spectrum that meets the required criteria, software must be available that allows for the comparison of sample spectra against the reference library spectra.

6.2.3 Data Library: NIST05

6.3 Carrier gas: Ultra high purity helium

6.4 Instrument columns and run conditions are posted in the instrument maintenance calendar.

6.5 Amber vials. Crimp top seals

6.6 Disposal pipettes

6.7 Micro syringes- 10µL, 250µL, 500µL, 1000µL. Hamilton 1700 series, Agilent Gold Standard

6.8 Volumetric flasks, Class A

6.9 Analytical Balance, capable of weighing ± 0.01 grams.

## 7.0 REAGENTS AND STANDARDS

7.1 All standards and reagent preparation, documentation and labeling must follow the requirements of SOP ST-QA-0002, current revision.

7.2 See recipes for standards and QC samples in the LIMS Reagent Log program.

7.3 At a minimum, a five point calibration curve is prepared. The low point should be at or below the reporting limit. Refer to Table 3 for typical calibration levels for all analytes. Other calibration levels may be used, depending on instrument capability, but the low standard must support the reporting limit and the high standard defines the range of the calibration.

7.4 An Internal Standard (IS) solution is prepared. Compounds in the I.S. Mix are: acenaphthene-d10, chrysene-d12, 1,4-dichlorobenzene-d4, naphthalene-d8, perylene-d12, and phenanthrene-d10.

7.5 Internal Standards are added to all standards and extracts to result in 40 ng injected onto the column. SIM Analysis Internal Standards are added to all standards and extracts to result in 4 ng injected onto the column.

7.6 GC/MS Tuning Standard: A methylene chloride solution containing 50 µg/mL of decafluorotriphenylphosphine (DFTPP) is prepared.

7.7 ICV standards, NIST traceable:

7.7.1 The Semivolatile ICV standard is a second source from the calibration standard, where a second viable source is available.

7.7.2 ICV standard is prepared and stored in the same way as calibration standards.

7.8 Standards are to be refrigerated at $\leq 6^{o}C$ when not in use. Refrigeration at less than $-10^{o}C$ may be used if it can be demonstrated that analytes do not fall out of solution at this temperature. The standards must be replaced at least 6 months after opening.

## 8.0 SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 TestAmerica St. Louis supplies sample containers and chemical preservatives in accordance with the method. TestAmerica St. Louis does not perform sample collection. Samplers should reference the methods referenced and other applicable sample collection documents for detailed collection procedures. Sample volumes and preservative information is given in ST-PM-0002.

8.2 Water samples are collected in amber glass, unpreserved and stored at 4 ± 2°C.

8.3 Soil samples are refrigerated at 4 ± 2°C.

8.4 The extraction holding time for Semivolatiles analysis in waters is 7 days.

8.5 The extraction holding time for Semivolatiles in soil/solid matrix is 14 days.

8.6 Extracts must be refrigerated at $\leq 6^{o}C$ and analyzed within 40 days of the beginning of the extraction.

## 9.0 QUALITY CONTROL

### 9.1 Batch

9.1.1 A sample batch is a maximum of 20 environmental samples, which are prepared together using the same process and same lot(s) of reagents.

9.1.2 Instrument conditions must be the same for all standards, samples and QC samples.

9.1.3 For this analysis, batch QC consists of a method blank, a Laboratory Control Sample (LCS), and Matrix Spike (MS)/ Matrix Spike Duplicate (MSD). In the event that there is insufficient sample to analyze a MS/MSD, an LCS Duplicate (LCSD) is prepared and analyzed.

### 9.2 Method Blank (MB)

9.2.1 A method blank is a blank matrix processed simultaneously with, and under the same conditions as, samples through all steps of the procedure.
9.2.2 A method blank must be prepared with every sample batch.
9.2.3 DI water is used for the Method Blank.
9.2.4 Sodium sulfate is used as the method blank for solid matrices.

9.3 **Laboratory Control Sample (LCS)**
9.3.1 An LCS is a blank matrix spiked with a known amount of analyte(s), processed simultaneously with, and under the same conditions as, samples through all steps of the analytical procedure.
9.3.2 An LCS must be prepared with every sample batch.
9.3.3 The LCS is comprised of sodium sulfate fortified with the target analyte(s).

9.4 **Matrix Spike (MS) /Matrix Spike Duplicate (MSD)**
9.4.1 A Matrix Spike is an aliquot of a field sample to which a known amount of target analyte(s) is added, and is processed simultaneously with, and under the same conditions as, samples through all steps of the analytical procedure.

9.5 **Surrogate**
9.5.1 A surrogate is a non-target analyte similar in chemical composition and behavior, which mimics the target analytes during preparation, extraction and analysis.
9.5.2 Surrogate(s) is added to every field sample, method blank, LCS and MS/MSD for analysis at the beginning of the sample preparation process.

9.6 **Procedural Variations/ Nonconformance and Corrective Action**
9.6.1 Any variation shall be completely documented using a Nonconformance Memo and approved by the Supervisor and QA Manager. See SOP ST-QA-0036 for details regarding the NCM process.
9.6.2 Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the Supervisor and QA Manager. See SOP ST-QA-0036 for details regarding the NCM process.

## 10.0 CALIBRATION AND STANDARDIZATION

10.1 Internal standard calibration is used.
10.1.1 Internal Standard Calibration Procedure: Internal standards are listed in Table 5. Use the base peak m/z as the primary m/z for quantitation of the standards. If interferences are noted, use one of the next two most intense masses for quantitation.
10.1.1.1 Compounds are assigned to the IS, generally with the closest retention time. See Table 5.

10.2 **Instrument Tuning**
10.2.1 The GC/MS system must be checked to see if acceptable performance criteria are achieved for DFTPP (decafluorotriphenylphosphine). See Table 1 in this SOP.
10.2.1.1 The DFTPP and calibration verification standard may be combined into a single standard as long as both tuning and calibration verification acceptance criteria for the project can be met without interferences.
10.2.1.2 **8270** - At the beginning of every twelve hour shift.
10.2.1.3 **625** - At the beginning of every 24 hour shift.
10.2.1.3.1 The time period begins at the moment of injection of DFTPP.
10.2.2 Inject 50 ng of the GC/MS tuning standard into the GC/MS system. Obtain a background-corrected mass spectrum of DFTPP and confirm that all the key m/z criteria in Table 1 are achieved. The performance criteria must be achieved before any samples, blanks, or standards are analyzed.
10.2.3 Degradation of DDT to DDE and DDD should not exceed 20%.

$$\% \text{ breakdown of DDT} = \frac{\text{sum of degradation peak areas (DDD \% DDE)}}{\text{sum of all peak areas (DDT \% DDE \% DDD)}} \times 100$$

10.2.4 Benzidine and pentachlorophenol should be present at their normal responses, and should not exceed a tailing factor of 2 given by the following equation:

$$\text{Tailing Factor} = BC/AB$$

Where the peak is defined as follows:

AC is the width at 10% height; DE is the height of peak and B is the height at 10% of DE. This equation compares the width of the back half of the peak to the width of the front half of the peak at 10% of the height.

10.3 **Initial Calibration**

10.3.1 Prepare calibration standards at a minimum of five concentration levels, six points for a quadratic fit, (see Table 3 for suggested concentrations) for each parameter of interest. It may be useful to analyze six calibration levels and use the lower five for most analytes and the upper five for analytes that have poor response. The low level standard should be at or below the reporting limit. The other standards define the working range of the detector.

10.3.2 Add the internal standard mixture to result in 40 ng on column. The concentrations of all analytes are listed in Table 3. Add the internal standard mixture to result in 4ng on column for SIM analysis.

10.3.3 Analyze each calibration standard and tabulate the area of the primary characteristic m/z against concentration for each compound and internal standard. The low level standard must be at or below the reporting limit.

10.3.4 Except in specific instances, it is NOT acceptable to remove points from a calibration curve for the purpose of meeting criteria. Refer to the TestAmerica corporate policy, "Calibration Curves."

10.3.5 It may be necessary to analyze more than one set of calibration standards to encompass all of the analytes required for some tests.

10.3.6 A new calibration curve must be generated after major changes to the system and may be required when the continuing calibration criteria cannot be met. Major changes include new columns, any significant changes in instrument operating parameters, and major instrument maintenance (e.g., cleaning the ion source).

10.3.7 Sample peak areas are compared to peak areas of the standards. The ratio of the detector response to the amount concentration of analyte in the calibration standard is defined as the response factor (RF) or calibration factor (CF).

10.3.8 **Initial Calibration Criteria (8270D)**

10.3.8.1 Minimum Response Factors

10.3.8.2 See Table 4 in this SOP for the minimum response factors. These minimum response factors are prescribed by SW method 8270D. For analytes not given a minimum response factor by the method, St. Louis has established a default minimum response factor of 0.01 for compound, except for Famphur, Hexachlorophene, Kepone and Phthalic Anhydride which have a minimum response factor of 0.001.

10.3.8.2.1 SW-846 chromatographic methods allow the use of both linear and non-linear models for the calibration data.

10.3.8.3 The first way is to begin with the simplest approach, the linear model through the origin, and then progress through other options until the calibration acceptance criteria are met. The second way is to use technical knowledge of the detector response to the target compound to choose the calibration model.

10.3.8.4 The option for non-linear calibration may be necessary to address specific instrumental techniques. However, it is not EPA's intent to allow non-linear calibration to be used to compensate for detector saturation or to avoid proper instrument maintenance.

10.3.8.5 **Linear calibration using the average response factor**

10.3.8.5.1 The Relative Standard Deviation (RSD) of the calibration points from the curve used must be ≤ 20% for each target analyte.

10.3.8.5.2 If the %RSD in the initial calibration is > 20%, then calibration using a linear regression may be employed.

10.3.8.6 **Linear calibration using a least squares regression**

The intercept of a linear calibration at zero response (i.e. the y-intercept) must have an absolute value less than the reporting limit for each analyte. Client requirements may be tighter, please check Client Requirement Memorandum (CRM) if identified in comments.

**Note**, for analyses utilizing an internal standard the Target variable ~~"b~~" does NOT equal the y-intercept. For analyses utilizing an internal standard, the Target variable ~~"b~~" must be multiplied by the associated internal standard concentration to derive the concentration at the y-intercept.

10.3.8.6.1 r (correlation coefficient) must be ≥ 0.995 OR $r^2$ (coefficient of difference) must be ≥ 0.990.

10.3.8.6.2 When calculating the calibration curves using the linear regression model, a minimum quantitation check on the viability of the lowest calibration point should be performed by re-fitting the response from the low concentration calibration standard back into the curve.

10.3.8.6.3 It is not necessary to re-analyze a low concentration standard; rather the data system can recalculate the concentrations.

10.3.8.6.4 The recalculated concentration of the low calibration point should be within ± 30% of the standard's true concentration.

10.3.8.6.4.1 Analytes which do not meet the minimum quantitation calibration re-fitting criteria should be considered ~~"o~~ut of control" and corrective action should be taken.

10.3.8.7 **Linear calibration using a least squares regression, forcing thru zero**

10.3.8.7.1 Forcing the curve through zero is not the same as including the origin as a fictitious point in the calibration. In essence, if the curve is forced through zero, the intercept is set to 0 *before* the regression is calculated, thereby setting the bias to favor the low end of the calibration range by ~~"p~~ivoting" the function around the origin to find the best fit and resulting in one less degree of freedom. It may be appropriate to force the regression though zero for some calibrations.

10.3.8.7.2 Curve must still meet criteria in 10.3.8.6.1 and 10.3.8.6.2

10.3.8.7.3 For samples requiring adherence to method 8000B, forcing through zero is ***NOT*** allowed.

10.3.8.8 **Linear calibration using a least squares regression, weighting of data points**

10.3.8.8.1 In linear, the points at the lower end of the calibration curve have less absolute variance than points at the high concentration end of the curve. This can cause severe errors in quantitation at the low end of the calibration; for this reason it may be preferable to increase the weighting of the lower concentration points, $1/Concentration^2$ weighting (often called $1/X^2$ weighting), to improve accuracy at the low end of the curve.

10.3.8.8.2 Curve must still meet criteria in 10.3.8.6.1 and 10.3.8.6.2

10.3.8.9 **Non-linear calibration**

10.3.8.9.1 In situations where the analyst knows that the instrument response does not follow a linear model over a sufficiently wide working range, or when the other approaches have not met the acceptance criteria, a non-linear calibration model may be employed.

10.3.8.9.2 The use of non-linear calibrations or second order regression calibrations are not allowed for South Carolina compliance samples.

10.3.8.9.3 It is not EPA's intent to allow non-linear calibration to be used to compensate for detector saturation or to avoid proper instrument maintenance. Thus, non-linear calibrations are not to be employed for analytes shown to consistently exhibit linear calibration for the analytes of interest.

10.3.8.9.3.1 These compounds are not to use non-linear calibrations:
1,4-Dioxane; Pyridine; n-Nitrosodimethylamine;
2-Fluorophenol; Aniline; Bis(2-chloroethyl)ether; Phenol-d5;
Phenol; 2-Chlorophenol; 1,3-Dichlorobenzene; 1,4-Dichlorobenzene; 1,2-Dichlorobenzene; Benzyl Alcohol;
2-Methylphenol; N-nitrosodinpropylamine; Hexachloroethane; 3 and 4-Methylphenol; Nitrobenzene-d5; Nitrobenzene; Isophorone;
2-Nitrophenol;
2,4-Dimethylphenol; Bis(2-chloroethoxy) methane;
2,4- Dichlorophenol; 1,2,4-Trichlorobenzene; Naphthalene;
Hexachlorobutadiene; 4-Chloro-3-Methylphenol;
2-Methylnaphthalene; 2,4,6-Trichlorophenol;
2-Fluorobiphenyl; 2,4,5-Trichlorophenol; 2-Chloronaphthalene;
Dimethylphathalate; Acenaphthylene; Acenaphthene; Dibenzofuran;
Diethylphthalate; Fluorene; 4-Chlorophenyl-phenylether; N-Nitrosodiphenylamine; Azobenzene; 4-Bromophenyl-phenylether;
Hexachlorobenzene; Phenanthrene; Anthracene; Carbazole; Di-n-Butylphthalate; Fluoranthene; Pyrene; Terphenyl-d14;
Butylbenzylphthalate; Benzo(a)Anthracene; Chrysene;
bis(2-ethylhexyl)Phthalate; 2-Picoline;
n-Nitrosomethylethylamine; Methyl methanesulfonate;
n-Nitrosodiethylamine; Ethyl Methanesulfonate; Pentachloroethane;
Acetophenone; n-Nitrosopyrrolidine;
n-Nitrosomorpholine; O-Toluidine; n-Nitrosopiperidine; o,o,o-Triethyl-Phosphorothioate; 2,6-Dichlorophenol;
Hexachloropropene; Benzothiazole;
n-Nitrosodi-n-butylamine; Safrole;
1,2,4,5-Tetrachlorobenzene; cis-Isosafrole; trans-Isosafrole; 1,4-Dinitrobenzene; 1,3-Dinitrobenzene; Pentachlorobenzene; 1-Naphthylamine; 2-Naphthylamine; Thionazin; 5-Nitro-o-toluidine;
Tri-n-butylphosphate; Sulfotepp; Diallate; Phorate; Phenacetin; Tris (2-chloroethyl) phosphate; 4-Aminobiphenyl; Pronamide;
Pentachloronitrobenzene; Disulfoton; Parathion; Isodrin; Aramite;
p- (Dimethylamino) azobenzene; Chlorobenzilate; 2-Acetylaminofluorene; 4,4'-Methylenebis (2)-Chloroaniline; 7,12-Dimethylbenz (a) anthracene;
3-Methylcholanthrene; Isosafrole; Octachlorostyrene;
Methyl methacrylate;
Ethyl methacrylate; Benzaldehyde; Caprolactam;
1-Methylnaphthalene; Biphenyl; Atrazine.

10.3.8.9.2.2 EPA Method 8000C suggests a 20% RSD limit be used when evaluating a calibration. The above compound list was constructed based on the 20% RSD criteria. TestAmerica St. Louis reserves the right to employ different calibration models when client mandated criteria are less than the 20% criteria found in method 8000C.

10.3.8.9.4 The intercept of the curve at zero response must be less than + or – the reporting limit for the analyte.

10.3.8.9.5 r (correlation coefficient) must be $\geq 0.995$ OR $r^2$ (coefficient of difference) must be $\geq 0.990$.

10.3.8.9.6 Due to the nature of SIM analysis, non-linear calibrations may be used.

10.3.9 **625 criteria**

10.3.9.1 Method 625 only requires a 3 point calibration. We routinely perform a 6 point calibration; however, 3 points may be removed from the curve if necessary to meet 625 calibration criteria.

10.3.9.1.1 Refer to the TestAmerica corporate policy, "Calibration Curves."

10.3.9.2 The Relative Standard Deviation (RSD) of the calibration points from the curve used must be < 35%.

10.3.9.3 If the %RSD in the initial calibration is > 35%, then calibration using a linear regression may be employed.

10.3.9.4 If a linear regression curve is used, the intercept of the curve at zero response must be less than ± the reporting limit for the analyte. It is recommended that for linear regression curves the line be set through the origin.

10.3.9.5 Use of $1/Concentration^2$ weighting is recommended to improve the accuracy of quantitation at the low end of the curve. The analyst should consider instrument maintenance to improve the linearity of response.

10.3.9.6 Weighting of data points

10.3.9.6.1 The points at the lower end of the calibration curve have less weight in determining the curve generated than points at the high concentration end of the curve. However, in environmental analysis, accuracy at the low end of the curve is very important. For this reason it is preferable to increase the weighting of the lower concentration points. $1/Concentration^2$ weighting (often called $1/X^2$ weighting) will improve accuracy at the low end of the curve and should be used if the data system has this capability.

10.4 **Initial Calibration Verification (ICV)**

10.4.1 An initial calibration verification standard is a different standard source than the one used for the initial calibration.

10.4.2 An ICV must be performed with every initial calibration.

10.4.3 The ICV performance must be within ± 30% D criteria.

10.4.3.1 Not meeting this requirement may be indicative of serious system malfunction or inaccuracies in the standards used for the initial calibration curve or ICV standard. Corrective action must be taken (including reanalysis of the ICV or analysis of a different ICV). Any decision to proceed with analysis of samples when the ICV is out-of-control must be taken with great care and in consultation with the QA department and the laboratory director. Any such action must be documented in an NCM.

10.5 **Continuing Calibration Verification (CCV)**

10.5.1 At the start of each 12 hour period (8270) or 24 hour period (EPA 625) the GC/MS tuning standard must be analyzed. A 50 ng injection of DFTPP must result in a mass spectrum for DFTPP which meets the criteria. See Table 1 in this SOP.

10.5.2 Following a successful DFTPP analysis the continuing calibration standard(s) are analyzed. The standards must contain all semivolatile analytes, including all required surrogates. A mid level calibration standard is used for the continuing calibration.

10.5.3 A CCV standard is analyzed every analysis tune clock immediately following the DFTPP tune.

10.5.3.1 **EPA 8270** – for each 12 hour tune time period

10.5.3.2 **EPA 625** – for each 24 hour tune time period

10.5.4 The CCV can be the same source or a second source from the calibration.

10.5.5 The internal standard response must be within 50-200 area counts (-50% to 100%) of the response in the mid level of the initial calibration. The internal standard retention times must be within 30 seconds of the retention times in the mid-level of the initial calibration.

10.5.6 **EPA 8270 Criteria**

10.5.6.1 Minimum Response Factors

10.5.6.2 See Table 4 in this SOP for the minimum response factors. These minimum response factors are prescribed by SW-846 method 8270D. For analytes not given a minimum response factor by the method, St. Louis has established a default minimum response factor of 0.01 per compound, except for Famphur, Hexachlorophene, Kepone and Phthalic Anhydride which have a minimum response factor of 0.001.

10.5.6.3 The CCV performance must be with ± 20% D criteria.

10.5.6.4 If a CCV has failed and the analyst can document the reason for failure (e.g. broken vial, carryover from the previous sample etc.) then a second CCV may be analyzed without any adjustments to the instrument. If this CCV meets criteria then sample analysis may continue; however the preceding samples must be reanalyzed. If this second CCV does not meet criteria, the analysis run is terminated. Instrument maintenance is performed and the instrument may require re-calibration (i.e. initial calibration).

10.5.7 **EPA 625 Criteria**

10.5.7.1 For each target analyte %D must be < 20%.

10.5.8 Calibration excursions are to be documented via a NCM.

10.6 Retention Time (RT) windows

10.6.1 Relative Retention Time (RRT)

10.6.1.1 In addition to normalizing the response (peak area) of the target compound to the response of the internal standard in that sample or extract for that injection, the retention times of the target compound and the internal standard may be used to calculate the relative retention time (RRT) of the target compound.

10.6.1.2 The RRT is expressed as a unit-less quantity:

$$RRT = \frac{\text{Retention time of the analyte}}{\text{Retention time of the internal standard}}$$

10.6.1.3 The RRT of each target analyte in each calibration standard should agree within ± 0.06 RRT units.

10.6.1.4 It is recognized here that with increasing retention times of the internal standard, target analytes will be able to more easily meet this criterion. Thus, care should be exercised when selecting the appropriate internal standards by retention times. The process of selecting internal standards to quantify target analytes should also include consideration of retention times as they should be similar.

10.6.1.5 If this criterion is not met and unless there are no other indicators of a component's identification such as a very unique but a high probability mass spectral match then that component may not be considered as identified by relative retention time.

10.6.1.6 The RRT evaluation allows the analyst to compensate for modest shifts in the chromatographic conditions that can occur due to interferences and simple day-to-day instrument variability. Many methods that employ internal standard calibration use more than one internal standard and the target compounds are related to the internal standards on the basis of the similarity of their respective chromatographic retention times (see Table 5).

10.6.2 Internal standard retention time

10.6.2.1 The retention times of the internal standards in the calibration verification standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from that in the mid-point standard level of the most recent initial calibration sequence, then the chromatographic system must be inspected for malfunctions and corrections must be made, as required. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

10.6.3 Retention Time Criteria

10.6.3.1 The retention times of all compounds in each continuing calibration must be within the retention time windows established.

## 11.0 PROCEDURE

11.1 Samples are prepared following ST-OP-0002.

11.2 South Carolina requires a separate certification for SIM analysis. At this time TestAmerica St. Louis does not hold that certification. SIM analysis can not be used for South Carolina compliance samples.

11.3 All standards and extracts are allowed to warm to room temperature before injecting.

11.4 All samples must be analyzed using the same instrument conditions as the initial calibration.

11.5 Add internal standard to the extract to result in 40ng injected on column. Mix thoroughly before injection into the instrument.

11.5.1 Add internal standard to the extract to result in 4ng injected on column for SIM analysis.

11.6 Inject the sample extract into the GC/MS system using the same injection technique as used for the standards.

11.7 The data system will determine the concentration of each analyte in the extract using calculations equivalent to those in section 12. Quantitation is based on the initial calibration, not the continuing calibration.

11.8 Perform all qualitative and quantitative measurements. When the extracts are not being used for analyses, refrigerate at -10°C to -20°C (if it can be demonstrated that analytes do not fall out of solution at this temperature), protected from light in screw cap vials equipped with un-pierced Teflon lined septa.

## 12.0 DATA ANALYSIS AND CALCULATIONS

12.1 External Standard Calculations

12.1.1 See instrument software (Target/Chrom) for calculations.

12.2 Manual Integrations

12.2.1 Identified compounds are reviewed for proper integration. Integrations are performed automatically by the data system. If necessary, manual integrations are performed and are documented by the analyst. Manual integrations are denoted with ~~–M~~" flag on the Target quantitation report. See TestAmerica Policy CA-Q-S-002, Acceptable Manual Integration Practices.

12.3 Qualitative identification

12.3.1 An analyte is identified by retention time and by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for standard reference may be obtained on the user's GC/MS by analysis of the calibration standards or from the NIST Library. Two criteria must be satisfied to verify identification: (1) elution of sample component at the same GC retention time as the standard component; and (2) correspondence of the sample component and the standard component characteristic ions.

12.3.1.1 Note: Care must be taken to ensure that spectral distortion due to co-elution is evaluated. The following analytes should be carefully reviewed:

| | | |
|---|---|---|
| 1,4-Dichlorobenzene-d4 | Aniline | Bis (2-Chloroethyl) ether |
| 1,3-Dichlorobenzene | 1,4-Dichlorobenzene | 1,2-Dichlorobenzene |
| Benzyl alcohol | 2-Methylphenol | 3,4-Methylphenol |
| 2,4-Dichlorophenol | 2,4,6-Trichlorophenol | 2,4,5-Trichlorophenol |
| Phenanthrene | Anthracene | Benz (a) anthracene |

| | | |
|---|---|---|
| Bis (2-ethylhexyl) phthalate | Chrysene | Di-n-octyl phthalate |
| Benzo (b) fluoranthene | Benzo (k) fluoranthene | Indeno (1,2,3-cd) pyrene |
| Benzo (g,h,i) perylene | p-Phenylenediamine | Safrole |
| Cis-Isosafrole | Trans-Isosafrole | 1,4-Dinitrobenzene |
| 1,3-Dinitrobenzene | 1-Naphthylamine | 2-Naphthylamine |
| 2,3,4,6-Tetrachlorophenol | Dinoseb | Sulfotepp |
| Diallate 1 & 2 | Methapyrilene | Aramite 1 & 2 |

12.3.2 The sample component retention time must compare to within ± 0.2 min. of the retention time of the standard component. For reference, the standard must be run within the same twelve hours as the sample.

12.3.3 All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) should be present in the sample spectrum.

12.3.4 The relative intensities of ions should agree to within ±30% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance should be between 20 and 80 percent.)

12.3.4.1 See Table 2 for primary, secondary and tertiary ion assignments.

12.3.5 If a compound cannot be verified by all the above criteria, but in the technical judgment of the analyst, the identification is correct, then the analyst shall report that identification and proceed with quantitation.

12.3.6 Retention time criteria for samples

12.3.6.1 If the retention time for any internal standard changes by more than 0.5 minutes from the last continuing calibration standard, the chromatographic system must be inspected for malfunctions and corrected. Reanalysis of samples analyzed while the system was malfunctioning is required.

12.3.6.2 If the retention time of any internal standard in any sample varies by more than 0.1 minute from the preceding continuing calibration standard, the data must be carefully evaluated to ensure that no analytes have shifted outside their retention time windows.

12.4 Library searches of peaks present in the chromatogram that are not target compounds (Tentatively Identified Compounds, TIC) may be performed if required by the client.

12.4.1 TICs are done as follows:

12.4.1.1 The computer will give quality matches in order from most likely to least likely. In order for us to call a TIC a certain compound, the quality match must be at least 90%. However, if the next two quality matches are within (around) 10% quality match of the first choice, the compound will be identified as an unknown because it is too close to call. Unknowns are put into a group if possible (such as Unknown alkanes) but if a group is not available it will be called Unknown. A compound will be also called unknown if the top three matches are all different groups of compounds and the quality match is < 90% (ex. If the top choice is an alkane, the second choice is an alcohol, the third choice is an acid).

12.4.1.2 The first 30 TICs, based on abundance, will be identified in a sample, unless a different number is specified by the client. See client requirement sheet.

12.5 Dilutions

12.3.7 If the concentrations of any analytes exceed the working range as defined by the calibration standards, then the sample must be diluted and reanalyzed.

12.5.1 A dilution should target the most concentrated analyte in the upper half (over 50% of the high level standard) of the client specific project requirements.

12.5.2 Samples may be diluted initially if the project reporting limits are above the laboratory's routine calibration lower limit, if there is physical evidence of matrix, or historical knowledge of the site.

12.6 Carryover

12.6.1 When a sample has a high response for a compound, there is a real possibility that some of the sample may carry over into the sample analyzed immediately afterward.

12.6.1.1 If a sample analyzed after a sample with high concentrations has negative results or is non-detect, carryover did not occur.

12.6.1.2 If a sample analyzed after a sample with high concentrations has positive results for the same analytes, carryover may have occurred.

12.6.1.2.1 This sample must be reanalyzed under conditions in which carryover can be confirmed to not have occurred.

## 13.0 DATA ASSESSMENT AND ACCEPTANCE CRITERIA; CORRECTIVE ACTIONS FOR OUT OF CONTROL DATA

13.1 This SOP lists requirements for the standard Quality Assurance criteria followed at TestAmerica St. Louis. If a client or program requires stricter quality controls (i.e. DoD, DOE, SC DHEC) the analyst is directed to the Client Requirement Memo for that client/project for limits.

13.2 The data assessment and corrective action process is detailed through the LIMS Nonconformance Memorandum (NCM) process. The NCM process is described in SOP: ST-QA-0036.

13.3 Method Blank

13.3.1 Acceptance Criteria:

13.3.1.1 No target analytes may be present in the method blank above the reporting limit.

13.3.1.2 The method blank must have acceptable surrogate recoveries.

13.3.1.3 Corrective Action for Method Blanks not meeting acceptance criteria:

13.3.1.3.1 Method Blank Contamination – Blank contamination above the RL (>1/2 RL for some programs – see specific Client Requirement Memos for details) requires re-prep of batch unless all associated samples are < RL or greater than 10 times the amount detected in the method blank.

13.3.1.3.2 Method Blank Surrogate excursion – If excursion is limited to the blank, data may be reported with an NCM. If surrogates are also outside criteria in samples, re-prep and re-anlaysis is required. In cases where the surrogate recovery is high and the samples are non-detect, the data may be reported with an NCM.

13.4 Laboratory Control Sample (LCS)

13.4.1 Acceptance Criteria: All control analytes must be within established control limits for accuracy (%Recovery) and precision (RPD).

13.4.1.1 For long analyte spike lists, marginal exceedances (ME) are allowed as follows:

13.4.1.2 less than 11 analytes in LCS, no analytes allowed in ME of the LCS control limit.

13.4.1.3 11-30 analytes in LCS, 1 analytes allowed in ME of the LCS control limit.

13.4.1.4 31-50 analytes in LCS, 2 analytes allowed in ME of the LCS control limit.

13.4.1.5 51-70 analytes in LCS, 3 analytes allowed in ME of the LCS control limit.

13.4.1.6 71-90 analytes in LCS, 4 analytes allowed in ME of the LCS control limit.

13.4.1.7 More than 90 analytes in LCS, 5 analytes allowed in ME of the LCS control limit.

13.4.1.8 No LCS recoveries may be outside the Marginal Exceedance limit.

13.4.1.9 Marginal exceedances must be random. If the same LCS analyte exceeds the control limit repeatedly, it is an indication of a systemic problem. The source of the error must be located and corrective action taken.

13.4.1.10 Marginal exceedance is not allowed by all programs. See Project/Program CRM for details. The use of marginal exceedances is not allowed for South Carolina Compliance samples.

13.4.2 The LCS should have acceptable surrogate recoveries.

13.4.3 Corrective Action for LCS not meeting acceptance criteria:

13.4.3.1 LCS Spike Recovery excursion (high) – Samples that are non-detect may be reported with an NCM (unless prohibited by client requirements). Samples with detects for the analyte

recovered high in the LCS are re-prepped and re-analyzed. . In cases where the surrogate recovery is high and the samples are non-detect, the data may be reported with an NCM.

13.4.3.2 LCS Spike Recovery excursion (low) – batch is re-prepped and re-analyzed.

13.4.3.3 LCS Surrogate Recovery excursion – If excursion is limited to the LCS, data may be reported with an NCM. If target analytes are in control in the LCS, data may be reported with an NCM. If surrogates are also outside criteria in samples, re-prep and re-analysis is required.

13.4.3.4 RPD excursion for LCS/LCSD – If target analytes recoveries are in control, data may be reported with an NCM.

13.5 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

13.5.1 All analytes should be within established control limits for accuracy (%Recovery) and precision (RPD).

13.5.2 Corrective Action for MS/MSD not meeting acceptance criteria:

13.5.2.1 MS/MSD Spike Rec. excursion may not necessarily warrant corrective action other than narration. If affected analyte concentration in the original sample is greater than four times the amount spiked, percent recovery information is ineffective. Data is reported with an NCM. If the excursion is due to a physically evident matrix interference, the data is reported with an NCM (the physical interference must be described in the NCM). If there is no evidence of interference and the RPD as well as spike recoveries out outside limits out, sample re-prep and re-analysis are required.

13.6 Sample result evaluation

13.6.1 Dilutions

13.6.1.1 If the response for any compound exceeds the working range of the analytical system, a dilution of the extract is prepared and analyzed. An appropriate dilution should be in the upper half of the calibration range.

13.6.1.2 Dilution: Sample– An NCM is created when dilutions are required.

13.6.1.3 Dilution: Surrogate(s)/spikes diluted out– An NCM is generated to document the surrogates/spikes being diluted out.

13.6.2 Carryover

13.6.2.1 When a sample has a high response for a compound, there is a real possibility that some of the sample may carry over into the sample analyzed immediately afterward.

13.6.2.2 If a sample analyzed after a sample with high concentrations is non-detect for the high concentration analyte, carryover did not occur.

13.6.2.3 If a sample analyzed after a sample with high concentrations has positive results for the same analytes, the results are questionable. This sample must be reanalyzed under conditions in which carryover can be confirmed to not have occurred.

13.6.3 Internal Standards

13.6.3.1 Acceptance Criteria:

13.6.3.1.1 If the EICP area for any of the internal standards in the calibration verification standard changes by a factor of two (-50% to +100%) from that in the mid-point standard level of the most recent initial calibration sequence, corrective action must be taken.

13.6.3.1.2 If the EICP area for any of the internal standards in samples, spikes and blanks changes by a factor of two (-50% to +100%) from the areas determined in the continuing calibration analyzed that day, corrective action must be taken. The samples, spikes or blanks should be reanalyzed or the data should be qualified. (Some programs may require that the midpoint of the initial calibration be used for ISTD monitoring. See the project CRM for specifics.)

13.6.3.2 Corrective Action for Internal Standards not meeting acceptance criteria:

13.6.3.2.1 Internal Standard excursion – high – High ISTD recovery indicates a potential low bias to analytical results. Instrument maintenance, if required, is done

and affected samples are reanalyzed. If ISTDs are outside criteria on the re-analysis, a matrix interference is suspected and data reported with an NCM.

13.6.3.2.2 Internal Standard excursion – low – Low ISTD recovery indicates the potential for a high bias to analytical results. Samples that are non-detect for affected analytes may be reported with an NCM. Samples with positive hits above the RL for analytes associated with the poor ISTD recovery require re-analysis. Instrument maintenance, if required, is done. If ISTDs are outside criteria on the re-analysis, a matrix interference is suspected and data reported with an NCM.

13.6.4 Surrogate

13.6.4.1 All Surrogates should be within established control limits for accuracy (%Recovery).

13.6.4.2 Corrective Action for Surrogate not meeting acceptance criteria:

13.6.4.2.1 Surrogate Spike Rec. excursion may not necessarily warrant corrective action other than narration.

13.7 Insufficient Sample

13.7.1 For each prescribed re-preparation corrective action, if there is insufficient sample to repeat the analysis, an NCM is created and a narrative comment stating such is included in the report's Case Narrative.

## 14.0 METHOD PERFORMANCE AND DEMONSTRATION OF CAPABILITY

14.1 Method performance data, Reporting Limits, and QC acceptance limits, are given in the LIMS.

14.2 Demonstration of Capability

14.2.1 Initial and continuing demonstrations of capability requirements are established in the QAM.

14.3 Training Qualification

14.3.1 The manager/supervisor has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience.

14.3.2 The analyst must have successfully completed the initial demonstration capability requirements prior to working independently. See requirements in the QAM.

14.4 Annually, the analyst must successfully demonstrate proficiency to continue to perform this analysis. See requirements in the QAM.

## 15.0 VALIDATION

15.1 Laboratory SOPs are based on standard reference EPA Methods that have been validated by the EPA and the lab is not required to perform validation for these methods. The requirements for lab demonstration of capability are included in LQM. Lab validation data would be appropriate for performance based measurement systems or non-standard methods. TestAmerica St. Louis will include this information in the SOP when accreditation is sought for a performance based measurement system or non-standard method.

## 16.0 WASTE MANAGEMENT AND POLLUTION PREVENTION

16.1 All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for ~~"~~Waste Management and Pollution Prevention."

16.2 Waste Streams Produced by the Method

16.2.1 The following waste streams are produced when this method is carried out.

16.2.1.1 Auto-sample vials containing Methylene Chloride are to be disposed of in the appropriate solvent vial waste accumulation container located within the GC/MS lab, for temporary storage. Once this temporary container is full or once it reaches a one-year collection time, this container must be dumped into the permanent solvent vial waste container located in the 90-day storage area, which is marked as a Type ~~"C~~" waste accumulation container.

16.2.1.2 Waste Methylene Chloride rinses are to be collected and disposed of within the solvent waste accumulation container located in the Organic Prep. Lab. This temporary storage container shall be dumped on a daily basis into the permanent waste accumulation container located in the 90-day storage area which is marked as a Type ~~"D~~" waste drum.

## 17.0 REFERENCES

17.1 SW846, Test Methods for Evaluating Solid Waste, Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS): Method 8000B, 8000C and 8270D.

17.2 40CFR Part 136: ~~"G~~uidelines Establishing Test Procedures for the Analysis of Pollutants, Appendix A, ~~"M~~ethods for Organic Chemical Analysis of Municipal and Industrial Wastewater", Code of Federal Regulations, Revised July1, 1995, Method 625.

17.3 TestAmerica St. Louis Quality Assurance Manual (QAM), current revision.

17.4 TestAmerica Corporate Environmental Health and Safety Manual (CW-E-M-002) and St. Louis Facility Addendum (ST-HS-0002), current revision.

17.5 TestAmerica Policy CA-Q-S-002, Acceptable Manual Integration Practices

17.6 TestAmerica Policy CA-T-P-002, Selection of Calibration Points

17.7 Associated SOPs, current revisions

17.7.1 ST-OP-0002, Extraction and Cleanup of Organic Compounds from Waters and Soils, Based on SW-846 3500 Series, 3600 Series, and 600 Series Methods
17.7.2 ST-PM-0002, Sample Receipt and Chain of Custody
17.7.3 ST-QA-0002, Standard and Reagent Preparation
17.7.4 ST-QA-0005, Calibration and Verification Procedure for Thermometers, Balances, Weights and Pipettes.
17.7.5 ST-QA-0014, Evaluation of Analytical Accuracy and Precision Through the Use of Control Charts
17.7.6 ST-QA-0016, IDL/MDL, LOD/LOQ Determination
17.7.7 ST-QA-0036, Non-conformance Memorandum (NCM) Process

## 18.0 CLARIFICATIONS, MODIFICATIONS TO THE REFERENCE METHOD

18.1 The quantitation and qualifier ions for some compounds have been changed from those recommended in SW-846 in order to improve the reliability of qualitative identification.

## 19.0 CHANGES TO PREVISION SOP REVISION

19.1 Table reference in Section 6.1 was corrected.
19.2 Y-intercept requirements added to Section 10.
19.3 Added requirement for 6 levels for a quadratic curve to Section 10
19.4 Added CLP allowance for reporting data within 10% of upper standard without dilution to Section 12
19.5 Clarification of criteria for TIC reporting added to Section 12.4.

19.6 Table 1: clarified Tune criteria and added allowance of other published DFTPP Tune criteria (i.e. EPA CLP)

19.7 Added Table 5, a listing of internal standards and associated analytes

19.8 Revision 13:

- 19.8.1 Grammatical /spelling corrections
- 19.8.2 Added SIM analysis to section 11

19.9 Revision 14:

- 19.9.1 Removed QuantIMS and Clouseau references – replaced with LIMs
- 19.9.2 Created hyperlinks to tables
- 19.9.3 Appended LVI Calibration Levels to Table 3
- 19.9.4 Combined fragmented Table 5 into one table
- 19.9.5 Added table of potentially mis-identifiable analytes to Section 12.3.
- 19.9.6 Removed CLP allowance for reporting data within 10% of upper standard without dilution from Section 12.
- 19.9.7 Revised Section 13 to remove Clouseau corrective action references and to provide specific corrective actions for non-conformances.

19.10 Revision 15:

- 19.10.1 Section 3, updated SIM definition
- 19.10.2 Section 7.5 Added SIM requirement
- 19.10.3 Section 7.7 ICV standard 2nd source where available to acquire
- 19.10.4 Section 10.1 corrected table references
- 19.10.5 Section 10.2 Added % breakdown calculation and added Benzidine and pentachlorophenol requirements
- 19.10.6 Section 10.3.8.9.2.1 removed compounds that are not to use non-linear calibration model
- 19.10.7 Removed 12.6.1.3
- 19.10.8 Section 13.6.2.3 removed chromatographic profile reference

19.11 Revision 16:

- 19.11.1 Section 1.1 Added a missing period
- 19.11.2 Section 10.2.1.2 Added a missing period
- 19.11.3 Section 10.2.2 Added a missing period
- 19.11.4 Section 10.5.2 Added a missing period
- 19.11.5 Section 12.2.1 Added a missing period
- 19.11.6 Section 13.4.3.1 Added a missing period
- 19.11.7 Section 13.4.3.4 Added a missing period
- 19.11.8 Section 10.3.8.2 Took comma out after Kepone and added the word ~~a~~nd"
- 19.11.9 Section 10.5.6.2 Took comma out after Kepone
- 19.11.10 Section 17.5 Changed policy number from 001 to 002
- 19.11.11 Section 2.1 Added possible concentration of 5 mL
- 19.11.12 Added Surrogates to Section 13
- 19.11.13 Table 3 – Changed calibration concentration levels

19.12 Revision 17:

- 19.12.1 Added note to Section 11 that South Carolina requires certification for SIM analysis.
- 19.12.2 Updated Section 13.4 to disallow the use of marginal exceedance for South Carolina compliance work.
- 19.12.3 Updated Section 10.3.8 to disallow the use of non-linear or second order calibrations for South Carolina compliance work.

**Table 1**
**DFTPP Key Ions and Ion Abundance Criteria***

| Mass | Ion Abundance Criteria |
|---|---|
| 51 | 30 - 60% of mass 198 |
| 68 | <2% of mass 69 |
| 70 | <2% of mass 69 |
| 127 | 40 - 60% of mass 198 |
| 197 | <1% of mass 198 |
| 198 | Base peak, 100% relative abundance |
| 199 | 5 - 9% of mass 198 |
| 275 | 10 - 30% of mass 198 |
| 365 | >1% of mass 198 |
| 441 | Present, but less than mass 443 |
| 442 | >40% of mass 198 |
| 443 | 17 - 23% of mass 442 |

* Tune criteria in use is a combination of 8270C and 8270D which is more stringent than either method. Alternatively, other documented tuning criteria (e.g. EPA CLP) may be used provided method performance is not aversely affected.

**Table 2**
**Analytes in Approximate Retention Time Order and Characteristic Ions**

| Primary Standard | | | |
|---|---|---|---|
| **Analyte** | **Primary** | **Secondary** | **Tertiary** |
| 1,4 Dioxane | 88 | 58 | 43 |
| n-Nitrosodimethylamine | 74* | 42 | 44 |
| Pyridine | 79 | 52 | — |
| Dimethylformamide | 44 | 73 | 42 |
| Cyclohexanol | 57 | 82 | 67 |
| **2-Fluorophenol (Surrogate Standard)** | 112 | 64 | 63** |
| **Phenol-d5 (Surrogate Standard)** | 99 | 42 | 71 |
| Aniline | 93 | 66 | 65 |
| Phenol | 94 | 65 | 66 |
| Bis(2-chloroethyl)ether | 93 | 63 | 95 |
| 2-Chlorophenol | 128 | 64 | 130 |
| 1,3-Dichlorobenzene | 146 | 148 | 111 |
| **1,4-Dichlorobenzene-d4 (Internal Standard)** | 152 | 150 | 115 |
| 1,4-Dichlorobenzene | 146 | 148 | 111 |
| Benzyl Alcohol | 108 | 79 | 77 |
| 1,2-Dichlorobenzene | 146 | 148 | 111 |
| 2-Methylphenol | 108* | 107 | 79 |
| 2,2'-oxybis(1-chloropropane)[1] | 45 | 77 | 121 |
| 3&4-Methylphenol | 107 | 108 | 79 |
| n-Nitroso-di-n-propylamine | 70 | 42 | 101 |
| Hexachloroethane | 117 | 201 | 199 |
| **Nitrobenzene-d5 (Surrogate Standard)** | 82 | 128 | 54 |
| Nitrobenzene | 77 | 123 | 65 |
| Isophorone | 82 | 95 | 138 |
| 2-Nitrophenol | 139 | 65 | 109 |
| 2,4-Dimethylphenol | 107* | 121 | 122 |
| Benzoic Acid | 122 | 105 | 77 |
| Bis(2-chloroethoxy)methane | 93 | 95 | 123 |

**Table 2**
**Analytes in Approximate Retention Time Order and Characteristic Ions**

| Primary Standard | | | |
|---|---|---|---|
| **Analyte** | **Primary** | **Secondary** | **Tertiary** |
| 2,4-Dichlorophenol | 162 | 164 | 98 |
| 1,2,4-Trichlorobenzene | 180 | 182 | 145 |
| **Naphthalene-d8 (Internal Standard)** | 136 | 68 | 54** |
| Naphthalene | 128 | 129 | 127 |
| 4-Chloroaniline | 127 | 129 | 65 |
| Hexachlorobutadiene | 225 | 223 | 227 |
| 4-Chloro-3-methylphenol | 107 | 144 | 142 |
| 2-Methylnaphthalene | 142 | 141 | — |
| Hexachlorocyclopentadiene | 237 | 235 | 272 |
| 2,4,6-Trichlorophenol | 196 | 198 | 200 |
| 2,4,5-Trichlorophenol | 196 | 198 | 200 |
| **2-Fluorobiphenyl (Surrogate Standard)** | 172 | 171 | — |
| 2-Chloronaphthalene | 162 | 164 | 127 |
| 2-Nitroaniline | 65 | 92 | 138 |
| Dimethylphthalate | 163 | 194 | 164 |
| Acenaphthylene | 152 | 151 | 153 |
| 2,6-Dinitrotoluene | 165 | 63 | 89 |
| **Acenaphthene-d10 (Internal Standard)** | 164 | 162 | 160 |
| 3-Nitroaniline | 138 | 108 | 92 |
| Acenaphthene | 153* | 152 | 154 |
| 2,4-Dinitrophenol | 184 | 63 | 154 |
| Dibenzofuran | 168 | 139 | — |
| 4-Nitrophenol | 109* | 139 | 65 |
| 2,4-Dinitrotoluene | 165 | 63 | 89 |
| Diethylphthalate | 149 | 177 | 150 |
| Fluorene | 166 | 165 | 167 |
| 4-Chlorophenylphenylether | 204 | 206 | 141 |
| 4-Nitroaniline | 138 | 92 | 108 |
| 4,6-Dinitro-2-methylphenol | 198 | 105 | 51 |

**Table 2**
**Analytes in Approximate Retention Time Order and Characteristic Ions**

| Primary Standard | | | |
|---|---|---|---|
| **Analyte** | **Primary** | **Secondary** | **Tertiary** |
| n-Nitrosodiphenylamine | 169 | 168 | 167 |
| **2,4,6-Tribromophenol (Surrogate Standard)** | 330 | 332** | 141 |
| Azobenzene | 77 | 51** | 105 |
| 4-Bromophenylphenylether | 248 | 250 | 141 |
| Hexachlorobenzene | 284 | 142 | 249 |
| Pentachlorophenol | 266 | 264 | 268 |
| **Phenanthrene-d10 (Internal Standard)** | 188 | 94 | 80 |
| Phenanthrene | 178 | 179 | 176 |
| Anthracene | 178 | 179 | 176 |
| Carbazole | 167 | 166 | 139 |
| Di-n-butylphthalate | 149 | 150 | 104 |
| Fluoranthene | 202 | 101 | 203 |
| Benzidine | 184 | 92 | 185 |
| Pyrene | 202 | 200 | 203 |
| **Terphenyl-d14 (Surrogate Standard)** | 244 | 122 | 212 |
| Butylbenzylphthalate | 149 | 91 | 206 |
| Benzo(a)Anthracene | 228 | 229 | 226 |
| **Chrysene-d12 (Internal Standard)** | 240 | 120 | 236 |
| 3,3'-Dichlorobenzidine | 252 | 254 | 126 |
| Chrysene | 228 | 226 | 229 |
| Bis(2-ethylhexyl)phthalate | 149 | 167 | 279 |
| Di-n-octylphthalate | 149 | 167 | 43 |
| Benzo(b)fluoranthene | 252 | 253 | 125 |
| Benzo(k)fluoranthene | 252 | 253 | 125 |
| Benzo(a)pyrene | 252 | 253 | 125 |
| **Perylene-d12 (Internal Standard)** | 264 | 260 | 265 |
| Indeno(1,2,3-cd)pyrene | 276 | 138 | 277 |
| Dibenz(a,h)anthracene | 278 | 139 | 279 |
| Benzo(g,h,i)perylene | 276 | 138 | 277 |

***** primary/secondary and/or tertiary ions are switched from order in Method
** not listed in the method

**Appendix IX Standard**

| Analyte | Primary | Secondary | Tertiary |
|---|---|---|---|
| Methyl methacrylate | 69 | 41 | 39 |
| Ethyl methacrylate | 69 | 41 | 39 |
| 2-Picoline | 93 | 66 | 92 |
| n-Nitrosomethylethylamine | 88 | 42 | 43 |
| Methyl methanesulfonate | 80 | 79 | 65 |
| **2-Fluorophenol (Surrogate Standard)** | 112 | 64 | 63** |
| n-Nitrosodiethylamine | 102 | 44 | 57 |
| Ethyl methanesulfonate | 79 | 109 | 97 |
| Benzaldehyde | 77 | 106 | 51 |
| **Phenol-d5 (Surrogate Standard)** | 99 | 42 | 71 |
| Pentachloroethane | 117 | 119 | 167 |
| **1,4-Dichlorobenzene-d4 (Internal Standard)** | 152 | 150 | 115 |
| Acetophenone | 105 | 77 | 120 |
| n-Nitrosopyrrolidine | 100 | 41 | 42 |
| n-Nitrosomorpholine | 116 | 56 | 86 |
| o-Toluidine | 106 | 107 | — |
| **Nitrobenzene-d5 (Surrogate Standard)** | 82 | 128 | 54 |
| n-Nitrosopiperidine | 114 | 42 | 55 |
| O,o,o-Triethyl-Phosphorothioate | 198 | 121 | 93 |
| a,a-Dimethyl-phenethylamine | 58 | 91 | — |
| **Naphthalene-d8 (Internal Standard)** | 136 | 68 | 54** |
| 2,6-Dichlorophenol | 162 | 164 | 63 |
| Hexachloropropene | 213 | 215 | 211 |
| Benzothiazole | 135 | 108 | 69 |
| Caprolactam | 55 | 113 | 42 |
| p-Phenylenediamine | 108 | 80 | — |
| n-Nitrosodi-n-butylamine | 84 | 57 | 41 |
| Safrole | 162 | 104 | 77 |
| Phthalic anhydride | 104 | 76 | 50 |
| 1-methylnaphthalene | 142 | 141 | 115 |

**Appendix IX Standard**

| Analyte | Primary | Secondary | Tertiary |
|---|---|---|---|
| 1,2,4,5-Tetrachlorobenzene | 216 | 214 | 218 |
| Isosafrole, cis | 162 | 104 | 131 |
| **2-Fluorobiphenyl (Surrogate Standard)** | 172 | 171 | — |
| Isosafrole, trans | 162 | 104 | 131 |
| Biphenyl | 154 | 153 | 152 |
| 1,4-Dinitrobenzene | 168 | 75 | 50 |
| 1,4-Naphthoquinone | 158 | 104 | 102 |
| 1,3-Dinitrobenzene | 168 | 75 | 76 |
| **Acenaphthene-d10 (Internal Standard)** | 164 | 162 | 160 |
| Pentachlorobenzene | 250 | 248 | 252 |
| 1-Naphthylamine | 143 | 115 | — |
| 2-Naphthylamine | 143 | 115 | — |
| 2,3,4,6-Tetrachlorophenol | 232 | 230 | 131 |
| 5-Nitro-o-toluidine | 152 | 77 | 106 |
| Thionazin | 107 | 96 | 143 |
| 1,3,5-Trinitrobenzene | 213* | 75 | 120 |
| **2,4,6-Tribromophenol (Surrogate Standard)** | 330 | 332** | 141** |
| Sulfotepp | 97 | 322 | 202 |
| Phorate | 75 | 97 | 121 |
| Phenacetin | 108 | 179 | 109 |
| Diallate 1 | 86 | 234 | 43 |
| Diallate 2 | 86 | 234 | 43 |
| Dimethoate | 87 | 93 | 125 |
| 4-Aminobiphenyl | 169 | 168 | 170 |
| Pentachloronitrobenzene | 237 | 142 | 214 |
| **Phenanthrene-d10 (Internal Standard)** | 188 | 94 | 80 |
| Pronamide | 173 | 175 | 145 |
| Disulfoton | 88 | 97 | 89 |
| 2-secbutyl-4,6-dinitrophenol (Dinoseb) | 211 | 163 | 147 |
| Methyl parathion | 109 | 125 | 263 |
| 4-Nitroquinoline-1-oxide | 190 | 128 | 75 |
| Parathion | 109 | 97 | 291 |
| Isodrin | 193 | 66 | 195 |

**Appendix IX Standard**

| Analyte | Primary | Secondary | Tertiary |
|---|---|---|---|
| Kepone | 272 | 274 | 237 |
| Methapyrilene | 97 | 58** | — |
| Octachlorostyrene | 308 | 343 | 154 |
| **Terphenyl-d14 (Surrogate Standard)** | 244 | 122 | 212 |
| Aramite 1 | 185 | 319 | — |
| Aramite 2 | 185 | 319 | — |
| p-(Dimethylamino)azobenzene | 120* | 225 | 77 |
| p-Chlorobenzilate | 251 | 139 | 253 |
| 3,3'-Dimethylbenzidine | 212 | 106 | — |
| 2-Acetylaminofluorene | 181 | 180 | 223 |
| Famphur | 218 | 125 | 93 |
| **Chrysene-d12 (Internal Standard)** | 240 | 120 | 236 |
| Hexachlorophene | 196 | 198 | 209 |
| 7,12-Dimethylbenz(a)anthracene | 256 | 241 | 120 |
| **Perylene-d12 (Internal Standard)** | 264 | 260 | 265 |
| 3-Methylcholanthrene | 268 | 252 | 126 |

***** primary/secondary and/or tertiary ions are switched from order in Method
** not listed in the method

**Table 3**
**Calibration Levels, Primary Standard, µg/mL[3]**

| Analyte | Level 1 | Level 2 | Level 3 | Level 4 | Level 5 | Level 6 | Level 7 | Level 8 | Level 9 |
|---|---|---|---|---|---|---|---|---|---|
| 1,4 Dioxane | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Pyridine | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| n-Nitrosodimethylamine | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Dimethylformamide | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Cyclohexanol | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Aniline | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Phenol | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Bis(2-chloroethyl)ether | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 2-Chlorophenol | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 1,3-Dichlorobenzene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 1,4-Dichlorobenzene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Benzyl alcohol | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 1,2-Dichlorobenzene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 2-Methylphenol | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 2,2'-oxybis(1-chloropropane)[1] | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 3&4-Methylphenol | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| n-Nitroso-di-n-propylamine | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Hexachloroethane | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Nitrobenzene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Isophorone | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 2-Nitrophenol | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 2,4-Dimethylphenol | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Benzoic acid | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| bis(2-Chloroethoxy)methane | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 2,4-Dichlorophenol | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 1,2,4-Trichlorobenzene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Naphthalene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 4-Chloroaniline | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Hexachlorobutadiene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |

**Table 3**
**Calibration Levels, Primary Standard, µg/mL[3]**

| Analyte | Level 1 | Level 2 | Level 3 | Level 4 | Level 5 | Level 6 | Level 7 | Level 8 | Level 9 |
|---|---|---|---|---|---|---|---|---|---|
| 4-Chloro-3-methylphenol | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 2-Methylnaphthalene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Hexachlorocyclopentadiene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 2,4,6-Trichlorophenol | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 2,4,5-Trichlorophenol | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 2-Chloronaphthalene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 2-Nitroaniline | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Dimethyl phthalate | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Acenaphthylene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 3-Nitroaniline | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Acenaphthene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 2,4-Dinitrophenol | 2 | 4 | 10 | 20 | 40 | 60 | 80 | 100 | 120 |
| 4-Nitrophenol | 2 | 4 | 10 | 20 | 40 | 60 | 80 | 100 | 120 |
| Dibenzofuran | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 2,4-Dinitrotoluene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 2,6-Dinitrotoluene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Diethylphthalate | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 4-Chlorophenyl phenyl ether | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Fluorene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 4-Nitroaniline | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 4,6-Dinitro-2-methylphenol | 2 | 4 | 10 | 20 | 40 | 60 | 80 | 100 | 120 |
| N-Nitrosodiphenylamine | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Azobenzene[2] | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 4-Bromophenyl phenyl ether | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Hexachlorobenzene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Pentachlorophenol | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Phenanthrene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Anthracene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Carbazole | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Di-n-butyl phthalate | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Fluoranthene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |

**Table 3**
**Calibration Levels, Primary Standard, µg/mL[3]**

| Analyte | Level 1 | Level 2 | Level 3 | Level 4 | Level 5 | Level 6 | Level 7 | Level 8 | Level 9 |
|---|---|---|---|---|---|---|---|---|---|
| Benzidine | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Pyrene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Butyl benzyl phthalate | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 3,3'-Dichlorobenzidine | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Benzo(a)anthracene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Bis(2-ethylhexyl)phthalate | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Chrysene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Di-n-octylphthalate | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Benzo(b)fluoranthene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Benzo(k)fluoranthene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Benzo(a)pyrene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Indeno(1,2,3-cd)pyrene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Dibenz(a,h)anthracene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Benzo(g,h,i)perylene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |

[1] 2,2'oxybis(1-chloropropane) was formally known as bis(2-chloroisopropyl)ether
[2] Azobenzene is formed by decomposition of 1,2-diphenlyhydrazine. If 1,2-diphenylhydrazine is requested, it will be analyzed as azobenzene.
[3] Lower concentration standards may be analyzed on a project specific basis.

**Calibration Levels, Appendix IX Standard, µg/mL**

| Semivolatiles | Level 1 | Level 2 | Level 3 | Level 4 | Level 5 | Level 6 | Level 7 | Level 8 | Level 9 |
|---|---|---|---|---|---|---|---|---|---|
| Methyl methacrylate | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Ethyl methacrylate | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 2-Picoline | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| n-Nitrosomethylethylamine | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Methyl methanesulfonate | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| n-Nitrosodiethylamine | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Ethyl methanesulfonate | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Benzaldehyde | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |

**Calibration Levels, Appendix IX Standard, µg/mL**

| Semivolatiles | Level 1 | Level 2 | Level 3 | Level 4 | Level 5 | Level 6 | Level 7 | Level 8 | Level 9 |
|---|---|---|---|---|---|---|---|---|---|
| Pentachloroethane | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Acetophenone | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| n-Nitrosopyrrolidine | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| n-Nitrosomorpholine | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| o-Toluidine | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| n-Nitrosopiperidine | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| O,o,o-Triethyl-Phosphorothioate | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| A,a-Dimethyl-phenethylamine | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 2,6-Dichlorophenol | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Hexachloropropene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Benzothiazole | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Caprolactam | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| p-Phenylenediamine | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| n-Nitrosodi-n-butylamine | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Safrole | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Phthalic anhydride | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 1-Methylnaphthalene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 1,2,4,5-Tetrachlorobenzene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Isosafrole, cis | .5 | 1 | 2.5 | 5 | 10 | 15 | 20 | 25 | 30 |
| Isosafrole, trans | .5 | 1 | 2.5 | 5 | 10 | 15 | 20 | 25 | 30 |
| Biphenyl | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 1,4-Dinitrobenzene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 1,4-Naphthoquinone | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 1,3-Dinitrobenzene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Pentachlorobenzene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 1-Naphthylamine | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 2-Naphthylamine | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 2,3,4,6-Tetrachlorophenol | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 5-Nitro-o-toluidine | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Thionazin | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 1,3,5-Trinitrobenzene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Sulfotepp | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Phorate | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |

**Calibration Levels, Appendix IX Standard, µg/mL**

| Semivolatiles | Level 1 | Level 2 | Level 3 | Level 4 | Level 5 | Level 6 | Level 7 | Level 8 | Level 9 |
|---|---|---|---|---|---|---|---|---|---|
| Phenacetin | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Diallate 1 | .5 | 1 | 2.5 | 5 | 10 | 15 | 20 | 25 | 30 |
| Diallate 2 | .5 | 1 | 2.5 | 5 | 10 | 15 | 20 | 25 | 30 |
| Dimethoate | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 4-Aminobiphenyl | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Pentachloronitrobenzene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Pronamide | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Disulfoton | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 2-sec butyl-4,6-dinitrophenol (Dinoseb) | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Methyl parathion | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 4-Nitroquinoline-1-oxide | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Parathion | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Isodrin | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Kepone | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Famphur | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Methapyrilene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Octachlorostyrene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Aramite 1 | .5 | 1 | 2.5 | 5 | 10 | 15 | 20 | 25 | 30 |
| Aramite 2 | .5 | 1 | 2.5 | 5 | 10 | 15 | 20 | 25 | 30 |
| p-(Dimethylamino)azobenzene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| p-Chlorobenzilate | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 3,3'-Dimethylbenzidine | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Hexachlorophene | 10 | 20 | 50 | 100 | 200 | 300 | 400 | 500 | 600 |
| 2-Acetylaminofluorene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Dibenz (a,j)acridine | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 7,12-Dimethylbenz(a)anthracene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 3-Methylcholanthrene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| **2-Fluorophenol (Surrogate Standard** | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| **Phenol-d5 (Surrogate Standard)** | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| **Nitrobenzene-d5 (Surrogate Standard)** | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| **2-Fluorobiphenyl (Surrogate Standard)** | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| **2,4,6-Tribromophenol (Surrogate Standard)** | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| **Terphenyl-d14 (Surrogate Standard)** | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |

**Calibration Levels SIM Standard, ug/mL**

| | | | | | | |
|---|---|---|---|---|---|---|
| **Naphthalene** | 0.2 | 0.5 | 1.0 | 2.0 | 5.0 | 10.0 |
| **Acenaphthylene** | 0.2 | 0.5 | 1.0 | 2.0 | 5.0 | 10.0 |
| **Acenaphthene** | 0.2 | 0.5 | 1.0 | 2.0 | 5.0 | 10.0 |
| **Fluorene** | 0.2 | 0.5 | 1.0 | 2.0 | 5.0 | 10.0 |
| **Phenanthrene** | 0.2 | 0.5 | 1.0 | 2.0 | 5.0 | 10.0 |
| **Pyrene** | 0.2 | 0.5 | 1.0 | 2.0 | 5.0 | 10.0 |
| **Benzo(a)anthracene** | 0.2 | 0.5 | 1.0 | 2.0 | 5.0 | 10.0 |
| **Chrysene** | 0.2 | 0.5 | 1.0 | 2.0 | 5.0 | 10.0 |
| **Benzo(b)fluoranthene** | 0.2 | 0.5 | 1.0 | 2.0 | 5.0 | 10.0 |
| **Benzo(k)fluoranthene** | 0.2 | 0.5 | 1.0 | 2.0 | 5.0 | 10.0 |
| **Benzo(a)pyrene** | 0.2 | 0.5 | 1.0 | 2.0 | 5.0 | 10.0 |
| **Indeno(1,2,3-cd)pyrene** | 0.2 | 0.5 | 1.0 | 2.0 | 5.0 | 10.0 |
| **Dibenz(a,h)anthracene** | 0.2 | 0.5 | 1.0 | 2.0 | 5.0 | 10.0 |
| **Anthracene** | 0.2 | 0.5 | 1.0 | 2.0 | 5.0 | 10.0 |
| **Fluoranthene** | 0.2 | 0.5 | 1.0 | 2.0 | 5.0 | 10.0 |
| **Benzo(g,h,i)perylene** | 0.2 | 0.5 | 1.0 | 2.0 | 5.0 | 10.0 |
| **2-Methylnaphthalene** | 0.2 | 0.5 | 1.0 | 2.0 | 5.0 | 10.0 |

**Table 3**

**LVI Calibration Levels, Primary Standard, µg/mL[3]**

| Analyte | Level 1 | Level 2 | Level 3 | Level 4 | Level 5 | Level 6 | Level 7 | Level 8 | Level 9 |
|---|---|---|---|---|---|---|---|---|---|
| 1,4 Dioxane | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Pyridine | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |

**Table 3**

**LVI Calibration Levels, Primary Standard, µg/mL[3]**

| Analyte | Level 1 | Level 2 | Level 3 | Level 4 | Level 5 | Level 6 | Level 7 | Level 8 | Level 9 |
|---|---|---|---|---|---|---|---|---|---|
| n-Nitrosodimethylamine | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Dimethylformamide | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Cyclohexanol | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Aniline | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Phenol | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Bis(2-chloroethyl)ether | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 2-Chlorophenol | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 1,3-Dichlorobenzene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 1,4-Dichlorobenzene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Benzyl alcohol | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 1,2-Dichlorobenzene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 2-Methylphenol | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 2,2'-oxybis(1-chloropropane)[1] | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 3&4-Methylphenol | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| n-Nitroso-di-n-propylamine | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Hexachloroethane | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Nitrobenzene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Isophorone | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 2-Nitrophenol | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 2,4-Dimethylphenol | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Benzoic acid | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| bis(2-Chloroethoxy)methane | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 2,4-Dichlorophenol | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 1,2,4-Trichlorobenzene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Naphthalene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 4-Chloroaniline | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Hexachlorobutadiene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 4-Chloro-3-methylphenol | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 2-Methylnaphthalene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Hexachlorocyclopentadiene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 2,4,6-Trichlorophenol | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 2,4,5-Trichlorophenol | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |

**Table 3**

**LVI Calibration Levels, Primary Standard, µg/mL[3]**

| Analyte | Level 1 | Level 2 | Level 3 | Level 4 | Level 5 | Level 6 | Level 7 | Level 8 | Level 9 |
|---|---|---|---|---|---|---|---|---|---|
| 2-Chloronaphthalene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 2-Nitroaniline | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Dimethyl phthalate | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Acenaphthylene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 3-Nitroaniline | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Acenaphthene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 2,4-Dinitrophenol | 2 | 4 | 10 | 20 | 40 | 60 | 80 | 100 | 120 |
| 4-Nitrophenol | 2 | 4 | 10 | 20 | 40 | 60 | 80 | 100 | 120 |
| Dibenzofuran | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 2,4-Dinitrotoluene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 2,6-Dinitrotoluene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Diethylphthalate | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 4-Chlorophenyl phenyl ether | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Fluorene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 4-Nitroaniline | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 4,6-Dinitro-2-methylphenol | 2 | 4 | 10 | 20 | 40 | 60 | 80 | 100 | 120 |
| N-Nitrosodiphenylamine | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Azobenzene[2] | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 4-Bromophenyl phenyl ether | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Hexachlorobenzene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Pentachlorophenol | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Phenanthrene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Anthracene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Carbazole | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Di-n-butyl phthalate | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Fluoranthene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Benzidine | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Pyrene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Butyl benzyl phthalate | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 3,3'-Dichlorobenzidine | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Benzo(a)anthracene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Bis(2-ethylhexyl)phthalate | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |

**Table 3**

**LVI Calibration Levels, Primary Standard, µg/mL[3]**

| Analyte | Level 1 | Level 2 | Level 3 | Level 4 | Level 5 | Level 6 | Level 7 | Level 8 | Level 9 |
|---|---|---|---|---|---|---|---|---|---|
| Chrysene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Di-n-octylphthalate | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Benzo(b)fluoranthene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Benzo(k)fluoranthene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Benzo(a)pyrene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Indeno(1,2,3-cd)pyrene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Dibenz(a,h)anthracene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Benzo(g,h,i)perylene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |

[1]2,2'oxybis(1-chloropropane) was formally known as bis(2-chloroisopropyl)ether
[2]Azobenzene is formed by decomposition of 1,2-diphenlyhydrazine. If 1,2-diphenylhydrazine is requested, it will be analyzed as azobenzene.
[3]Lower concentration standards may be analyzed on a project specific basis.

**LVI Calibration Levels, Appendix IX Standard, µg/mL**

| Semivolatiles | Level 1 | Level 2 | Level 3 | Level 4 | Level 5 | Level 6 | Level 7 | Level 8 | Level 9 |
|---|---|---|---|---|---|---|---|---|---|
| Methyl methacrylate | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Ethyl methacrylate | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 2-Picoline | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| n-Nitrosomethylethylamine | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Methyl methanesulfonate | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| n-Nitrosodiethylamine | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Ethyl methanesulfonate | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Benzaldehyde | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Pentachloroethane | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Acetophenone | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| n-Nitrosopyrrolidine | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| n-Nitrosomorpholine | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| o-Toluidine | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| n-Nitrosopiperidine | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| O,o,o-Triethyl-Phosphorothioate | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| A,a-Dimethyl-phenethylamine | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |

**LVI Calibration Levels, Appendix IX Standard, µg/mL**

| Semivolatiles | Level 1 | Level 2 | Level 3 | Level 4 | Level 5 | Level 6 | Level 7 | Level 8 | Level 9 |
|---|---|---|---|---|---|---|---|---|---|
| 2,6-Dichlorophenol | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Hexachloropropene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Benzothiazole | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Caprolactam | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| p-Phenylenediamine | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| n-Nitrosodi-n-butylamine | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Safrole | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Phthalic anhydride | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 1-Methylnaphthalene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 1,2,4,5-Tetrachlorobenzene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Isosafrole, cis | .5 | 1 | 2.5 | 5 | 10 | 15 | 20 | 25 | 30 |
| Isosafrole, trans | .5 | 1 | 2.5 | 5 | 10 | 15 | 20 | 25 | 30 |
| Biphenyl | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 1,4-Dinitrobenzene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 1,4-Naphthoquinone | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 1,3-Dinitrobenzene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Pentachlorobenzene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 1-Naphthylamine | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 2-Naphthylamine | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 2,3,4,6-Tetrachlorophenol | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 5-Nitro-o-toluidine | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Thionazin | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 1,3,5-Trinitrobenzene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Sulfotepp | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Phorate | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Phenacetin | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Diallate 1 | .5 | 1 | 2.5 | 5 | 10 | 15 | 20 | 25 | 30 |
| Diallate 2 | .5 | 1 | 2.5 | 5 | 10 | 15 | 20 | 25 | 30 |
| Dimethoate | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 4-Aminobiphenyl | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Pentachloronitrobenzene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Pronamide | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Disulfoton | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |

**LVI Calibration Levels, Appendix IX Standard, µg/mL**

| Semivolatiles | Level 1 | Level 2 | Level 3 | Level 4 | Level 5 | Level 6 | Level 7 | Level 8 | Level 9 |
|---|---|---|---|---|---|---|---|---|---|
| 2-sec butyl-4,6-dinitrophenol (Dinoseb) | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Methyl parathion | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 4-Nitroquinoline-1-oxide | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Parathion | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Isodrin | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Kepone | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Famphur | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Methapyrilene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Octachlorostyrene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Aramite 1 | .5 | 1 | 2.5 | 5 | 10 | 15 | 20 | 25 | 30 |
| Aramite 2 | .5 | 1 | 2.5 | 5 | 10 | 15 | 20 | 25 | 30 |
| p-(Dimethylamino)azobenzene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| p-Chlorobenzilate | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 3,3'-Dimethylbenzidine | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 2-Acetylaminofluorene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Dibenz (a,j)acridine | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Hexachlorophene | 10 | 20 | 50 | 100 | 200 | 300 | 400 | 500 | 600 |
| 7,12-Dimethylbenz(a)anthracene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| 3-Methylcholanthrene | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| **2-Fluorophenol (Surrogate Standard** | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| **Phenol-d5 (Surrogate Standard)** | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| **Nitrobenzene-d5 (Surrogate Standard)** | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| **2-Fluorobiphenyl (Surrogate Standard)** | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| **2,4,6-Tribromophenol (Surrogate Standard)** | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| **Terphenyl-d14 (Surrogate Standard**) | 1 | 2 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |

**Table 4**
**Minimum Response Factor Criteria**

| Semivolatile Compounds | Minimum Response Factor (RF) |
|---|---|
| Benzaldehyde | 0.010 |

**Table 4**
**Minimum Response Factor Criteria**

| Semivolatile Compounds | Minimum Response Factor (RF) |
|---|---|
| Phenol | 0.800 |
| Bis(2-chloroethyl)ether | 0.700 |
| 2-Chlorophenol | 0.800 |
| 2-Methylphenol | 0.600 |
| 2,2'-Oxybis-(1-chloropropane) | 0.010 |
| Acetophenone | 0.010 |
| 4-Methylphenol | 0.600 |
| N-Nitroso-di-n-propylamine | 0.500 |
| Hexachlorethane | 0.300 |
| Nitrobenzene | 0.200 |
| Isophorone | 0.400 |
| 2-Nitrophenol | 0.100 |
| 2,4-Dimethylphenol | 0.200 |
| Naphthalene | 0.700 |
| 4-Chloroanline | 0.010 |
| Hexachlorobutadiene | 0.010 |
| Caprolactam | 0.010 |
| 4-Chloro-3-methylphenol | 0.200 |
| 2-Methylnaphthalene | 0.400 |
| Hexachlorocyclopentadiene | 0.050 |
| 2,4,6-Trichlorophenol | 0.200 |
| 2,4,5-Trichlorophenol | 0.200 |
| 1,1'-Biphenyl | 0.010 |
| 2-Chloronaphthanlene | 0.800 |
| 2-Nitroaniline | 0.010 |
| Dimethyl phthalate | 0.010 |

**Table 4**
**Minimum Response Factor Criteria**

| Semivolatile Compounds | Minimum Response Factor (RF) |
|---|---|
| 2,6-Dinitrotulene | 0.200 |
| Acenaphthylene | 0.900 |
| 3-Nitroaniline | 0.010 |
| Acenaphthene | 0.900 |
| 2,4-Dinitrophenol | 0.010 |
| 4-Nitrophenol | 0.010 |
| Dibenzofuran | 0.800 |
| 2,4-Dinitrotoluene | 0.200 |
| Diethyl phthalate | 0.010 |
| 1,2,4,5-Tetrachlorobenzene | 0.010 |
| 4-Chlorophenyl-phenyl ether | 0.400 |
| Fluorene | 0.900 |
| 4-Nitroaniline | 0.010 |
| 4,6-Dinitro-2-methylphenol | 0.010 |
| N-Nitrosodiphenylamine | 0.010 |
| Hexachlorobenzene | 0.100 |
| Atrazine | 0.010 |
| Pentachlorophenol | 0.050 |
| Phenanthrene | 0.700 |
| Anthracene | 0.700 |
| Carbazole | 0.010 |
| Di-n-butyl phthalate | 0.010 |
| Fluoranthene | 0.600 |
| Pyrene | 0.600 |
| Butyl benzyl phthalate | 0.010 |
| 3,3'-Dichlorobenzidine | 0.010 |

**Table 4**
**Minimum Response Factor Criteria**

| Semivolatile Compounds | Minimum Response Factor (RF) |
|---|---|
| Benzo(a)anthracene | 0.800 |
| Chrysene | 0.700 |
| Bis-(2-ethylhexyl)phthalate | 0.010 |
| Di-n-octyl phthalate | 0.010 |
| Benzo(b)fluoranthene | 0.700 |
| Benzo(k)fluoranthene | 0.700 |
| Benzo(a)pyrene | 0.700 |
| Indeno(1,2,3-cd)pyrene | 0.500 |
| Dibenz(a,h)anthracene | 0.400 |
| Benzo(g,h,i)perylene | 0.500 |
| 2,3,4,6-Tetrachlorophenol | 0.010 |

TestAmerica St. Louis has established a default minimum response factor of 0.01 for compound not identified in this table, except for Famphur, Hexachlorophene, Kepone, Phthalic Anhydride which have a minimum response factor of 0.001.

**Table 5**

**Semi-Volatile Internal Standards with Corresponding Analytes***

| 1,4-Dichlorobenzene-d4 | Naphthalene-d8 | Acenaphthene-d10 | Phenanthrene-d10 | Chrysene-d12 | Perylene-d12 |
|---|---|---|---|---|---|
| 1,4-Dioxane | Acetophenone | cis-Isosafrole | 5-Nitro-o-toluidine | Benzidine | Benzo(b)fluoranthene |
| Methyl methacrylate | N-Nitrosopyrrolidine | 1,2,4,5-Tetrachlorobenzene | 4,6-Dinitro-2-methylphenol | Pyrene | Benzo(k)fluoranthene |
| Pyridine | N-Nitrosomorpholine | Hexachlorocyclopentadiene | N-Nitrosodiphenylamine | Terphenyl-d14 | 7,12-Dimethyl benz(a)anthracene |
| N-Nitrosodimethylamine | O-Toluidine | 2,4,6-Trichlorophenol | Tri-n-butyl phosphate | Aramite 1 | Hexachlorophene |
| N,N-Dimethylformamide | Nitrobenzene-d5 | 2,4,5-Trichlorophenol | Azobenzene | Kepone | Benzo(a)pyrene |
| Ethyl methacrylate | Nitrobenzene | 2-Fluorobiphenyl | Sulfotep | Aramite 2 | 3-methylcholanthrene |
| 2-Picoline | N-Nitrosopiperidine | trans-Isosafrole | Diallate 1 | p-(dimethylamino) azobenzene | Indeno (1,2,3-cd) pyrene |
| N-Nitrosomethylethylamine | Isophorone | Biphenyl | 1,3,5-Trinitrobenzene | Chlorobenzilate | Dibenz(a,h)anthracene |
| Methyl methanesulfonate | 2-Nitrophenol | 2-Chloronaphthalene | Phorate | 3,3'-Dimethylbenzidine | Benzo(g,h,i)perylene |
| 2-Fluorophenol | 2,4-Dimethylphenol | 2-Nitroaniline | 4-Bromophenyl phenyl ether | Butyl benzyl phthalate | |
| Cyclohexanol | Bis (2-chloroethoxy) methane | 1,4-Naphthoquinone | Phenacetin | 2-Acetylaminofluorene | |
| N-Nitrosodiethylamine | o,o,o-Triethylphosphorothioate | 1,4-Dinitrobenzene | Diallate 2 | Famphur | |
| Ethyl methanesulfonate | Benzoic acid | Dimethylphthalate | Hexachlorobenzene | Benzo (a) anthracene | |
| Benzaldehyde | 2,4-Dichlorophenol | 1,3-Dinitrobenzene | Dimethoate | 4,4'-methylenebis (2-Chloroaniline) | |
| Phenol-d5 | a,a-Dimethylphenethylamine | Acenaphthylene | Atrazine | 3,3'-Dichlorobenzidine | |
| Phenol | 1,2,4-Trichlorobenzene | 2,6-Dinitrotoluene | Tris(2-chloroethyl) phosphate | Chrysene | |
| Aniline | Naphthalene | 3-Nitroaniline | 4-Aminobiphenyl | Bis (2-ethylhexyl) phthalate | |
| Pentachloroethane | 4-Chloroaniline | Acenaphthene | Pentachlorophenol | Di-n-octyl phthalate | |
| Bis (2-chloroethyl) ether | 2,6-Dichlorophenol | 2,4-Dinitrophenol | Pronamide | | |
| 2-Chlorophenol | Hexachloropropene | 4-Nitrophenol | Pentachloronitrobenzene | | |
| 1,3-Dichlorobenzene | Hexachlorobutadiene | Dibenzofuran | Phenanthrene | | |

**Table 5**

**Semi-Volatile Internal Standards with Corresponding Analytes***

| 1,4-Dichlorobenzene-d4 | Naphthalene-d8 | Acenaphthene-d10 | Phenanthrene-d10 | Chrysene-d12 | Perylene-d12 |
|---|---|---|---|---|---|
| 1,4-Dichlorobenzene | Benzothiazole | Pentachlorobenzene | Disulfoton | | |
| 1,2-Dichlorobenzene | Caprolactam | 2,4-Dinitrotoluene | Anthracene | | |
| Benzyl alcohol | N-Nitroso-di-n-butylamine | 1-Naphthylamine | Dinoseb | | |
| 2-Methylphenol | p-Phenylenediamine | 2-Naphthylamine | Carbazole | | |
| Bis (2-chloroisopropyl) ether | 4-Chloro-3-methylphenol | 2,3,4,6-Tetrachlorophenol | Methyl parathion | | |
| 3,4-Methylphenol | Safrole | Diethylphthalate | Di-n-butyl phthalate | | |
| N-Nitroso-di-n-propylamine | 2-Methylnaphthalene | Fluorene | Parathion | | |
| Hexachloroethane | | 4-Chlorophenyl phenyl ether | 4-Nitroquinoline-1-oxide | | |
| | | Thionazin | Methapyrilene | | |
| | | 4-Nitroaniline | Isodrin | | |
| | | 2,4,6-Tribromophenol | Fluoranthene | | |
| | | | | | |

* ISTD assignment is based on instrument operating conditions and column type and may vary slightly from this listing.

**Table 6a Acid Surrogates with Corresponding Analytes**

| 2-Fluorophenol | Phenol-d5 | 2,4,6-Tribromophenol |
|---|---|---|
| none | Phenol | 2,4,6-Trichlorophenol |
| | 2-Clorophenol | 2,4,5-Trichlorophenol |
| | 2-Methylphenol | 2,4-Dinitrophenol |
| | 3,4-Methylphenol | 4-Nitrophenol |
| | 2-Nitrophenol | 2,3,4,6-Tetrachlorophenol |
| | 2,4-Dimethylphenol | 4,6-Dinitro-2-methyl phenol |
| | Benzoic acid | Pentachlorophenol |
| | 2,4-Dichlorophenol | |
| | 2,6-Dichlorophenol | |
| | 4-Chloro-3-methyl -phenol | |

## Table 6b Base/Neutral Surrogates with Corresponding Analytes

| **Nitrobenzene-d5** | **2-Fluorobiphenyl** | **Terphenyl-d14** |
|---|---|---|
| 1,4-Dioxane | Benzothiazole | Phenanthrene |
| Methyl methacrylate | Caprolactam | Disulfoton |
| Pyridine | N-Nitrosodi-n-butylamine | Anthracene |
| N-Nitrosodimethylamine | p-Phenylenediamine | Dinoseb |
| Dimethylformamide | Safrole | Carbazole |
| Ethyl methacrylate | 2-Methylnaphthalene | Methyl parathion |
| 2-Picoline | 1-Methylnaphthalene | Di-n-butyl phthalate |
| N-Nitrosomethylethylamine | cis-Isosafrole | Parathion |
| Methyl methanesulfonate | 1,2,4,5-Tetrachlorobenzene | 4-Nitroquinoline-1-oxide |
| Cyclohexanol | Hexachlorocyclopentadiene | Methapyrilene |
| N-Nitrosodiethylamine | trans-Isosafrole | Isodrin |
| Ethyl methanesulfonate | Biphenyl | Fluoranthene |
| Benzaldehyde | 2-Chloronaphthalene | Benzidine |
| Aniline | 2-Nitroaniline | Pyrene |

Pentachloroethane
Bis (2-Chloroethyl) ether
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Naphthoquinone
1,4-Dinitrobenzene
Dimethyl phthalate
1,3-Dinitrobenzene
Aramite 1 & 2
Kepone
p-(dimethylamino) azobenzene

## Table 6b Base/Neutral Surrogates with Corresponding Analytes

| Nitrobenzene-d5 | 2-Fluorobiphenyl | Terphenyl-d14 |
|---|---|---|
| 1,4-Dichlorobenzene | Acenapthylene | Chlorobenzilate |
| Benzyl alcohol | 2,6-Dinitrotoluene | 3,3-Dimethylbenzidine |
| 2,2'-oxybis (1-Chloro propane) | 3-Nitroaniline | Butyl benzyl phthalate |
| Acetophenone | Acenapthene | 2-Acetylaminofluorene |
| N-Nitrosopyrrolidine | Dibenzofuran | Famphur |
| N-Nitrosodinpropylamine | Pentachlorobenzene | Benz (a) anthracene |
| N-Nitrosomorpholine | 2,4-Dinitrotoluene | 4,4'-Methylenebis (2-Chloro -aniline) |
| o-Toluidine | 1-Naphthylamine | 3,3'-Dichlorobenzidine |
| Hexachloroethane | 2-Naphthylamine | Chrysene |
| Nitrobenzene | Diethyl phthalate | Bis (2-ethylhexyl) phthalate |
| N-Nitrosopiperidine | Fluorene | Di-n-octyl phthalate |
| Isophorone | 4-Chlorophenyl phenyl ether | Benzo (b) fluoranthene |
| Bis (2-Chloroethoxy) Methane | Thionazin | Benzo (k) fluoranthene |
| O,o,o-Triethylphosphoro Thioate | 5-Nitro-o-toluidine | 7,12-Dimethylbenz (a) anthracene |
| A,a-Dimethylphenethyl Amine | 4-Nitroaniline | Hexachlorophene |
| 1,2,4-Trichlorobenzene | N-Nitrosodiphenylamine | Benzo (a) pyrene |
| Naphthalene | Tri-n-butyl phthalate | 3-methylcholanthrene |
| 4-Chloroaniline | Azobenzene | Indeno (1,2,3-cd) pyrene |
| Hexachloropropene | Sulfotepp | Dibenz (a,h) anthracene |
| Hexachlorobutadiene | Diallate 1 & 2 | Benzo (g,h,i) perylene |
| | 1,3,5-Trinitrobenzene | |
| | Phorate | |
| | 4-Bromophenyl phenyl ether | |
| | Phenacetin | |
| | Hexachlorobenzene | |
| | Dimethoate | |
| | Atrazine | |
| | Tris(2-chloroethyl)phosphate | |
| | 4-Aminobiphenyl | |

Pronamide
Pentachloronitrobenzene

# Title: EXTRACTION AND CLEANUP OF ORGANIC COMPOUNDS FROM WATERS AND SOILS

**Approvals (Signature/Date):**

Jeff Winkler 9-16-14
Jeff Winkler Date
Extractable Dept. Supervisor

Michael Ridenhower 9/16/14
Michael Ridenhower Date
Health & Safety Manager / Coordinator

Marti Ward 9-16-14
Marti Ward Date
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Elaine Wild Date
Laboratory Director

**This SOP was previously identified as SOP No. ST-OP-0002 Rev. 22**



**Facility Distribution No.:** 0 **Distributed To:** See Electronic Distribution Sheet

## 1.0 SCOPE AND APPLICATION

1.1. This SOP describes procedures for extraction preparation of semivolatiles, pesticide, PCB, and hydrocarbon organic analytes in aqueous, TCLP leachate, and soil matrices for analysis by Gas Chromatography (GC) and Gas Chromatography / Mass Spectrometry (GC/MS).

1.2. This SOP is based on SW-846 Methods 3500C, 3510C, 3520C, 3550C, 3600C, 3620C, 3650B, 3660B, AND 3665A.

1.3. Sample homogenization is not covered in this SOP. Refer to SOP ST-QA-0038.

1.4. The clean up methods: GPC , florisil, sulfuric acid, sulfur removal are described.

1.5. The procedures are based on SW-846 and 600 series methodology and are acceptable for measurements made to comply with the Resource Conservation and Recovery Act (RCRA) and for wastewater testing.

1.6. See individual analysis SOPs: ST-GC-0005, ST-GC-0013, ST-GC-0015, ST-GC-0016, and ST-MS-0001 for analytical requirements.

## 2.0 SUMMARY OF METHOD

2.1. Continuous Liquid/Liquid Extraction

2.1.1 A measured volume of sample, typically 1 liter, is placed into a continuous liquid/liquid extractor, adjusted, if necessary, to a specific pH and extracted with methylene chloride for 18-24 hours.

2.2. Separatory Funnel Extraction

2.2.1 A measured volume of sample, typically 1 liter, is adjusted, if necessary, to a specified pH and serially extracted with appropriate solvent using a separatory funnel.

2.2.2 For an LVI extraction, a measured volume of sample, typically 200 mL is adjusted, if necessary, to a specified pH and serially extracted with methylene chloride using a 500 mL separatory funnel.

2.3. Sonication Extraction

2.3.1 A measured weight of sample, typically 30 g, is mixed with anhydrous sodium sulfate to form a free flowing powder. This is solvent extracted three times using an ultrasonic horn.

2.4. Waste Dilution

2.4.1 This method is used for materials that are soluble in an organic solvent.

2.5. Cleanup

2.5.1 Procedures are presented for removing interferents from sample extracts, and for drying and concentrating of the extract to final volume for analysis.

## 3.0 DEFINITIONS

3.1. See the TestAmerica St. Louis Quality Assurance Manual (ST-QAM) for a glossary of common laboratory terms and data reporting qualifiers.

3.2. Lower Volume Initiative (LVI): procedures which provide for the collection of reduced volume of water samples while maintaining standard and achievable reporting limits.

## 4.0 INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus. All these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2. Visual interferences or anomalies (such as foaming, emulsions, odor, etc.) must be documented.

## 5.0 SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), Radiation Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.2. Specific Safety Concerns or Requirements

5.2.1 The use of separatory funnels to extract aqueous samples with Methylene Chloride creates excessive pressure very rapidly. Initial venting should be done immediately after the sample container has been sealed and inverted. Vent the funnel into the hood away from people and other samples. This is considered a high-risk activity, and must be performed in a ventilated hood and safety glasses or goggles must be worn.

5.2.2 Nitrile gloves should be used when performing this procedure. Latex and vinyl gloves provide no significant protection against organic solvents.

5.2.3 During Kuderna-Danish (KD) concentration technique (if used), do not allow the extract to boil to dryness. The solvent vapors remaining in the KD apparatus may superheat and create an explosion or fire hazard. The KD apparatus has ground glass joints which can become stuck. Technicians must use Kevlar or other cut/puncture resistant gloves when separating stuck joints. Broken glassware must be disposed of or repaired.

5.2.4 The addition of Sulfuric Acid or Potassium Permanganate to the sample extract has the potential to create an exothermic reaction. Both can cause severe burns.

5.2.5 Ultrasonic disrupters can produce high intensity noise and must be used in an area with adequate noise protection.

5.3 Primary Materials Used

5.3.1 The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

| Material (1) | Hazards | Exposure Limits (2) | Signs of Exposure |
|---|---|---|---|
| Sulfuric Acid | Corrosive Oxidizer | 1 mg/m3 (TWA) | Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may |

| | | | |
|---|---|---|---|
| | Dehydrator<br>Poison<br>Carcinogen | | include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness. |
| Sodium Hydroxide | Corrosive<br>Poison | 2 ppm<br>(TWA) | This material will cause burns if comes into contact with the skin or eyes. Inhalation of Sodium Hydroxide dust will cause irritation of the nasal and respiratory system. |
| Acetone | Flammable | 1000 ppm<br>(TWA) | Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache. |
| Methanol (Methyl Alcohol) | Flammable<br>Poison<br>Irritant | 200 ppm<br>(TWA) | A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes. |
| Hexane | Flammable<br>Irritant | 500 ppm<br>(TWA) | Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes. |
| Acetonitrile | Flammable<br>Poison | 40 ppm<br>(TWA) | Early symptoms may include nose and throat irritation, flushing of the face, and chest tightness. Prolonged exposure to high levels of vapors may cause formation of cyanide anions in the body. |
| Methylene chloride | Carcinogen<br>Irritant | 25 ppm<br>(TWA)<br>125 ppm<br>(STEL) | Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin. |
| 1 – Always add acid to water to prevent violent reactions. | | | |
| 2 – Exposure limit refers to the OSHA regulatory exposure limit. | | | |
| TWA – Time Weighted Average | | | |
| STEL – Short Term Exposure Limit | | | |

## 6.0 EQUIPMENT AND SUPPLIES

6.1. Labware is cleaned to remove any residual organics. Please refer to SOP ST-OP-0001 for detailed glassware cleaning procedures.

6.2. Separatory Funnel: 2 L; 500 mL

6.3. Balance:

6.3.2 For Waters - greater than 1400 g capacity, accurate +/- 0.1 g

6.3.3 For Soils – accurate to +/- 0.01 g

6.4. pH indicator paper, wide-range, peroxide test strips, chlorine test strips

6.5. Graduated cylinder: 1 liter. (other sizes may be used)

6.6. Solvent Dispenser Pump or 100 mL Graduated Cylinder

6.7. Continuous Liquid/Liquid Extractors

6.8. Round or flat Bottom: 250, 500 mL or 1 L

6.9. Boiling Chips: Contaminant free, approximately 10/40 mesh (Teflon® PTFE, carbide or equivalent).

6.10. Cooling Condensers

6.11. Heating Mantle: Rheostat controlled

6.12. Beakers: 250, 400 & 1000 mL, graduated (Note: used as backup equipment)

6.13. Mason Jars

6.14. 250 mL and 500 mL chem. bottles

6.15. Sonicator (at least 300 watts)

6.16. Sonicator horn, 3/4 inch

6.17. Kuderna-Danish (K-D) Apparatus: 500 mL, 250mL

6.18. Concentrator Tip: 10 mL, attached to K-D with clips Class A

6.19. Snyder Column: Three ball macro

6.20. Water Bath: Heated, with concentric ring cover, capable of temperature control (± 5°C) up to 95°C. The bath must be used in a hood or with a solvent recovery system.

6.21. Vials: Glass, 2 mL, 4 mL, and 40 mL capacity with Teflon®-lined screw cap

6.22. Nitrogen Blowdown Apparatus

6.23. Syringes: 10µl – 1000 µl

6.24. 0.45 micron PTFE filter

6.25. Phase Separation Paper (filter paper)

6.26. Poly Funnel: 75 X 75 mm

6.27. Transfer Pipettes

6.28. Aluminum foil

6.29. Muffle ovens

6.30. Drying Ovens

| EQUIPMENT AND SUPPLIES FOR CLEANUP |
|---|
| Gel permeation chromatography system (OI Analytical Autoprep 2000 with OI Analytical 1096TB Autosampler).<br>Bio Beads: (S-X3) -200-400 mesh, 70 gm (Bio-Rad Laboratories, Richmond, CA, Catalog 152-2750 or equivalent).<br>Chromatographic column: 700 mm x 25 mm ID glass column. Flow is upward.<br>Ultraviolet detector: Fixed wavelength (254 nm) and a semi-prep flow-through cell. |

## 7.0 REAGENTS AND STANDARDS

7.1 All standards and reagent preparation, documentation and labeling must follow the requirements of SOP ST-QA-0002, current revision.

7.2 DI water, organic free

7.3 Sodium hydroxide (NaOH), Pellets: Reagent Grade.
7.3.1 Sodium hydroxide solution, 10 N: Dissolve 40 g of NaOH in reagent water and dilute to 1000 mL. Depending on purity of NaOH pellets, 37% KOH is needed.

7.4 Sulfuric acid ($H_2SO_4$), Concentrated: Reagent Grade.
7.4.1 Sulfuric acid (1:1): Carefully add 500 mL of $H_2SO_4$ to 500 mL of reagent water. Mix well.

7.5 90:10 Hexane:Acetone

7.6 Sodium sulfate ($Na_2SO_4$), J.T. Baker Catalog No. 3375-07-5345200, Granular, Anhydrous (ST certified).
7.6.1 Purify by heating at 400°C a minimum of four hours.

7.7 Sand
7.7.1 Muffle for 2 hours at 400°C; cool in drying oven for four hours at 105°C

7.8 Extraction/Exchange Solvents: Methanol, Methylene chloride, Hexane, Acetonitrile, Acetone, and 1:1 Methylene chloride/Acetone mixed solvent, pesticide quality or equivalent

7.9 Nitrogen: reagent grade.

7.10 Supelco Superclean ENVI Florisil Cartridges - precertified

7.11 Organic standards are purchased as certified solutions or prepared from neats.
7.11.1 Refer to SOP ST-QA-0002, “Standards and Reagent Preparation” for the required storage conditions and shelf lives of the standards used in this procedure. All stock standards must be protected from light. Standard solutions must be replaced by the manufacturer’s expiration date or 6 months after opening the ampoule (or making the standard if from neat materials), whichever is shorter.
7.11.2 Standards must be allowed to come to room temperature before use.

7.11.3 Surrogate spiking standards are prepared as dilutions of the stock standards. See recipe in the LIMS Reagent program.

7.11.3.1 The same spiking solution is used for the matrix spike and the Laboratory Control Sample. Spiking standards are purchased or prepared as dilutions of the stock standards. See recipe in the LIMS Reagent program.

7.12 5% Aqueous Potassium Permanganate – Reagent grade. This chemical is a powerful oxidizer and should be handled with care. Consult MSDS for more information if using for the first time.

7.13 GPC calibration solution - prepare or purchase a solution in methylene chloride that contains the following analytes in the concentrations listed below:

| Analyte | mg/mL |
|---|---|
| Corn Oil | 25.0 |
| Bis (2-ethylhexyl) phthalate | 1.0 |
| Methoxychlor | 0.2 |
| Perylene | 0.02 |
| Sulfur | 0.08 |

## 8.0 SAMPLE COLLECTION PRESERVATION AND STORAGE

8.1 TestAmerica St. Louis supplies sample containers and chemical preservatives in accordance with the method. TestAmerica St. Louis does not perform sample collection. Samplers should reference the methods referenced and other applicable sample collection documents for detailed collection procedures. Sample volumes and preservative information is given in ST-PM-0002**.**

8.2 Water samples are unpreserved and stored at 4 ± 2˚C.

8.3 Soil samples are refrigerated at 4 ± 2˚C.

8.4 Holding Times

8.4.1 Extraction is initiated within 7 days of the sampling date for aqueous samples, 14 days for solid and waste samples.

8.4.2 For TCLP leachates, the extraction is initiated within seven days from when the TCLP Leach tumbling has been completed, excluding the filtration step. If the filtration step requires extended time, then this time counts as part of the seven day holding time.

8.4.3 Analysis of the extracts is completed within forty days of extraction.

8.4.4 Holding times do not apply to PCB method 8082A.

## 9.0 QUALITY CONTROL

9.1. **Batch**

9.1.1 A sample batch is a maximum of 20 environmental samples, which are prepared together using the same process and same lot(s) of reagents. Where no preparation method exists (e.g. water sample volatile organics, water sample anion analysis ) the batch is comprised of a maximum of 20 environmental samples which are analyzed together with the same process, lots of reagents and personnel.

9.1.2 Instrument conditions must be the same for all standards, samples and QC samples.

9.1.3 Batch QC consists of a method blank, a Laboratory Control Sample (LCS), and Matrix Spike (MS) and Matrix Spike Duplicate (MSD). In the event that there is insufficient sample to analyze a MS/MSD, an LCS Duplicate (LCSD) is prepared and analyzed.

9.1.4 A method blank and LCS may be shared across QC programs provided the actual “sample

batch" does not exceed 20 environmental samples. Duplicates (and MS/MSD if applicable) must be performed, as required by clients, for each separate QC program.

9.2 **Method Blank**

9.2.1 A method blank is a blank matrix processed simultaneously with, and under the same conditions as, samples through all steps of the procedure.

9.2.2 A method blank must be prepared with every sample batch.

9.2.3 Surrogates are spiked into the method blank at the same level as the samples.

9.2.4 Aqueous Method Blanks use 1000 mL of DIwater spiked with the surrogates. Solid method blanks use 30 g of sodium sulfate spiked with the surrogates.

9.2.5 LVI Method blank uses 200 mL of DI water spiked with the surrogates.

9.2.6 TCLP method blanks use 100 mL of leachate fluid (200 mL for BNA) spiked with the surrogates. Use the leaching fluid type (1 or 2) that was used in leaching the samples. If both fluid types are used in a batch, a method blank with each fluid is prepared.

9.3 **Laboratory Control Sample**

9.3.1 An LCS is a blank matrix spiked with a known amount of analyte(s), processed simultaneously with, and under the same conditions as, samples through all steps of the analytical procedure.

9.3.2 An LCS must be prepared with every sample batch.

9.3.3 Aqueous LCS use 1000 mL of DI water fortified with the organic analytes of interest.

9.3.4 LVI LCS uses 200 mL of DIwater fortified with the organic analytes of interest.

9.3.5 Solid LCS use 30 g of sodium sulfate fortified with the organic analytes of interest.

9.3.6 TCLP LCS use 100 mL (or 200 mL for BNA) of leachate fluid. Use the leaching fluid type (1 or 2) that was used in leaching the samples. If both fluid types were used in a batch, a LCS with each fluid is prepared.

9.4 **Matrix Spike (MS) /Matrix Spike Duplicate (MSD)**

9.4.1 A Matrix Spike is an aliquot of a field sample to which a known amount of target analyte(s) is added, and is processed simultaneously with, and under the same conditions as, samples through all steps of the analytical procedure.

9.4.2 MS/MSD samples do not count towards the 20 environmental samples in a sample batch.

9.4.3 MS/MSD samples, when requested, must be performed with every sample batch and every LIMS batch.

9.4.4 If there is insufficient sample to perform an MS/MSD, a duplicate LCS is analyzed. An NCM is written to document the insufficient volume and the utilization of an LCSD to demonstrate precision.

9.5 **Surrogates**

9.5.1 Surrogates are organic compounds which are similar to the target analyte(s) in chemical composition and behavior in the analytical process, but which are not normally found in environmental samples.

9.5.2 Each applicable sample, blank, LCS and MS/MSD is spiked with surrogate standards. Surrogate spike recoveries must be evaluated by determining whether the concentration (measured as percent recovery) falls within the required recovery limits.

9.6 **Procedural Variations/ Nonconformance and Corrective Action**

9.6.1 Any variation shall be completely documented using a Nonconformance Memo and approved by the Supervisor and QA Manager. See SOP ST-QA-0036 for details regarding the NCM process.

9.6.2 Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the Supervisor and QA Manager. See SOP ST-QA-0036 for details regarding the NCM process.

## 10.0 CALIBRATION AND STANDARDIZATION

10.1 Balance calibration must be checked daily when used. Refer to SOP ST-QA-0005, "Calibration and Verification Procedure for Thermometers, Balances, Weights and Pipette".

10.2 Thermometers must be checked as prescribed in SOP ST-QA-0005, "Calibration and Verification Procedure for Thermometers, Balances, Weights and Pipette".

10.3 If Class A concentrator tips are not available the Concentrator tip calibration is checked gravimetrically at the 5 and 10 mL marks when new lots are received.
- 10.3.1 Place the empty tip into a suitable container to allow tip to remain upright, place on balance and tare.
- 10.3.2 Add DI water exactly to the 5 mL/10 mL mark and record weight. Criteria is ±3% (9.7 to 10.3 mL).
- 10.3.3 This is not required for Class A concentrator tips.

10.4 Sonicators are calibrated (tuned) each day of use.
CAUTION: Hearing protection must be worn when tuning the sonicators.
- 10.4.1 See work instruction ST-WI-0010 for tuning instructions for the different horns.

10.5 Florisil cartridge performance check – required if pre-certified cartridges are not used)
- 10.5.1 Every lot number of Florisil must be tested before use.
  - 10.5.1.1 Check with the lab to ensure lot check was performed for the lot in use.
  - 10.5.1.2 If check was not performed by another TestAmerica location
    - 10.5.1.2.1 Add 0.5 ug/mL of 2,4,5-trichlorophenol solution and 0.5 mL of GC Standard Mix A (midpoint concentration) to 9 mL hexane.
    - 10.5.1.2.2 Add the concentrate to a pre-washed Florisil cartridge and elute with 9 mL hexane/acetone [(90:10)(v/v)].
    - 10.5.1.2.3 Rinse cartridge with 1.0 mL hexane two additional times.
    - 10.5.1.2.4 Concentrate eluate to 1.0 mL final volume and transfer to vial.
      - 10.5.1.2.4.1 Concentration may be done by any of the techniques given in section 11.
    - 10.5.1.2.5 Analyze the solution by GC/EC.
      - 10.5.1.2.5.1 The test sample must show 80 to 120% recovery of all pesticide analytes with <5% trichlorophenol recovery, and no peaks interfering with target compounds can be detected.
      - 10.5.1.2.5.2 The trichlorophenol standard has a lifetime of six months. The cartridge has a lifetime of one year or the manufacturer's expiration date, whichever is shorter.
      - 10.5.1.2.5.3 Alternatively, this standard may be purchased as a stock solution.

10.6 See individual analysis SOPs: ST-GC-0005, ST-GC-0013, ST-GC-0015, ST-GC-0016, and ST-MS-0001 for instrument calibration requirements.

## 11.0 PROCEDURE

11.1 Aqueous Samples – Preparation (SW846 3500C)
- 11.1.1 Weigh full sample bottle, without the cap.
  - 11.1.1.1 If a sample is known or suspected (based upon client knowledge, project scope, or

site history) to have a high density (>1.2 g/mL, e.g. a brine or waste) or a low density (<0.98 g/mL, e.g. mixed solvent), the sample density will be measured and the volume determined arithmetically (sample mass divided by the density equals the volume).

11.1.2 Thoroughly mix the liquid sample in accordance with SOP ST-QA-0038.

11.1.3 The normal sample volume is 1 liter. LVI sample volume is 200 mL.

11.1.3.1 Other sample volumes may be used to obtain specific reporting limits, and reduced sample volumes, diluted to 1 liter with DI water, may be used for very dirty samples. See manager/supervisor for instruction.

11.1.3.2 LVI is not to be used for South Carolina work. The state requires certification for this method and TestAmerica St. Louis does not have the certification at this time.

11.1.4 Pour sample aliquot into a Separatory Funnel or Continuous Liquid/Liquid extraction vessel. Details available in section 11.2 and 11.3 respectively..

11.1.5 Take pH of sample

11.1.5.1 For Pesticides record pH on extraction log to demonstrate pH between 5 and 9

11.1.5.2 As necessary, adjust sample pH as indicated in Table 1.

11.1.5.3 For Base.Neutral/Acids the typical order of extraction is as follows: reduce pH to 1-2 with 1:1 $H_2SO_4$. Then, perform the extraction with 100 mL of methylene chloride. Repeat the extraction in acid twice more using 50mL methylene chloride. Adjust pH to 13-14 with NaOH. Add 100 mLs of methylene chloride and perform extraction. Repeat the following last two base extractions with 50 mLs of methylene chloride. (NOTE: for SIM analysis, only the base portion of the extraction needs to be performed.)

11.1.5.4 For LVI Base Neutral/Acids follow steps above using 40mL, 20mL, 20mL methylene chloride for acids and again for base

11.1.5.5 Check each sample with pH paper after each pH adjustment. Record adjusted pH.

11.1.5.6 For method EPA 608, check for residual chlorine and record.

11.1.6 For all analyses (except SIM PAH which is 10uL), add 0.5 mL surrogate solution (Table 3) to samples and QC.

11.1.7 Spike LCS and MS/MSD with spiking mix applicable to the requested analysis.

11.1.7.1 Document spiking volumes and standard numbers on the bench sheet.

11.1.7.2 Change the caps on the standards and return spiking solutions to the refrigerator as soon as possible.

11.1.8 After the sample bottle is emptied, rinse the container with approximately 60 mL of the extraction solvent. (For LVI extraction 20 mL of the extraction solvent is used.) Gently swirl the solvent in the container, rinsing the sides of the container thoroughly and add solvent rinse to the extraction vessel.

11.1.8.1 If the entire sample volume is not used the container cannot be solvent rinsed. Organic materials adhering to the container walls will be absent in the extraction process. An NCM is written documenting that the container rinse could not be performed.

11.1.9 Weigh the empty sample bottle, without the cap.

11.1.9.1 Volume is calculated by gravimetric determination assuming a sample density of 1. Samples that are not aqueous or are suspected to have a density greater than 1.2 will have aliquots taken for density analysis to correct volume for density.

11.1.10 Using a graduated cylinder, measure 100 mL of leachate for TCLP pesticides and PCBs , 200 mL of leachate for TCLP semivolatiles and 200mL for LVI. For TCLPs dilute to about 1 liter with DI water. For BNA, make acidic after dilution.

11.2 Aqueous Samples - Continuous Liquid/Liquid Extraction (SW846 3520C)

11.2.1 Add approximately 350 – 500 mL (amount differs due to vessel size) of methylene chloride to the extractor body.

11.2.2 Add 3 to 5 boiling chips to the round-bottom distilling flask.

11.2.3 Attach cold condenser (about 10°C). Turn on heating mantle. Inspect joints for leaks once solvent has begun cycling. Extract for 18-24 hours. (24 hours required for 600 series.)
11.2.4 Turn off the heating mantle and allow the extractor to cool.
11.2.4.1 For **semivolatiles analysis**, a second extraction at a basic pH is required (see Table 1).
11.2.4.2 Detach the condenser and adjust the pH of the sample in the extractor body to the pH indicated in Table 1 with a minimum amount of 10 N NaOH.
11.2.4.3 Measure with pH paper and record the adjusted pH on the bench sheet.
11.2.4.3.1 If desired, the acid and base fractions may be kept separate by replacing the boiling flask with a clean flask and fresh solvent.
11.2.4.4 Reattach the condenser and turn on heating mantle. Extract for 18-24 hours. (24 hours required for 600 series.)
11.2.5 Line the funnel with filter paper or place glass wool in the funnel stem.
11.2.6 Add 10-20 g of anhydrous sodium sulfate to the funnel .
11.2.7 Place the prepared funnel on a labeled amber bottle or labeled K-D flask.
11.2.8 Filter extracts through the prepared funnel into a K-D flask.
11.2.8.1 If concentration does not begin immediately, place extract in labeled amber jars and secure the lids.
11.2.9 Dispose of solvent and water remaining in the extractor in the appropriate waste container.
11.2.10 Proceed to Section 11.6 for concentration.

11.3 Aqueous Water - Separatory Funnel Liquid/Liquid Extraction (SW846 3510C)
11.3.1 Add 60 mL methylene chloride to the Separatory funnel. 100mL for semi-volatiles
11.3.1.1 For LVI extractions, add 20mL methylene chloride to the seperatory funnel.
11.3.2 Seal and shake or rotate the separatory funnel vigorously for 1 minute with periodic venting to release excess pressure.
**Warning: Dichloromethane creates excessive pressure very rapidly! Therefore, initial venting should be done immediately after the separatory funnel has been sealed and inverted. Vent into hood away from analysts and other samples.**
11.3.3 Allow the organic layer to separate from the water phase until complete visible separation has been achieved.
11.3.3.1 If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. If the emulsion cannot be broken (recovery of <80% of the methylene chloride), transfer the sample, solvent, and emulsion into the extraction chamber of a continuous extractor and proceed as described in continuous liquid-liquid extraction.
11.3.3.1.1 The sample must be extracted as part of a valid 3510C batch.
**NOTE:** 15 - 20 mL of methylene chloride is expected to dissolve in 1 L of water. Thus, solvent recovery could be as low as 40 mL from the first shake and still be acceptable. Subsequent shakes should recover at least 50 mL of solvent. For LVI extraction, a solvent recovery of 15 mL is acceptable for the first extraction. Subsequent shakes should recover at least 18 mL.
11.3.4 Line a funnel with filter paper or place glass wool in the funnel stem.
11.3.5 Add 10-20 g of anhydrous sodium sulfate to the funnel.
11.3.6 Place the prepared funnel on a pre-rinsed K-D flask.
11.3.6.1 Condition each sodium sulfate filled funnel with methylene chloride before each drain and rinse with methylene chloride after each drain.
11.3.7 Drain solvent extract from the separatory funnel (Methylene chloride is the bottom layer) through the prepared filtration funnel into a clean glass container or K-D flask.

11.3.8 Close the stopcock just before the water level begins draining out of the separatory funnel. If the sodium sulfate becomes saturated with water add more to the funnel or replace the existing sodium sulfate with fresh drying agent.
11.3.8.1 If concentration does not begin immediately, place extract in labeled amber jars and secure the lids.
11.3.9 Repeat the extraction steps 11.3.5-11.3.10 two more times with a fresh 60 mL, 50mL for semi-volatiles or 20 mL for LVI extraction of methylene chloride. Use the same funnel and sodium sulfate for all three extractions.
11.3.10 Combine the three solvent extracts in the K-D flask or labeled amber jar.
11.3.10.1 For **Semivolatiles analysis**, a second extraction at a basic pH is required (see Table 1).
11.3.10.2 Adjust the pH of the sample in the separatory funnel to the pH indicated in Table 1 with a minimal amount of 10 N NaOH.
11.3.10.3 Measure with pH paper and record the adjusted pH on the bench sheet.
11.3.10.4 Serially extract with three portions of methylene chloride for semi-volatiles using 100 mL, 50 mL and 50 mL.
11.3.10.5 For LVI semi-volatiles serially extract with three portions of Methylene Chloride using 20 mL, 20 mL and 20 mL. or 40mL, 20mL, 20mL for semi-volatiles
11.3.11 Dispose of solvent and water remaining in the extractor in the appropriate waste container.
11.3.12 Proceed to Section 11.6 for concentration.

11.4 Solids and Waste Sonication Extraction (SW846 3550C)
11.4.1 Decant and discard any water layer on a sediment/soil sample.
11.4.1.1 Document if a water layer was discarded.
11.4.2 Homogenize the sample by mixing thoroughly. See SOP ST-QA-0038 for details.
11.4.3 Weigh approximately 30 g of sample into a 250 or 400 mL beaker or Mason Jar.
11.4.4 Record the weight to the nearest 0.01g in the appropriate column on the bench sheet.
11.4.5 Use approximately 30 g of sodium sulfate for the method blank and the LCS.
11.4.6 Spike samples and QC with surrogate.
11.4.7 Spike LCS and MS/MSD with spiking mix applicable to the requested analysis.
11.4.7.1 Document spiking volumes and standard numbers on the bench sheet.
11.4.7.2 Return spiking solutions to the refrigerator as soon as possible.
11.4.8 Mix sample with a spatula adding enough anhydrous sodium sulfate (approximately 30 g) to be free flowing. (If the sample is not free flowing extraction efficiency may be reduced)
11.4.9 Add a minimum of 100 mL of solvent to the mason jar.

**Semivolatile GC/MS**
**1:1 Methylene Chloride / Acetone**

**Organochlorine Pesticides, PCBs**
**1:1 Methylene Chloride / Acetone**

**TPH Hydrocarbons by FID (DRO, etc.)**
**Methylene Chloride**

11.4.10 Place the bottom surface of the disrupter horn tip approximately ½ inch below the surface of the solvent, but above the sediment layer.
11.4.11 Set sonicator between 7 and 8 (to achieve the required 300 watt power level) with mode switch on pulse, and percent- duty cycle knob set at 50% and record the sonicator ID.
11.4.12 Sonicate for 3 minutes, making sure the entire sample is agitated.
11.4.13 Line a funnel with filter paper.
11.4.14 Add 10-20 g of anhydrous sodium sulfate to the funnel. Condition funnel with methylene chloride before each drain.

11.4.15 Place the prepared funnel on an amber bottle or K-D flask.
Decant and filter extract through the prepared funnel into the amber bottle or K-D flask,.
If concentration is not to begin immediately, place extract in labeled amber jars and secure the lids.

11.4.16 Repeat the extraction steps 11.4.9-11.4.16 two more times with fresh a 100 mL amount of solvent each time. Use the same funnel and sodium sulfate for all three extractions. Decant extraction solvent after each sonication, combing all three extractions.

11.4.16.1 Dump remaining soil from mason jar on top of sodium sulfate filled funnel, rinsing the jar with methylene choride into KD flask or amber jar.

11.4.17 Rinse funnel with an additional 10 – 20 mL of the methylene chloride.

11.4.18 Proceed to Section 11.6 for concentration.

11.5 Waste Dilution (SW846 3580)

11.5.1 This method is used for non-aqueous liquid or solid materials (e.g. oils, organic product) that are soluble in an organic solvent or samples known to contain high concentrations of target analytes.

11.5.1.1 Waste dilutions are reported in ug/L for liquids and ug/kg for soils.

11.5.1.2 For liquids, sample density must be performed to reflect volume of sample.

11.5.1.2.1 Aliquot 10 mL of sample and deliver aliquot to Wet Chemistry Supervisor, or designee, for density determination.

11.5.2 Pre-weigh empty Class A concentrator tip.

11.5.3 Add 1g of sample to the tip. Record the weight.

11.5.4 Use 1g of mineral oil for Method Blank and LCS.

11.5.5 For Semivolatiles, add 2 mL spike solution to QC samples and 1 mL surrogate solution (Table 3) for all samples. For all other analyses, add 0.5 mL of surrogate solution (Table 3) to samples and 0.5 mL of spike solution to QC samples.

11.5.6 Bring final volume to 10 mL with appropriate solvent.

11.5.6.1 Methylene Chloride for GC/MS Semivolatiles, TPH and Phenol analysis

11.5.6.2 Hexane for Pesticide and PCB analysis.

11.5.7 Mix thoroughly approximately 1 minute.

11.5.8 Proceed to cleanup if method specified.

11.5.9 Vial samples.

11.6 Initial Concentration

11.6.1 Different final extract volumes are required, depending on analysis, matrix and cleanup. Refer to Table 2 for the appropriate final volumes and concentrations.

11.6.2 Kuderna-Danish (KD) Method:

11.6.2.1 Assemble a KD concentrator by attaching a 10 mL Class A concentrator tip to the 500 mL KD flask.

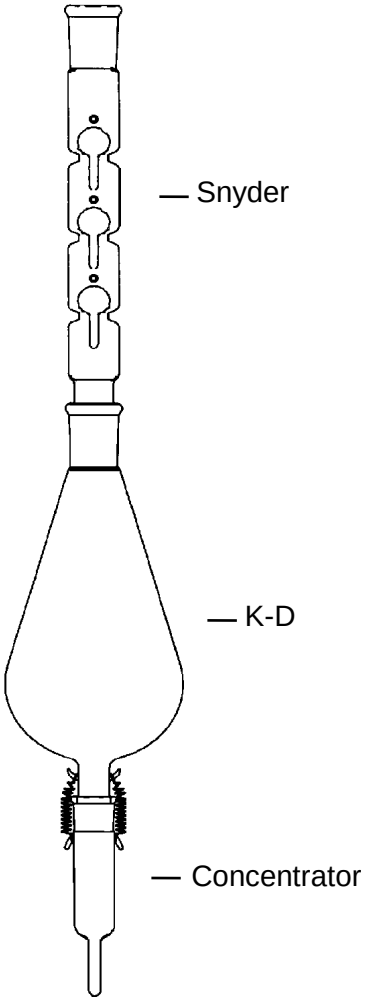
11.6.2.2 Transfer the sample to the KD flask.

11.6.2.3 Rinse extract container with methylene chloride and add rinse to KD flask.

11.6.2.4 Add one or two boiling chips to KD flask.

11.6.2.5 Attach a three ball Snyder Column.

11.6.2.5.1 Ensure that the balls are not stuck and that the column is working properly.




11.6.2.6 Set water bath at 85 - 95 °C depending on the analysis.
- 11.6.2.6.1 For Semivolatiles, Phenols, PAHs, and TPH, set temperature at approximately 90°C.
- 11.6.2.6.2 For Pesticides and PCBs, set temperature at approximately 95°C.

11.6.2.7 Record water bath temperature on the extraction log.

11.6.2.8 Place the KD apparatus in water bath so that the tip of the concentrator tip is submerged. The water level should not reach the joint between the concentrator and the KD flask.
- 11.6.2.8.1 The balls should actively chatter but the chambers should not flood.

11.6.2.9 Semivolatiles, Phenols and PAH Initial Concentration
- 11.6.2.9.1 Concentrate to 10 mL.
- 11.6.2.9.2 Remove extract from water bath.
- 11.6.2.9.3 Let cool and remove the concentrator tip from the KD flask.

11.6.2.10 Pesticide and PCB Initial Concentration
- 11.6.2.10.1 Concentrate to 5-10 mL.
  - 11.6.2.10.1.1 If the KD flask is removed from the water bath prior to solvent exchange, a new boiling chip must be added to the flask to prevent "bumping" of the solvent.
- 11.6.2.10.2 Add approximately 60 mL hexane to the top of the Snyder Column, remove column after solvent exchange.

11.6.2.10.3 Return extract to water bath.
11.6.2.10.4 Concentrate to 5-8 mL.
11.6.2.10.5 Remove extract from water bath.
11.6.2.10.6 Let cool and remove the concentrator tip from the KD flask.

11.6.3 Concentrating extracts to dryness can cause the loss of analytes.
11.6.3.1 Remove the KD apparatus from the water bath and allow it to cool for a minimum of 10 minutes. The level of the extract should be below the level of the tip joint. If the level of the extract is above the level of the concentrator tip joint, continue to distill the solvent as necessary. Again, allow the KD flask to cool for a minimum of 10 minutes.
11.6.3.2 If nessecary, dilute the extract to the desired final volume in the concentrator tip.
11.6.3.3 If the desired final volume is less than the remaining extract, nitrogen evaporation (see next section) may be used to further concentrate the sample to 5 or 10 mL.
11.6.3.4 Transfer the extract to a vial for storage and document the final volume.

11.7 Final Concentration
11.7.1 Nitrogen Evaporators are used for the final concentration of extract.
11.7.2 Nitrogen Evaporation Concentration Method
11.7.2.1 Semivolatiles, Pesticides, PCB, TPH, Phenol Final Concentration
11.7.2.1.1 Place the pre-rinsed concentrator tip in the rack of the nitrogen evaporation apparatus.
11.7.2.1.2 Lower the nitrogen tip to approximately ½" above the surface of the solvent.
11.7.2.1.3 Turn on the nitrogen gas and observe the solvent in the concentrator tip.
11.7.2.1.4 The nitrogen flow should be a gentle stream forming a slight depression on the surface of the solvent and should not create splattering of the extract.
11.7.2.1.5 Gas flow can be adjusted using the flow control knobs located at the top of each gas tip.
11.7.2.1.6 Place the concentrator tip in a warm water bath at approximately 35°C.
11.7.2.1.6.1 If during the course of the evaporation sample residue appears to be adhering to the sides of the tip, rinse the sides of the evaporation tip with approximately 1 mL of clean solvent. The first rinse should be about half way through the process, with the second rinse when the solvent volume gets close to 1 mL.
11.7.2.1.7 Concentrating extracts to dryness can cause analytes to be lost.
11.7.2.1.8 Concentrate the solvent slightly below the required final volume and then draw the extract into a syringe.
11.7.2.1.9 Rinse the evaporation tip with a small amount of solvent and draw additional solvent into the syringe to make up the required final volume.
11.7.2.1.10 Transfer the extract to a vial for storage and document the final volume.

11.8 Cleanup Techniques [SW846 3620C(Florist Cleanup), SW846 3660B (Sulfur Cleanup)]
11.8.1 The following techniques may be used to remove interferences that may cause column deterioration and/ or loss of detector sensitivity.
11.8.2 Cleanup procedures may be done in combination. If done in combination, they must be

performed in the order listed.

11.8.2.1 Florisil column cleanup is particularly useful for cleanup of pesticides analysis and is applied to these samples. It separates compounds with a different polarity from the target analytes.

11.8.2.2 Sulfur cleanup is generally applied to samples for analysis by ECD since the detector responds strongly to sulfur. It is performed after Florisil cleanup. Sulfur cleanup is performed by the analyst. See SOP: ST-GC-0015 for instruction.

11.8.2.3 Sulfuric acid cleanup is applied to samples requiring analysis for Polychlorinated Biphenyls (PCBs) only. Most organic matter is destroyed by sulfuric acid.

11.8.3 Florisil Cartridge Cleanup

11.8.3.1 Florisil cleanup is used for all soil pesticides extracts and may be applied to Pesticide water extract or other method extracts, at the discretion of the Manager/Supervisor or request of the client. See Client Requirement sheet.

11.8.3.1.1 If semivolatile,TPH or Phenol extracts require Florisil Clean up, the extract must be exchanged into Hexane. Consult Manager/Supervisor for instruction.

11.8.3.2 Place one Florisil cartridge into a vacuum manifold for each sample and associated QC extract.

11.8.3.3 Pre-elute each cartridge with 5 mL of hexane/acetone (9:1).

11.8.3.4 Using a pipette bulb, apply pressure to each cartridge so that the flow is a constant, continual drip. Do not allow the cartridges to go dry.

11.8.3.4.1 Stop applying pressure to the cartridge and remove the manifold top, before the cartridge goes dry.

11.8.3.5 Label 10 mL concentrator tips or comparable vessel (disposable vial) and place into the manifold. Tips and vials are conditioned with hexane.

11.8.3.6 Replace the manifold top.

11.8.3.7 Make sure that the solvent line from each cartridge is placed inside the appropriate tip.

11.8.3.8 Add 1.0 mL of the extract to the appropriate Florisil cartridge

11.8.3.9 Apply pressure using the pipette bulb.

11.8.3.10 Elute through the column with about 8 mL of hexane/acetone (90:10)

11.8.3.11 Collect into the labeled vessel held in the rack inside the vacuum manifold.

11.8.3.12 Concentrate the extract to 1 mL using the Nitrogen Evaporator See 11.7.2

11.8.4 Sulfuric Acid Cleanup

11.8.4.1 All PCB (only) extracts are taken through the sulfuric acid cleanup procedure.

11.8.4.2 Use an equal volume of concentrated sulfuric acid to sample extract volume

11.8.4.2.1 Add concentrated sulfuric acid to empty, labeled vial.

11.8.4.2.2 Carefully add the sample extract to the vial and cap.

11.8.4.3 QC extracts are also taken through this clean up procedure.

11.8.4.4 There must be no water present in the extract or the reaction may shatter the sample container. A face shield, splash guard, or hood sash must be used when performing acid clean-up.

11.8.4.5 Shake or vortex for about thirty seconds and allow to settle.

11.8.4.5.1 If extract will not settle, centrifuge.

11.8.4.6 Remove the sample extract (top layer) from the sulfuric acid using a pipette and transfer to a clean, labeled vial being careful not to transfer the sulfuric acid (bottom layer).

11.8.4.6.1 It is not necessary to remove all the extract since the final volume has already been determined.

11.8.4.6.2 Transfer small amounts of sulfuric acid along with the extract will destroy the chromatographic column.

11.8.4.7 If the hexane layer becomes highly colored after shaking with the sample extract, transfer the hexane extract to a clean vial and repeat the cleanup procedure until

color is no longer being removed by the acid, or a maximum of 3 acid cleanups. Document it if this is required.

11.8.4.8 If extract color persists after completion of the sulfuric acid cleanup, a potassium permanganate cleanup *may* be employed if deemed necessary by the analyst or requested by the client. Document it if this procedure is performed.

11.8.4.9 Slowly add 5 mL of 5 percent aqueous potassium permanganate solution to the hexane fraction. Caution: Permanganate is a powerful oxidizer and a violent reaction, while uncommon, may occur

11.8.4.10 Seal the vial tightly and shake or vortex for 30 second

11.8.4.10.1 If extract does not form two distinct layers within a few minutes, centrifuge.

11.9 Gel Permeation Chromatography - A generally applicable technique which can be used to prepare extracts for analysis. It is capable of separating high molecular weight material from the sample analytes, and so is particularly useful if tissue or vegetable matter is part of the sample, and for many soil samples.

11.9.1 Gel Permeation Chromatography (GPC)

Note: GPC system (OI Analytical Autoprep 2000 with OIA 1096TB Autosampler)

11.9.1.1 GPC Column Preparation

11.9.1.2 Weigh out 70 g of Bio Beads (SX-3) into a 400-mL beaker.

11.9.1.3 Add approximately 300 mL of methylene chloride and stir gently.

11.9.1.4 Cover with aluminum foil and allow the beads to swell for a minimum of 12 hours. Maintain enough solvent to sufficiently cover the beads at all times.

11.9.1.5 Position and tighten the outlet bed support (top) plunger assembly in the tube by inserting the plunger and turning it clockwise until snug. Install the plunger near the column end but no closer than 5 cm (measured from the gel packing to the collar).

11.9.1.6 Turn the column upside down from its normal position with the open end up. Place the tubing from the top plunger assembly into a waste beaker below the column.

11.9.1.7 Swirl the bead/solvent slurry to get a homogeneous mixture and pour the mixture into the open end of the column. Transfer as much as possible with one continuous pour trying to minimize bubble formation. Pour enough to fill the column. Wait for the excess solvent to drain out before pouring in the rest. Add additional methylene chloride to transfer the remaining beads and to rinse the beaker and the sides of the column. If the top of the gel begins to look dry, add more methylene chloride to rewet the beads.

11.9.1.8 Wipe any remaining beads and solvent from the inner walls of the column with a laboratory tissue. Loosen the seal slightly on the other plunger assembly (long plunger) and insert it into the column. Make the seal just tight enough so that any beads on the glass surface will be pushed forward, but loose enough so that the plunger can be pushed forward.

**CAUTION**: Do not tighten the seal if beads are between the seal and the glass surface because this can damage the seal and cause leakage.

11.9.1.9 Push the plunger until it meets the gel, then compress the column bed about 4 cm.

11.9.1.10 Connect the column inlet to the solvent reservoir and place the column outlet tube in a waste container. Pump methylene chloride through the column into a glass beaker at a rate of 5 mL/min. for one hour. Inspect the glass beaker to ensure that gel beads do not escape from the column.

11.9.1.11 If observing beads in the beaker, continue pumping for several more minutes and check again for bead leakage. If gel beads are still present in the column effluent after 30 minutes, then disassemble, clean, inspect, and repack the column.

11.9.1.12 Closely monitor the column pressure. High pressure occurs occasionally while rewetting the gel, especially for the 100% methylene chloride column. If pressure continues to rise above 15 psi, reverse the flow direction through the column by exchanging the input and output column lines at the GPC column bypass ports until pressure begins to fall. Replace the connections in their original configuration. The pressure should begin to decline to between 7 and 10 psi as the gel uniformly saturates and swells. If pressure remains high, check for any restrictions or blockages.

11.9.1.13 After washing the column for at least one hour, connect the column outlet tube to the inlet side of the UV detector. Connect the system outlet to the outlet side of the UV detector. Placing a restrictor (made from a piece of capillary tubing of 1/16"OD x 10/1000"ID x 2") in the outlet tube from the UV detector will prevent bubble formation which causes a noisy UV baseline. The restrictor will not effect the flow rate. After pumping methylene chloride through the column for an additional 1-2 hours, adjust the inlet bed support plunger until approximately 6-10 psi back-pressure is achieved. Push the plunger in to increase pressure or slowly pull outward to reduce pressure.

11.9.1.14 When the GPC column is not to be used for several days, connect the column inlet and outlet lines to prevent column drying and/or channeling. If channeling occurs, the gel must be removed from the column, re-swelled, and re-poured as described above. If drying occurs, pump methylene chloride through the column until the observed column pressure is constant and the column appears wet. Always recalibrate after column drying has occurred to verify that retention volumes have not changed.

11.9.2 Initial Calibration of the GPC Column

11.9.2.1 Before use, the GPC must be calibrated based on monitoring the elution of standards with a UV detector connected to the GPC column.

11.9.2.2 Pump solvent through the GPC column for 2 hours. Verify that the flow rate is 4.5-5.5 mL/min. Corrective action must be taken if the flow rate is outside this range. Record the column pressure (should be 6-10 psi) and room temperature ($22^{o}$C is ideal).

**Note**: Changes in pressure, solvent flow rate, and temperature conditions can affect analyte retention times and must be monitored. If the flow rate and/or column pressure do not fall within the above ranges, a new column should be prepared.

11.9.2.3 Inject the calibration solution, for which the component concentrations can be found in section 7.1.1, and retain a UV trace that meets the following requirements (See resolution calculation in section 11.4.3.7.1):

Peaks must be observed and should be symmetrical for all compounds in the calibration solution.
Corn oil and phthalate peaks must exhibit >85% resolution.
Phthalate and methoxychlor peaks must exhibit >85% resolution.
Methoxychlor and perylene peaks must exhibit >85% resolution.
Perylene and sulfur peaks must not be saturated and must exhibit >90% baseline resolution.

11.9.2.4 A UV trace that does not meet the criteria in paragraph 11.4.3.2.3 indicates the need for system maintenance and/or the need for a new column.

11.9.2.5 Determine appropriate dump and collect cycles by following calculations 11.9.7.2 and 11.9.7.3, respectively.

11.9.2.6 The calibrated GPC program for pesticides/PCB should dump >85% of the phthalate and should collect >95% of the methoxychlor and perylene. Use a wash time of 10 minutes.

11.9.2.7 For semivolatile extracts, initiate a column eluate collection just before the elution of bis (2-ethylhexyl) phthalate and after the elution of the corn oil. Stop eluate collection shortly after the elution of perylene. Stop collection before sulfur elutes. Use a wash time of 10 minutes after the elution of sulfur.

11.9.2.8 Reinject the calibration solution after appropriate dump and collect cycles have been set.

11.9.2.9 Measure and record the volume of collected GPC eluate in a graduated cylinder.

11.9.2.10 The retention times for both bis(2-ethylhexyl) phthalate and perylene must not vary more than +/- 5% between calibrations.

11.9.3 GPC calibration check

11.9.3.1 Check the calibration of the GPC immediately after the initial calibration and at least every 7 days thereafter, while the column is in use.

11.9.3.2 Inject the calibration solution, and obtain a UV trace. If the retention times of bis(2-ethylhexyl)phthalate or perylene have changed by more than $\pm$ 5% use this run as the start of a new initial calibration. Otherwise, proceed with the recovery check. Excessive retention time shifts may be caused by poor laboratory temperature control or system leaks, an unstabilized column, or high laboratory temperature causing outgassing of methylene chloride. Pump methylene chloride through the system and check the retention times each day until stabilized.

11.9.4 GPC Recovery Check for Pesticides/ PCBs

11.9.4.1 The recovery from the GPC must be verified immediately after the initial calibration and at least every 7 days, when the instrument is in use. Two recovery check solutions are used. The first mixture is prepared by diluting 1.0 mL of the pesticide matrix spiking solution (Table 6) to 10 mL in methylene chloride. The second mixture is prepared by diluting 1 mL of the PCB only matrix spiking solution (Table 6) to 10 mL with methylene chloride.

11.9.4.2 Load the pesticide matrix spike mixture, the PCB mixture, and a methylene chloride blank onto the GPC using the GC dump and collect values.

**Note**: If the analysis is for PCBs only, then the pesticide recovery check is not necessary.

11.9.4.3 After collecting the GPC calibration check fraction, concentrate, solvent exchanging to hexane. Adjust the final volume to 5.0 mL, and analyze by GC/EC. Refer to concentration, section 11.3.

11.9.4.4 The methylene chloride blank may not exceed more than one half the reporting limit of any analyte. And if the recovery of each of the single component analytes is 80-110% and if the Aroclor pattern is the same as previously run standards, then the analyst may use the column. If the above criteria are not met, there may be a need for system maintenance.

11.9.5 GPC Recovery Check for Semivolatiles

11.9.5.1 The recovery from the GPC must be verified immediately after the initial calibration and at least every 7 days, when the instrument is in use. Dilute 1.0 mL of the semivolatiles matrix spiking solution (Table 6) to 10 mL in methylene chloride.

11.9.5.2 Load the matrix spike mixture and a methylene chloride blank onto the GPC using the semivolatiles dump and collect values.

11.9.5.3 After collecting the GPC recovery check fraction, concentrate to 0.5 mL, and analyze by GC/MS. Refer to the concentration section 11.3.

11.9.5.4 Recovery of the matrix spike analytes should be at least 60%. The blank should not contain any analytes at or above the reporting limit. If these conditions are met the column may be used for sample analysis. Otherwise correct the contamination problem, or extend the collect time to improve recovery of target analytes.

11.9.6 Sample Extract Cleanup

11.9.6.1 Reduce the sample extract volume to 1-2 mL, then adjust to 10 mL with methylene chloride prior to cleanup. This reduces the amount of acetone in the extract.

11.9.6.2 Start the pump and let the flow stabilize for 2 hours. The solvent flow rate should be 4.5-5.5 mL/min. The ideal laboratory temperature to prevent outgassing of the methylene chloride is 22$^{o}$C. The normal backpressure is 6-10 psi.

11.9.6.3 In order to prevent overloading of the GPC column, highly viscous sample extracts must be diluted prior to cleanup. Any sample extract with a viscosity greater than that of a 1:1 glycerol:water solution (by visual comparison) must be diluted and loaded into several loops.

11.9.6.4 Samples being loaded onto the GPC should be filtered with a 5 micron (or less) filter disk. Attach a filter to a 10 mL Luerlok syringe and filter the 10 mL sample extract into the sample tube.

11.9.6.5 Load the filtered samples into the proper sample tubes and place on the GPC.

11.9.6.6 Set the collect, dump, and wash times determined by the calibration procedure.

11.9.6.7 Switch to the run mode and start the automated sequence. Process each sample using the collect and dump cycle times established by the calibration procedure.

11.9.6.8 Collect each sample in a suitable glass container. Monitor sample volumes collected.

11.9.6.9 Any samples that were loaded into 2 or more positions must be recombined.

11.9.6.10 Concentrate semivolatile sample extracts to 0.5 mL in methylene chloride.

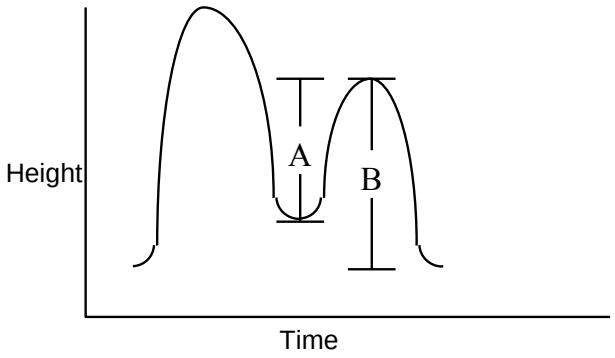
11.9.6.11 Solvent exchange the pesticide/PCB sample extracts into hexane and concentrate to 5.0 mL.

11.9.7 Calculations

11.9.7.1 Resolution

To calculate the resolution between two peaks on a chromatograph, divide the depth of the valley between the peaks by the peak height of the smaller peak being resolved and multiply by 100.

Resolution Calculation




$$\% \text{ Resolution } = \frac{A}{B} \times 100$$

Where: A = depth of valley to height of smaller peak

B = peak height of smaller peak

11.9.7.2 Dump Time

11.9.7.2.1 Mark on the chromatograph the injection point and the point where collection is to begin. Measure the distance from the injection point to the point of collection. Divide the distance by the chart speed.

$$\text{Dump time (min)} = \frac{\text{Distance (cm) from injection to collection start}}{\text{Chart speed (cm / min)}}$$

11.9.7.3 Collection Time

$$\text{Collection time (min)} = \frac{\text{Distance (cm) between collection start and stop}}{\text{Chart speed (cm / min)}}$$

11.10 Deliver extract and extraction log paperwork to the analyst.
11.11 See individual analysis SOPs: ST-GC-0005, ST-GC-0013, ST-GC-0015, ST-GC-0016, ST-LC-0001, and ST-MS-0001 for extract analysis.
11.12 If not immediately analyzed, extracts are stored in designated refrigerators.

## 12 DATA ANALYSIS AND CALCULATIONS

12.1 Commonly used calculations (e.g. % recovery and RPD) and standard instrument software calculations are given in the TestAmerica St. Louis ST-QAM.

12.2 See individual analysis SOPs: ST-GC-0005, ST-GC-0013, ST-GC-0015, ST-GC-0016,and ST-MS-0001 for specific calculations.

## 13.0 DATA ASSESSMENT AND ACCEPTANCE CRITERIA; CORRECTIVE ACTIONS FOR OUT OF CONTROL DATA

13.1 Data assessment does not pertain to this sample preparation procedure.

13.2 Samples requiring re-preparation are submitted to the preparation lab with an NCM detailing the issue. The NCM process is described in SOP: ST-QA-0036. Specific information is given in the applicable analysis SOP.

## 14.0 METHOD PERFORMANCE AND DEMONSTRATION OF CAPABILITY

14.1 Method performance data, Reporting Limits, and QC acceptance limits, are maintained in the LIMS.

14.2 Demonstration of Capability
- 14.2.1 Initial and continuing demonstrations of capability requirements are established in the ST-QAM.

14.3 Training Qualification
- 14.3.1 The manager/supervisor has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience.
- 14.3.2 The analyst must have successfully completed the initial demonstration capability requirements prior to working independently. See requirements in the ST-QAM.

14.4 Annually, the analyst must successfully demonstrate proficiency to continue to perform this analysis. See requirements in the ST-QAM.

## 15.0 VALIDATION

15.1 Laboratory SOPs are based on standard reference EPA Methods that have been validated by the EPA and the lab is not required to perform validation for these methods. The requirements for lab demonstration of capability are included in ST-QAM. Lab validation data would be appropriate for performance based measurement systems or non-standard methods. TestAmerica St. Louis will include this information in the SOP when accreditation is sought for a performance based

measurement system or non-standard method

## 16.0 WASTE MANAGEMENT AND POLLUTION PREVENTION

16.1 All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Environmental Health and Safety Manual for "Waste Management and Pollution Prevention."

16.2 Waste Streams Produced by the Method

16.2.1 The following waste streams are produced when this method is carried out:

16.2.1.1 Sulfuric acid waste from the clean up will be disposed of in the acid waste barrel after removal of the hexane layer.

16.2.1.2 Contaminated disposable glass or plastic materials utilized in the analysis are disposed of in the sanitary trash.

16.2.1.3 Solid materials (soil, gloves, soiled paper products) are collected in the container labeled "Non-Regulated Material" for disposal.

16.2.1.4 If the labware was used for the analysis of radioactive samples and contains radioactivity at level of 100 cpm over background as determined by a GM meter, the labware will be collected in waste barrels designated for solid rad waste for disposal by the EH&S Coordinator.

16.2.1.5 Methylene chloride saturated water and sample volume remaining after extraction is disposed of in the base waste barrel.

16.2.1.6 Solvent rinses from the labware cleaning procedure are disposed of in the flammable solvent waste stream.

## 17.0 REFERENCES

17.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update III (December 1996) and Update IV, February 2007. Sections 3500C, 3510C, 3520C, 3580A, 3550C, 3600C, 3620C, 3650B, 3660B, AND 3665A.

17.2 TestAmerica St. Louis Quality Assurance Manual (ST-QAM), current revision

17.3 TestAmerica Corporate Environmental Health and Safety Manual (CW-E-M-001) and St. Louis Facility Addendum (SOP ST-HS-0002), current revisions.

17.4 Associated SOPs:

17.4.1 Corporate White Paper CA-Q-W-010 LVI Technique for Organic Prep & Analysis
17.4.2 ST-OP-0001, Labware Preparation for Organic analysis.
17.4.3 ST-PM-0002, Sample Receipt and Chain of Custody
17.4.4 ST-QA-0002, "Standards and Reagent Preparation."
17.4.5 ST-QA-0005, "Calibration and Verification Procedure for Thermometers, Balances, Weights and Pipettes"
17.4.6 ST-QA-0016, IDL/MDL Determination
17.4.7 ST-QA-0036, "Non-Conformance Memorandum (NCM) Process"
17.4.8 ST-QA-0038, "Procedure for Compositing and Sub-sampling"
17.4.9 ST-QA-0039 "Sample Transfer Utility"
17.4.10 ST-GC-0005, "Extractable Total Petroleum Hydrocarbons Iowa OA-2 and Method 8015 by GC"
17.4.11 ST-GC-0013, "Extraction and Analysis of Phenols by SW846-8040A"
17.4.12 ST-GC-0015, "PCB Gas Chromatography Analysis Method SW-846 8000C/8082A"

17.4.13 ST-GC-0016, "Pesticide Gas Chromatography Analysis Method SW-846 8000C/8081B and EPA 608"
17.4.14 ST-MS-0001, "GC/MS Analysis Based on Methods 8270C and 625"

## 18.0 CLARIFICATIONS, MODIFICATIONS TO THE REFERENCE METHOD

18.1 Some surrogate spiking concentrations are modified from those recommended in SW-846, in order to make the concentrations more consistent with the calibration levels in the determinative methods.
18.2 For the 600 series methods, an 18-24 hour CLLE extraction time has been demonstrated to yield acceptable LCS recoveries.
18.3 For method 625, the acid fraction is performed first and then followed by the base/neutral extraction. It has been demonstrated that this procedure yields acceptable LCS recoveries.
18.4 Aqueous sample volumes are determined by weight.
18.5 The lab uses a modified 3665A sulfuric acid clean up. The permanganate step is not traditionally used.
18.6 Method 3510C and 3520C state that water bath temperatures may be elevated so that concentration is completed with 10-20 minutes. TestAmerica St. Louis prefers to keep the water bath temperature lower for semivolatiles extracts and thus concentrating time is greater than 20 minutes.
18.7 The solvent rinsing of the extraction glassware when transferring the extract to the KD flask is not performed. Once the organics are extracted from the water and in the solvent layer, adhesion to the glassware is no longer a significant concern.

## 19.0 CHANGES FROM PREVIOUS REVISION

19.1. Clarified pH requirements and BNA extraction order in Section 11.1.5
19.2. Added Section 11.9: GPC cleanup procedure.
19.3. Rev. 15:
- 19.3.1. Added ovens to equipment in Section 6
- 19.3.2. Added Class A description to Concentrator tips in Section 6
- 19.3.3. Updated Section 10.3 to include Class A concentrator tips and calibration requirement
- 19.3.4. Updated Sonicator settings in Section 11.4 (from 10 to ~7.5)
- 19.3.5. Updated the use of methylene chloride/acetone blend in section 11.3.1 and 11.3.10.
- 19.3.6. Added volume of spike solution added to QC samples in Section 11.5.5
- 19.3.7. Updated the procedure steps in section 11.7.2.2.9.
- 19.3.8. Added SOP ST-QA-0039 to Reference Section 17

19.4. Rev 16:
- 19.4.1. Updated GPC section 11.9.
- 19.4.2. Added documentation of sonicator in section 11.4.
- 19.4.3. Added residual chlorine check to section 11.1.

19.5 Rev 17:
- 19.5.1 Added Methanol to solvents in Section 7
- 19.5.2 Updated Table 2: removed hexane as solvent for Pest/PCBs; replaced with methanol

19.6 Rev, 18:
- 19.6.1 Removed acetone blend for separatory funnel in section 11.3.
- 19.6.2 Updated PAH analysis extract blend throughout section 11.3.

19.7 Rev, 19:
- 19.7.1 Added Potassium Permanganate to the list of reagents in section 7.0.
- 19.7.2 Updated instructions for added Potassium Permanganate throughout section 11.8.4.
- 19.7.3 Updated Sep Funnel Liquid Extraction in section 11.3.

19.8 Rev 20:
- 19.8.1 Updated Section 11.4 to read the same as Method 3550C regarding the amount of sample weighed up and the requirements for recording of the amount used.

19.9 Rev 21:

19.9.1 11.1.1.1.: Addition of density limits

19.10 Rev 22

19.10.1 Removed references to Method 8310, PAHs and SOP ST-LC-0001. Method no longer supported by laboratory.
19.10.2 Added information on Lower Volume Initiative (LVI) to SOP.
19.10.3 Updated balance and syringe information in Section 6.
19.10.4 Added chlorine and peroxide test strips to Section 6.
19.10.5 Added acidic sodium sulfate and Hexane:Acetone mix to Section 7
19.10.6 Removed references to Standards Log program; replaced with LIMS reagent program.
19.10.7 Added info on PCB holding time to Section 8.
19.10.8 Clarified QC batching and requirements in Section 9.1.
19.10.9 Updated TCLP volumes in Sections 9.2 and 9.3.
19.10.10 Updated BNA extraction procedure in Section 11.1.5.
19.10.11 Added funnel conditioning information to Section 11.3.
19.10.12 Removed Turbovap procedure from Concentration Section 11.7.
19.10.13 Updated Clean-up information in Section 11.8.
19.10.14 Updated Section 14 to indicate performance and QC data for methods is maintained in LIMS.
19.10.15 Updated tables.

19.11 Revsion 23:

19.11.1 Added note to Section 11.1.3 that LVI requires South Carolina certification if to be used for South Carolina compliance samples.

Table 1

| Liquid /Liquid Extraction Conditions | | |
|---|---|---|
| Determinative Method | Initial Ext. pH | Secondary Ext. pH |
| Semivolatiles: 8270, 625 | <2 | >13 |
| PAHs: 8270 | >11 | None |
| Pest/PCB: 8081/8082 & 608 | 5-9 | None |
| Hydrocarbons (TPH): 8015 | as received | None |
| Phenol: 8041 | <2 | None |

**Table 2**

| Final Volume and Exchange Solvents if no cleanup is used | | | |
|---|---|---|---|
| Type | Exchange Solvent for Analysis | Final Volume for Analysis (mL) | Final Volume for LVI Analysis (mL) |
| Semivolatiles: 8270, 625 | N/A | 1.0 | 1.0 |
| PAHs: 8270 | N/A | 1.0 | |
| Pesticides/PCBs: 8081/8082 & 608 | Hexane | 10.0 (routine waters and soils) | 2.0 |
| Hydrocarbons (TPH): 8015 | N/A | 1.0 | |
| Phenol: 8041 | N/A | 1.0 | |

| Final Volumes and exchange solvents if Florisil cleanup is used | | | |
|---|---|---|---|
| Type | Exchange Solvent for Florisil | Final Volume for Florisil | Final Volume and solvent for Analysis |
| Pesticides | 90:10 Hexane/Acetone | 10 mL (1 mL aliquot used) | 1 mL, hexane |

Note: Different final volumes may be necessary to meet special client reporting limit requirements.

**Table 3**

| Determinative Method | Surrogate Standard ID | Amount | Spike Standard | Amount | LVI Spike | LVI surr |
|---|---|---|---|---|---|---|
| Semivolatiles: 8270, 625 | BNA SURR | 500 µL | BNA/TCLP | 1 mL | | |
| 8270 SIM | BNA SURR | 10 µL | 8270 SIM | 1 mL | | |
| Pesticides: 8081 & 608 | PEST SURR | 500 µL | PEST | 500 µL | 100 µL | 100 |
| PCBs: 8082 & 608 (if PCB only) | PCB SURR | 500 µL | PCB | 500 µL | 100 µL | 100 |
| Hydrocarbons (TPH): 8015 | TPH SURR | 500 µL | TPH | 500 µL | | |
| Phenol: 8040 | PHENOL SURR | 500 µL | Phenol | 500 µL | | |

# Title: ANALYSIS OF NITROAROMATIC AND NITROAMINE EXPLOSIVES BY HPLC [SW846 8000C and 8330B]

**Approvals (Signature/Date):**

| | |
|---|---|
| Ben Hicks 8/7/13<br>Organics Department Manager Date | Michael Ridenhower 8/6/13<br>Health & Safety Manager / Coordinator Date |
| Marti Ward 8.6.13<br>Quality Assurance Manager Date | Elaine Wild 8/7/13<br>Laboratory Director Date |

**This SOP was previously identified as SOP No. ST-LC-0002 Rev. 17**



**Facility Distribution No.: 0** **Distributed To: See Electronic Distribution Sheet**

## 1.0 SCOPE AND APPLICATION

1.1 This procedure provides instructions for the analysis of nitroaromatic and nitramine explosives by high performance liquid chromatography (HPLC) with UV detection in water, soil and sediment samples.

1.2 This SOP uses Low-level solid phase extraction method 3535A for low concentration water samples and the sonication extraction method 3550C or a shaker table (8330B) for soil, sediment, and wipe samples.

1.3 This SOP is based on EPA SW-846 Method 8000C and 8330B.

1.4 The laboratory target analytes supported by this method, the reporting limits, method detection limits and QC limits are maintained in the Laboratory Information Management System (LIMS).

1.4.1 Additional compounds may be amenable to this procedure. The minimum requirement for non-standard analytes is that the reporting limit be set at the lowest required concentration that can actually be detected by the instrument. When an MDL study can not be conducted, the MDL is set equal to the reporting limit.

## 2.0 SUMMARY OF METHOD

2.1 After the initial preparation step, (SOP ST-OP-0008) the sample is introduced to the HPLC and concentrations of target analytes are measured by the detector response within a defined retention time window, relative to the response to standard concentrations. Analysis on a second column provides confirmation of the identification of the target analyte, as does spectra identification, if client requested.

## 3.0 DEFINITIONS

3.1 See the TestAmerica Quality Assurance Manual (ST-QAM) for a glossary of common laboratory terms and data reporting qualifiers.

## 4.0 INTERFERENCES

4.1 Solvents, reagents, glassware and other sample processing hardware may yield discrete artifacts and/or elevated baselines, causing misinterpretation of chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running laboratory method blanks.

4.2 2,4-DNT and 2,6-DNT elute at similar retention times (retention time difference of ~0.2 minutes). A large concentration of one isomer may mask the response of the other isomer. If these isomers cannot be resolved, an isomeric mixture should be reported.

4.3 Tetryl decomposes rapidly in methanol/water solutions, as well as with heat. All aqueous samples expected to contain Tetryl should be diluted with acetonitrile prior to filtration. SAMPLES EXPECTED TO CONTAIN TETRYL SHOULD NOT BE EXPOSED TO TEMPERATURES ABOVE ROOM TEMPERATURE

4.4 Degradation products of Tetryl appear as a shoulder on the 2,4,6-TNT peak. Tetryl has also been observed to degrade into 4-amino-2,6-dinitrotoluene.

## 5.0 SAFETY

5.1 Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), Radiation Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.2 Primary Materials Used

5.2.1 The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

| Material (1) | Hazards | Exposure Limit (2) | Signs and symptoms of exposure |
|---|---|---|---|
| Methanol (Methyl Alcohol) | Poison Flammable | 200 ppm (TWA) | Inhalation symptoms may include headache, drowsiness, nausea, vomiting, blurred vision and blindness. Symptoms of skin contact may parallel inhalation exposure and can cause skin to become dry and cracked. Eye contact can cause irritation. |
| Acetonitrile | Flammable Poison | 40 ppm (TWA) | Early symptoms may include nose and throat irritation, flushing of the face, and chest tightness. Prolonged exposure to high levels of vapors may cause formation of cyanide anions in the body. |
| 1 – Always add acid to water to prevent violent reactions. | | | |
| 2 – Exposure limit refers to the OSHA regulatory exposure limit. | | | |
| TWA – Time Weighted Average | | | |

## 6.0 EQUIPMENT AND SUPPLIES

6.1 HPLC system: The lab utilizes two HPLC systems, one Agilent 1100 and one Agilent 1200. Chemstation software collects data which is transferred to Chromserver. The data then is automatically processed and uploaded to the LIMS through Chrom.

6.2 Restek Allure C18 reverse phase HPLC column, 250 x 4.6 mm, 5µm [primary/quantitative column].

6.3 Phenomenex Luna Phenyl-Hexyl, 150 x 4.6 mm, 3 µm [confirmation column]

6.4 Phenomenex Synergi Polar – RP 80A, 250 x 4.60 mm, 4 micron [confirmation column]

6.5 High pressure injection syringes, 10-µL, 25-µL, 50-µL, 100-µL, 500-µL, 1000-uL, Hamilton liquid syringe or equivalent

6.6 Volumetric flasks, 10-mL, 100-mL, 1000-mL with screw tops

6.7 Wipes-4-ply rayon/polyester 4”x4” Avant Gauze PRM25444

6.8 Sand – reagent grade

## 7.0 REAGENTS AND STANDARDS

7.1 All standards and reagent preparation, documentation and labeling must follow the requirements of SOP ST-QA-0002, current revision.

7.2 HPLC grade water

7.3 Acetonitrile, HPLC grade

7.4 Methanol, HPLC grade

7.5 Calcium chloride, reagent grade (Fisher Scientific) A 5 g/L aqueous calcium chloride solution is prepared.

7.6 HPLC Mobile Phases. The following solutions:

7.6.1 HPLC Primary Mobile Phase: 55 (± 2%) /45 (± 2%) methanol/water at 1.0 mL/min [isocratic], UV detection at 254 nm. Note: The 215 nm wavelength is also monitored for nitroglycerin and PETN, if applicable. Special analytes may be detected at other wavelengths.

7.6.2 HPLC Confirmation Mobile Phase: 40/60 methanol/water at 1.0 (± 0.4) mL/min., UV detection at 254 nm. Note: The 215 nm wavelength is also monitored for nitroglycerin and PETN, if applicable.

7.7 Stock Standards

7.7.1 It is recommended that diluted standards be purchased as stock solutions with a concentration no greater than 1000 mg/L (ppm). Standard solutions may also be prepared using Standard Analytical Reference Materials (SARMs). **Before neat materials are to be used, contact the EH&S Coordinator immediately for revision of this procedure.** IF USING NEAT STANDARDS PLEASE NOTE: HMX, RDX, Tetryl, and 2,4,6-TNT are explosives and the neat material must be handled carefully. See section 5.0 Safety, for guidance. Drying at ambient temperature requires several days. DO NOT DRY AT HEATED TEMPERATURES!

7.7.1.1 Place about 10 mg (weighed to the nearest 0.1 mg) of a single analyte into a 10-mL volumetric flask and dilute to volume with acetonitrile. Invert the flask several times until dissolved. Calculate the concentration of the stock solution from the actual weight used (nominal concentration = 1,000 mg/L).

7.7.1.2 Store at < 6 °C and protect from light.

7.7.1.3 Stock standards must be replaced after **six months** or sooner if comparison with quality control samples indicates a problem.

7.7.1.4 Standard solutions may also be purchased as prepared certified solutions. The vendor specified expiration dates will apply until ampoules are opened and mix is used.

7.7.2 Intermediate Stock Standard Solutions

7.7.2.1 Prepare an intermediate stock standard solution at 2000 ug/L for low level and 20,000 for high level per analyte in acetonitrile.

**NOTE:** If the analytical column cannot achieve separation of 2,4-DNT and 2,6-DNT, it will be necessary to prepare a separate intermediate stock solution of 2,6-DNT.

7.7.2.2 Intermediate stock standards must be replaced after **30 days** or sooner if comparison with quality control samples indicates a problem.

7.7.3 Calibration Standards

7.7.3.1 Calibration standards, at a minimum of five concentration levels, are prepared through dilution of the intermediate stock standard solutions by 50% (v/v) with 5 g/L calcium chloride solution. One of the concentration levels should be at or below the reporting limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the

working range of the HPLC. See Table 2 for suggested calibration standard concentrations.

7.7.3.2 Calibration standards must be stored at a temperature less than zero degrees C at (< 0 °C) and stored in the dark, and prepared fresh on the day of calibration.

7.7.4 Surrogate Standards

7.7.4.1 1,2-Dinitrobenzene is the surrogate typically used for this method. The surrogate standards are prepared and stored in the same way as the calibration standards.

7.7.4.2 Table 2 lists suggested concentrations for surrogate standards for initial calibration.

7.7.4.3 The working surrogate mix concentration is 40 µg/mL.

7.7.5 Quality Control (QC) Standards

7.7.5.1 Calibration verification standards (second source verification standards) are prepared and stored in the same way as calibration standards. They must be made from a stock independently prepared from that used for the calibration standards.

## 8.0 SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 TestAmerica St. Louis supplies sample containers and chemical preservatives in accordance with the method. TestAmerica St. Louis does not perform sample collection. Samplers should reference the methods referenced and other applicable sample collection documents for detailed collection procedures. Sample volumes and preservative information is given in ST-PM-0002.

8.2 Aqueous samples should be collected in 1-L glass bottles and soil samples should be collected in 4-oz glass jars. Samples are protected from light and stored at 4 ± 2 ˚C. Sample extracts are stored at a temperature < 0 ˚C, protected from light and isolated from all potential contaminants and all standards.

8.3 Holding Times

8.3.1 Extraction is initiated within 7 days of the sampling date for aqueous samples, and 14 days of the collection date for solid and waste samples.

8.3.2 In the case, where drying/homogenization techniques and/or incremental sampling techniques are employed, the hold time may be assessed from when the composited sample is created, in the field or in the laboratory. Homogenization and incremental sampling techniques are diverse and vary depending on the nature of the material, methodologies and project objectives. Please reference the project's Client Requirements Memorandum regarding compositing and hold times.

## 9.0 QUALITY CONTROL

9.1 **Batch**

9.1.1 A sample batch is a maximum of 20 environmental samples, which are prepared together using the same process and same lot(s) of reagents.

9.1.2 Instrument conditions must be the same for all standards, samples and QC samples.

9.1.3 For this analysis, batch QC consists of a method blank, a Laboratory Control Sample (LCS), and Matrix Spike (MS)/ Matrix Spike Duplicate (MSD). In the event that there is insufficient sample to analyze a MS/MSD, an LCS Duplicate (LCSD) is prepared and analyzed.

9.1.3.1 Matrix Spike (MS) and Matrix Spike Duplicate (MSD) may be performed upon client request, and are noted in the Client Requirement Sheets and Log-in.

9.2 **Method Blank (MB)**

9.2.1 A method blank is a blank matrix processed simultaneously with, and under the same conditions as, samples through all steps of the procedure. DI water is used for water samples, reagent sand for soils and solids, and Avant Gauze wipe for wipes.

9.2.2 A method blank must be prepared with every sample batch.

9.3 **Laboratory Control Sample (LCS)**

9.3.1 An LCS is a blank matrix spiked with a known amount of analyte(s), processed simultaneously with, and under the same conditions as, samples through all steps of the analytical procedure. DI water is used for water samples, reagent sand for soils and solids, and Avant Gauze wipe for wipes.

9.3.2 An LCS must be prepared with every sample batch.

9.4 **Matrix Spike (MS) /Matrix Spike Duplicate (MSD)**

9.4.1 A Matrix Spike is an aliquot of a field sample to which a known amount of target analyte(s) is added, and is processed simultaneously with, and under the same conditions as, samples through all steps of the analytical procedure.

9.5 **Surrogate**

9.5.1 A surrogate is a non-target analyte similar in chemical composition and behavior, which mimics the target analytes during preparation, extraction and analysis.

9.5.2 Surrogate(s) is added to every field sample, method blank, LCS and MS/MSD for analysis at the beginning of the sample preparation process.

9.6 **Instrument Blanks**

9.6.1 An instrument blank (consisting of 1:1 acetonitrile to 5 g/L calcium chloride solution) is periodically analyzed to assess instrument performance.

9.7 **Procedural Variations/ Nonconformance and Corrective Action**

9.7.1 Any variation shall be completely documented using a Nonconformance Memo and approved by the Supervisor and QA Manager. See SOP ST-QA-0036 for details regarding the NCM process.

9.7.2 Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the Supervisor and QA Manager. See SOP ST-QA-0036 for details regarding the NCM process.

## 10.0 CALIBRATION AND STANDARDIZATION

10.1 **Initial Calibration**

10.1.1 External standard calibration is used. Prepare standards containing each analyte of interest at a minimum of five concentration levels. The low level standard should be at or below the reporting limit. The other standards define the working range of the detector. Recommended calibration levels are given in Table 2.

10.1.1.1 A new calibration curve must be generated after major changes to the system or when the continuing calibration criteria cannot be met. Major changes include new columns, any significant changes in instrument operating parameters, and major instrument maintenance (e.g., UV lamp replacement).

10.1.1.2 Except in specific instances, it is NOT acceptable to remove points from a calibration curve for the purpose of meeting criteria. Refer to the corporate policy, "Selection of Calibration Points."

10.1.2 SW-846 chromatographic methods allow the use of both linear and non-linear models for the calibration data.

10.1.2.1 The first way is to begin with the simplest approach, the linear model through the origin, and then progress through other options until the calibration acceptance criteria are met. The second way is to use technical knowledge of the detector response to the target compound to choose the calibration model.

10.1.2.2 The option for non-linear calibration may be necessary to address specific instrumental techniques. However, it is not EPA's intent to allow non-linear calibration to be used to compensate for detector saturation or to avoid proper instrument maintenance.

10.1.3 **Linear calibration using the average response factor**

10.1.3.1 The Relative Standard Deviation (RSD) of the calibration points from the curve used must be ≤ 20% for each target analyte.

10.1.3.2 If the %RSDs in the initial calibration is > 20%, then calibration using a linear regression may be employed.

10.1.4 **Linear calibration using a least squares regression**

10.1.4.1 The intercept of the curve at zero response must be less than ± the reporting limit for the analyte.

10.1.4.2 r (correlation coefficient) must be ≥ 0.995 **OR** $r^2$ (coefficient of difference) must be ≥ 0.990.

10.1.4.3 **Linear calibration using a least squares regression, forcing thru zero**

10.1.4.3.1 Forcing the curve through zero is not the same as including the origin as a fictitious point in the calibration. In essence, if the curve is forced through zero, the intercept is set to 0 *before* the regression is calculated, thereby setting the bias to favor the low end of the calibration range by "pivoting" the function around the origin to find the best fit and resulting in one less degree of freedom. It may be appropriate to force the regression though zero for some calibrations.

10.1.4.3.2 Curve must still meet criteria in 10.4.3.1 and 10.4.3.2.

10.1.4.4 **Linear calibration using a least squares regression, weighting of data points**

10.1.4.4.1 In linear, the points at the lower end of the calibration curve have less absolute variance than points at the high concentration end of the curve. This can cause severe errors in quantitation at the low end of the calibration. For this reason it may preferable to increase the weighting of the lower concentration points. $^{1}/_{Concentration^2}$ weighting (often called $^{1}/_{X^2}$ weighting) to improve accuracy at the low end of the curve.

10.1.4.4.2 Curve must still meet criteria in 10.4.3.1 and 10.4.3.2.

10.1.5 **Non-linear calibration**

10.1.5.1 In situations where the analyst knows that the instrument response does not follow a linear model over a sufficiently wide working range, or when the other approaches have not met the acceptance criteria, a non-linear calibration model may be employed.

10.1.5.1.1 It is not EPA's intent to allow non-linear calibration to be used to compensate for detector saturation or to avoid proper instrument maintenance. Thus, non-linear calibrations are not be employed for analytes shown to consistently exhibit linear calibration for the analytes of interest.

10.1.5.2 The intercept of the curve at zero response must be less than ± the reporting limit for the analyte.

10.1.5.3 r (correlation coefficient) must be ≥ 0.995 OR $r^2$ (coefficient of difference) must be ≥ 0.990.

10.1.5.4 a quadratic calibration curve requires six standards.

10.2 Initial Calibration Verification (ICV)

10.2.1 An initial calibration verification standard must be analyzed before any samples are analyzed for the initial calibration curve. The value calculated is compared to the expected value and should meet the 30% difference criteria or client requirements before the samples are analyzed. The ICV standard is a separate/second source standard.

10.2.2 Not meeting this requirement may be indicative of serious system malfunction or inaccuracies in the standards used for the initial calibration curve or ICV standard. Corrective action must be taken (including reanalysis of the ICV or analysis of a different ICV). Any decision to proceed with analysis of samples when the ICV is out-of-control must be taken with great care and in consultation with the QA department and the laboratory director. Any such action must be documented in an NCM.

10.3 Continuing Calibration Verification.

10.3.1 Analyte response factors must be verified at the beginning of each, after every 10 samples, and at the end of the analysis sequence through the analysis of a mid-level calibration standard.

- Any individual compounds with %D ≤ 20% meet the calibration criteria.
- It is not necessary to run a calibration standard at the beginning of the sequence if samples are analyzed immediately after the completion of the initial calibration.
- If highly contaminated samples are expected, it is acceptable to analyze blanks or rinses at any point in the run.

10.3.2 Corrective Actions for Continuing Calibration: If the %D for any analyte is > 20% corrective action must be taken. This may include minor instrument adjustments, reconditioning or stabilizing the HPLC system, followed by reanalyzing the standard. If the %D is still unacceptable, a new calibration curve must be prepared.

10.3.3 Corrective Action for Samples: Any samples which are not bracketed by compliant continuing calibration standards must be re-injected.

10.4 Retention Time Windows

10.4.1 Retention Time Windows:

10.4.1.1 Retention time windows must be determined for all analytes. Make an injection of all analytes of interest each day over a three day period. Calculate the standard deviation of the three retention times for each analyte. Plus or minus three times the standard deviation of the retention times of each analyte defines the retention time window.

10.4.1.2 The centers of the windows are updated with the midpoint standard of the initial calibration or the opening daily CCV.

10.4.1.3 If the retention time window as calculated above is less than ± 0.2 minutes, use ± 0.2 minutes as the retention time window. This allows for slight variations in retention times caused by sample matrix.

10.4.1.4 The laboratory must calculate new retention time windows each time a new column is installed. Until these standards have been run on the new column, the retention time windows from the old column may be used, updated with the retention times from the new initial calibration.

10.4.2 Corrective Action for Retention Times

10.4.2.1 The retention times of all compounds in each continuing calibration must be within the retention time windows established. If this condition is not met, all samples analyzed after the last compliant standard must be reanalyzed.

## 11.0 PROCEDURE

11.1 Sample Introduction

11.1.1 Add 500 µL Calcium chloride solution (5 g/L) to 500 µL sample extract and QC extract.

11.1.2 Allow extracts to warm to ambient temperature before injection.

11.1.3 Samples are introduced by direct injection of the extract. Samples, standards, and QC must be introduced using the same procedure.

11.2 Perform all qualitative and quantitative measurements.

11.3 Return extract to freezer when not in use.

11.3.1 Once Calcium chloride addition is made to the extract, and the extract is frozen, the extract is no longer suitable for analysis. If reanalysis is needed, a fresh extract aliquot must be taken through 11.1.1 – 11.1.3.

## 12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Qualitative Identification

12.1.1 Tentative identification occurs when a peak is found within the retention time window for an analyte, at a concentration above the Reporting Limit (RL).

12.1.2 Compound identifications which are calculated to be above the RL on the C-18 column are confirmed by analysis on the CLPH column.

12.1.2.1 If requested, the laboratory will report confirmed analyte levels which are calculated to be below the RL but above the laboratory MDL. The data for these hits will be flagged to indicate that the value is estimated.

12.1.3 Sample results are reported only from the C-18 column. The confirmation column, when used, meets all QC requirements. The CLPH column, while not used for reporting, is quantitative in nature.

12.2 Calibration Range

12.2.1 If concentrations of any analytes exceed the working range as defined by the calibration standards, then the sample must be diluted and reanalyzed. Dilutions should target the most concentrated analyte in the upper half (over 50%) of the calibration range.

12.3 Dilutions

12.3.1 Samples may be screened to determine the appropriate dilution for the initial run.

12.3.2 Reporting Dilutions

The most concentrated dilution with no target compounds above the calibration range will be reported. Other dilutions will only be reported at client request.

12.4 Interferences

12.4.1 If peak detection is prevented by interferences, then elevation of reporting levels and/or lack of positive identification must be addressed in the case narrative.

12.5 Calculations are performed using Chrom.

## 13.0 DATA ASSESSMENT AND ACCEPTANCE CRITERIA; CORRECTIVE ACTIONS FOR OUT OF CONTROL DATA

13.1 The data assessment and corrective action process is detailed through the LIMS Nonconformance Memorandum (NCM) process. The NCM process is described in SOP: ST-QA-0036.

13.2 Method Blank

13.2.1 No target analytes may be present in the method blank above the reporting limit.

13.2.2 The method blank must have acceptable surrogate recoveries.

13.2.3 Corrective Action for Method Blanks not meeting acceptance criteria:

13.2.3.1 Method Blank Contamination – Blank contamination above the RL (>1/2 RL for some programs – see specific Client Requirement Memos for details) requires re-prep of batch unless all associated samples are < RL or greater than 10 times the amount detected in the method blank.

13.2.3.2 Method Blank Surrogate excursion – If excursion is limited to the blank, data may be reported with an NCM. If surrogates are also outside criteria in samples, re-prep and re-anlaysis is required. In cases where the surrogate recovery is high and the samples are non-detect, the data may be reported with an NCM

13.3 Laboratory Control Sample (LCS)

13.3.1 Acceptance Criteria:

13.3.1.1 All control analytes should be within established control limits for accuracy (%Recovery) and precision (RPD).

13.3.1.1.1 For long analyte spike list, marginal exceedances (ME) are allowed as follows:

13.3.1.1.2 < 11 analytes in LCS, no analytes allowed in ME of the LCS control limit.

13.3.1.1.3 11-30 analytes in LCS, 1 analytes allowed in ME of the LCS control limit.
13.3.1.1.4 31-50 analytes in LCS, 2 analytes allowed in ME of the LCS control limit.
13.3.1.1.5 51-70 analytes in LCS, 3 analytes allowed in ME of the LCS control limit.
13.3.1.1.6 71-90 analytes in LCS, 4 analytes allowed in ME of the LCS control limit.
13.3.1.1.7 > 90 analytes in LCS, 5 analytes allowed in ME of the LCS control limit.
13.3.1.1.8 No LCS recoveries may be outside the Marginal Exceedance limit.
13.3.1.1.9 Marginal exceedances must be random. If the same LCS analyte exceeds the control limit repeatedly, it is an indication of a systemic problem. The source of the error must be located and corrective action taken.

13.3.1.2 The LCS should have acceptable surrogate recoveries.
13.3.1.3 Corrective Action for LCS not meeting acceptance criteria:
13.3.1.3.1 LCS Spike Recovery excursion (high) – Samples that are non-detect may be reported with an NCM (unless prohibited by client requirements). Samples with detects for the analyte recovered high in the LCS are re-prepped and re-analyzed. . In cases where the surrogate recovery is high and the samples are non-detect, the data may be reported with an NCM
13.3.1.3.2 LCS Spike Recovery excursion (low) – batch is re-prepped and re-analyzed.
13.3.1.3.3 LCS Surrogate Recovery excursion – If excursion is limited to the LCS, data may be reported with an NCM. If target analytes are in control in the LCS, data may be reported with an NCM. If surrogates are also outside criteria in samples, re-prep and re-analysis is required.
13.3.1.4 RPD excursion for LCS/LCSD – If target analytes recoveries are in control, data may be reported with an NCM.

13.4 Matrix Spike/Matrix Spike Duplicate (MS/MSD)
13.4.1 All analytes should be within established control limits for accuracy (%Recovery) and precision (RPD).
13.4.2 Corrective Action for MS/MSD not meeting acceptance criteria:
13.4.2.1 MS/MSD Spike Rec. excursion may not necessarily warrant corrective action other than narration. If affected analyte concentration in the original sample is greater than four times the amount spiked, percent recovery information is ineffective. Data is reported with an NCM. If the excursion is due to a physically evident matrix interference, the data is reported with an NCM (the physical interference must be described in the NCM). If there is no evidence of interference and the RPD as well as spike recoveries out outside limits out, sample re-prep and re-analysis are required.

13.5 Surrogate
13.6.1 All Surrogates should be within established control limits for accuracy (%Recovery).
13.6.2 Corrective Action for Surrogate not meeting acceptance criteria:
13.6.2.1 Surrogate Spike Rec. excursion may not necessarily warrant corrective action other than narration. In cases where the surrogate recovery is high and the associated analytes in the sample are non-detect, the data may be reported with an NCM. Samples with low surrogate recovery require re-prep and re-anlaysis.

13.6 Sample result evaluation
13.6.1 Dilutions

13.6.1.1 If the response for any compound exceeds the working range of the analytical system, a dilution of the extract is prepared and analyzed. An appropriate dilution should be in the upper half of the calibration range.

13.6.1.1.1 Dilution: Sample– An NCM is written to document the reason for the dilution.

13.6.1.1.2 Dilution: Internal Standard diluted out– An NCM is written to document the reason for the dilution

13.6.1.1.3 Dilution: Internal Standard and/or Spike(s) diluted out An NCM is written to document the reason for the dilution.

13.6.2 Carryover

13.6.2.1 When a sample has a high response for a compound, there is a real possibility that some of the sample may carry over into the sample analyzed immediately afterward.

13.6.2.2 If a sample analyzed after a sample with high concentrations has negative results, carryover did not occur.

13.6.2.3 If a sample analyzed after a sample with high concentrations has positive results for the same analytes, or if the chromatographic profile resembles the previous sample, the results are questionable. This sample must be reanalyzed under conditions in which carryover can be confirmed to not have occurred.

13.7 Insufficient Sample

13.7.1 For each prescribed re-preparation corrective action, if there is insufficient sample to repeat the analysis a narrative comment stating such is included in the report narrative.

## 14.0 METHOD PERFORMANCE AND DEMONSTRATION OF CAPABILITY

14.1 Method performance data, Reporting Limits, and QC acceptance limits, are given in the appendix of this SOP.

14.2 Demonstration of Capability

14.2.1 Initial and continuing demonstrations of capability requirements are established in the ST-QAM.

14.3 Training Qualification

14.3.1 The manager/supervisor has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience.

14.3.2 The analyst must have successfully completed the initial demonstration capability requirements prior to working independently. See requirements in the ST-QAM.

14.4 Annually, the analyst must successfully demonstrate proficiency to continue to perform this analysis. See requirements in the ST-QAM.

## 15.0 VALIDATION

15.1 Laboratory SOPs are based on published methods (EPA, DOE, ASTM, Eichrom, Standard Methods) and do not require validation by the laboratory. The requirements for laboratory demonstration of capability are included in the ST-QAM. Laboratory validation data would be appropriate for performance based measurement systems, non-standard methods and significant modifications to published methods. Data from said validations is held in the QA department.

## 16.0 WASTE MANAGEMENT AND POLLUTION PREVENTION

16.1 All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

16.2 Waste Streams Produced by the Method

16.2.1 The following waste streams are produced when this method is carried out.

16.2.1.1 Solvent and water from the HPLC. Solvent waste must be accumulated in the appropriate waste accumulation container, labeled as Drum Type "D".

16.2.1.2 Contaminated disposable glass or plastic materials utilized in the analysis are disposed of in the sanitary trash. If the labware was used for the analysis of radioactive samples and contains radioactivity at a level of 100 cpm over background as determined by a GM meter, the lab ware will be collected in waste barrels designated for solid rad waste for disposal by the EH&S Coordinator.

## 17.0 REFERENCES

17.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, January 1998, Method 8330A.

17.2 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, October 2006, Method 8330B.

17.3 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, December 1996, Section 8000C.

17.4 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, November 1998, Method 3535A.

17.5 TestAmerica Quality Assurance Manual (ST-QAM), current revision

17.6 TestAmerica Corporate Environmental Health and Safety Manual (CW-E-M-001) and St. Louis Facility Addendum (SOP ST-HS-0002), current revisions.

17.7 TestAmerica Policy CA-Q-S-001, Acceptable Manual Integration Practices

17.8 TestAmerica Policy CA-T-P-0002, Selection of Calibration Points

17.9 Associated SOPs, current revisions

17.9.1 ST-QA-0002, Standard and Reagent Preparation

17.9.2 ST-QA-0014, Evaluation of Analytical Accuracy and Precision Through the Use of Control Charts

17.9.3 ST-QA-0016, IDL/MDL Determination

17.9.4 ST-QA-0036, Non-conformance Memorandum (NCM) Process

17.9.5 ST-QA-0038 Procedure for Compositing and Subsampling

17.9.6 ST-PM-0002 Sample Receipt and Chain of Custody

17.9.7 ST-OP-0008 Extraction of Nitroaromatic and Nitroamine Explosives for Waters and Soils, Based on SW-846 3500 Series Methods

## 18.0 CLARIFICATIONS, MODIFICATIONS TO THE REFERENCE METHOD

18.1 None

## 19.0 CHANGES TO PREVIOUS SOP REVISION

19.1 Rev. 12 No Changes, Annual Review.

19.2 Revision 13:

19.2.1 Section 6.1, changed the number of Agilent pieces of equipment used.

19.2.2 Section 12.1.3.1, changed the qualifier assigned to "S".

19.3 Revision 14:

19.3.1 Updated the number of HPLC systems used in section 6.1.

19.3.2 Updated the use of Phenomenex Synergi Polar columns in section 6.4.

19.4 Revision 15:

19.4.1 Updated the steps for preparing low level intermediate stock standard in section 7.7.2.

19.4.2 Updated the amount of calcium chloride solution needed to make QC extract in section 11.0.

19.4.3 Updated grammatical errors.

19.5 Revision 16:

19.5.1 Inserted requirement for quadratic curve for non-linear calibrations in section 10.1.

19.5.2 Updated information regarding retention times in section 10.4.

19.6 Revision 17:

19.6.1 Grammatical and formatting corrections through out

19.6.2 Removal of QuantIMS and Clouseau references and replaced with LIMS

19.6.3 Section 6.0 updated to add equipment

19.6.4 Section 8.0 updated

19.6.5 Section 9.0 updated to indicate the composition of the MB and LCS

19.7 Revision 18:

19.7.1 Updated section 6 equipment list

19.7.2 Section 7, removal of QC Standard 16 mg/mL and 40 ug/mL verbiage

19.7.3 Section 12, removed further confirmation of hits identified by C18 from Qualitative Identification section and updated calculation software.

19.7.4 Updated section 13 with corrective actions

19.7.5 Updated section 15

**Calibration Standards**
**Water (Final Concentration) µg/L**

| Compound | Level 1 | Level 2 | Level 3 | Level 4 | Level 5 | Level 6 | Level 7 | Level 8 |
|---|---|---|---|---|---|---|---|---|
| HMX | 0.125 | 0.25 | 1.25 | 2.50 | 5.00 | 12.5 | 25.0 | 50.0 |
| RDX | 0.125 | 0.25 | 1.25 | 2.50 | 5.00 | 12.5 | 25.0 | 50.0 |
| 1,3,5-Trinitrobenzene | 0.125 | 0.25 | 1.25 | 2.50 | 5.00 | 12.5 | 25.0 | 50.0 |
| 1,3-Dinitrobenzene | 0.125 | 0.25 | 1.25 | 2.50 | 5.00 | 12.5 | 25.0 | 50.0 |
| Tetryl | 0.125 | 0.25 | 1.25 | 2.50 | 5.00 | 12.5 | 25.0 | 50.0 |
| Nitrobenzene | 0.125 | 0.25 | 1.25 | 2.50 | 5.00 | 12.5 | 25.0 | 50.0 |
| 2,4,6-Trinitrotoluene | 0.125 | 0.25 | 1.25 | 2.50 | 5.00 | 12.5 | 25.0 | 50.0 |
| 4-Amino-2,6-dinitrotoluene | 0.125 | 0.25 | 1.25 | 2.50 | 5.00 | 12.5 | 25.0 | 50.0 |
| 2-Amino-2,4-dinitrotoluene | 0.125 | 0.25 | 1.25 | 2.50 | 5.00 | 12.5 | 25.0 | 50.0 |
| 2,6-Dinitrotoluene | 0.125 | 0.25 | 1.25 | 2.50 | 5.00 | 12.5 | 25.0 | 50.0 |
| 2,4-Dinitrotoluene | 0.125 | 0.25 | 1.25 | 2.50 | 5.00 | 12.5 | 25.0 | 50.0 |
| 2-Nitrotoluene | 0.125 | 0.25 | 1.25 | 2.50 | 5.00 | 12.5 | 25.0 | 50.0 |
| 3-Nitrotoluene | 0.125 | 0.25 | 1.25 | 2.50 | 5.00 | 12.5 | 25.0 | 50.0 |
| 4-Nitrotoluene | 0.125 | 0.25 | 1.25 | 2.50 | 5.00 | 12.5 | 25.0 | 50.0 |
| Nitroglycerin | 0.312 | 0.624 | 3.12 | 6.24 | 12.5 | | | |
| PETN | 0.312 | 0.624 | 3.12 | 6.24 | 12.5 | | | |
| MNX | 0.025 | 0.05 | 0.125 | 0.25 | 0.625 | 1.25 | 2.50 | 5.00 |
| DNX | 0.025 | 0.05 | 0.125 | 0.25 | 0.625 | 1.25 | 2.50 | 5.00 |
| TNX | 0.025 | 0.05 | 0.125 | 0.25 | 0.625 | 1.25 | 2.50 | 5.00 |

**Soil (Final Concentration) ug/kg**

| Compound | Level 1 | Level 2 | Level 3 | Level 4 | Level 5 | Level 6 | Level 7 | Level 8 |
|---|---|---|---|---|---|---|---|---|
| HMX | 125 | 250 | 1250 | 2500.00 | 5000.00 | 12500 | 25000.0 | 50000.0 |
| RDX | 125 | 250 | 1250 | 2500.00 | 5000.00 | 12500 | 25000.0 | 50000.0 |
| 1,3,5-Trinitrobenzene | 125 | 250 | 1250 | 2500.00 | 5000.00 | 12500 | 25000.0 | 50000.0 |
| 1,3-Dinitrobenzene | 125 | 250 | 1250 | 2500.00 | 5000.00 | 12500 | 25000.0 | 50000.0 |
| Tetryl | 125 | 250 | 1250 | 2500.00 | 5000.00 | 12500 | 25000.0 | 50000.0 |
| Nitrobenzene | 125 | 250 | 1250 | 2500.00 | 5000.00 | 12500 | 25000.0 | 50000.0 |
| 2,4,6-Trinitrotoluene | 125 | 250 | 1250 | 2500.00 | 5000.00 | 12500 | 25000.0 | 50000.0 |
| 4-Amino-2,6-dinitrotoluene | 125 | 250 | 1250 | 2500.00 | 5000.00 | 12500 | 25000.0 | 50000.0 |
| 2-Amino-2,4-dinitrotoluene | 125 | 250 | 1250 | 2500.00 | 5000.00 | 12500 | 25000.0 | 50000.0 |
| 2,6-Dinitrotoluene | 125 | 250 | 1250 | 2500.00 | 5000.00 | 12500 | 25000.0 | 50000.0 |
| 2,4-Dinitrotoluene | 125 | 250 | 1250 | 2500.00 | 5000.00 | 12500 | 25000.0 | 50000.0 |
| 2-Nitrotoluene | 125 | 250 | 1250 | 2500.00 | 5000.00 | 12500 | 25000.0 | 50000.0 |
| 3-Nitrotoluene | 125 | 250 | 1250 | 2500.00 | 5000.00 | 12500 | 25000.0 | 50000.0 |
| 4-Nitrotoluene | 125 | 250 | 1250 | 2500.00 | 5000.00 | 12500 | 25000.0 | 50000.0 |
| Nitroglycerin | 312 | 624 | 3120 | 6240.00 | 12480.0 | | | |
| PETN | 312 | 624 | 3120 | 6240.00 | 12480.0 | | | |
| MNX | 25 | 50 | 125 | 250.00 | 625 | 1250 | 2500.00 | 5000.00 |
| DNX | 25 | 50 | 125 | 250.00 | 625 | 1250 | 2500.00 | 5000.00 |
| TNX | 25 | 50 | 125 | 250.00 | 625 | 1250 | 2500.00 | 5000.00 |

*NOTE: Level concentration may be slightly varied.

# Title: EXTRACTION of NITROAROMATIC and NITRAMINE EXPLOSIVES for WATERS and SOILS

**Approvals (Signature/Date):**

Alicia Flaker 5/19/14
Alicia Flaker Date
Organics Analyst

Michael Ridenhower 5-19-14
Michael Ridenhower Date
Health & Safety Manager / Coordinator

Marti Ward 5-19-14
Marti Ward Date
Quality Assurance Manager

Elaine Wild 5/19/14
Elaine Wild Date
Laboratory Director

**This SOP was previously identified as SOP No. ST-OP-0008 Rev. 9**



**Facility Distribution No.:** 0 **Distributed To:** See Electronic Distribution Sheet

## 1.0 SCOPE AND APPLICATION

1.1. This SOP describes procedures for the preparation of nitroaromatic and nitramine explosives by high performance liquid chromatography (HPLC) with UV detection and HPLC with atmospheric pressure, chemical ionization (APCI) mass spectrometry/mass spectrometry (MS/MS), in water, soil and sediment samples. Sample homogenization is not covered in this SOP. Refer to SOP ST-QA-0038.

1.2. This SOP is based on SW-846 Methods 8000C, 8330A, 8321, and 8330B.

1.3. The laboratory target analytes supported by this method, the reporting limit, method detection limits and QC limits are maintained in the Laboratory Information Management System (LIMS).

## 2.0 SUMMARY OF METHOD

2.1. Nitroaromatic and nitramine analytes are prepared for analysis using one of the following procedures:

2.1.1 Low-level solid phase extraction method: Aqueous samples of low concentration are extracted and concentrated using solid phase extraction (SPE). Analytes from a 500 mL sample are adsorbed onto the sorbent material in a SPE cartridge, and then eluted with acetonitrile. The concentrated extract is diluted 1:1 with a 5 g/L solution of calcium chloride prior to analysis for HPLC, diluted 1:1 with $H_2O$ (HPLC grade) for LCMSMS.

2.1.2 Sonication method: Soil and sediment samples are extracted using acetonitrile in a cooled ultrasonic bath. The concentrated extract is diluted 1:1 with a 5 g/L solution of calcium chloride prior to analysis.

2.1.3 Orbital Shaker Table Method: Soil, sediment and wipe samples are extracted into acetonitrile on an orbital shaker table. The concentrated extract is diluted 1:1 with a solution of calcium chloride prior to analysis for HPLC, diluted 1:1 with $H_2O$ (HPLC grade) for LCMSMS.

## 3.0 DEFINITIONS

3.1. See the St. Louis Quality Assurance Manual (ST-QAM) for a glossary of common laboratory terms and data reporting qualifiers.

3.2. There are no specific definitions for this procedure.

## 4.0 INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus. All these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2. Tetryl decomposes rapidly in methanol/water solutions, as well as with heat. All aqueous samples expected to contain Tetryl should be diluted with acetonitrile prior to filtration. SAMPLES EXPECTED TO CONTAIN TETRYL SHOULD NOT BE EXPOSED TO TEMPERATURES ABOVE ROOM TEMPERATURE.

## 5.0 SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), Radiation Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.2. Specific Safety Concerns or Requirements

5.2.1 2,4,6-TNT is the analyte most often detected in high concentrations in soil samples. Soil samples as high as 2% 2,4,6-TNT can be safely ground. Samples containing higher concentrations should not be ground. The project manager or client must provide information as to whether the samples are suspected to contain explosives at a level greater than 2%. Visual observation of soil samples taken from a site expected to contain explosives is also important. Lumps of material that have a chemical appearance should be suspect and not ground. Explosives are generally a very finely ground grayish-white material.

5.3 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: **This list does not include all materials used in the method.** The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

| Material (1) | Hazards | Exposure Limits (2) | Signs of Exposure |
|---|---|---|---|
| Acetonitrile | Flammable<br>Poison | 40 ppm<br>(TWA) | Early symptoms may include nose and throat irritation, flushing of the face, and chest tightness. Prolonged exposure to high levels of vapors may cause formation of cyanide anions in the body. |
| Methanol<br>(Methyl Alcohol) | Flammable<br>Poison<br>Irritant | 200 ppm<br>(TWA) | A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes. |
| Hydrochloric Acid | Corrosive<br>Poison | 5 ppm-<br>Ceiling | Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage. |

| |
|---|
| 1 – Always add acid to water to prevent violent reactions. |
| 2 – Exposure limit refers to the OSHA regulatory exposure limit. |
| TWA – Time Weighted Average |

## 6.0 EQUIPMENT AND SUPPLIES

6.1. Labware is cleaned to remove any residual organics. Please refer to SOP ST-OP-0001 for detailed glassware cleaning procedures.

6.2. Temperature controlled ultrasonic bath

6.3. Vortex mixer

6.4. Muffle Oven

6.5. Analytical balance

6.6. 10-µL, 25-µL, 50-µL, 100-µL, 500-µL, 1000-µL, 0.2-mL, 0.3-mL Hamilton liquid syringe or equivalent

6.7. Disposable cartridge filters – 0.45 µm Teflon filter

6.8. SPE Cartridges (Resprep RDX, 500 mg/6 mL or Waters Porapak RDX, 500 mg/6mL) or equivalent

6.9. Volumetric flasks (Class A), 100-mL, 10-mL, 1000-mL with screw tops

6.10. Scintillation, 12-mL, or volatile vials, 40-mL, screw top with Teflon liners.

6.11. Mortar and Pestle

6.12. Puck Mill

6.13. Orbital shaker table.

6.14. Wipes- 4-ply rayon/polyester 4”x4” Avant Gauze PRM25444

## 7.0 REAGENTS AND STANDARDS

7.1 All standards and reagent preparation, documentation and labeling must follow the requirements of SOP ST-QA-0002, current revision.

7.2 HPLC grade water is used both for the instrumentation mobile phase as well as at the extraction level.

7.3 Acetonitrile, HPLC grade

7.4 Methanol, HPLC Grade

7.5 Sodium Chloride, ASC grade

7.6 Sand, purified (JT Baker)

7.7 Ammonium acetate, HPLC grade

7.8 0.1M HCL

7.8.1 Add 10 mL of 12 M HCL to 1200 mL of HCLP grade water

7.9 Stock Standards

7.9.1 It is recommended that diluted standards be purchased as stock solution with a concentration no greater than 1000 mg/L (ppm).

7.9.2 Standard solutions may also be prepared using Standard Analytical Reference Materials (SARMs).

7.9.2.1 **NOTE: IF USING NEAT STANDARDS PLEASE NOTE: HMX, RDX, Tetryl, and 2,4,6-TNT are explosives and the neat material must be handled carefully. Drying at ambient temperature requires several days. DO NOT DRY AT HEATED TEMPERATURES**.

7.9.2.2 Place about 10 mg (weighed to the nearest 0.1 mg) of a single analyte into a 10 mL volumetric flask and dilute to volume with acetonitrile. Invert the flask several times until dissolved. Calculate the concentration of the stock solution from the actual weight used (nominal concentration = 1,000 mg/L).

7.9.2.3 Store at < 6 ˚C and protect from light.

7.9.2.4 Stock standards must be replaced after six months or sooner if comparison with quality control indicates a problem.

7.9.2.5 Standard solution may also be purchased as prepared certified solutions. The vendor specified expiration dates will apply until ampoules are opened and mix is used.

7.10 Intermediate Stock Standard Solutions

7.10.1 Prepare an intermediate stock standard solution at 2000 µg/L for low level and 20,000 for high level per analyte in acetonitrile.
**NOTE: If the analytical column cannot achieve separation of 2,4-DNT and 2,6-DNT, it will be necessary to prepare a separate intermediate stock solution of 2,6-DNT.**

7.10.2 Intermediate stock standards must be replaced after 30 days or sooner if comparison with quality control samples indicated a problem.

7.11 Surrogate Standards

7.11.1 1,2-Dinitrobenzene is the surrogate used for this method. The surrogate standards are prepared and stored in the same way as the calibration standards.

7.12 MDNA Stock Standards

7.12.1 A neat MDNA standard is purchased. Stock solution preparation is similar to section 7.9.2 using 1:1 methanol and 0.1 M HCL as solvents.

## 8.0 SAMPLE COLLECTION PRESERVATION AND STORAGE

8.1 TestAmerica St. Louis supplies sample containers and chemical preservatives in accordance with the method. TestAmerica St. Louis does not perform sample collection. Samplers should reference the methods referenced and other applicable sample collection documents for detailed collection procedures. Sample volumes and preservative information is given in ST-PM-0002**.**

8.2 Aqueous samples should be collected in 1-L glass bottles and soil samples should be collected in 4-oz glass jars. Samples are protected from light and stored at 4 ± 2 ˚C. Sample extracts are stored at a temperature < 0 ˚C, protected from light and isolated from all potential contaminants and all standards.

8.3 Holding Times

8.3.1 Extraction is initiated within 7 days of the sampling date for aqueous samples, and 14 days of the collection date for solid and waste samples.

8.3.2 In the case, where drying/homogenization techniques and/or incremental sampling techniques are employed, the hold time may be assessed from when the composited sample is created, in the field or in the laboratory. Homogenization and incremental sampling techniques are diverse and vary depending on the nature of the material, methodologies and project objectives. Please reference the project's Client Requirements Memorandum regarding compositing and hold times.

## 9.0 QUALITY CONTROL

9.1. **Batch**

9.1.1 A sample batch is a maximum of 20 environmental samples, which are prepared together using the same process and same lot(s) of reagents. Where no preparation method exists (e.g. water sample volatile organics, water sample anion analysis) the batch is comprised of a maximum of 20 environmental samples which are analyzed together with the same process, lots of reagents and personnel.

9.1.2 Instrument conditions must be the same for all standards, samples and QC samples.

9.1.3 For this analysis, batch QC consists of a method blank, a Laboratory Control Sample (LCS), and Matrix Spike (MS) and Matrix Spike Duplicate (MSD). In the event that there is insufficient sample to analyze a sample duplicate, an LCS Duplicate (LCSD) is prepared and analyzed.

9.2 **Method Blank**

9.2.1 A method blank is a blank matrix processed simultaneously with, and under the same conditions as, samples through all steps of the procedure.

9.2.2 A method blank must be prepared with every sample batch.

9.2.3 Surrogates are spiked into the method blank at the same level as the samples.

9.2.4 Aqueous method Blanks use 500 mL of HPLC water spiked with the surrogates.

9.2.5 Solid method blanks use either 2 or 10 g of muffled sand spiked with the surrogates depending on method variation.

9.2.6 Wipe method blanks use blank wipes.

9.3 **Laboratory Control Sample**

9.3.1 An LCS is a blank matrix spiked with a known amount of analyte(s), processed simultaneously with, and under the same conditions as, samples through all steps of the analytical procedure.

9.3.2 An LCS must be prepared with every sample batch.

9.3.3 Aqueous LCS use 500 mL of HPLC water fortified with the organic analytes of interest, including surrogates.

9.3.4 Solid LCS use either 2 or 10 g of muffled sand fortified with the organic analytes of interest, including surrogates, depending on method variation.

9.3.5 Wipe LCS use blank wipe fortified with the organic analytes of interest, including surrogates, depending on method variation.

9.4 **Matrix Spike (MS) /Matrix Spike Duplicate (MSD)**

9.4.1 A Matrix Spike is an aliquot of a field sample to which a known amount of target analyte(s) is added, and is processed simultaneously with, and under the same conditions as, samples through all steps of the analytical procedure.

9.4.2 MS/MSD samples do not count towards the 20 environmental samples in a sample batch.

9.4.3 MS/MSD samples, when requested, must be performed with every sample batch and every LIMS batch.

9.4.4 If there is insufficient sample to perform an MS/MSD, a duplicate LCS is analyzed. An NCM is written to document the insufficient volume and the utilization of an LCSD to demonstrate precision.

9.4.5 There is no MS/MSD for wipe sample batches due to the nature of the sample. A LCS/LCSD will be performed to demonstrate precision.

9.5 **Surrogates**

9.5.1 Surrogates are organic compounds which are similar to the target analyte(s) in chemical composition and behavior in the analytical process, but which are not normally found in environmental samples.

9.5.2 Each applicable sample, blank, LCS and MS/MSD is spiked with surrogate standards. Surrogate spike recoveries must be evaluated by determining whether the concentration (measured as percent recovery) falls within the required recovery limits.

9.6 **Procedural Variations/ Nonconformance and Corrective Action**

9.6.1 Any variation shall be completely documented using a Nonconformance Memo and approved by the Supervisor and QA Manager. See SOP ST-QA-0036 for details regarding the NCM process.

9.6.2 Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the Supervisor and QA Manager. See SOP ST-QA-0036 for details regarding the NCM process.

## 10.0 CALIBRATION AND STANDARDIZATION

10.1 Balance calibration must be checked daily when used. Refer to SOP ST-QA-0005.

10.2 Thermometers must be checked as prescribed in SOP ST-QA-0005.

10.3 See the analysis of SOPs: ST-LC-0002 and ST-LC-0005 for instrument calibration requirements.

## 11.0 PROCEDURE

11.1 Solid phase extraction (SPE) for aqueous samples

11.1.1 Measure 500 mL of sample gravimetrically and record the pH.

11.1.2 Add the appropriate amount of surrogate based on the middle range of the initial calibration. If the sample is an LCS or MS/MSD, add the appropriate amount of spike and surrogate based on the mid level of the ICAL. Do not agitate the contents of the container while pouring the 500 mL.

11.1.2.1 If a sample is known or suspected (based upon client knowledge, project scope, or site history) to have a high density (>1.2 g/mL, e.g. a brine or waste) or a low density (<0.98 g/mL, e.g. mixed solvent), the sample density will be measured and the volume determined arithmetically (sample mass divided by the density equals the volume).

11.1.2.2 Volume is calculated by gravimetric determination assuming a sample density of 1. Samples that are not aqueous, or suspected of having a density greater than 1.2, will have aliquots taken for density analysis to correct volume for density.

11.1.3 Prior to conditioning the cartridges, the connector caps, straws and PTFE tubing thoroughly rinsed with methanol and then acetonitrile.

11.1.4 Adjust the flow rate through the solid-phase extraction cartridge to approximately 10 mL/min with the vacuum pressure. It is important not to allow the cartridge to go dry at any point during the conditioning stage or during the addition of sample to the cartridge.

11.1.5 Precondition the RDX cartridge with acetonitrile.

11.1.6 Condition the cartridge with **HPLC grade** water.

11.1.7 Begin dripping the sample through the solid phase extraction cartridge at a rate of approximately 10 mL/min. Do not pre-filter the sample unless the sample is suspected to cause clogging. Do not let the solid phase extraction tube go completely dry during the running of the sample through the cartridge. If the tube clogs after sample loading, measure the amount of the sample that was successfully filtered and use that volume for the extraction constant. A cartridge is considered clogged when there can be no more sample drawn through it.

11.1.8 When there is 10 to 20 mL of sample left in the container, use 5 to 10 mL **HPLC grade** water to rinse the interior of the cartridge in order to insure that all the contents have been removed.

11.1.9 If the tube is not clogged, rinse the column with 10 mL HPLC grade water. After rinsing the cartridge allow any excess water to be drawn though. The cartridge is then dried with nitrogen.

**Note:** After extraction is finished the cartridge must be dry in order to insure that no water is being carried over into the final extract.

11.1.10 Put the sample collection vials in the rack and slowly elute with acetonitrile into a 4mL amber vial by pulsing the pipette bulb once and adjust eluent to a final volume of 2.5 mL allowing the acetonitrile to be pulled by gravity (this may take several minutes).

11.2 Extraction of Soil/Sediment Samples Method 8330A & 8321

11.2.1 Allow sample to air dry at least 18 hours. After drying, weigh the sample until constant mass is achieved. The period in between measurements may not be less than one hour.

11.2.2 See SOP ST-QA-0038 for the procedure for sub-sampling.

11.2.3 Place a 2.0 g sub-sample of each soil sample in a 40 mL glass vial. Add the appropriate amount of surrogate based on the middle range of the initial calibration. If the sample is an LCS or MS/MSD, add the appropriate amount of spike and surrogate based on the mid level of the ICAL Bring to 10.0mL with acetonitrile. Vortex swirl for one minute. Place in an ultrasound bath for 18 ± 2 hours or an orbital shaker table for 18 ± 2 hours.

11.2.4 After extraction remove from the bath or shaker table and centrifuge for 15 minutes if necessary.

11.2.5 Place extract in a syringe and filter through a 0.45 µm Teflon filter. Discard the first 3 mL of filtrate and retain the remainder in a Teflon capped vial for HPLC/LCMSMS analysis.

11.3 Extraction of Soil/Sediment Samples Method 8330B

11.3.1 Allow sample to air dry at least 18 hours. After drying, weigh the sample until constant mass is achieved. The period in between measurements may not be less than one hour.

11.3.2 **Sample Grinding:** Samples from ammunition plants or depots must be

thoroughly ground using an acetonitrile rinsed mortar and pestle. Samples from firing ranges must have oversized fractions removed by passing the entire sample through a 2mm sieve. Weigh both fractions and then pulverize the entire sample that passed the 2 mm sieve in a puck mill (5 cycles with a 60 second duration for each cycle). **Note:** Heat will accumulate in the dish which may lead to unwanted loss of analytes. Blind PTs in which the sample and entire puck assembly are kept below 0 °C until the time of grinding have shown excellent recoveries. It is highly recommended to grind while both the sample and puck assembly are cold.

11.3.3 See SOP ST-QA-0038 for the procedure for sub-sampling.

11.3.4 To obtain a sub-sample, the entire sample is spread out on a clean surface in a fume hood to a thickness of 1-2 cm. At least thirty different portions of approximately 0.3 g each are collected from random locations throughout the sample.

11.3.5 Place a 10.0 g sub-sample of each soil sample in a 2 oz wide mouth bottle. Add the appropriate amount of surrogate based on the middle range of the initial calibration. If the sample is an LCS or MS/MSD, add the appropriate amount of spike and surrogate based on the mid level of the ICAL. Bring to 20.0 mL with acetonitrile, cap with Teflon-lined cap, vortex swirl for one minute, and place in a cooled ultrasonic bath for 18 ± 2 hours or on an orbital shaker table for 18 ± 2 hours.

11.3.6 After extraction remove from the bath or shaker table and centrifuge for 15 minutes if necessary.

11.3.7 Place extract in a syringe and filter through a 0.45 µm Teflon filter. Discard the first 3 mL of filtrate and retain the remainder in a Teflon capped vial for HPLC analysis.

11.4 Extraction of Wipe Samples Method 8330/8321

11.4.1 Place wipe into a 50-mL polypropylene centrifuge tube (or appropriately sized jar). Add about 10 mL of acetonitrile (or enough to submerge the wipe). Add the appropriate amount of surrogate, based on the middle range of the initial calibration (for an LCS or MS/MSD, add the appropriate amount of spike). Vortex samples for half of an hour.

11.4.2 Place in an orbital shaker for 1 hour. For each sample, squeeze the wipe three times.

11.4.3 Repeat step 11.4.2 one more time.

11.4.4 Vortex each sample for 10 seconds.

11.4.5 Transfer the extract into a syringe and filter through a 0.45 µm Teflon filter. Discard the first 3 mL of filtrate and retain the remaining sample in a Teflon capped vial for HPLC/LCMSMS analysis.

11.5 Methylene Dinitramine (MDNA)/ETU Preparation

11.5.1 Pipette 5ml of sample into clean and labeled VOA vial.

11.5.2 Verify that each MDNA sample has a pH of less than 2. (unpreserved samples will not have any MDNA present as the compound degrades quickly in neutral water) If the MDNA sample pH is greater than 2, contact the project manger.

11.5.3 For MDNA, use 5ml of 0.1 M HCL as fluid for the method blanks and LCS. For ETU use DI water.

11.5.4 Add appropriate amount of 1,2-Dinitrobenzene surrogate to all samples including QC.

11.5.5 Add MDNA/ETU spikes to LCS and MS/MSD.

11.5.6 Record the standard identification and volume of all additions onto the preparation sheet.

11.5.7 Add 5 mL of methanol to all samples.

11.5.8 Mix thoroughly

11.5.9 Add internal standards to extract just prior to injection.

## 12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Commonly used calculations (e.g. % recovery and RPD) and standard instrument software calculations are given in the TestAmerica St. Louis ST-QAM.

12.2 See individual analysis SOPs: ST-LC-0002 and ST-LC-0005 for specific calculations.

## 13.0 DATA ASSESSMENT AND ACCEPTANCE CRITERIA; CORRECTIVE ACTIONS FOR OUT OF CONTROL DATA

13.1 Data assessment does not pertain to this sample preparation procedure.

13.2 Samples requiring re-preparation are submitted to the preparation lab with an NCM detailing the issue. The NCM process is described in SOP: ST-QA-0036. Specific information is given in the applicable analysis SOP.

## 14.0 METHOD PERFORMANCE AND DEMONSTRATION OF CAPABILITY

14.1. Method performance data, Reporting Limits, and QC acceptance limits, are given in the associated analytical SOP

14.2. Demonstration of Capability

14.2.1. Initial and continuing demonstrations of capability requirements are established in the ST-QAM.

14.3. Training Qualification

14.3.1. The manager/supervisor has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience.

14.3.2. The analyst must have successfully completed the initial demonstration capability requirements prior to working independently. See requirements in the ST-QAM.

14.4. Annually, the analyst must successfully demonstrate proficiency to continue to perform this analysis. See requirements in the ST-QAM.

## 15.0 VALIDATION

15.1 Laboratory SOPs are based on published methods (EPA, DOE, ASTM, Eichrom, Standard Methods) and do not require validation by the laboratory. The requirements for laboratory demonstration of capability are included in the ST-QAM. Laboratory validation data would be appropriate for performance based measurement systems, non-standard methods and significant modifications to published methods. Data from said validations is held in the QA department.

## 16.0 WASTE MANAGEMENT AND POLLUTION PREVENTION

16.1 All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for “Waste Management and Pollution Prevention.”

16.2 Waste Streams Produced by the Method

The following waste streams are produced when this method is carried out:

- Contaminated disposable glass or plastic materials utilized in the analysis are disposed of in the sanitary trash.
- Solid materials (soil, gloves, soiled paper products) are collected in the container labeled "Non-Regulated Material" for disposal.
- If the labware was used for the analysis of radioactive samples and contains radioactivity at level of 100 cpm over background as determined by a GM meter, the labware will be collected in waste barrels designated for solid rad waste for disposal by the EH&S Coordinator.
- Solvent rinses from the labware cleaning procedure are disposed of in the flammable solvent waste stream.

## 17.0 REFERENCES

17.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods SW846 February 2007 Method 8330A.

17.2 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods SW846 February 2007, Method 8321B

17.3 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, March 2003 Section 8000C.

17.4 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, October 2006 Method 8330B.

17.5 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, February 2007 Method 3535A.

17.6 St. Louis Quality Assurance Manual (ST-QAM), current revision

17.7 Corporate Environmental Health and Safety Manual (CW-E-M-001) and St. Louis Facility Addendum (SOP ST-HS-0002), current revisions.

17.8 Associated SOPs, current revisions:

17.8.1 ST-OP-0001, Labware Preparation for Organic Analysis
17.8.2 ST-PM-0002, Sample Receipt and Chain of Custody
17.8.3 ST-QA-0002, "Standards and Reagent Preparation."
17.8.4 ST-QA-0005, "Calibration and Verification Procedure for Thermometers, Balances, Weights and Pipettes"
17.8.5 ST-QA-0036, "Non-Conformance Memorandum (NCM) Process"
17.8.6 ST-LC-0002, "Analysis of Nitroaromatic and Nitroamine Explosives by HPLC."
17.8.7 ST-LC-0005, Analysis of Nitroaromatic and Nitramine Explosives by APCI/LC/MS/MS
17.8.8 ST-QA-0038, "Procedure for Compositing and Sub sampling."

## 18.0 CLARIFICATIONS, MODIFICATIONS TO THE REFERENCE METHOD

18.1 Some surrogate spiking concentrations are modified from those recommended in SW-846, in order to make the concentrations more consistent with the calibration levels in the determinative methods.

18.2 Aqueous sample volumes are determined by weight.

## 19.0 CHANGES FROM PREVIOUS REVISION

19.1. Updated section 9.2 regarding amounts of reagent water used with surrogates and also, updated the amount muffled sand used with surrogates.
19.2. 12/23/2010; REV5, Updated section 11.2.3 regarding ultrasound times.
19.3. Rev 6:
- 19.3.1. Updated dilution information in section 2.1.
- 19.3.2. Added shaker table to equipment list.
- 19.3.3. Updated spike and surrogate amounts in section 11.
- 19.3.4. Added cartridge conditioning information to section 11.1.
- 19.3.5. Added constant weight determination to section 11.2 and 11.3.

19.4. Rev 7:
- 19.4.1. Through-out: removed references to Clouseau and Quantims – replaced with LIMS
- 19.4.2. Updated volume of intermediate stock standard solution from 5000ug/L to 2000 ug/L in Section 7.11
- 19.4.3. Removed references to tables no longer in SOP from Section 7.12
- 19.4.4. Added MDNA stock standard information to Section 7.13
- 19.4.5. Updated size of vial used in soil prep (Section 11.2.3)
- 19.4.6. Removed specific amount of surrogate to add in Section 11.4.4 as amount depends upon concentration
- 19.4.7. grammatical and spelling errors corrected
- 19.4.8. added grinding information for 8330B – altered language
- 19.4.9. § 11.1.1.1.: Addition of density limits
- 19.4.10. § 11.1.1.2.: Addition of volume calculation by gravimetric determination

19.5. Rev 8:
- 19.5.1. Grammatical errors corrected through out
- 19.5.2. Added §2.1.3, reference to wipe samples
- 19.5.3. Added §7.0, wipes
- 19.5.4. Added §9.0, material used for MB, LCS and MS/MSD
- 19.5.5. Added §11.0, procedure for processing wipes

19.6. Rev 9:
- 19.6.1. Updated §8.0

19.7. Rev. 10
- 19.7.1. Annual review, no changes.

# Title: ANALYSIS OF PERCHLORATE IN WATER, WIPES, SOILS AND SOLID WASTES BY LC/MS/MS [SW-846 6850]

**Approvals (Signature/Date):**

| | |
|---|---|
| Ben Hicks 8/7/13<br>Ben Hicks Date<br>Chemistry Department Manager | Michael Ridenhower 8/7/13<br>Michael Ridenhower Date<br>Health & Safety Manager / Coordinator |
| Marti Ward 8.7.13<br>Marti Ward Date<br>Quality Assurance Manager | Elaine Wild 8/7/13<br>Elaine Wild Date<br>Laboratory Director |

**This SOP was previously identified as SOP No. ST-LC-0004 Rev. 4**



**Facility Distribution No.: 0** **Distributed To: See Electronic Distribution Sheet**

## 1.0 SCOPE AND APPLICATION

1.1 This procedure provides instructions for the analysis of perchlorate by high performance liquid chromatography (HPLC) coupled with electrospray ionization (ESI) and tandem mass spectrometry detection (MS/MS) in water, wipes, soil and solid waste samples.

1.2 This SOP is based on EPA SW-846 Method 6850.

1.3 The laboratory target analytes supported by this method, the reporting limits, method detection limits and QC limits are maintained in the Laboratory Information Management System (LIMS).

## 2.0 SUMMARY OF METHOD

2.1 Water samples are filtered to remove solids and pretreated to remove common anions in the sample matrix. The pretreatment minimizes the effect of signal suppression caused by these common anions.

2.2 Soil and solid samples are mixed with reagent water at a 10:1 ratio (water to soil/solid) and are vortexed and shaken to provide sample agitation/mixing. A 20:1 ratio is used for wipes (20 ml to 1 wipe). The resulting extract is filtered to remove solids and pretreated to remove common anions in the sample extract. The pretreatment minimizes the effect of signal suppression caused by these common anions.

2.3 After the initial preparation steps, the sample is introduced to the HPLC allowing for perchlorate separation from the sample matrix. Following separation perchlorate is ionized via negative electrospray ionization, isolated in the first quadrupole and transferred to a collision cell for fragmentation. The resulting fragments are isolated in the second quadrupole and transferred to the detector where they are measured by the detector response relative to the response of the perchlorate standard concentrations and quantitated. Perchlorate is formed from the two naturally occurring isotopes of chlorine ($^{35}Cl$ and $^{37}Cl$) which produce perchlorate with molecular weights of 99 and 101 amu. The two parent ions for perchlorate (m/z = 99 and 101) are selected at the first quadrupole. The parent ions are then fragmented in the collision cell and the resulting daughters (m/z = 83 and 85) are used for quantitation. The 83/85 isotopic ratio reflects the isotopic ratio of the naturally occurring $^{35}Cl/^{37}Cl$. The presence of the two parent to daughter transitions 99>83 and 101>85 and the ratio of the detected ions are used as the confirmation of the presence of perchlorates.

2.4 Calibration is based on internal standardization using oxygen-18-labeled perchlorate, i.e., $Cl^{18}O_4^-$, m/z = 107. The 107>89 m/z transition is monitored for the labeled perchlorate. Use of the labeled perchlorate helps control calibration drift and provides a retention time reference point.

## 3.0 DEFINITIONS

3.1 See the TestAmerica Quality Assurance Manual (ST-QAM) for a glossary of common laboratory terms and data reporting qualifiers.

3.2 Ionization Suppression: Ionic species co-eluting with perchlorate can cause suppression of the perchlorate signal.

## 4.0 INTERFERENCES

4.1 Solvents, reagents, glassware and other sample processing hardware may yield discrete artifacts and/or elevated baselines, causing interference to the sample analysis. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running laboratory method blanks.

4.2 Some samples of laboratory detergents (e.g., Alconox) have been shown to contain concentrations of perchlorate in the low part-per-million concentrations. Using disposable labware and rinsing volumetric flasks with de-ionized water, rather than washing in detergent, is helpful to avoid background contamination.

4.3 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed with solvent between samples. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of an instrument blank to check for cross contamination.

4.4 Hydrogen sulfate ion ($H^{34}SO_4^-$), which is formed from a minor sulfur isotope, is commonly present in samples. $H^{34}SO_4^-$ elutes before perchlorate, but at high concentrations can tail into the retention time window of the perchlorate peak and elevate its baseline at m/z 99. Quantitation of perchlorate based on m/z 83 and 89 avoids this potential interference from $H^{34}SO_4^-$.

4.5 Potential problems may arise when analyzing samples containing high levels of total dissolved solids (TDS) (i.e. salts of chloride, sulfate, carbonate, bicarbonate, etc.). Ionization suppression can occur when high levels of dissolved salts are introduced into the mass spectrometer, resulting in reduction in the perchlorate analyte transition peaks. The degree of ionization suppression will depend on the type and concentration of the interfering ions present, and whether they overlap with perchlorate when eluted. Ionization Suppression is monitored in each sample by including oxygen-18 labeled perchlorate as an internal standard. To ensure accurate quantitation, the internal standardization technique is used. Any samples producing internal standard recoveries outside +/- 50% are routinely reanalyzed. If there is evidence of the sample matrix affecting the internal standard recovery, the sample may be diluted and reanalyzed to reduce sample matrix effects on the analysis.

4.6 Retention time shifts may occur as competing anions in the sample take up active sites on the stationary phase. In such samples, perchlorate will elute earlier than in the calibration standards. The $Cl^{18}O_4^-$ peak will also shift, and therefore is used to confirm the identification of the native perchlorate peak.

## 5.0 SAFETY

5.1 Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), Radiation Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.2 Primary Materials Used

5.2.1 The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

| Material (1) | Hazards | Exposure Limit (2) | Signs and symptoms of exposure |
|---|---|---|---|
| Ammonium Hydroxide | Corrosive | 25 PPM (TWA) | Harmful if inhaled. Severe irritation or burns of respiratory system. Irritation may lead to pulmonary edema and lung inflammation. Causes severe irritation of the upper respiratory tract with coughing, burns, breathing difficulty, and possible death. Causes severe eye burns. May cause irreversible eye injury/blindness. Contact may cause ulceration of the conjunctiva and cornea. Eye damage may be delayed. Harmful if ingested. Severe burns to the mouth, throat, and stomach, nausea, vomiting and diarrhea. |
| (1) Always add acid to water to prevent violent reactions | | | |
| (2) Exposure limit refers to OSHA regulatory exposure limit | | | |
| TWA – Time Weighted Average | | | |

## 6.0 EQUIPMENT AND SUPPLIES

6.1 Liquid Chromatograph (Agilent HPLC 1100)/tandem Mass Spectrometer System (Micromass Quattro Ultima)

The analytical system consists of a liquid chromatograph for separation of sample analytes, electrospray ionization source, and tandem mass spectrometer for fragmentation and detection of sample analytes.

6.2 The liquid chromatograph should have a programmable solvent delivery system and all necessary accessories including injection loop, analytical columns, column heater, pump, in-line degasser, etc.

6.3 Any analytical column capable of providing adequate separation of perchlorate from the sample matrix may be used. An example of a suitable column is a Dionex Ion Pac AG16 Guard 2x50mm.

6.4 The mass spectrometer system must have an ESI interface capable of generating gas phase ions of perchlorate from the liquid phase . A matrix diversion valve may be necessary to divert pre-eluting common anions to waste prior to the elution of perchlorate from the analytical column. The use of the matrix diversion valve will also help reduce buildup of salts in the electrospray source and mass spectrometer.

6.5 Masslynx software collects data which is processed and uploaded to the LIMS through Chrom. A data system must be interfaced to the mass spectrometer allowing continuous analyte signal acquisition and storage on machine readable media for all mass spectra obtained. The data system must have software that can search any LC/MS/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. The software must also be capable of integrating the abundances between specified time.

6.6 Volumetric flasks, various volumes.

6.7 Automatic precision pipettes and disposable tips, various volumes.

6.8 Analytical balance capable of measuring to +/- 0.001 g accuracy.

6.9 Shaker

6.10 Vortex Mixer

6.11 Centrifuge – adequate for clarifying soil extracts prior to filtration.

6.12 Disposable 50 mL polypropylene centrifuge tubes or equivalent.

6.13 Disposable 20 mL sterile luerlock syringe w/o needle or equivalent.

6.14 PTFE or Tuffryn membrane 0.45 µm pore size syringe filters.

6.15 Disposable pipettes.

6.16 Solid phase sample pretreatment cartridge, Dionex 2.5 cc BA/AG/H On Guard II® or equivalent

6.17 Sample vials of sufficient volume to allow for replicate analyses.

6.18 Disposable autosampler vials.

6.19 Wipes- 4-ply rayon/polyester 4"x4" Avant Gauze PRM25444

## 7.0 REAGENTS AND STANDARDS

7.1 All standards and reagent preparation, documentation and labeling must follow the requirements of SOP ST-QA-0002, current revision.

7.2 HPLC grade water
7.2.1 DI water ≥ 18 Mohm-cm may be used as an alternative

7.3 Sand – reagent grade

7.4 Nitrogen gas – 99+%

7.5 Argon gas – 99+%

7.6 Ammonium Hydroxide, $NH_4OH$ (28.0 – 30.0% as NH3), ACS grade

7.7 Sodium chloride, NaCl, ACS grade

7.8 Sodium sulfate, $Na_2SO_4$, ACS grade

7.9 Sodium carbonate, $Na_2CO_3$, ACS grade

7.10 Sodium bicarbonate, $NaHCO_3$, ACS grade

7.11 50 mM $NH_4OH$ – Prepare by diluting 3.4 mL of concentrated $NH_4OH$ to 1 L using HPLC grade water.

7.12 5 mM $NH_4OH$ Mobile phase eluant – Prepare by diluting 100 mL of 50 mM $NH_4OH$ to 1.0 L using HPLC grade water.

7.13 Stock Standards

7.13.1 It is recommended that diluted standards be purchased as stock solutions with a concentration no greater than 1000 mg/L (ppm). Standard solutions may also be prepared using Standard Analytical Reference Materials (SARMs). **Before neat materials are to be used, contact the EH&S Coordinator immediately for revision of this procedure.**

7.13.1.1 Store at < 6˚C and protect from light.

7.13.1.2 Stock standards must be replace after **one year** or sooner if comparison with quality control samples indicates a problem.

7.13.1.3 Standard solutions may also be purchased as prepared certified solutions. The vendor specified expiration dates will apply until ampoules are opened and mix is used.

7.13.2 Intermediate Stock Standard Solutions

7.13.2.1 Prepare an intermediate stock standard solution at 1.0 µg/mL in reagent grade water.

7.13.2.2 Intermediate stock standards must be replaced after six months or sooner if comparison with quality control samples indicates a problem.

7.13.3 Calibration Standards

7.13.3.1 Calibration standards, at a minimum of six concentration levels, are prepared through dilution of the intermediate stock standard solutions with HPLC grade water. Spike each calibration standard using the exact same volume of internal spiking solution such that the final internal spike concentration is exactly the same (i.e., 10.0 µg/L $Cl^{18}O_4^-$) for each calibration standard. One of the concentration levels should be at or below the reporting limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples and define the working range of the LC/MS/MS. See Table 2 for suggested calibration standard concentrations.

7.13.3.2 Calibration standards must be stored at a temperature less than six degrees C (<6°C) and stored in the dark.

7.13.4 Internal Standard, Oxygen-18 ($^{18}O$)-Labeled Perchlorate

7.13.4.1 The internal standard is obtained from commercial sources. The standard is oxygen-18 labeled perchlorate, $Cl^{18}O_4^-$, with a purity $\geq$ 90% where < 10% of the oxygen present is $^{16}O$. Opened internal standard expiration is one (1) year and may be stored at room temperature.

7.13.4.2 The internal standard concentration in each standard and sample is 10.0 µg/L. An alternate internal standard spiking volume or concentration may be used, provided it falls within the same concentration range as the external calibration curve. **The volume of the internal standard added to the sample or sample extracts should be such that minimal dilution of the extract occurs.**

7.13.5 Dissolved Salt Solution (DSS)

7.13.5.1 The DSS is prepared in a matrix of HPLC grade water that contains 1000mg/L each of chloride, carbonate, bicarbonate and sulfate ions.

7.13.6 NaCsI Mass Calibration Solution – obtained from a commercial source.

7.13.7 Second Source Initial Calibration Verification (ICV) Standard

7.13.7.1 Calibration verification standards (second source verification standards) are prepared and stored in the same way as calibration standards. They must be made from a stock independently prepared from that used for the calibration standards.

## 8.0 SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 TestAmerica St. Louis supplies sample containers and chemical preservatives in accordance with the method. TestAmerica St. Louis does not perform sample collection. Samplers should reference the methods referenced and other applicable sample collection documents for detailed collection procedures. Sample volumes and preservative information is given in ST-PM-0002.

8.2 Aqueous samples should be collected in clean 125 mL polyethylene bottles and whenever possible, should be steriley filtered in the field at the time of collection using 0.2 µm PTFE membrane filtration

in order to remove potentially perchlorate-degrading microbes. Soil samples should be collected in clean 4oz amber glass jars. Care should be taken to avoid temperature extremes during shipment and storgage. Samples and extracts should be stored with headspace to reduce potential anaerobic biodegradation and isolated from all potential contaminants and all standards.

8.3 Soils, wipes and solid samples should be extracted within twenty eight days of sample collection.

8.4 Aqueous and sample extracts should be analyzed within twenty eight days of collection and/or extraction.

## 9.0 QUALITY CONTROL

9.1 **Batch**

9.1.1 A sample batch is a maximum of 20 environmental samples, which are prepared together using the same process and same lot(s) of reagents.

9.1.2 Instrument conditions must be the same for all standards, samples and QC samples.

9.1.3 For this analysis, batch QC consists of a Method Blank, a Laboratory Control Sample (LCS), and Matrix Spike (MS)/ Sample Duplicate (SD). In the event that there is insufficient sample to analyze a MS/MSD or SD, an LCS Duplicate (LCSD) is prepared and analyzed.

9.1.3.1 Matrix Spike (MS) and Matrix Spike Duplicate (MSD) may be performed upon client request, and are noted in the Client Requirement Sheets and Log-in.

9.2 **Method Blank (MB)**

9.2.1 A method blank is a blank matrix processed simultaneously with, and under the same conditions as, samples through all steps of the procedure.

9.2.2 DI or HPLC water is used for water samples, reagent sand for soils and solids, and Avant Gauze blank wipe for wipes

9.2.3 A method blank must be prepared with every sample batch.

9.2.4 Method Blank results must be below the reporting limt or client specific limit.

9.3 **Laboratory Control Sample (LCS)**

9.3.1 An LCS is a blank matrix spiked with a known amount of analyte(s), processed simultaneously with, and under the same conditions as, samples through all steps of the analytical procedure.

9.3.2 DI or HPLC water is used for water samples, reagent sand for soils and solids, and Avant Gauze for wipes

9.3.3 An LCS must be prepared with every sample batch.

9.3.4 Recovery criteria for the LCS is 80 – 120%.

9.4 **Matrix Spike (MS) /Sample Duplicate (SD)**

9.4.1 A Matrix Spike is an aliquot of a field sample to which a known amount of target analyte(s) is added, and is processed simultaneously with, and under the same conditions as, samples through all steps of the analytical procedure.

9.4.2 A Sample Duplicate is an additional aliquot of a field sample taken through the entire analytical process to demonstrate precision.

9.4.3 The control limits for the matrix spike percent recovery are 80 – 120% for water and 70 – 130% for soils.

9.4.4 The method control limit for RPD is 15% for all samples near or above the mid-range of the calibration curve, and 50% for sample concentrations near the low range of the calibration curve.

9.5 **Internal Standard (IS)**

9.5.1 Oxygen-18 labeled perchlorate is added to every standard, instrument blank, method blank, sample, spiked sample, and dilution tested. For all water, wipe, soil and solid samples the IS addition is made directly to the sample aliquot prior to filtration, extraction and sample pretreatment cartridges. Dilution analyses may be required to either adjust the sample perchlorate concentration into the analytical range, or to reduce matrix effects. For diluted samples that have been extracted with the IS, the IS is added to the diluted extract.

9.5.2 Recovery limit is -50% to +50% of the average IS area counts of the CCV level calibration standards. Client specific limits may be different. Review appropriate Client Requiement Memo for details.

9.6 **Interference Check Standard (ICS)**

9.6.1 A DSS (Dissolved Solid Spike) is analyzed in every analytical batch to demonstrate sufficient analyte separation and lack of excessive ion suppression.

9.6.1.1 Methodologies for perchlorates by LC/MS/MS require that a sample spiked at approximately 2 times the limit of detection (LODV verification) be included in every analytical run. A method blank containing historic anionic interferences is also required with every analytical run to test the robustness of the preparation cleanup. TestAmerica St. Louis has combined these two requirements into the ICS which contains twice as much interfering anions as required by the method and is spiked at the RL with perchlorate. The DSS is subjected to the same preparation and analyzed in the same manner as the samples.

9.6.1.2 The recovery at the LODV for the spiked perchlorate must be within 30% of the true value.

9.6.1.3 In addition, ion suppression is monitored by evaluation of the internal response. The IS response may not exceed -50% to +50% of the CCV level in the ICAL.

9.7 **Instrument Blanks (IB)**

9.7.1 An Instrument Blank is a blank matrix that does not undergo any sample preparation steps.

9.7.2 An instrument blank is analyzed when high level STD or samples are analyzed. Since samples are analyzed in an automated sequence an instrument blank is not typically inserted into the sequence following sample analysis to evaluate for high concentration carryover. Sample analyses that immediately follow a high concentration sample must be evaluated for potential carryover and reanalyzed if carryover is suspected.

9.8 **$^{35}Cl/^{37}Cl$ Isotope Ratio**

9.8.1 For tandem mass spectrometry, the $^{35}Cl/^{37}Cl$ isotope ratio is monitored for both the parent ion at masses 99/101 and the daughter ion at masses 83/85 in each sample, spiked sample, standard, and blank. The theoretical value for the ratio, based on the natural abundance of the respective isotopes, is 3.06.

9.9 **Procedural Variations/ Nonconformance and Corrective Action**

9.9.1 Any variation shall be completely documented using a Nonconformance Memo and approved by the Supervisor and QA Manager. See SOP ST-QA-0036 for details regarding the NCM process.

9.9.2 Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the Supervisor and QA Manager. See SOP ST-QA-0036 for details regarding the NCM process.

## 10.0 CALIBRATION AND STANDARDIZATION

10.1 **Mass Calibration and Mass Calibration Check**

10.1.1 The LC/MS/MS settings such as mass windows, source conditions and voltage settings are checked each time the instrument is set up for perchlorate analysis. Perchlorate is used for the check of optimization as needed.

10.1.2 After major maintenance a mass calibration is performed using the NaCsI solution. The NaCsI solution is introduced at the ESI interface, after the HPLC. The solution is analyzed in the ESI negative mode. The instrument is tuned to the masses shown at the conclusion of this SOP.

10.2 **Initial Calibration**

10.2.1 Internal standard calibration is used. Prepare standards containing each analyte of interest at a minimum of six concentration levels. The low level standard should be at or below the reporting limit. The other standards define the working range of the detector. Recommended full calibration levels are given in the attachment Table at the end of this SOP. The concentration of level 1 may be adjusted based on the reporting limit..

10.2.1.1 A new calibration curve must be generated after major changes to the system or when the continuing calibration criteria cannot be met. Major changes include any significant changes in instrument operating parameters, and major instrument maintenance.

10.2.1.2 Except in specific instances, it is NOT acceptable to remove points from a calibration curve for the purpose of meeting criteria. Refer to the TestAmerica corporate policy, "Selection of Calibration Points."

10.2.2 **Linear calibration using the average response factor**

10.2.2.1 The Relative Standard Deviation (RSD) of the calibration points from the curve used must be $\leq$ 20% for each target analyte.

10.2.2.2 If the %RSDs in the initial calibration is > 20%, then calibration using a linear regression may be employed.

10.2.3 **Linear calibration using a least squares regression**

10.2.3.1 The intercept of the curve at zero response must be less than + or – the reporting limit for the analyte.

10.2.3.2 r (correlation coefficient) must be $\geq$ 0.995 OR $r^2$ (coefficient of determination) must be $\geq$ 0.990.

10.2.3.3 **Linear calibration using a least squares regression, forcing thru zero**

10.2.3.3.1 Forcing the curve through zero is not the same as including the origin as a fictitious point in the calibration. In essence, if the curve is forced through zero, the intercept is set to 0 *before* the regression is calculated, thereby setting the bias to favor the low end of the calibration range by "pivoting" the function around the origin to find the best fit and resulting in one less degree of freedom. It may be appropriate to force the regression though zero for some calibrations.

10.2.3.4 **Linear calibration using a least squares regression, weighting of data points**

10.2.3.4.1 In linear, the points at the lower end of the calibration curve have less absolute variance than points at the high concentration end of the curve. This can cause severe errors in quantitation at the low end of the calibration. For this reason it may preferable to increase the weighting of the lower concentration points. $1/Concentration^2$ weighting (often called $1/X^2$ weighting) to improve accuracy at the low end of the curve.

10.3 Initial Calibration Verification (ICV)

10.3.1 An initial calibration verification standard must be analyzed before any samples are analyzed to ensure the accuracy of the calibration. The value calculated is compared to

the expected value and should meet the 15% difference criteria before the samples are analyzed. The ICV standard is a separate/second source standard.

10.3.2 Not meeting this requirement may be indicative of serious system malfunction or inaccuracies in the standards used for the initial calibration curve or ICV standard. Corrective action must be taken (including reanalysis of the ICV or analysis of a different ICV). Any decision to proceed with analysis of samples when the ICV is out-of-control must be taken with great care and in consultation with the QA department and the laboratory director. Any such action must be documented in an NCM.

10.4 Continuing Calibration Verification.

10.4.1 A CCV may be a second source or the same source as the initial calibration standards and should be made to represent the midpoint of the curve.

10.4.2 Analyte response factors must be verified at the beginning of each analytical run (by either an ICV or a CCV), after every 10 samples and at the end of the analysis run through the analysis of a CCV.

10.4.3 The calibration verification is acceptable if the %D ≤ 15%.

10.4.3.1 If a CCV has failed and the analyst can document the reason for failure (e.g. broken vial, carryover from the previous sample etc.) then a second CCV may be analyzed without any adjustments to the instrument.

10.4.3.2 If this CCV meets criteria then sample analysis may continue; however the preceding samples must be reanalyzed.

10.4.3.3 If this second CCV does not meet criteria, the analysis run is terminated. Instrument maintenance is performed and the instrument may require re-calibration (i.e. initial calibration).

10.4.4 Analyte response factors must be verified at the beginning of each analytical sequence, after every 10 samples and at the end of the analytical sequence at a concentration level within the calibration range for the method.

10.4.4.1 Any individual compounds with %D ≤ 15% meet the calibration criteria.

10.4.4.2 It is not necessary to run a calibration standard at the beginning of the sequence if samples are analyzed immediately after the completion of the initial calibration.

10.4.4.3 If highly contaminated samples are expected, it is acceptable to analyze blanks or rinses at any point in the run.

10.5 Retention Time Windows

10.5.1 Retention Time Windows:

10.5.1.1 A retention time window study is not necessary when using internal standard calibration. However, it is always a good practice and can be a useful diagnostic tool to monitor analyte and internal standard retention times and peak area counts in all samples and standards to observe drifting method performance, poor injection execution , unintended changes in the eluant strength or flow rates, column overloading, and high ionic matrix effects or fouling, so as to anticipate the need for system inspection and/or maintenance.

10.5.1.2 The sample perchlorate RT is compared to the RT of the internal standard peak. The relative retention time (RRT) should be 1.0 +/- 2% (0.98 – 1.02).

## 11.0 PROCEDURE

11.1 Preparation of aqueous samples

11.1.1 Aqueous samples are analyzed with the addition of the internal standard. The sample aliquot size is 10 mL dispensed into a 50 mL disposable polypropylene centrifuge tube.

11.1.2 Prepare a method blank by dispensing 10 mL of reagent grade water into a 50 mL disposable polypropylene centrifuge tube.

11.1.3 Prepare an LCS by dispensing 10 mL of reagent grade water into a 50 mL disposable polypropylene centrifuge tube and adding 100 µL of the 1.0 µg/mL primary intermediate stock standard solution.

11.1.4 Prepare a matrix spike (MS) sample by dispensing a second 10 mL aliquot of the selected sample into a 50 mL disposable polypropylene centrifuge tube and adding 100 µL of the 1.0 µg/mL primary intermediate stock standard solution. Prepare a matrix spike duplicate (MSD) by dispensing a third 10 mL aliquot of the selected sample into a 50 mL disposable polypropylene centrifuge tube and adding 100 µL of the 1.0 µg/mL primary intermediate stock standard solution.

11.1.5 Prepare a DSS sample by dispensing a 10 mL aliquot of the dissolved salt solution into a 50 mL disposable polypropylene centrifuge tube and adding 100 µL of a 0.05 µg/mL primary working standard solution.

11.1.6 Add 100 µL of the 1.0 µg/mL internal standard solution to each sample and QC sample. Place the cap on the centrifuge tube and vortex until well mixed.

11.1.7 If necessary, filter the sample using a plastic 20 cc disposable sterile luerlock syringe fitted with a 0.45-µm PTFE or Tuffryn membrane filter. Dispense the sample into another 50 mL disposable polypropylene centrifuge tube. If any sample in the batch requires this filtration step prior to pretreatment then all associated QC samples must undergo this same step.

11.1.8 Fit a new plastic 20 cc disposable sterile luerlock syringe with a Dionex 2.5 cc BA/AG/H On Guard II® sample treatment cartridge. Precondition the cartridge by passing 15 mL of reagent grade water through the ion exchange resin and dispensing it to waste. To maximize loading of the cartridge bed be sure not to exceed the recommended flow rate of 2 mL/min. Do not allow the resin to go dry. After conditioning load 10m/L of sample on the cartridge and elute at a rate of 2 mL/min discarding the first 6 mL of sample eluant. The first 6 mL of the sample eluant is discarded because it is diluted by the water remaining in the cartridge following the activation process. Fit a 0.45-µm PTFE or Tuffryn filter onto the end of the luerlock syringe and filter the remaining 4 mL of sample eluant into an appropriately sized autosampler vial at a rate of 2.0 mL/min. The sample is now ready for analysis.

11.2 Preparation of soil and solid samples

11.2.1 Soil and solid samples are analyzed with the addition of internal standard. The sample aliquot size is 2.0 g weighed into a disposable 50 ml polypropylene centrifuge tube.

11.2.2 Prepare a method blank by weighing 2.0 g of reagent grade sand into a disposable 50 mL polypropylene centrifuge tube.

11.2.3 Prepare an LCS by weighing 2.0 g of reagent grade sand into a disposable 50 mL polypropylene centrifuge tube and adding 200 µL of the 1.0 µg/mL primary intermediate stock standard solution.

11.2.4 Prepare a matrix spike (MS) sample by weighing a second 2.0 g aliquot of the selected sample into a disposable 50 ml polypropylene centrifuge tube and adding 200 µL of the 1.0 µg/mL primary intermediate stock standard solution. Prepare a matrix spike duplicate (MSD) sample by weighing a third 2.0 g aliquot of the selected sample into a disposable 50 mL polypropylene centrifuge tube and adding 200 µL of the 1.0 µg/mL primary intermediate stock standard solution.

11.2.5 Prepare a DSS sample by weighing a 2.0 g of reagent grade sand into a disposable 50 mL polypropylene centrifuge tube and add 200 µL of a 0.05 µg/mL primary working standard solution.

11.2.6 Add 200 µL of the 1.0 µg/mL internal standard solution to each sample and QC sample. Add 20 mL of reagent water to the centrifuge tube of each sample and QC sample except the DSS. To the DSS add 20 mL of the dissolved salt solution. Cap each centrifuge tube and vortex until well mixed.

11.2.7 Place the samples on the shaker and shake them for 15 minutes.

11.2.8 Vortex the samples once more after shaking to ensure sample agitation.

11.2.9 Centrifuge the samples for 15 minutes to help clarify the leachate. Use centrifuge settings that provide an adequate separation.

11.2.10 Fit a new plastic 20cc disposable sterile luerlock syringe with a Dionex 2.5cc BA/AG/H OnGuard II sample treatment cartridge. For water samples, pour the entire sample into the syringe and run 5mL of the sample at 2mL/minute back to the centrifuge tube. For soils pour 10mL of the sample into the syringe and run the first 5mL to waste. Attach a 0.45-um PTFE or Tuffryn membrane filter after the treatment cartridge and collect the next 1.5mL into a labeled vial. The sample is now ready for analysis.
**Note: In the event of samples that are high in dissolved salts an obvious coloration change take place in the treatment cartridges, this usually occurs in waste water samples. The sample may require additional passes through additional treatment cartridges.**

11.3 Preparation of wipes

11.3.1 Wipes are analyzed with the addition of internal standard. The sample aliquot size is one wipe placed into a disposable 50 mL polypropylene centrifuge tube. Add 20 mL, maybe more depending on the size or the wipe, of HPLC water for final volume.

11.3.2 Prepare a method blank by placing one blank wipe into a disposable 50 mL polypropylene cenrifuge tube. Add 20 mL of HPLC water for final volume.

11.3.3 Prepare an LCS/LCSD by placing one blank wipe into a disposable 50 mL polypropylene centrifuge tube and adding 200 µL of the 1.0 µg/mL primary intermediate stock standard solution. Add 20 mL of HPLC water for final volume.

11.3.4 If requested and provided, prepare a matrix spike (MS) by placing a duplicate wipe sample into a disposable 50 mL polypropylene centrifuge tube and adding 200 µL of the 1.0 µg/mL primary intermediate stock standard solution. Add 20 mL of HPLC water for final volume.

11.3.5 If requested and provided, prepare a sample duplicate (Dup) by placing a duplicate sample wipe into a disposable 50 mL polypropylene centrifuge tube. Add 20 mL of HPLC water for final volume.

11.3.6 Prepare a DSS sample by placing one blank wipe into a disposable 50 mL polypropylene centrifuge tube and add 200 µL of a 0.05 µg/mL primary working standard solution.

11.3.7 Shake the tube for 10 minutes, squeeze the wipe three times

11.3.8 Repeat step 11.3.7 at least two times

11.3.9 Fit a new plastic 20cc disposable sterile luerlock syringe with a Dionex 2.5cc BA/AG/H OnGuard II sample treatment cartridge. Pour 10mL of the sample into the syringe and run the first 5mL to waste. Attach a 0.45-um PTFE or Tuffryn membrane filter after the treatment cartridge and collect the next 1.5mL into a labeled vial. The sample is now ready for analysis.

11.4 Perform all qualitative and quantitative measurements

11.5 Store the extract vial with a little headspace to prevent anaerobic conditions

## 12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Qualitative Identification

12.1.1 Perchlorate is identified by relative retention time, detection of the 99 > 83 and 101 > 85 m/z characteristic ion transitions, and the 83:85 ion ratios. Retention time and the 107 > 89 m/z ion transitions are used for the identification of the oxygen-18 labeled perchlorate. Compare the retention times of the m/z 83 peak and the m/z 89 peak. The retention times should not vary by more than 0.2 min. Identification occurs when a peak is found within the above listed criteria, at a concentration above the Reporting Limit (RL).

12.1.2 The natural abundance of $^{35}Cl$ is 75.5%, with the remaining 24.5% of natural chlorine occurring as $^{37}Cl$. The expected ratio of $^{35}Cl$ to $^{37}Cl$ is 3.06. Therefore the expected ratio of the perchlorate daughter ion 83 m/z to the daughter ion 85 m/z is also 3.06. The measured ratio should fall between 2.3 and 3.8. If it does not the sample needs to be reanalyzed.

12.1.3 If the identification is in doubt because of retention time shifts combined with poor chromatography, then additional sample analysis may be required, including dilutions and/or spike additions to confirm the identification of perchlorate.

12.2 Calibration Range

12.2.1 If concentrations of any analytes exceed the working range as defined by the calibration standards, then the sample must be diluted and reanalyzed. Dilutions should target the most concentrated analyte in the upper half (over 50%) of the calibration range.

12.3 Dilutions

12.3.1 Samples may be screened to determine the appropriate dilution for the initial run.

12.3.2 Reporting Dilutions

The most concentrated dilution with no target compounds above the calibration range will be reported. Other dilutions will only be reported at client request.

12.4 Interferences

12.4.1 If peak detection is prevented by interferences, then elevation of reporting levels and/or lack of positive identification must be addressed in the case narrative.

12.5 Calculations are performed using commercially available, MassLynx LC/MS/MS, software.

## 13.0 DATA ASSESSMENT AND ACCEPTANCE CRITERIA; CORRECTIVE ACTIONS FOR OUT OF CONTROL DATA

13.1 The data assessment and corrective action process is detailed through the LIMS Nonconformance Memorandum (NCM) process. The NCM process is described in SOP: ST-QA-0036.

13.2 Method Blank

13.2.1 Acceptance Criteria:

13.2.1.1 No target analytes may be present in the method blank above the reporting limit.

13.2.1.2 The method blank must have acceptable surrogate recoveries.

13.2.1.3 Corrective Action for Method Blanks not meeting acceptance criteria:

13.2.1.3.1 Method Blank Contamination – Blank contamination above the RL (>1/2 RL for some programs – see specific Client Requirement Memos for details) requires re-prep of batch unless all associated samples are < RL or greater than 10 times the amount detected in the method blank.

13.2.1.4 Method Blank Surrogate excursion – If excursion is limited to the blank, data may be reported with an NCM. If surrogates are also outside criteria in samples, re-prep and re-anlaysis is required. In cases where the surrogate recovery is high and the samples are non-detect, the data may be reported with an NCM.

13.3 Instrument Blank

13.3.1 Acceptance Criteria:

13.3.1.1 No target analytes may be present in the instrument blank above the reporting limit.

13.3.1.2 The instrument blank must have internal standard area counts that are within +/- 50% of the average of the internal standard area counts of the calibration standards performed on the same day as the analysis.

13.3.2 Corrective Action for Instrument Blanks not meeting acceptance criteria:

13.3.2.1 Instrument Blank Contamination – Reanalyze the instrument blank until no carryover/contamination is observed, then reanalyze all samples analyzed since the contaminated blank. If reanalysis is not possible document reasons in NCM.

13.4 Laboratory Control Sample (LCS)

13.4.1 Acceptance Criteria:

13.4.1.1 All control analytes should be within established control limits for accuracy (%Recovery) and precision (RPD).

13.4.1.2 The LCS should have internal standard area counts that are within -50% to +50% of the average of the internal standard area counts of the calibration standards performed on the same day as the analysis.

13.4.1.3 Corrective Action for LCS not meeting acceptance criteria:

13.4.1.3.1 LCS Spike Recovery excursion (high) – Samples that are non-detect may be reported with an NCM (unless prohibited by client requirements). Samples with detects for the analyte recovered high in the LCS are re-prepped and re-analyzed. . In cases where the surrogate recovery is high and the samples are non-detect, the data may be reported with an NCM

13.4.1.3.2 LCS Spike Recovery excursion (low) – batch is re-prepped and re-analyzed.

13.4.1.3.3 LCS Surrogate Recovery excursion – If excursion is limited to the LCS, data may be reported with an NCM. If target analytes are in control in the LCS, data may be reported with an NCM. If surrogates are also outside criteria in samples, re-prep and re-analysis is required.

13.4.1.4 RPD excursion for LCS/LCSD – If target analytes recoveries are in control, data may be reported with an NCM.

13.5 Matrix Spike/Sample Duplicate/Matrix Spike Duplicate (MS/SD/MSD)

13.5.1 All analytes should be within established control limits for accuracy (%Recovery) and precision (RPD).

13.5.2 Corrective Action for MS/SD/MSD not meeting acceptance criteria:

13.5.2.1 MS/SD/MSD Spike Rec/RPD. excursions may not necessarily warrant corrective action other than narration. If affected analyte concentration in the original sample is greater than four times the amount spiked, percent recovery information is ineffective. Data is reported with an NCM. If the excursion is due to a physically evident matrix interference, the data is reported with an NCM (the physical interference must be described in the NCM). If there is no evidence of interference and the RPD as well as spike recoveries out outside limits out, sample re-prep and re-analysis are required.

13.6 Internal Standard

13.6.1.1 All samples should have internal standard area counts that are within -50% to +50% of the average of the internal standard area counts of the calibration standards performed on the same day as the analysis.

13.6.1.2 Sample Internal Standard Recovery excursion – The samples, spikes or blanks should be reanalyzed or the data should be qualified. (Some programs may require that the midpoint of the initial calibration be used for ISTD monitoring. See the project CRM for specifics.).

13.6.1.3 Internal Standard Recovery excursion may not necessarily warrant corrective action other than narration. High ISTD recovery indicates a potential low bias to analytical results. Instrument maintenance, if required, is done and affected samples are reanalyzed. If ISTDs are outside criteria on the re-analysis, a matrix interference is suspected and data reported with an NCM.

13.7 Sample result evaluation

13.7.1 Dilutions

13.7.1.1 If the response for any compound exceeds the working range of the analytical system, a dilution of the extract is prepared and analyzed. An appropriate dilution should be in the upper half of the calibration range.

13.7.1.1.1 Dilution: Sample– An NCM is written to document the reason for the dilution.

13.7.1.1.2 Dilution: Internal Standard diluted out– An NCM is written to document the reason for the dilution

13.7.1.1.3 Dilution: Internal Standard and/or Spike(s) diluted out An NCM is written to document the reason for the dilution.

13.7.2 Carryover

13.7.2.1 When a sample has a high response for a compound, there is a real possibility that some of the sample may carry over into the sample analyzed immediately afterward.

13.7.2.2 If a sample analyzed after a sample with high concentrations has negative results, carryover did not occur.

13.7.2.3 If a sample analyzed after a sample with high concentrations has positive results for the same analytes, or if the chromatographic profile resembles the previous sample, the results are questionable. This sample must be reanalyzed under conditions in which carryover can be confirmed to not have occurred.

13.8 Insufficient Sample

13.8.1 For each prescribed re-preparation corrective action, if there is insufficient sample to repeat the analysis a narrative comment stating such is included in the report narrative.

## 14.0 METHOD PERFORMANCE AND DEMONSTRATION OF CAPABILITY

14.1 Method performance data, Reporting Limits, MDLs, and QC acceptance limits, are maintained in LIMS

14.2 Method Detection Limit

14.2.1 Each laboratory must generate a valid method detection limit for the analyte of interest. The MDL must be below the reporting limit for the analyte. See SOP ST-QA-0016 regarding our MDL procedure.

14.3 Ion Suppression control capability

14.3.1 Laboratories that analyze samples that contain high levels of total dissolved solids (TDS) (i.e., > 1000 mg/L) should determine the approximate sample matrix levels that can be tolerated by the LC/MS/MS system before the loss of column capacity brings about a significant reduction in the analyte signal.

14.3.1.1 Using the sodium salts of chloride, sulfate, carbonate and bicarbonate prepare a dissolved salt solution (DSS) fortified with 0.5 ug/L (0.25 µg/L for DoD) perchlorate containing 1000 mg/L each of the anions chloride, sulfate, carbonate and bicarbonate in reagent water. Analyze the prepared sample. The perchlorate recovery should be within 70-130% of the theoretical value and the internal standard recovery should be within -50% to +50% of the average of the internal standard area counts of the calibration standards performed on the same day as the analysis. If the perchlorate and internal standard recoveries meet the acceptance criteria, then the measured conductivity of this solution is the conductivity limit of the analytical system.

14.4 Demonstration of Capability

14.4.1 Initial and continuing demonstrations of capability requirements are established in the ST-QAM.

14.5 Training Qualification

14.5.1 The manager/supervisor has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience.

14.5.2 The analyst must have successfully completed the initial demonstration capability requirements prior to working independently. See requirements in the ST-QAM.

14.6 Annually, the analyst must successfully demonstrate proficiency to continue to perform this analysis. See requirements in the ST-QAM.

## 15.0 VALIDATION

15.1 Laboratory SOPs are based on published methods (EPA, DOE, ASTM, Eichrom, Standard Methods) and do not require validation by the laboratory. The requirements for laboratory demonstration of capability are included in the ST-QAM. Laboratory validation data would be appropriate for performance based measurement systems, non-standard methods and significant modifications to published methods. Data from said validations is held in the QA department.

## 16.0 WASTE MANAGEMENT AND POLLUTION PREVENTION

16.1 All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

16.2 Waste Streams Produced by the Method

16.2.1 The following waste streams are produced when this method is carried out.

16.2.1.1 Solvent and water from the HPLC. Solvent waste must be accumulated in the appropriate waste accumulation container, labeled as Drum Type "D".

16.2.1.2 Contaminated disposable glass or plastic materials utilized in the analysis are disposed of in the sanitary trash. If the lab ware was used for the analysis of radioactive samples and contains radioactivity at a level of 100 cpm over background as determined by a GM meter, the lab ware will be collected in waste barrels designated for solid rad waste for disposal by the EH&S Coordinator.

## 17.0 REFERENCES

17.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, January 2005, Method 331.

17.2 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, January 2007, Method 6850

17.3 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, December 1996, Section 8000C.

17.4 DoD Perchlorate Handbook, May 2007

17.5 TestAmerica Quality Assurance Manual (ST-QAM), current revision

17.6 TestAmerica Corporate Environmental Health and Safety Manual (CW-E-M-001) and St. Louis Facility Addendum (SOP ST-HS-0002), current revisions.

17.7 TestAmerica Policy CA-Q-S-001, Acceptable Manual Integration Practices

17.8 TestAmerica Policy CA-T-P-0002, Selection of Calibration Points

17.9 Associated SOPs, current revisions:

17.9.1 ST-QA-0002, Standard and Reagent Preparation

17.9.2 ST-QA-0014, Evaluation of Analytical Accuracy and Precision Through the Use of Control Charts

17.9.3 ST-QA-0016, IDL/MDL Determination

17.9.4 ST-QA-0036, Non-conformance Memorandum (NCM) Process

17.9.5 ST-QA-0038 Procedure for Compositing and Subsampling

17.9.6 ST-PM-0002 Sample Receipt and Chain of Custody

## 18.0 CLARIFICATIONS, MODIFICATIONS TO THE REFERENCE METHOD

18.1 TestAmerica St. Louis used the Fortified Dissolved Salt Solution (DSS) sample as the verification standard for the reporting limit. The lab does not run a separate LLOQ standard.

## 19.0 CHANGES TO PREVIOUS SOP REVISION

19.1 Updated section 7.13 regarding the preparation of standards.

19.2 Updated the internal recovery limits throughout entire SOP.

19.3 Added Low-Level table to calibration standards table.

19.4 Rev. 3:

19.4.1 Updated section 11.2.10 and deleted section 11.2.11.

19.5 Rev 4:

19.5.1 Updated information on internal calibration standardizations in section 2.4.

19.5.2 Updated section 6.0 to include Mass Spec System used and suitable analytical columns.

19.5.3 Corrected the replacement requirement for stock standards to one year in Section 7.0.

19.5.4 Updated Perchlorate calibration standards, LC operating conditions and recommended Mass Spec operating conditions in Attachment 1.

19.6 Rev 5:

19.6.1 Added procedures for the preparation and analysis of wipe samples to Sections 2, 6, 8, 9 and 11

19.6.2 Updated instrument and software in Section 6.

19.6.3 Removed QuantIMS and Clouseau references – replaced with LIMS

19.6.4 Revised Section 13 to remove Clouseau corrective action references and to provide specific corrective actions for non-conformances.

19.6.5 Updated section 15

## Attachment

**Calibration Standards**
**Water (Final Concentration) µg/L**

| Compound | Level 1 | Level 2 | Level 3 | Level 4 | Level 5 | Level 6 | Level 7 | Level 8 |
|---|---|---|---|---|---|---|---|---|
| Perchlorate | 0.2 | 0.5 | 1.0 | 2.5 | 5.0 | 10.0 | 20.0 | 50.0 |

**Calibration Standards Soil (Final Concentration) µg/Kg**

| Compound | Level 1 | Level 2 | Level 3 | Level 4 | Level 5 | Level 6 | Level 7 | Level 8 |
|---|---|---|---|---|---|---|---|---|
| Perchlorate | 2.0 | 5.0 | 10.0 | 25.0 | 50.0 | 100.0 | 200.0 | 500.0 |

**Calibration Standards Low-Level Waters (Final Concentration) µg/L**

| Compound | Level 1 | Level 2 | Level 3 | Level 4 | Level 5 | Level 6 | Level 7 | Level 8 |
|---|---|---|---|---|---|---|---|---|
| Perchlorate | 0.02 | 0.05 | 0.1 | 0.5 | 1.0 | 2.0 | 5.0 | 10 |

**Characteristic Ions and Scan Conditions**

| Analyte | Parent/Daughter Ion (m/z) | Dwell Time (sec) |
|---|---|---|
| Perchlorate ($^{37}Cl$) | 101/85 | 0.40 |
| Perchlorate ($^{35}Cl$) | 99/83 | 0.40 |
| Perchlorate ($^{35}Cl^{18}O_4^-$) | 107/89 | 0.40 |

**LC Operating Conditions**

| Parameter | Setting |
|---|---|
| Columns | Dionex Ion Pac AG-16® guard column |
| Column Temperature | 25-30°C |
| Eluent Flow Rate | 0.5 – 0.7 mL/min |
| Eluent Identification | 5 mM $NH_4OH$ |
| Solvent Program | Isocratic |
| Injection Volume | 50 µL/20 µL |

**Recommended Mass Spectrometer Operating Conditions**

| Parameter | Setting (Recommended) |
|---|---|
| Scan Mode | ESI, Negative Ion |
| Capillary Current | 0.2 kV |
| Multiplier Voltage | 650 Volts |
| Desolvation Temperature | 450°C |
| Source Temperature | 120°C |
| Desolvation Gas Flow | 600 - 1000 L/hr |
| Cone Gas Flow | 50 - 100 L/hr |

**Calibration Masses for NaCsI Solution**

| Amu |
|---|
| 126.9045 |
| 276.7987 |
| 426.6929 |
| 576.5872 |
| 726.4814 |
| 876.3757 |

Note: All ion abundances are 100%

# Title: INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROSCOPY, SPECTROMETRIC METHOD FOR TRACE ELEMENT ANALYSES [SW-846 6010C; EPA 200.7]

Approvals (Signature/Date):

Kristen Ely 6/17/13
Kristen Ely Date
Metals Supervisor

Michael Ridenhower 6/17/13
Michael Ridenhower Date
Health & Safety Manager / Coordinator

Marti Ward 6.17.13
Marti Ward Date
Quality Assurance Manager

Elaine Wild 6/17/13
Elaine Wild Date
Laboratory Director

**This SOP was previously identified as SOP No. ST-MT-0003 Rev. 14**



**Facility Distribution No.: 0** **Distributed To: See Electronic Distribution Sheet**

## 1.0 SCOPE AND APPLICATION

1.1 This procedure describes the analysis of trace elements including metals in solution by Inductively Coupled Plasma -Atomic Emission Spectroscopy (ICP-AES) using SW-846 Method 6010C and EPA Method 200.7.

1.2 This method is applicable to surface, and saline waters; soil and waste samples.

1.3 The aqueous sample digestion procedure is found in SOP: ST-IP-0013, Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by ICP Spectroscopy, and ICP/MS (Method 3010A, EPA 200.7 and EPA 200.8) and the soil sample digestion procedure is found in SOP: ST-IP-0002, Acid Digestion of Soils, SW846 Method 3050B for ICP, and ICP/MS.

1.4 The laboratory target analytes supported by this method, the reporting limits, method detection limits and QC limits are maintained in the Laboratory Information Management System (LIMS).

1.4.1 Additional elements may be amendable to this method provided the laboratory has established a MDL and the elements meets the QC requirements as prescribed in the associated preparation and analytical SOP.

## 2.0 SUMMARY OF METHOD

2.1 This method describes a technique for the determination of multi elements in solution using simultaneous optical systems and axial or radial viewing of the plasma. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by a radio frequency inductively coupled plasma (ICP). The spectra are dispersed by a grating spectrometer and the intensities of the emission lines are monitored by photomultiplier tubes. The photocurrents from the photomultiplier tubes are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background must be measured adjacent to analyte lines during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interferences and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences should also be recognized and appropriate actions taken.

## 3.0 DEFINITIONS

3.1 See the TestAmerica St. Louis Quality Assurance Manual (ST-QAM) for a glossary of common laboratory terms and data reporting qualifiers.

3.2 EPA and SW methodology use different terminology. Our SOP references the SW 846 terminology:

3.2.1 The ICV satisfies the QCS requirements found in method 200.7.
3.2.2 The LCS satisfies the requirements of the LFB found in method 200.7.
3.2.3 The MS satisfies the requirements of the LFM found in method 200.7.
3.2.4 The ICS (A and/or AB) satisfies the requirements of the SIC found in method 200.7.
3.2.5 The CCV satisfies the requirements of the IPC found in method 200.7.

3.3 Linear Dynamic Range (LDR): A standard at the upper limit must be prepared, analyzed and quantitated against the normal calibration curve. The calculated value must be within 10% (±10%) of the true value. At a minimum, the range should be checked every six months. TestAmerica St. Louis uses the high point of the single-point initial calibration as its' LDR check.

3.4 Dissolved Metals: Those elements which pass through a 0.45 um membrane filter. (Sample is acidified after filtration)

3.5 Suspended Metals: Those elements retained by a 0.45 um filter.

3.6 Total Metals: The concentration determined on an unfiltered sample following vigorous digestion.

3.7 Dilution Test – the terminology "dilution test" found in later versions of 200.7 and 6010C is referred to as a Serial Dilution in this SOP.

## 4.0 INTERFERENCES

4.1 Spectral, physical and chemical interference effects may contribute to inaccuracies in the determinations of trace elements by ICP. Spectral interferences are caused by
- 4.1.1 Overlap of a spectral line from another element.
- 4.1.2 Unresolved overlap of molecular band spectra.
- 4.1.3 Background contribution from continuous or recombination phenomena.
- 4.1.4 Stray light from the line emission of high concentration elements.

4.2 A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background correction is not required in cases where a background corrective measurement would actually degrade the analytical result.

4.3 Inter-element correction factors (IECs) are necessary to compensate for spectral overlap. Inter-element interferences occur when elements in the sample emit radiation at wavelengths so close to that of the analyte that they contribute significant intensity to the analyte channel. If such conditions exist, the intensity contributed by the matrix elements will cause an excessively high (or sometimes low) concentration to be reported for the analyte. Inter-element corrections IECs must be applied to the analyte to remove the effects of these unwanted emissions.

4.4 Physical interferences are generally considered to be effects associated with sample transport, nebulization and conversion within the plasma. These interferences may result in differences between instrument responses for the sample and the calibration standards. Physical interferences may occur in the transfer of solution to the nebulizer (e.g., viscosity effects), at the point of aerosol formation and transport to the plasma (e.g., surface tension) or during excitation and ionization processes within the plasma itself. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, dilution of the sample, use of a peristaltic pump, mass flow controller, use of an internal standard and/or use of a high solids nebulizer can reduce the effect.

4.5 Chemical interferences are characterized by molecular compound formation, ionization effects and solute vaporization effects. Normally these effects are not significant with the ICP technique but if observed can be minimized by buffering the sample, matrix matching or standard addition procedures.

## 5.0 SAFETY

5.1 Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), Radiation Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.2 SPECIFIC SAFETY CONCERNS OR REQUIREMENTS
- 5.2.1 The ICP plasma emits strong UV light, harmful to vision. Analysts must avoid looking directly at the plasma.

5.3 PRIMARY MATERIALS USED

5.3.1 The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

| Material (1) | Hazards | Exposure Limit (2) | Signs and symptoms of exposure |
|---|---|---|---|
| Nitric Acid | Corrosive Oxidizer Poison | 2 ppm (TWA)<br><br>4 ppm (STEL) | Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage. |
| Hydrochloric Acid | Corrosive Poison | 5 ppm (Ceiling) | Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage. |
| Hydrogen Peroxide 30% | Oxidizer Corrosive Fire (increases flammability of combustible, organic, and readily oxidizable materials) | 1 ppm (TWA) | Irritation to respiratory tract and burning of mucous membrane of nose and throat. Pain, redness, and blurred vision in eyes. |
| 1 – Always add acid to water to prevent violent reactions. | | | |
| 2 – Exposure limit refers to the OSHA regulatory exposure limit. | | | |
| TWA – Time Weighted Average | | | |
| STEL – Short Term Exposure Limit | | | |
| Ceiling – At no time should this exposure limit be exceeded. | | | |

## 6.0 EQUIPMENT AND SUPPLIES

6.1 Inductively Coupled Plasma Atomic Emission Spectrometer equipped with autosampler and background correction

6.2 Instrument Software: Thermo 61T uses Thermo Spec Version 6.2

6.3 Instrument Software: Thermo 6500 uses iTeva

6.4 Radio Frequency Generator

6.5 Argon gas supply, welding grade or better

6.6 Chiller (water cooling device)

6.7 Calibrated automatic pipettes or Class A glass volumetric pipettes

6.8 Class A volumetric flasks

6.9 Glass beads

## 7.0 REAGENTS AND STANDARDS

7.1 All standards and reagent preparation, documentation and labeling must follow the requirements of SOP ST-QA-0002, current revision.

7.2 Concentrated nitric acid ($HNO_3$), trace metal grade

7.3 Concentrated hydrochloric acid (HCl), trace metal grade

7.4 DI water from the Millipore unit
- 7.4.1 Water must be free of the analytes of interest as demonstrated through the analysis of method blanks. Water must be shown to have a resistivity greater than or equal to 16.67 Mohm-cm.

7.5 Standards, NIST traceable
- 7.5.1 Purchased as custom multi-element mixes or as single-element solutions.
- 7.5.2 All standards must be stored in FEP fluorocarbon or unused polyethylene or polypropylene bottles.
- 7.5.3 Working calibration and calibration verification solutions may be used for up to 1 month and must be replaced sooner if verification from an independent source indicates a problem. Standards should be prepared in a matrix of 5% hydrochloric and 5% nitric acid.

7.6 Profile Standard
- 7.6.1 61T Trace ICP: 5 ppm Arsenic standard

7.7 Internal Standard
- 7.7.1 61T Trace ICP: 2 ppm yttrium
- 7.7.2 6500: 1 ppm yttrium

## 8.0 SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 TestAmerica St. Louis supplies sample containers and chemical preservatives in accordance with the method. TestAmerica St. Louis does not perform sample collection. Samplers should reference the methods referenced and other applicable sample collection documents for detailed collection procedures. Sample volumes and preservative information is given in ST-PM-0002.

8.2 Aqueous samples for total metals must be digested before analysis using an appropriate digestion procedure, ST-IP-0013.

8.3 Soil or waste samples are digested before analysis using an appropriate digestion procedure. Method 3050B of SW846 is the appropriate digestion procedure, ST-IP-0002.

8.4 Digestate holding time is 6 months from sample collection.

## 9.0 QUALITY CONTROL

9.1 **Batch**
- 9.1.1 A sample batch is a maximum of 20 environmental samples, which are prepared together using the same process and same lot(s) of reagents.
- 9.1.2 Instrument conditions must be the same for all standards, samples and QC samples.
- 9.1.3 For this analysis, batch QC consists of a method blank, a Laboratory Control Sample (LCS), and Matrix Spike (MS)/ Matrix Spike Duplicate (MSD). In the event that there is insufficient sample to analyze a MS/MSD an LCS Duplicate (LCSD) is prepared and analyzed.

9.2 **Method Blank (MB)**

9.2.1 A method blank is a blank matrix processed simultaneously with, and under the same conditions as, samples through all steps of the procedure.

9.2.2 A method blank must be prepared with every sample batch.

9.2.3 DI water is used as the MB for water batches; glass beads are used for soil batches.

9.2.4 See Section 13 for acceptance criteria.

9.3 **Laboratory Control Sample (LCS)**

9.3.1 An LCS is a blank matrix spiked with a known amount of analyte(s), processed simultaneously with, and under the same conditions as, samples through all steps of the analytical procedure.

9.3.2 An LCS must be prepared with every sample batch.

9.3.3 DI water, spiked with the analytes of interest, is used as the LCS for water batches; A purchased soil QC standard is used for soil batches. Spiked glass beads are used as the LCS for analytes not included in the purchased solid QC standard.

9.3.4 See Section 13 for acceptance criteria.

9.4 **Matrix Spike (MS) /Matrix Spike Duplicate (MSD)**

9.4.1 A Matrix Spike is an aliquot of a field sample to which a known amount of target analyte(s) is added, and is processed simultaneously with, and under the same conditions as, samples through all steps of the analytical procedure.

9.4.2 See Section 13 for acceptance criteria.

9.5 **Serial Dilution**

9.5.1 A dilution test is performed to determine whether significant physical or chemical interferences exist due to the sample matrix.

9.5.2 The test is performed by running a sample at a 5x (1:5) dilution.

9.5.3 Samples identified as field blanks cannot be used for dilution tests.

9.5.4 The serial dilution results shall agree within ± 10% of the undiluted sample results, if the undiluted sample results are greater than 10 times the reporting limit. There is no criteria for sample results less than 10 times the reporting limit.

9.6 **Post Digestion Spike (PDS)**

9.6.1 A post digestion spike is a sample which has been fortified with target analytes of interest after the digestion process.

9.6.2 A PDS is only analyzed at client request.

9.6.3 See Section 13 for acceptance criteria

9.7 **Method of Standard Addition** (MSA)

9.7.1 This technique involves adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample interferent that may enhance or depress the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift.

9.7.2 MSAs are not considered standard batch QC and if required by the client, must appear on the client requirements memo or in the comment section of LIMS.

9.7.3 MSA is required by SW846 Method 1311 when the MS/MSD recovery is less than 50%, analyte concentration is less than and within 20% of its regulatory limit.

9.8 **Procedural Variations/ Nonconformance and Corrective Action**

9.8.1 Any variation shall be completely documented using a Nonconformance Memo and approved by the Supervisor and QA Manager. See SOP ST-QA-0036 for details regarding the NCM process.

9.8.2 Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the Supervisor and QA Manager. See SOP ST-QA-0036 for details regarding the NCM process.

## 10.0 CALIBRATION AND STANDARDIZATION

10.1 Set up the instrument with the operating parameters recommended by the manufacturer. Allow the instrument to become thermally stable before calibration (minimum 30 minutes of warm-up is required).

10.2 Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures. Flush the system with the calibration blank between each standard. Refer to each ICP instrument manual for a detailed set up and operation protocols.

10.3 A minimum of two exposures for each standard, field sample and QC sample is required. The average of the exposures is reported.
10.3.1 For Trace ICP analyses, the result of the sum channel is used for reporting.

10.4 Rinse Time Determination
10.4.1 Prior to calibration and between each sample/standard the system is rinsed with the calibration blank solution. The minimum rinse time between analytical samples is 60 seconds unless following the protocol outlined in this SOP it can be demonstrated that a shorter rinse time may be used.
10.4.1.1 To determine the appropriate rinse time for a particular ICP system, a linear range verification standard should be aspirated as a regular sample followed by the analysis of a series of rinse blanks. The length of time required to reduce the analyte signals to < RL will define the rinse time for a particular ICP system. For some analytes it may be impractical to set the rinse time based on the linear range standard result (i.e., analyte not typically detected in environmental samples at that level and an excessive rinse time would be required at the linear range level). The concentration levels used to establish the rinse time must be taken into consideration when reviewing the data.

10.5 **Background Correction Points**
10.5.1 A background correction technique is applied to compensate for variable background contribution. This is performed by setting background points during initials instrument set up and matrix matching.

10.6 **Inter-element Corrections** (IECs)
10.6.1 The IECs are verified on a daily basis by analyzing the ICSA and ICSAB solutions at the beginning of every analytical run. An IEC must be established to compensate for any interelement interference which results in a false analyte signal greater than ± the RL. To determine IECs, run a single element standard at the high level calibration standard. To calculate an IEC, divide the observed concentration of the analyte by the observed concentration of the "interfering element."
10.6.2 IEC factors are updated every 6 months or after significant maintenance have been performed.

10.7 **Profile**
10.7.1 To monitor and prevent instrument spectral drift, a profile is performed on a daily basis.
10.7.2 For the 61T Trace ICP, a 5 ppm Arsenic standard is aspirated. When 0 ± 0.05 has been achieved, a calibration can begin.
10.7.2.1 If profile is not within 0 ± 0.05 adjust profile knob and re-run profile until ± 0.05 is achieved.
**10.7.3 For the 6500, wavelengths are checked internally**

10.8 **Linear dynamic Range**
10.8.1 Prior to running the instrument, the upper limit of quantitation must be established for each analyte.
10.8.2 This upper limit is tested by running a standard containing high concentrations of the analytes against a calibration curve.
10.8.3 The LDR standard must recover within ten percent of its true value.
10.8.4 The concentration of the LDR standard is equal to that of the high calibration standard.
10.8.5 LDR study is performed every six months or after significant instrument maintenance.

10.9 **Initial Calibration**

10.9.1 Single point Calibration

10.9.1.1 Instrument calibration consists of a minimum of high level standard plus a method blank.

10.9.1.2 Calibration criteria:

10.9.1.2.1 The resulting curve must be verified by a low level and mid-level verification standard

10.9.1.2.2 Both the low level standard (CRI) must recover in the range of 70 – 130% and the mid level verification standard (ICV) must be within 90% – 110% of its' true value.

10.9.1.2.3 The low level verification standard must be at or below the laboratory's routine reporting limit.

10.9.2 Multi-point Calibration: (alternative)

10.9.2.2 A calibration curve, consisting of 3 standards and a blank, must be analyzed daily.

10.9.2.3 Calibration criteria:

10.9.2.3.1 Correlation Coefficient of > 0.998

10.9.2.3.2 The low level standard in the curve must be at or below the laboratory's routine reporting limit.

10.9.2.3.2.1 If a client requested reporting limit is below the laboratory's routine reporting limit and thus below the low level verification standard, the laboratory will discuss with the client, prior to sample analysis, how to proceed with this requirement.

10.10 **Initial Calibration Verification/Initial Calibration Blank** (ICV/ICB)

10.10.1 The initial calibration accuracy is verified by analyzing a second source standard (ICV) and a low level verification standard (CRI) that can be from the same source as the calibration standards.

10.10.2 ICV Frequency:

10.10.2.2 Perform with each initial calibration

10.10.3 ICV Criteria:

10.10.3.2 **Method 200.7**, the ICV result must fall within 5% of the true value for that solution with relative standard deviation < 3% from replicate (minimum of two) exposures.

10.10.3.3 **Method 6010C**, the ICV must fall within 10% of the true value for that solution with relative standard deviation < 5% from replicate (minimum of two) exposures.

10.10.4 CRI recovery criteria is 70 –130%. (6010C only)

10.10.5 ICB Frequency:

10.10.5.2 An ICB is analyzed immediately following the ICV to monitor low level accuracy and system cleanliness.

10.10.6 ICB Criteria:

10.10.6.2 The ICB result must fall within ± the RL from zero.

10.10.7 If either the ICV or ICB fail to meet criteria, the analysis should be terminated, the problem corrected, the instrument recalibrated and the calibration re-verified.

10.10.7.2 Not meeting this requirement may be indicative of serious system malfunction or inaccuracies in the standards used for the initial calibration curve or ICV standard. Corrective action must be taken (including reanalysis of the ICV, or analysis of a different ICV). Any decision to proceed with analysis of samples when the ICV is out-of-control must be taken with great care and in consultation with the QA department and the laboratory director. Any such action must be documented in an NCM.

10.11 **Continuing Calibration Verification/Continuing Calibration Blank (CCV/CCB)**

10.11.1 Calibration is monitored throughout the analytical run through the analysis of a known standard.

10.11.2 A CCV may be a second source or the same source as the calibration

10.11.3 CCV Frequency:

10.11.3.2 Analyte response factors must be verified at the beginning of each analytical run (by either an ICV or a CCV), after every 10 samples and at the end of the analysis run through the analysis of a mid-level calibration standard.

10.11.4 CCV Criteria:

10.11.4.2 The CCV must fall within 10% of the true value for that solution with relative standard deviation < 5% from replicate (minimum of two) exposures.

10.11.4.3 If a CCV has failed and the analyst can document the reason for failure (e.g. mis-injection, etc.) then a second CCV may be analyzed without any adjustments to the instrument. If this CCV meets criteria then sample analysis may continue; however the preceding 10 samples must be reanalyzed. If this second CCV does not meet criteria, the analysis run is terminated. Instrument maintenance is performed and the instrument may require re-calibration (i.e. initial calibration). Samples after the last acceptable CCV require re-analysis.

10.11.5 CCB Frequency:

10.11.5.2 A CCB is analyzed immediately following each CCV.

10.11.6 CCB Criteria:

10.11.6.2 The CCB result must fall within ± the reporting limit.

10.11.6.3 A failed CCB does not necessarily require reanalysis of associated samples. Samples with results greater than ten times the concentration found in the bracketing blank may be reported with an NCM. Samples with concentrations less than ten times that found in the blank must be reanalyzed and be bracketed by passing CCBs.

10.12 **Interference Check Analysis** (ICSA/ICSAB)

10.12.1 The validity of the interelement correction factors is demonstrated through the successful analysis of interference check solutions.

10.12.2 **ICSA**:

10.12.2.2 The ICSA contains only interfering elements. Refer to Table II for the details of ICSA composition.

10.12.2.3 Custom multi-element ICS solutions must be used.

10.12.2.4 Elements known to be interferents on a required analyte must be included in the ICP run when that analyte is determined. Aluminum, iron, calcium and magnesium must always be included in all ICP runs.

10.12.3 **ICSAB**:

10.12.3.2 The ICSAB contains analytes and interferents.

10.12.3.3 Refer to Table II for the details of ICSAB composition.

10.12.3.4 Custom multi-element ICS solutions must be used.

10.12.4 ICSA/ICSAB Frequency:

10.12.4.2 For **6010C**: The ICSA and ICSAB must run with each initial calibration or every 12 hours whichever is shorter.

10.12.4.3 For **200.7**: The ICSA and ICSAB must run at the beginning and the end of the run.

10.12.5 ICSA/ICSAB Criteria:

10.12.5.2 The ICSAB results for interferents must fall within 80 – 120% of the true value.

10.12.5.3 ICSA results for the non-interfering elements with RLs < 10 µg/L must fall within ± 2x RL from zero. ICSA results for the non-interfering elements with RLs > 10 µg/L must fall within ± 1x RL from zero.

10.13 Calibration Sequence

Profile Standard
Initial Calibration (3 standards plus a blank)
ICV
ICB
CRI
ICSA*
ICSAB*
CCV

CCB
10 samples (analysis runs)
CCV
CCB
10 samples (repeat every 10 analysis runs)
CCV
CCB
**8 samples (CCV/CCB pairs as required to complete run)**
**ICSA (200.7 only)**
**ICSAB (200.7 only)**
**CCV**
**CCB**
End

* If sequence time is longer than 12 hours, the ICSA and ICSAB standard must be re-analyzed every twelve hours.

## 11.0 PROCEDURE

11.1 The aqueous sample digestion procedure is found in SOP: ST-IP-0013, Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by ICP Spectroscopy, and ICP/MS (Method 3010A, EPA 200.7 and EPA 200.8)
11.1.1 For 200.7 analyses, dissolved samples must be digested

11.2 The soil sample digestion procedure is found in SOP: ST-IP-0002, Acid Digestion of Soils, SW846 Method 3050B for ICP, and ICP/MS.

11.3 The use of a high solids nebulizer and mass flow controller is utilized and the calibration and QC standards are matrix matched.
11.3.1 Normal acid concentrations are 5% HCl and 5% $HNO_3$

11.4 Instrument conditions, including rinse times, must be the same for all standards and samples.

11.5 Load autosampler with standards and digestates in accordance with the sequence given in section 10.

11.6 Analyze samples.

11.7 When analysis is completed, return unused digestate to proper storage area.

## 12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Commonly used calculations (e.g. % recovery and RPD) and standard instrument software calculations are given in the TestAmerica St. Louis LQM.

12.2 A minimum of <u>two</u> <u>exposures</u> for each standard, field sample and QC sample is required. The average of the exposures is reported.

12.3 For Trace ICP analyses, the result of the sum channel is used for reporting.
All measurements must fall within the defined linear range where spectral interference correction factors are valid.
12.3.1 Dilute and reanalyze all samples for required analytes that exceed the linear range.
12.3.2 Acid strength must be maintained in the dilution of samples.

12.4 If an inter-element correction exists for an analyte which exceeds the linear range, the IEC may be applied. Even if an over-range analyte may not be required to be reported for a sample, if that analyte is an interferent for any requested analyte in that sample, the sample must be diluted.

12.5 The procedure for standard additions is to split the sample into several even aliquots in separate volumetric flasks of the same volume. The first flask is then diluted to volume with the selected diluent. A standard containing the analyte is then added in increasing volumes to the subsequent flasks and each flask is then diluted to volume with the selected diluent. The instrument response is then measured for all of the diluted solutions and the data is plotted with volume of standards added in the x-axis and instrument response in the y-axis. Linear regression is performed and the slope (m) and y-intercept (b) of the calibration curve are used to calculate the concentration of the analyte in the sample.

12.6 An internal standard (IS), yttrium or other suitable element, is added to all solution to correct and monitor physical interference. Physical interferences are generally considered to be effects associated with samples transport, nebulization and conversion within the plasma. These interferences may result in differences between instrument responses for the sample and the calibration standards. Physical interferences may occur in the transfer of solution to the nebulizer, at the point of aerosol formation and transport to the plasma or during excitation and ionization processes within the plasma itself. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If internal standard recoveries are abnormally high, then the dilution of the sample may be necessary to overcome the interferences.

## 13.0 DATA ASSESSMENT AND ACCEPTANCE CRITERIA; CORRECTIVE ACTIONS FOR OUT OF CONTROL DATA

13.1 The data assessment and corrective action process is detailed through the Nonconformance Memorandum (NCM) process in LIMS. The NCM process is described in SOP: ST-QA-0036.

13.2 Method Blank (MB)
- 13.2.1 Acceptance Criteria: No target analytes may be present in the method blank above the reporting limit.
- 13.2.2 Project specific requirements if more stringent than our routine procedure (e.g. no target analytes present above ½ RL), will be noted on the client requirements memo or in the comment section of LIMS.
- 13.2.3 Corrective Action for Method Blanks not meeting acceptance criteria:
  - 13.2.3.1 Method Blank Contamination – If the Method Blank concentration exceeds the applicable criteria the batch must be re-prepped unless the concentration of all associated samples is less than the RL or greater than ten times the concentration found in the blank.

13.3 Laboratory Control Sample (LCS)
- 13.3.1 Acceptance Criteria: All control analytes should be within established control limits for accuracy (%Recovery) and precision (RPD).
  - 13.3.1.1 Control limits are found in LIMS.
- 13.3.2 Corrective Action for LCS not meeting acceptance criteria:
  - 13.3.2.1 LCS Spike Recovery excursion (high) – Samples with results less than the RL may be reported with an NCM (unless prohibited by client requirements). Samples with detects for the analyte with a high bias in the LCS are re-prepped and re-analyzed.
  - 13.3.2.2 LCS Spike Recovery excursion (low) – the batch is re-prepped and re-analyzed for the affected analytes.

13.4 Matrix Spike/Matrix Spike Duplicate (MS/MSD)
- 13.4.1 Analytes should be within control limits for accuracy (%Recovery) and precision (RPD).
- 13.4.2 Corrective Action for MS/MSD not meeting acceptance criteria:
  - 13.4.2.1 MS/MSD Spike Recovery excursion: may not necessarily warrant corrective action other than narration
- 13.4.3 If the affected analyte concentration in the original sample is greater than four times the amount spiked, recovery information is ineffective and the data is reported with an NCM.
- 13.4.4 If the excursion is due to a physically evident matrix interference, the data is reported with an NCM.

13.4.5 In cases where the MS and/or MSD don't meet criteria, but the RPD is in control, data may be reported with and NCM.

13.4.6 When the MS/MSD recoveries and the %RPD are outside criteria, the batch is re-prepped and re-analyzed for the affected analytes.

13.5 Serial Dilution (SD)

13.5.1 The serial dilution results shall agree within ± 10% of the undiluted sample results, if the undiluted sample results are greater than 10 times the reporting limit. There is no criteria for sample results less than 10 times the reporting limit.

13.5.2 Corrective Action: Serial dilution failure is documented in an NCM and the reported data is flagged. If multiple analytes fail the serial dilution test, the analyst may re-prep and re-analyze the samples.

13.6 Post Digestion Spike (PDS)

13.6.1 The method stipulates that a PDS be performed. If the PDS is acceptable, the laboratory is not required to perform a serial dilution. Since the laboratory has elected to perform the serial dilution routinely, the outcome of the PDS is not critical and a PDS is only analyzed at client request.

13.6.2 Acceptance Criteria

13.6.2.1 **6010C** Criteria: The acceptance criteria is 80% – 120%, with a spike concentration between 10-100 times the MDL, UNLESS, other project/program criteria is given.

13.6.2.2 **200.7** Criteria: The acceptance criteria is 85% – 115%, with a spike concentration between 20-100 times the MDL, UNLESS, other project/program criteria is given.

13.6.3 Corrective Action: There is no qualification made to the data based on the performance of the PDS, however a failed PDS is documented with a Non-conformance memo (NCM) and noted in the report narrative.

13.6.4 The PDS is not reported in the data package unless a client project or program requires it. This requirement is noted by the Project Manager in the client requirement memo and/ or in the comment section of LIMS

13.7 Sample result evaluation

13.7.1 Dilutions

13.7.1.1 If the response for any compound exceeds the working range of the analytical system, a dilution of the extract is prepared and analyzed. An appropriate dilution should be in the upper half of the calibration range.

13.7.2 For samples requiring dilution an NCM is created to document the reason for the dilution.

13.7.3 Insufficient Sample

13.7.3.1 For any prescribed re-preparation corrective action, if there is insufficient sample to repeat the analysis, a narrative comment stating such is included in the report narrative.

13.8 Internal Recovery Standard (IS)

13.8.1 In house internal standard recovery criteria is 70% –130% of the intensity of that standard in the initial calibration standard for all samples and the QC standards.

13.8.2 If this criteria is not met, the sample should be diluted and re-analyzed until the IS recoveries are within specified limits.

## 14.0 METHOD PERFORMANCE

14.1 Method performance data, reporting limits, and QC acceptance limits, are maintained in the LIMS.

14.2 Demonstration of Capability

14.2.1 Initial and continuing demonstrations of capability requirements are established in the ST-QAM.

14.3 Training Qualification

14.3.1 The manager/supervisor has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience.

14.3.2 The analyst must have successfully completed the initial demonstration capability requirements prior to working independently. See requirements in the ST-QAM.

14.3.3 Annually, the analyst must successfully demonstrate proficiency to continue to perform this analysis. See requirements in the ST-QAM.

## 15.0 VALIDATION

15.1 Laboratory SOPs are based on published methods (EPA, DOE, ASTM, Eichrom, Standard Methods) and do not require validation by the laboratory. The requirements for laboratory demonstration of capability are included in the ST-QAM. Laboratory validation data would be appropriate for performance based measurement systems, non-standard methods and significant modifications to published methods. Data from said validations is held in the QA department.

## 16.0 WASTE MANAGEMENT AND POLLUTION PREVENTION

16.1 All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

16.2 Waste Streams Produced by the Method

16.3 The following waste streams are produced when this method is carried out.

16.3.1 Acidic sample waste generated. All acidic waste will be accumulated in the appropriate waste accumulation container, labeled as Drum Type "A" or "B."

16.3.2 Contaminated disposable glass or plastic materials utilized in the analysis are disposed of in the sanitary trash. If the lab ware was used for the analysis of radioactive samples and contains radioactivity at a level of 100 cpm over background as determined by a GM meter, the lab ware will be collected in waste barrels designated for solid rad waste for disposal by the EH&S Coordinator.

## 17.0 REFERENCES

17.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Method 6010C, February 2007.

17.2 Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry, Method 200.7.

17.3 Thermo Jarrell Ash Corporation Customer Training Manual, ICAP 61/91E Course

17.4 TestAmerica Laboratory Quality Assurance Manual (ST-QAM), current revision

17.5 TestAmerica Corporate Safety Manual CW-E-M-001) and St. Louis Facility Addendum (SOP ST-HS-0002), current revisions.

17.6 Associated SOPs, current revisions;

17.6.1 ST-IP-0002, Acid Digestion of Soils, SW846 Method 3050B for ICP, ICP/MS, and GFAA

17.6.2 ST-IP-0013, Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by ICP Spectroscopy, and ICP/MS (Method 3010A, EPA 200.7 and EPA 200.8)

17.6.3 ST-QA-0002, Standard and Reagent Preparation

17.6.4 ST-PM-0002, Sample Receipt and Chain of Custody

17.6.5 ST-QA-0014, Evaluation of Analytical Accuracy and Precision Through the Use of Control Charts

17.6.6 ST-QA-0016, IDL/MDL Determination

17.6.7 ST-QA-0036, Non-conformance Memorandum (NCM) Process

## 18.0 CLARIFICATIONS, MODIFICATIONS TO THE REFERENCE METHOD

18.1 Modifications/interpretations from both Methods 6010C and 200.7.

18.1.1 Method 6010C and Method 200.7 recommend that whenever a new or unusual matrix is encountered, a series of tests be performed prior to reporting concentration data for that analyte. The dilution test helps determine if a chemical or physical interference exists. Because TestAmerica laboratories receive no prior information from clients regarding when to expect a new or unusual matrix, TestAmerica may select to perform a dilution test on one sample in each

prep batch. According to the method, the post digestion spike (PDS) determines any potential matrix interferences. At TestAmerica labs, matrix interference is determined by evaluating data for the LCS and MS/MSD. TestAmerica requires documented, clear guidance when a new or unusual matrix will be received for a project and a request to perform the dilution test or PDS on a client-identified sample.

18.2 Modifications from Method 200.7.

18.2.1 TestAmerica St. Louis digests all aqueous samples. Method 200.7 allows for the digestion step to be omitted under certain conditions.

18.2.2 Method 200.7 defines the IDL as the concentration equivalent to a signal, due to the analyte, which is equal to three times the standard deviation of a series of ten replicate measurements of the calibration blank signal at the same wavelength. TestAmerica labs utilize the CLP IDL definition.

18.2.3 The calibration blank is prepared in an acid matrix of 5% $HNO_3$/5% HCl instead of the specified 2% $HNO_3$/10% HCl matrix as the former matrix provides for improved performance relative to the wide variety of digestate acid matrices which result from the various EPA preparation protocols applied.

18.2.4 Method specifies that "Analysis of the IPC (ICSA/AB) solution immediately following calibration must verify that the instrument is within ± 5% of calibration with a relative standard deviation < 3% from replicate integrations ≥ 4." TestAmerica uses a minimum of two exposures.

18.2.5 200.7 indicates that the QCS (ICV) should be prepared at a concentration near 1 ppm. The ICV specified in this SOP deviates from the 1ppm criteria . For the analytes, this SOP specifies ICV concentrations which are appropriate to the range of calibration. The intent of the ICV, verification of calibration standard accuracy, is independent of the ICV concentration used.

18.2.6 The ICS criteria applied by this SOP differ from those stated in the method. Method 200.7 states that results should fall within the established control limits of 3 times the standard deviation of the calibration blank for that analyte. The control limits listed in this SOP are those applicable to the EPA designed solution.

18.2.7 Method 200.7 states the CCB should be less than the IDL, but > the lower 3-sigma control limit of the calibration blank. The intent of this requirement is to ensure that the calibration is not drifting at the low end. TestAmerica has adopted an absolute control limit of ± the reporting limit for calibration blank criteria.

18.3 Modifications from Method 6010C.

18.3.1 Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit. Common lab contaminants are allowed up to two times the reporting limit in the blank following consultation with the client.

18.3.2 Method 6010C requires the analysis of a Lower Limit of Quantitation Check Sample (LLQC) to establish and confirm the lowest quantitation limit. TestAmerica St. Louis fills this requirement with the running of a MDL verification standard which is taken through the entire sample preparation procedure. The method suggested recovery criteria of ± 30% is not applied.

18.3.3 Method 6010C suggests the analysis of a Low Level Continuing Calibration Verification (LLCCV) standard. This standard should be at the laboratory limit of quantitation and be run periodically throughout an analytical sequence. TestAmerica St. Louis runs this standard only at the beginning of each analytical run.

18.3.4 Method 6010C stipulates that a PDS be performed. If the PDS is acceptable, the laboratory is not required to perform a serial dilution. Since the laboratory has elected to perform the serial dilution routinely, the outcome of the PDS is not critical and a PDS is only analyzed at client request.

## 19.0 CHANGES TO PREVIOUS REVISION

19.1 12/30/2010; REV 10, Modifications (Sec 18.0), removed Section 18.6 that stated that MSA requirement Method 1311 is not applied.

19.2 Clarified CCB requirements in section 10.11

19.3 Rev. 11:

19.3.1 Updated section 10.12.5 ICSA Criteria: non-interfering elements with RL < 10 must be ± 2X the RL from zero; results for non-interfering elements with RL > 10 must fall within ± 1X RL from zero.

19.4 Rev. 12:

19.4.1 Removed the exception taken to the MSA requirement in section 18.

19.4.2 Added instrument software and hardware to section 6.0.

19.4.3 Added MSA requirements for MS/MSD recovery in section 9.7.

19.4.4 Updated new data analysis and calculations in section 12.0.

19.5 Rev 13:

19.5.1 Updated adjustments to profile in section 10.7.

19.6 Rev 14:

19.6.1 Added specific reference CRI recovery criteria for method 6010C in section 10.10.

19.7 Rev 15:

19.7.1 Removed references to “Clouseau” and “QuantIMS” – replaced with “LIMS”

19.7.2 Removed all references to the 61E

19.7.3 Updated section 4.0 with discussion of physical interferences.

19.7.4 Added internal standard discussion to section 7.7 and 12.0

19.7.5 Added CCB corrective action guidance to Section 10.1

19.7.6 Updated Corrective Action information in Section 13, replacing references to the Clouseau NCM database with actual corrective actions to be taken.

19.7.7 Removed section 10.2.1 and 10.2.2 (information was already in section 10.7)

19.7.8 Added reference to 6500 to section 10

19.7.9 Updated section 9.6

19.7.10 Updated section 18.3

**TABLE I. ICP Calibration and Calibration Verification Standards**

| Element | Calibration Level | ICV (ug/L) | CCV (ug/L) |
|---|---|---|---|
| Aluminum | 100000 | 40000 | 40000 |
| Antimony | 10000 | 4000 | 4000 |
| Arsenic | 10000 | 4000 | 4000 |
| Barium | 10000 | 4000 | 4000 |
| Bismuth | 10000 | 4000 | 4000 |
| Beryllium | 10000 | 4000 | 4000 |
| Boron | 10000 | 4000 | 4000 |
| Cadmium | 10000 | 4000 | 4000 |
| Calcium | 50000 | 20000 | 20000 |
| Chromium | 10000 | 4000 | 4000 |
| Cobalt | 10000 | 4000 | 4000 |
| Copper | 10000 | 4000 | 4000 |
| Iron | 100000 | 40000 | 40000 |
| Lead | 10000 | 4000 | 4000 |
| Lithium | 10000 | 4000 | 4000 |
| Magnesium | 50000 | 20000 | 20000 |
| Manganese | 10000 | 4000 | 4000 |
| Molybdenum | 10000 | 4000 | 4000 |
| Nickel | 10000 | 4000 | 4000 |
| Phosphorous | 10000 | 4000 | 4000 |
| Potassium | 100000 | 40000 | 40000 |
| Selenium | 10000 | 4000 | 4000 |
| Silicon | 10000 | 4000 | 4000 |
| Silver | 2000 | 1000 | 1000 |
| Sodium | 100000 | 40000 | 40000 |
| Strontium | 10000 | 4000 | 4000 |
| Tellurium | 10000 | 4000 | 4000 |
| Thallium | 10000 | 4000 | 4000 |
| Tin | 10000 | 4000 | 4000 |
| Titanium | 10000 | 4000 | 4000 |
| Thorium | 10000 | 4000 | 4000 |
| Uranium | 10000 | 4000 | 4000 |
| Vanadium | 10000 | 4000 | 4000 |
| Zinc | 10000 | 4000 | 4000 |
| Zirconium | 10000 | 4000 | 4000 |
| | | | |

**TABLE II. Interference Check Sample Concentrations**

| Element | ICSA (ug/L) | ICSAB (ug/L) |
|---|---|---|
| Aluminum | 500000 | 500000 |
| Antimony | - | 1000 |
| Arsenic | - | 1000 |
| Barium | - | 500 |
| Beryllium | - | 500 |
| Bismuth | - | 1000 |
| Boron | - | 1000 |
| Cadmium | - | 1000 |
| Calcium | 500000 | 500000 |
| Chromium | - | 500 |
| Cobalt | - | 500 |
| Copper | - | 500 |
| Iron | 200000 | 200000 |
| Lead | - | 1000 |
| Lithium | - | 1000 |
| Magnesium | 500000 | 500000 |
| Manganese | - | 500 |
| Molybdenum | - | 1000 |
| Nickel | - | 1000 |
| Phosphorus | - | 500 |
| Potassium | - | 20000 |
| Selenium | - | 1000 |
| Silicon | - | 1000 |
| Silver | - | 1000 |
| Sodium | - | 20000 |
| Strontium | - | 1000 |
| Sulfur | - | 20000 |
| Thallium | - | 1000 |
| Thorium | - | 1000 |
| Tin | - | 1000 |
| Titanium | - | 500 |
| Uranium | - | 1000 |
| Vanadium | - | 500 |
| Zinc | - | 1000 |
| Zirconium | - | 1000 |

FORM: ORG-0034 TCLP MSA Spreadsheet Location: \\TAFS\Lab\St Louis\Public\QA\FORMS\ORG

# Title: ACID DIGESTION OF SOILS [SW-846 3050B FOR ICP, ICP/MS]

**Approvals (Signature/Date):**

| | |
|---|---|
| Kristen Ely 1/29/14<br>Kristen Ely Date<br>Metals Supervisor | Michael Ridenhower 1/29/14<br>Michael Ridenhower Date<br>Health & Safety Manager / Coordinator |
| Marti Ward 1.27.14<br>Marti Ward Date<br>Quality Assurance Manager | Elaine Wild 1/30/14<br>Elaine Wild Date<br>Laboratory Director |

**This SOP was previously identified as SOP No. ST-IP-0002 Rev. 16**



**Facility Distribution No.: 0** **Distributed To: See Electronic Distribution Sheet**

## 1.0 SCOPE AND APPLICATION

1.1 This procedure describes the preparation of soil samples for the analysis of metals by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP), and Inductively Coupled Plasma Atomic Emission/Mass Spectrometry (ICP/MS).

1.2 This procedure is based on SW-846 Method 3050B.

1.3 Additional metals may be processed by this method, assuming that performance criteria of the determinative method are met.

1.4 This method is not a total digestion, but will dissolve almost all metals that could become "environmentally available". By design, metals bound in silicate structures are not dissolved by this procedure as they are not usually mobile in the environment. This SOP can be applied to metals in solids, sludge, waste and sediment.

1.5 The laboratory target analytes supported by this method, the reporting limits, method detection limits and QC limits are maintained in the Laboratory's Information Management System (LIMS).

## 2.0 SUMMARY OF METHOD

2.1 A representative 0.5 g (wet weight) portion of sample is digested in nitric acid and hydrogen peroxide. The digestate is refluxed with hydrochloric acid for ICP, ICP/MS analysis. The digestates are then diluted to 50 mL.

## 3.0 DEFINITIONS

3.1 See the TestAmerica St. Louis Quality Assurance Manual (ST-QAM) for a glossary of common laboratory terms and data reporting qualifiers.

3.2 Total Metals: The concentration determined on an unfiltered sample following digestion.

## 4.0 INTERFERENCES

4.1 Potential sources of trace metals contamination include: metallic or metal-containing labware (e.g., talc gloves which contain high levels of zinc). Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them.

4.2 The entire work area, including the bench top and fume hood, should be thoroughly cleaned on a routine schedule in order to minimize the potential for environmental contamination.

4.3 Specific analytical interferences are discussed in the respective analytical SOPs: ST-MT-0001 (ICP/MS) and ST-MT-0003 (ICP).

## 5.0 SAFETY

5.1 Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), Radiation Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.2 SPECIFIC SAFETY CONCERNS OR REQUIREMENTS

Samples that contain high concentrations of carbonates or organic material or samples that are at elevated pH can react violently when acids are added. Hydrogen peroxide (H2O2) is a strong oxidizer and is corrosive. The digestion must be cooled sufficiently before the addition of H2O2 to avoid a reaction and possible violent effervescence, or boiling over of the digestion. A splash/splatter hazard is possible and a face shield should be worn.

5.3 PRIMARY MATERIALS USED

5.3.1 The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

| **Material (1)** | **Hazards** | **Exposure Limit (2)** | **Signs and Symptoms of exposure** |
|---|---|---|---|
| Hydrochloric Acid | Corrosive Poison | 5ppm (Ceiling) | Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage. |
| Hydrofluoric Acid | Poison<br>Corrosive<br>Dehydrator | 3 ppm-TWA | Severely corrosive to the respiratory tract. Corrosive to the skin and eyes. Permanent eye damage may occur. Skin contact causes serious skin burns, which may not be immediately apparent or painful. Symptoms may be delayed 8 hours or longer. **THE FLUORIDE ION READILY PENETRATES THE SKIN CAUSING DESTRUCTION OF DEEP TISSUE LAYERS AND BONE DAMAGE.** |
| Nitric Acid | Corrosive Oxidizer Poison | 2ppm (TWA) 4ppm (STEL) | Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage. |
| Hydrogen Peroxide | Oxidizer Corrosive | 1ppm (TWA) | Vapors are corrosive and irritating to the respiratory tract. Vapors are very corrosive and irritating to the eyes and skin. |
| 1 – Always add acid to water to prevent violent reactions. | | | |
| 2 – Exposure limit refers to the OSHA regulatory exposure limit | | | |
| TWA – Time Weighted Average | | | |
| STEL – Short Term Exposure Limit | | | |
| Ceiling – At no time should this exposure limit be exceeded. | | | |

## 6.0 EQUIPMENT AND SUPPLIES

6.1 Hot block, capable of maintaining a temperature of 90 °C – 95 °C.

6.2 Thermometer, temperature range of 0-250 °C.

6.3 Laboratory fume hood.

6.4 Hot block digestion vessels

6.5 Watch glasses, ribbed or equivalent

6.6 Vacuum filters – 0.45 µm

6.7 Analytical balance capable weighing to the nearest 0.001g.

6.8 Pipettes or reagent dispensers, micro pipettes 0.05 -10 mL

6.9 3 mm glass silica beads

6.10 Centrifuge tubes

6.11 Vacuum pump

6.12 Tongue Depressors (for taking aliquots of sample)

## 7.0 REAGENTS AND STANDARDS

7.1 All standards and reagent preparation, documentation and labeling must follow the requirements of SOP ST-QA-0002, current revision.

7.2 DI water: Obtained by the use of a Milli-Q System

7.3 Matrix Spike Standard, NIST traceable

7.4 ERA soil laboratory control samples (LCS) or LCS aqueous standard, NIST traceable

7.5 Nitric acid ($HNO_3$), concentrated, trace metal grade

7.6 Hydrochloric acid (HCl), concentrated, trace metal grade

7.7 30% Hydrogen peroxide ($H_2O_2$), Ultrex Grade.

## 8.0 SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 TestAmerica St. Louis supplies sample containers and chemical preservatives in accordance with the method. TestAmerica St. Louis does not perform sample collection. Samplers should reference the

methods referenced and other applicable sample collection documents for detailed collection procedures. Sample volumes and preservative information is given in ST-PM-0002.

8.2 Samples are to be collected in plastic or glass containers.

8.3 All soils must be refrigerated to $4^{o}C \pm 2^{o}C$.

8.4 The analytical holding time for metals is 6 months.

## 9.0 QUALITY CONTROL

9.1 Batch

9.1.1 A sample batch is a maximum of 20 environmental samples, which are prepared together using the same process and same lot(s) of reagents. Where no preparation method exists (e.g. water sample volatile organics, water sample anion analysis ) the batch is comprised of a maximum of 20 environmental samples which are analyzed together with the same process, lots of reagents and personnel.

9.1.2 Instrument conditions must be the same for all standards, samples and QC samples.

9.1.3 For this analysis, batch QC consists of a Method Blank (MB), a Laboratory Control Sample (LCS), and a Matrix Spike/ Matrix Spike Duplicate (MS/MSD). In the event that there is insufficient sample to analyze a sample duplicate, a LCS Duplicate (LCSD) is prepared and analyzed.

9.1.3.1. Matrix Spike (MS) and Sample Duplicate (SD) may be performed upon client request, and are noted in LIMS .

9.2 Method Blank

9.2.1 A method blank is a blank matrix processed simultaneously with, and under the same conditions as, samples through all steps of the procedure.

9.2.2 A method blank must be prepared with every sample batch.

9.2.3 For Soil analyses, the method blank is comprised of glass beads

9.2.3.1. . Boron and Silicon are not performed using glass beads due to contamination issues.

9.3 Laboratory Control Sample

9.3.1 A LCS is a blank matrix spiked with a known amount of analyte(s), processed simultaneously with, and under the same conditions as, samples through all steps of the analytical procedure.

9.3.2 A LCS must be prepared with every sample batch.

9.3.3 For Soil analyses, the LCS is a purchased Standard Reference Material

9.3.3.1. If requested, the laboratory may perform a LCS consisting of glass beads fortified with target analytes

9.3.3.2. Boron and Silicon are not performed using glass beads due to contamination issues. The LCS standard for these analytes is preserved with hydrofluoric acid which breaks down the glass beads causing contamination.

9.4 Matrix Spike (MS) /Matrix Spike Duplicate (MSD)

9.4.1 A Matrix Spike is an aliquot of a field sample to which a known amount of target analyte(s) is added, and is processed simultaneously with, and under the same conditions as, samples through all steps of the analytical procedure.

9.4.2 MS/MSD samples do not count towards the 20 environmental samples in a sample batch.

9.4.3 MS/MSD samples, when requested, must be performed with every sample batch and every LIMS batch.

9.4.4 If there is insufficient sample to perform a MS/MSD, a duplicate LCS is analyzed. A NCM is written to document the insufficient volume and the utilization of a LCSD to demonstrate precision.

9.5 Sample Duplicate

9.5.1 A Sample Duplicate is an additional aliquot of a field sample taken through the entire analytical process to demonstrate precision.

9.5.2 A Sample Duplicate is only performed upon client request.

9.5.3 If there is insufficient sample to perform a Sample Duplicate, a duplicate LCS is analyzed. A NCM is written to document the insufficient volume and the utilization of a LCSD to demonstrate precision.

9.6 Procedural Variations/ Nonconformance and Corrective Action

9.6.1 Any variation shall be completely documented using a Nonconformance Memo and approved by the Supervisor and QA Manager. See SOP ST-QA-0036 for details regarding the NCM process.

9.6.2 Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the Supervisor and QA Manager. See SOP ST-QA-0036 for details regarding the NCM process.

## 10.0 CALIBRATION AND STANDARDIZATION

10.1 Hot block/Hot plate must be checked daily when in use.

10.1.1 Temperature is documented in LIMS.

10.1.2 A calibrated thermometer is suspended in sand in a digestion vessel of water and brought to the proper temperature.

10.1.2.1. See SOP ST-QA-0005 for information regarding calibration of thermometers.

10.2 Instrument calibration is discussed in the respective analytical SOPs: ST-MT-0001 (ICP/MS) and ST-MT-0003 (ICP).

## 11.0 PROCEDURE

### NOTE:

**For DOE Antimony soil prep, see section 11.23.**

**For Tc99 soil prep, see SOP ST-RC-0125 (Determination of Technetium-99 Using Eichrom TEVA Resin)**

11.1 Label digestion vessel with sample ID or QC identifier.

11.2 Homogenize the sample by mixing thoroughly. See SOP ST-QA-0038 for details.

11.3 Weigh a 0.5 g – 0.6g portion of sample and the batch QC and record the weight in LIMS.

11.3.1 Larger sample sizes (typically 2 g) may be used if needed to meet the reporting limits.

11.4 Measure 0.5 g of glass beads into a digestion vessel for the MB (and LCS, if applicable)

11.5 Spike MS/MSD with spiking mix applicable to the requested analysis.

11.5.1.1. Document spiking volumes and standard numbers in LIMS

11.5.1.2. Reagent volumes are adjusted to reflect the sample volume used.

11.6 Add 2.5mL 1:1 $HNO_3$

11.7 Place watch glasses on digestion vessels

11.8 Place digestion vessels in hot block at 90°C - 95°C and reflux for 10 minutes.

11.8.1 **Do not allow the sample to boil or go dry during the digestion.** Allowing so may result in the loss of volatile metals. If this occurs the sample must be re-prepared. Antimony is easily lost by volatilization from hydrochloric media.

11.9 Take samples out and cool.

11.10 Add 1.25 mL $HNO_3$.

11.11 Return covered vessels to hot block.

11.12 Reflux at 90°C - 95°C for 30 minutes.

11.13 Add DI water as needed to ensure that the volume of solution is not reduced to less than 5 mL.

11.13.1 If brown fumes are observed, additional 1.25 mL aliquots of concentrated nitric acid until no more fumes are evolved.

11.14 Remove vessels from block and allow the samples to cool.

11.15 Add 1 mL of DI water and 2 mL of 30 % $H_2O_2$.

11.15.1 Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. If this occurs, add a minimal amount of DI water until sample settles, to ensure no loss of sample. If any amount of sample is lost, a re-digestion must be done.

11.16 Return covered vessel to hot block and heat sample until effervescence subsides.

11.17 While in block, continue adding 30% $H_2O_2$ in 1 mL aliquots with warming until effervescence is minimal or sample appearance is unchanged.

11.4.17.1 NOTE: Do not add more than a total of 5 mL of 30 % $H_2O_2$. If more then 5 mL of 30 % $H_2O_2$ is needed then the sample will be re-prepped using a smaller aliquot of sample.

11.18 Continue heating for 1 hour.

11.19 Remove vessel from hot block and allow to cool.

11.20 Add 2.5 mL HCL and reflux, on hot block, for an additional 15 minutes without boiling.

11.21 Remove vessel from hot block and allow to cool.

11.22 Wash down the vessel wall with DI water to dissolve any precipitation to a final volume 50 mL.

11.23 Particles in the digestate should then be removed by allowing the sample to settle.

11.23.1 Alternatively if the digestate needs to be run immediately or if the digestate, due to its physical appearance, is determined to need more than settling to remove particles, the digestate is filtered using a vacuum pump and a 0.45 µm filter.

11.24 Sample preparation is complete. Store digestates in designated cabinet. Print out the load sheet, which is then given to the analyst.

11.25 Hot Acid Prep for Antimony

11.25.1 Label digestion vessel with sample ID or QC identifier.

11.25.2 Homogenize the sample by mixing thoroughly. See SOP ST-QA-0038 for details.

11.25.3 Weigh a 0.5 g – 0.6g portion of sample and the batch QC and record the weight on in LIMS.

11.25.3.1. Weigh out 0.5g - 0.6g glass beads for blank and LCS.

11.25.4 Spike MS/MSD with spiking mix applicable to the requested analysis.

11.25.4.1. Document spiking volumes and standard numbers in LIMS

11.25.5 .Add 2.5 mL of $HNO_3$ and 2.5 mL of HCL.

11.25.6 Place digestion vessels in the hot block at 90-95°C and heat for 15 minutes.

11.25.7 Filter through vacuum filter while samples are still hot.

11.25.8 Rinse filter with 1.2 mL of hot HCL.

11.25.9 Rinse filter with 5 mL of hot DI water 4 times for a total of 20 mL.

11.25.10 Rinse the sample debris off the filter paper and place back into original digestion vessel.

11.25.11 Add 2.5 mL of HCL.

11.25.12 Return vessels to hot block.

11.25.13 Place watch glasses on the digestion vessels.

11.25.14 Reflux at 90-95°C for 20 minutes.

11.25.15 Filter while still hot through vacuum filter, adding original filtrate.

11.25.16 Rinse 3 times with DI water.

11.25.17 Bring samples to a final volume of 50 mL with DI water.

11.25.18 Sample preparation is complete. Store digestates in designated cabinet. Print out the load sheet, which is then given to the analyst.

## 12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Commonly used calculations (e.g. % recovery and RPD) and standard instrument software calculations are given in the TestAmerica St. Louis ST-QAM.

12.2 Specific calculations are included in the respective analytical SOPs: ST-MT-0001 (ICP/MS) and ST-MT-0003 (ICP).

## 13.0 DATA ASSESSMENT AND ACCEPTANCE CRITERIA; CORRECTIVE ACTIONS FOR OUT OF CONTROL DATA

13.1 Data assessment, acceptance criteria and corrective actions are included in the respective analytical SOPs: ST-MT-0001 (ICP/MS) and ST-MT-0003 (ICP).

13.2 Data assessment does not pertain to this sample preparation procedure.

13.3 Samples requiring re-preparation are submitted to the preparation lab with a NCM detailing the issue. The NCM process is described in SOP: ST-QA-0036.

## 14.0 METHOD PERFORMANCE AND DEMONSTRATIONS OF CAPABILITY

14.1 Method performance data, reporting limits, and QC acceptance limits, are maintained in LIMS.

14.2 Demonstration of Capability

14.2.1 Initial and continuing demonstrations of capability requirements are established in the ST-QAM.

14.3 Training Qualification

14.3.1 The manager/supervisor has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience.

14.3.2 The analyst must have successfully completed the initial demonstration capability requirements prior to working independently. See requirements in the ST-QAM.

14.4 Annually, the analyst must successfully demonstrate proficiency to continue to perform this analysis. See requirements in the ST-QAM.

## 15.0 VALIDATION

15.1 Laboratory SOPs are based on published methods (EPA, DOE, ASTM, Eichrom, Standard Methods) and do not require validation by the laboratory. The requirements for laboratory demonstration of capability are included in the ST-QAM. Laboratory validation data would be appropriate for performance based measurement systems, non-standard methods and significant modifications to published methods. Data from said validations is held in the QA department.

## 16.0 WASTE MANAGEMENT AND POLLUTION PREVENTION

16.1 All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

16.2 Waste Streams Produced by the Method

16.2.1 The following waste streams are produced when this method is carried out.

16.2.2 Acidic sample waste generated. All acidic waste will be accumulated in the appropriate waste accumulation container, labeled as Drum Type "A" or "B".

16.2.3 Contaminated disposable glass or plastic materials utilized in the analysis are disposed of in the sanitary trash. If the labware was used for the analysis of radioactive samples and contains radioactivity at a level of 100 cpm over background as determined by a GM meter, the labware will be collected in waste barrels designated for solid rad waste for disposal by the EH&S Coordinator.

## 17.0 REFERENCES

17.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Method 3050B.

17.2 DOE Methods Compendium RP550 Technitium-99 Analysis using Extraction Chromatography

17.3 TestAmerica St. Louis Quality Assurance Manual (ST-QAM), current revision

17.4 Corporate Environmental Health and Safety Manual (CW-E-M-001) and St. Louis Facility Addendum (SOP ST-HS-0002), current revisions

17.5 Associated SOPs, current revisions

17.5.1 ST-PM-0002, Sample Receipt and Chain of Custody

17.5.2 ST-QA-0002, Standard and Reagent Preparation

17.5.3 ST-QA-0005, Calibration and Verification Procedure for Thermometers, Balances, Weights and Pipettes

17.5.4 ST-QA-0014, Evaluation of Analytical Accuracy and Precision Through the Use of Control Charts

17.5.5 ST-QA-0016, IDL/MDL Determination

17.5.6 ST-QA-0036, Non-conformance Memorandum (NCM) Process

17.5.7 ST-QA-0038, Procedure for Compositing and Subsampling

17.5.8 ST-IP-0004, Labware Preparation for Inorganic and Trace Metal Analysis

17.5.9 ST-RC-5006 Decontamination of Laboratory Glassware

17.5.10 ST-RC-0125 Determination of Technetium-99 Using Eichrom Teva Resin

17.5.11 ST-MT-0001, Analysis of Metals by Inductively Coupled Plasma/Mass Spectrometry

17.5.12 ST-MT-0003, Inductively Coupled Plasma-Atomic Emission Spectroscopy, Method for Trace Element Analysis

## 18.0 CLARIFICATIONS, MODIFICATIONS TO THE REFERENCED METHOD

18.1 TestAmerica St. Louis uses a 0.5g sample aliquot size instead of the 1g aliquot in the method. TestAmerica St. Louis can achieve the necessary detections without using such a large sample volume.

18.2 Additionally, sample reagent volumes needed for digestion have been reduced to reflect the reduction in sample volume.

18.3 Acid strength has been reduced to allow for ICP/MS analysis.

18.3.1 TestAmerica St. Louis conducted a study of varying acid strengths to establish a successful medium between digestion efficiency and instrument tolerance.

18.4 The final acid concentration in the digestate is 10% acid.

## 19.0 CHANGES TO PREVIOUS REVISION

19.1 Glass beads added to equipment (Section 6)
19.2 Balance capability and pipette volumes changed in section 6.
19.3 Additional information added to LCS composition in section 9.3.
19.4 Plunger removed from section 11.21 due to zinc contamination.
19.5 Blank & LCS composition updated in section 11.23.
19.6 Grammatical corrections.
19.7 Rev. 13; updated the Hydrogen peroxide from reagent grade to ultrex grade in section 7.0.
19.8 Rev. 13; copied 9.3.3.2 and added it to the end of section 9.2.
19.9 Rev. 13; Updated the use of glass beads in section 9.2 and cause of contamination issues in section 9.3.3.2.
19.10 Rev. 13: Adjusted reagent volumes used to reflect sample volume used in section 11.3.3.2.
19.11 Rev 14:
- 19.11.1 Removed filter step from section 2.1
- 19.11.2 Added HF acid to safety table in Section 5
- 19.11.3 Added TC-99 soil prep equipment to Section 6
- 19.11.4 Added TC-99 soil prep reagents and standards to Section 7.
- 19.11.5 Added soil prep for TC-99, section 11.24
- 19.11.6 Added Eichrom method references to Section 17.

19.12 Rev 15:
- 19.12.1 Annual Review, No Changes.

19.13 Rev 16:
- 19.13.1 Removed Technetium 99 tracer prep procedure from section 7.0 replaced Tc-99m with rhenium as tracer.
- 19.13.2 Updated solid sample preparation for Technetium 99 by ICPMS in 11.24.
- 19.13.3 Removed references to Q'tims – old laboratory LIMS system.

19.14 Rev. 17:
- 19.14.1 Grammatical corrections throughout
- 19.14.2 Removed Tc99 soil prep (and all related references) . Referenced the Rad SOP.
- 19.14.3 Added procedure for insufficient sample for batch QC, section 9.4.4
- 19.14.4 Added sample duplicate only done by client request in section 9.5.2
- 19.14.5 Clarified through out the SOP that references to a digestion log was referring to LIMS, not an actual log book
- 19.14.6 Changed sample volume in section 11.3
- 19.14.7 Updated section 11.25 (Hot Antimony Prep) to make it resemble the prep steps in our normal prep.

# Title: PREPARATION AND ANALYSIS OF MERCURY IN SOLID SAMPLES BY COLD VAPOR ATOMIC ABSORPTION SPECTROSCOPY [SW-846 7471B]

**Approvals (Signature/Date):**

| | |
|---|---|
| Kristen Ely — 8/21/14<br>Kristen Ely — Date<br>Inorganic Manager | Michael Ridenhower — 8/21/14<br>Michael Ridenhower — Date<br>Health & Safety Manager / Coordinator |
| Marti Ward — 8.21.14<br>Marti Ward — Date<br>Quality Assurance Manager | Elaine Wild — 8/21/14<br>Elaine Wild — Date<br>Laboratory Director |

**This SOP was previously identified as SOP No. ST-MT-0007 Rev. 13**



**Facility Distribution No.:** 0 **Distributed To:** See Electronic Distribution Sheet

## 1.0 SCOPE AND APPLICATION

1.1 This procedure describes the preparation and analysis of mercury by Cold Vapor Atomic Absorption (CVAA) Spectroscopy using SW-846 Method 7471B.

1.2 CVAA analysis provides for the determination of total mercury (organic and inorganic). The combination of the oxidants, potassium permanganate, has been found to give 100% recovery with both types of compounds. Detection limits, sensitivity and optimum concentration ranges for mercury analysis will vary with the matrices, instrumentation and volume of sample used.

1.3 Method 7471B is applicable to the preparation and analysis of mercury in soils, sediments, bottom deposits and sludge-type materials. All matrices require sample preparation prior to analysis.

1.4 The laboratory target analytes supported by this method, the reporting limits, method detection limits and QC limits are maintained in the Laboratory Information Management System (LIMS).

## 2.0 SUMMARY OF METHOD

2.1 This SOP describes a technique for the determination of mercury in solution. The procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. A representative portion of the sample is digested in hydrochloric and nitric acids. Organic mercury compounds are oxidized with potassium permanganate and the mercury reduced to its elemental state with stannous chloride and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance is measured as a function of mercury concentration. Concentration of the analyte in the sample is determined by comparison of the sample absorbance to the calibration curve (absorbance vs. concentration).

## 3.0 DEFINITIONS

3.1 See the TestAmerica St. Louis Quality Assurance Manual (ST-QAM) for a glossary of common laboratory terms and data reporting qualifiers.

## 4.0 INTERFERENCES

4.1 Potassium permanganate, which is used to breakdown organic mercury compounds, also eliminates possible interferences from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of inorganic mercury from reagent water.

4.2 Copper has also been reported to interfere with recovery of mercury; however, copper concentrations as high as 10 mg/L had no effect on the recovery of mercury from spiked samples.

4.3 Interference from certain volatile organic materials that absorb at this wavelength may also occur. If suspected, a preliminary run without stannous chloride can determine if this type of interference is present. While the possibility of absorption from certain organic substances present in the sample does exist, this problem is not routinely encountered. This is mentioned only to caution the analyst of the possibility. If this condition is found to exist, the mercury concentration in the sample can be determined by subtracting the result of the sample run without the reducing reagent (stannous chloride) from that obtained with the reducing reagent.

4.4 Samples containing high concentrations of oxidizable organic materials, as evidenced by high COD levels, may not be completely oxidized by this procedure. When this occurs the recovery of mercury will be low. The problem can be eliminated by reducing the volume of original sample used.

## 5.0 SAFETY

5.1 Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), Radiation Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.2 SPECIFIC SAFETY CONCERNS OR REQUIREMENTS

5.2.1 Samples that contain high concentrations of carbonates or organic material or samples that are at elevated pH can react violently when acids are added.

5.3 PRIMARY MATERIALS USED

5.3.1 The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

| Material[(1)] | Hazards | Exposure Limit[(2)] | Signs and symptoms of exposure |
|---|---|---|---|
| Mercury (1,000 ppm in Reagent) | Oxidizer<br>Corrosive<br>Poison | 0.1 mg/m$^3$ for Hg Compounds (Ceiling) | Extremely toxic. Causes irritation to the respiratory tract. Causes irritation. Symptoms include redness and pain. May cause burns. May cause sensitization. Can be absorbed through the skin with symptoms to parallel ingestion. May affect the central nervous system. Causes irritation and burns to eyes. Symptoms include redness, pain, and blurred vision; may cause serious and permanent eye damage. |
| Nitric Acid | Corrosive<br>Oxidizer<br>Poison | 2 ppm (TWA)<br>4 ppm (STEL) | Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage. |
| Hydrochloric Acid | Corrosive<br>Poison | 5 ppm (Ceiling) | Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage. |
| Potassium Permanganate | Oxidizer | 5 mg/m$^3$ for Mn Compounds (Ceiling) | Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Dry crystals and concentrated solutions are caustic causing redness, pain, severe burns, brown stains in the contact area and possible hardening of outer skin layer. Diluted solutions are only mildly irritating to the skin. Eye contact with crystals (dusts) and concentrated solutions causes severe irritation, redness, and blurred vision |

| Material[1] | Hazards | Exposure Limit[2] | Signs and symptoms of exposure |
|---|---|---|---|
| | | | and can cause severe damage, possibly permanent. |
| 1 – Always add acid to water to prevent violent reactions. | | | |
| 2 – Exposure limit refers to the OSHA regulatory exposure limit. | | | |
| TWA – Time weighted average | | | |
| STEL – Short term exposure limit | | | |
| Ceiling – At no time should this exposure limit be exceeded | | | |

## 6.0 EQUIPMENT AND SUPPLIES

6.1 Temperature controlled hot block (capable of maintaining a temperature of 95 ± 3 °C).

6.2 Leeman Labs Hydra AA Mercury Analyzer.

6.3 Teledyne Leeman Hydra II Mercury Analyzer

6.4 Hydra II AA software: Envoy version 2.8

6.5 Hydra AA software: WinHg version 1.4

6.6 150 mL plastic containers or equivalent

6.7 Argon gas supply, welding grade or equivalent.

6.8 Pipettes

6.9 Volumetric flasks, class A

6.10 Top-loading balance, capable of reading ± 0.001 g

6.11 Thermometer (capable of reading 95 ± 3 °C)

6.12 Disposable cups or tubes.

6.13 Glass Beads

6.14 Boiling Chips

## 7.0 REAGENTS AND STANDARDS

7.1 All standards and reagent preparation, documentation and labeling must follow the requirements of SOP ST-QA-0002, current revision.

7.2 DI Water (Type II or better), obtained from the Milli-Q unit

7.3 Nitric acid ($HNO_3$), concentrated, trace grade

7.4 Hydrochloric Acid (HCl), concentrated, trace grade

7.5 Aqua Regia: Prepare immediately before use by carefully adding three volumes of concentrated HCl to one volume of concentrated $HNO_3$.

7.6 Stannous chloride - Dissolve 100 g of stannous chloride into 1000 mL of 10% HCl.

7.7 Hydroxylamine sulfate/12% sodium hydroxide solution, a certified stock standard is purchased
**NOTE**: Hydroxylamine hydrochloride (12%) may be used in place of hydroxylamine sulfate. (120 g →1000 mL)

7.8 Potassium permanganate, 5% solution (w/v) -certified stock reagent is purchased.
7.8.1 Alternately, dissolve 5 g of potassium permanganate for every 100 mL of DI water.

7.9 Mercury Calibration standards

7.9.1 Calibration Stock (100 ppm) in 5%HNO3, purchased from vendor.

7.9.2 Calibration Intermediate mercury standard (0.1 ppm): Add 2 mL of concentrated $HNO_3$ to a 100 mL volumetric flask. Add 0.1 mL of the stock Calibration mercury standard and dilute to a 100 mL final volume in DI water.

7.9.2.1 The calibration intermediate standard must be made daily.

7.9.3 Calibration standards: Transfer 0.0, 0.2, 0.5, 1.0, 5.0 and 10.0 mL aliquots of the Calibration Intermediate mercury standard into sample prep bottles and proceeding as specified in Section 11.1

7.9.3.1 The calibration standards must be made daily

7.9.3.2 All standards must be processed through the entire analytical procedure including sample preparation

7.10 Mercury Check Standard

7.10.1 The initial calibration verification (ICV) standard must be made from a different stock solution than that of the calibration standards.

7.10.2 QC Stock (100 ppm) in 5% $HNO_3$ , purchased from vendor

7.10.3 QC Intermediate mercury standard (0.1 ppm) – Add 2 mL of concentrated $HNO_3$ to a 100 mL volumetric flask. Add 0.1 mL of the stock QC mercury standard and dilute to a 100 mL final volume in DI water.

7.10.3.1 The QC intermediate standard must be made daily.

7.10.4 ICV standard: Transfer 2.5 mL aliquots of the QC intermediate mercury standard into sample prep bottles and proceeding as specified in Section 11.1

7.10.4.1 The ICV must be made daily

7.10.4.2 All standards must be processed through the entire analytical procedure including sample preparation.

## 8.0 SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 TestAmerica St. Louis supplies sample containers and chemical preservatives in accordance with the method. TestAmerica St. Louis does not perform sample collection. Samplers should reference the methods referenced and other applicable sample collection documents for detailed collection procedures. Sample volumes and preservative information is given in ST-PM-0002.

8.2 The sample holding time for mercury is 28 days from time of collection to the time of analysis.

8.3 Soil samples do not require chemical preservation but must be stored at 4 °C ± 2 °C until the time of analysis.

## 9.0 QUALITY CONTROL

9.1 **Batch**

9.1.1 A sample batch is a maximum of 20 environmental samples, which are prepared together using the same process and same lot(s) of reagents. Where no preparation method exists (e.g. water sample volatile organics, water sample anion analysis) the batch is comprised of a maximum of 20 environmental samples which are analyzed together with the same process, lots of reagents and personnel.

9.1.2 Instrument conditions must be the same for all standards, samples and QC samples.

9.1.3 For this analysis, batch QC consists of a method blank, a Laboratory Control Sample (LCS), and Matrix Spike (MS) and Matrix Spike Duplicate (MSD) In the event that there is insufficient sample to analyze a MS/MSD, an LCS Duplicate (LCSD) is prepared and analyzed.

9.1.3.1 At the instrument, a Serial dilution (SD) is performed with every batch.

9.1.4 Samples having different QC codes, due to non-standard client specific QC requirements, must be batched separately in the LIMS. A method blank and LCS may be shared across QC codes provided the actual "sample batch" does not exceed 20 environmental samples. Duplicates (and MS/MSD if applicable) must be performed for each separate QC code.

9.2 **Method Blank**

9.2.1 A method blank is a blank matrix processed simultaneously with, and under the same conditions as, samples through all steps of the procedure.

9.2.2 A method blank must be prepared with every sample batch.

9.2.3 For Soil analyses, the method blank is comprised of either glass beads or boiling chips.

9.2.4 See section 13 for acceptance criteria

9.3 **Laboratory Control Sample**

9.3.1 An LCS is a blank matrix spiked with a known amount of analyte(s), processed simultaneously with, and under the same conditions as, samples through all steps of the analytical procedure.

9.3.2 An LCS must be prepared with every sample batch.

9.3.3 For Soil analyses, the LCS is a commercially prepared purchased solid reference material containing mercury.

9.3.3.1 Alternately, the LCS may be comprised of glass beads or boiling chips fortified with mercury, if client requirements request or QC criteria dictate such.

9.3.4 See section 13 for acceptance criteria

9.4 **Matrix Spike (MS) /Matrix Spike Duplicate (MSD)**

9.4.1 A Matrix Spike is an aliquot of a field sample to which a known amount of target analyte(s) is added, and is processed simultaneously with, and under the same conditions as, samples through all steps of the analytical procedure.

9.4.2 MS/MSD samples do not count towards the 20 environmental samples in a sample batch.

9.4.3 MS/MSD samples must be performed with every sample batch and every LIMS batch.

9.4.3.1 If there is insufficient sample to perform a MS and/or MSD, a duplicate LCS is analyzed. A NCM is written to document the insufficient volume and the utilization of a LCSD to demonstrate precision.

9.4.4 See section 13 for acceptance criteria

9.5 **Sample Duplicate (DU)**

9.5.1 A Sample Duplicate is an additional aliquot of a field sample taken through the entire analytical process to demonstrate precision.
9.5.2 Certain client project requirements may request a sample duplicate in lieu of a MSD. Please check in the comment section in LIMS.

9.6 **Serial Dilution (SD)**
9.6.1 A sample digestate is diluted 1:5 and reanalyzed to assess the present of a matrix interference.
9.6.2 A serial dilution is performed with every analytical batch.
9.6.3 Agreement within 10% between the concentration for the undiluted sample and five times the concentration for the diluted sample indicates the absence of interferences.

9.7 **Post Digestion Spikes (PDS)**
9.7.1 A known amount of mercury is added to the sample chosen for MS/MSD to bring the concentration of mercury to 2 to 5 times the original concentration. If the sample's mercury concentration is below the detection limit, spike at a concentration between the low and mid-level standard.
9.7.2 At client's request, a post digestion spike is performed when MS/MSD fails..
9.7.3 See section 13 for acceptance criteria

9.8 **Method of Standard Addition (MSA)**
9.8.1 This technique involves adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample interferent that may enhance or depress the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift.
9.8.2 Method SW-846 1311 requires that the Method Standard Addition (MSA) be used when matrix spike recovery is less than 50% and the measured sample results is within the range of 80-120% of the Toxicity Characteristics Limit.

9.9 **Procedural Variations/ Nonconformance and Corrective Action**
9.9.1 Any variation shall be completely documented using a Nonconformance Memo and approved by the Supervisor and QA Manager. See SOP ST-QA-0036 for details regarding the NCM process.
9.9.2 Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the Supervisor and QA Manager. See SOP ST-QA-0036 for details regarding the NCM process.

## 10.0 CALIBRATION AND STANDARDIZATION

10.1 Initial Calibration
10.1.1 Calibration standards must be processed through the preparation procedure, section 11.
10.1.1.1 Due to the differences in preparation protocols, separate calibration and calibration verification standards must be prepared for aqueous and solid matrices.
10.1.1.2 Record the prep of the calibration standard in LIMS
10.1.2 Calibration must be performed daily (every 24 hours) and each time the instrument is set up.
10.1.3 Set up the instrument with the operating parameters recommended by the manufacturer.
10.1.4 Allow the instrument to become thermally stable before beginning calibration.
10.1.5 Calibrate the instrument according to instrument manufacturer's instructions, using a minimum of five standards and a blank.
10.1.5.1 One standard must be at the reporting limit. . The other standards define the working range of the detector, with the highest level standard establishing the linear range of the instrument.

10.1.5.2 Analyze standards in ascending order beginning with the blank.

10.1.6 Calibration criteria:

10.1.6.1 A correlation coefficient must be ≥ 0.995

10.1.6.2 If the calibration curve does not meet method requirements, perform maintenance and perform another calibration curve.

10.2 Initial Calibration Verification (ICV)

10.2.1 An ICV is a second source verification of the calibration.

10.2.2 An ICV must be performed with every calibration.

10.2.3 ICV criteria:

10.2.3.1 ICV recovery must be ± 10% of the known true value.

10.2.3.1.1 If the ICV fails to meet criteria (± 10%), the analysis is terminated, the problem corrected, the instrument recalibrated and the calibration re-verified.

10.2.3.1.2 If it is suspected that the failure was attributed to a poor sample introduction to the instrument, the ICV may be rerun once, provided no samples have been analyzed after the failing ICV. If the second ICV is acceptable, analysis may continue.

10.3 Initial Calibration Blank (ICB)

10.3.1 Analyze the initial continuing calibration blank (ICB) immediately following the ICV.

10.3.2 ICB criteria:

10.3.2.1 The absolute value of the ICB result must be less than or equal to the reporting limit (RL).

10.3.2.1.1 If the result is not within the control level, terminate the analysis, correct the problem, and recalibrate the instrument if necessary

10.3.2.1.2 Certain client programs may require more stringent ICB criteria, please see comments in LIMS.

10.4 Low Level Check (LLC) aka CRA (when requested by client)

10.4.1 Can be the same source as the calibration

10.4.2 An LLC is analyzed at the beginning of each analytical run when requested

10.4.3 LLC must be spiked at RL.

10.4.4 LLC Criteria

10.4.4.1 Must fall within 30% of the known value

10.4.4.2 If the result is not within the control level, terminate the analysis, correct the problem and recalibrate.

10.4.4.3 If it is suspected that the failure was attributed to a poor sample introduction to the instrument, the LLC may be rerun once, provided any samples analyzed after the failing LLC are also re-analyzed. If the second LLC is acceptable, analysis may continue.

10.5 Continuing Calibration Verification (CCV)

10.5.1 A CCV is analyzed after every 10 samples and at the end of the analytical sequence run.

10.5.2 CCV criteria:

10.5.2.1 The CCV must fall within 20% of the known true value.

10.5.2.1.1 If the CCV does not meet QC criteria, the analysis must be terminated, the problem corrected, the instrument recalibrated, and the preceding 10 samples reanalyzed.

10.5.2.1.2 If it is suspected that the failure was attributed to a poor sample introduction to the instrument, the CCV may be rerun once, provided any samples bracketing the failing CCV are also re-analyzed. If the second CCV is acceptable, analysis may continue.

10.6 Continuing Calibration Blank (CCB)

10.6.1 Analyze a continuing calibration blank (CCB) immediately following the CCV.
10.6.2 CCB criteria:
10.6.2.1 The absolute value of the CCB result must be less than or equal to the reporting limit (RL).
10.6.2.1.1 If the result is not within the control level, terminate the analysis, correct the problem, and recalibrate the instrument if necessary
10.6.2.1.2 Certain client programs may require more stringent CCB criteria. (see comments in LIMS).

## 11.0 PROCEDURE

11.1 To prepare aliquots
11.1.1 Calibration:
11.1.1.1 Pipette 0.0, 0.2, 0.5, 1.0, 5.0 and 10.0 mL aliquots of the calibration intermediate standard into a series of sample digestion vessel. Bring up all to 10 mL final volume with DI water.
11.1.2 ICV
11.1.2.1 Pipette 2.5 mL of QC intermediate into a sample digestion vessel and bring up to a 10 mL final volume with DI water
11.1.3 LLC
11.1.3.1 Pipette 0.2 mL calibration into a digestion vessel and bring up to a final volume of 10 mL.
11.1.4 CCV
11.1.4.1 To prepare the CCV, pipette 5.0 mL of QC intermediate into a sample digestion vessel and bring up all to a 10 mL final volume with DI water.
11.1.5 Sample
11.1.5.1 Transfer 0.6 – 0.7 g of well-mixed sample to a clean sample digestion vessel.
11.1.5.2 Reduced sample size can be used as long as a representative sample can be obtained and the reagent levels are adjusted to maintain the sample to reagent ratio.
11.1.5.3
11.1.6 MS/MSD
11.1.6.1 Spike MS/MSD with 1 mL of the QC intermediate.

11.2 Sample Digestion:
11.2.1 To each **standard** vessel: Add 5 mL of aqua regia.
11.2.2 To each **sample** vessel: Add 5 mL of reagent water and 5 mL of aqua regia.
11.2.3 Heat for 2 minutes in a hot block at 95 ± 3 °C
11.2.4 Cool.
11.2.5 Add 50 mL of DI water.
11.2.6 Add 15 mL of potassium permanganate solution, mix thoroughly
11.2.7 Let stand until purple color persists for 15 minutes, adding additional portions of permanganate solution if needed. If additional portions of permanganate solution are needed, an equivalent portion must also be added to all QC and client samples being prepped. Amount must be equal to that of the highest amount added to any sample.
11.2.8 Heat for 30 minutes in the hot block at 95 ± 3 °C
11.2.9 Cool.
11.2.10 Add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate.
11.2.11 Bring sample to a final volume of 100 mL with DI water.

11.3 Sample Analysis:
11.3.1 The samples must be allowed to cool to room temperature prior to analysis or a decrease in the response signal can occur.

11.3.2 Follow instructions provided by instrument manufacturer.

11.3.3 Baseline correction is acceptable as long as it is performed after every sample or after the CCV and CCB; resloping is acceptable as long as it is immediately preceded and followed by a compliant CCV and CCB.

11.3.4 Analytical sequence:

Instrument Initial Calibration (5 standard plus a blank)
ICV
ICB
LLC (only if required by client)
CCV
CCB
Maximum 10 samples
CCV
CCB
Repeat sequence of 10 samples between CCV/CCB pairs as required
CCV
CCB

**NOTE:** Samples include the method blank, LCS, LCS dup, MS, MSD, DU, field samples and sample dilutions.

**NOTE:** Analytical sequence must close with a CCV/CCB pair.

**NOTE:** If the instrument stops during the sequence, the instrument may be restarted. When restarting the instrument, the run must begin with an acceptable CCV/CCB only if the run has been stopped for more than 2 hours.

## 12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Commonly used calculations (e.g. % recovery and RPD) and standard instrument software calculations are given in the TestAmerica St. Louis ST-QAM.

12.2 Sample results are reported to three significant figures in accordance with the significant figure policy.

12.3 All measurements must fall within the defined calibration range to be valid. Dilute and reanalyze all samples for analytes that exceed the highest calibration standard.

## 13.0 DATA ASSESSMENT AND ACCEPTANCE CRITERIA; CORRECTIVE ACTIONS FOR OUT OF CONTROL DATA

13.1 The data assessment and corrective action process is detailed through the LIMS Nonconformance Memorandum (NCM) process. The NCM process is described in SOP: ST-QA-0036.

13.2 Method Blank (MB)

13.2.1 Acceptance Criteria: No target analytes may be present in the method blank above the reporting limit.

13.2.2 Project specific requirements if more stringent than our routine procedure (e.g. no target analytes present above ½ RL), will be in comments in LIMS.

13.2.3 Corrective Action for Method Blanks not meeting acceptance criteria:

13.2.3.1 Method Blank Contamination – If the Method Blank concentration exceeds the applicable criteria, the batch must be re-prepped unless the concentration of all associated samples is less than the RL or greater than ten times the concentration found in the blank.

13.3 Laboratory Control Sample (LCS)

13.3.1 Acceptance Criteria:

13.3.1.1 All control analytes should be within established control limits for accuracy (%Recovery) and precision (RPD).

13.3.1.2 Limits can be found in LIMS.

13.3.2 Corrective Action for LCS not meeting acceptance criteria:

13.3.2.1 LCS Spike Recovery excursion (high) – Samples with results less than the RL may be reported with an NCM (unless prohibited by client requirements). Samples with detects for the analyte with a high bias in the LCS are re-prepped and re-analyzed.

13.3.2.2 LCS Spike Recovery excursion (low) – the batch is re-prepped and re-analyzed for the affected analytes.

13.4 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

13.4.1 Analytes should be within control limits for accuracy (%Recovery) and precision (RPD).

13.4.2 MS/MSD Recovery criteria: 80% – 120%

13.4.3 Corrective Action for MS/MSD not meeting acceptance criteria:

13.4.3.1 MS/MSD Spike Recovery excursion: may not necessarily warrant corrective action other than narration

13.4.3.2 If the affected analyte concentration in the original sample is greater than four times the amount spiked, recovery information is ineffective and the data is reported with an NCM.

13.4.3.3 If the excursion is due to a physically evident matrix interference, the data is reported with an NCM.

13.4.3.4 In cases where the MS and/or MSD don't meet criteria, but the RPD is in control, data may be reported with and NCM.

13.4.3.5 When the MS/MSD recoveries and the %RPD are outside criteria, the batch is re-prepped and re-analyzed for the affected analytes.

13.5 Post Digestion Spike (PDS)

13.5.1 A PDS is only done when requested by the client.

13.5.2 The method stipulates that a PDS be performed on the sample chosen for MS/MSD.

13.5.2.1 The acceptance criteria is 80% – 120%, with a spike concentration between 10–100 times the RL UNLESS, other project/program criteria is given.

13.6 Serial Dilution (SD)

13.6.1 The serial dilution results shall agree within ± 10% of the undiluted sample results, if the undiluted sample results are greater than 10 times the reporting limit. There is no criteria for sample results less than 10 times the reporting limit.

13.6.2 Corrective Action: Serial dilution failure is documented in an NCM and the reported data is flagged. If multiple analytes fail the serial dilution test, the analyst may re-prep and re-analyze the samples.

13.7 Sample result evaluation

13.7.1 Analyses must fall within the calibration range.

13.7.2 Dilutions

13.7.2.1 If the response for any compound exceeds the working range of the analytical system, a dilution of the extract is prepared and analyzed. An appropriate dilution should be in the upper half of the calibration range.

13.7.2.1.1 An NCM will be written for any samples that are diluted.

13.7.3 Carryover

13.7.3.1 When a sample has a high response for a compound, there is a real possibility that some of the sample may carry over into the sample analyzed immediately afterward.

13.7.3.2 If a sample analyzed after a sample with high concentrations has negative results, carryover did not occur.

13.7.3.3 If a sample analyzed after a sample with high concentrations has positive results for the same analytes, the results are questionable. This sample must be reanalyzed under conditions in which carryover can be confirmed to not have occurred.

13.8 Insufficient Sample

13.8.1 For each prescribed re-preparation corrective action, if there is insufficient sample to repeat the analysis a narrative comment stating such is included in the report narrative. The insufficient sample description is included in the Clouseau NCM within the type defining the excursion.

## 14.0 METHOD PERFORMANCE AND DEMONSTRATIONS OF CAPABILITY

14.1 Method performance data, Reporting Limits, and QC acceptance limits, are given in LIMS.

14.2 Demonstration of Capability

14.2.1 Initial and continuing demonstrations of capability requirements are established in the ST-QAM.

14.3 Training Qualification

14.3.1 The manager/supervisor has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience.

14.3.2 The analyst must have successfully completed the initial demonstration capability requirements prior to working independently. See requirements in the ST-QAM.

14.4 Annually, the analyst must successfully demonstrate proficiency to continue to perform this analysis. See requirements in the ST-QAM.

## 15.0 VALIDATION

15.1 Laboratory SOPs are based on published methods (EPA, DOE, ASTM, Eichrom, Standard Methods) and do not require validation by the laboratory. The requirements for laboratory demonstration of capability are included in the ST-QAM. Laboratory validation data would be appropriate for performance based measurement systems, non-standard methods and significant modifications to published methods. Data from said validations is held in the QA department.

## 16.0 WASTE MANAGEMENT AND POLLUTION PREVENTION

16.1 All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

16.2 Waste Streams Produced by this Method

16.2.1 Acidic sample waste

16.2.1.1 All acidic waste will be accumulated in the appropriate waste accumulation container, labeled as Drum Type "A"

16.2.1.2 Contaminated disposable glass or plastic materials utilized in this analysis are disposed of in the sanitary trash. If the lab ware was used for the analysis of radioactive samples and contains radioactivity at a level of 100 cpm over background as determined by a GM meter, the lab ware will be collected in waste barrels designated for solid rad waste and disposed of by the EH&S Coordinator.

## 17.0 REFERENCES

17.1 Test Methods for Evaluating Solid Waste , Physical/Chemical Methods, SW-846, 3rd Edition, Revision 2, January 1998, Method 7471B (Mercury).

17.2 TestAmerica St. Louis Quality Assurance Manual (ST-QAM), current revision.

17.3 TestAmerica Corporate Environmental Health and Safety Manual (CW-E-M-001) and St. Louis Facility Addendum (ST-HS-0002), current revisions.

17.4 Associated SOPs, current revisions:

- 17.4.1 ST-QA-0002, Standard and Reagent Preparation
- 17.4.2 ST-QA-0005, Calibration and Verification Procedure for Thermometers, Balances, Weights and Pipettes
- 17.4.3 ST-QA-0016, IDL/MDL Determination
- 17.4.4 ST-QA-0014, Evaluation of Analytical Accuracy and Precision Through the Use of Control Charts
- 17.4.5 ST-QA-0036, Non-conformance Memorandum (NCM) Process
- 17.4.6 ST-PM-0002, Sample Receipt and Chain of Custody
- 17.4.7 ST-IP-0004, Labware Preparation for Inorganic and Trace Metals Analysis

## 18.0 CLARIFICATIONS, MODIFICATIONS AND ADDITIONS TO REFERENCE METHOD

18.1 Stannous chloride is used in place of Stannous sulfate.

18.2 TestAmerica St. Louis uses less DI water in steps 11.1.5.12 and 11.1.5.13 than the method suggests. The laboratory considers the volume of 15 mL not to be significant enough to render compensation/adjustment when diluting sample to final volume. The lab has adjusted the final volume of the standards and samples by 15 mL.

18.3 TestAmerica uses an ERA solid reference material for the LCS. Control limits supplied by ERA are used to determine acceptability of the LCS recovery.

## 19.0 CHANGES TO PREVIOUS REVISION

19.1 Removed sulfuric acid from section 5.0. It is no longer used in this method.

19.2 Updated section 10.0 by adding Low Level Check (LLC)

19.3 Added instructions on how to prepare an ICV, LLC and CCV in section 11.0

19.4 Added LLC, CCV and CCB to the list of analytical sequences in section 11.2.

19.5 Rev. 10;

- 19.5.1 Updated post digestion spike section 9.7; removed serial dilution requirements.
- 19.5.2 Updated MSA section 9.8; removed suggested criteria for MSA analysis.
- 19.5.3 Added Method 1311 MSA requirements, section 18.4.

19.6 Rev. 11:

- 19.6.1 Added instrument hardware and software to section 6.0.
- 19.6.2 Added requirement to document preparation of calibration standard to section 10.1.
- 19.6.3 Clarified instructions on addition of permanganate solution in section 11.4.

19.7 Rev. 12:

- 19.7.1 Updated requirement for prepping all client and QC samples in section 11.4.3.8.

19.8 Rev. 13:

- 19.8.1 Removed references to QuantIMS and Clouseau
- 19.8.2 Section 6, updated top-loading balance and DI water requirements

19.8.3 Section 9, recovery criteria and updated post digestion spike recovery criteria

19.8.4 Section 10, updated Low Level Check and Continuing Calibration Blank

19.8.5 Section 11, added sample amount for CCV preparation

19.8.6 Section 13 updated

19.8.7 Section 15 updated

19.8.8

19.9 Rev 14

19.9.1 Added glass beads and boiling chips to section 6, added reference to boiling chips throughout SOP

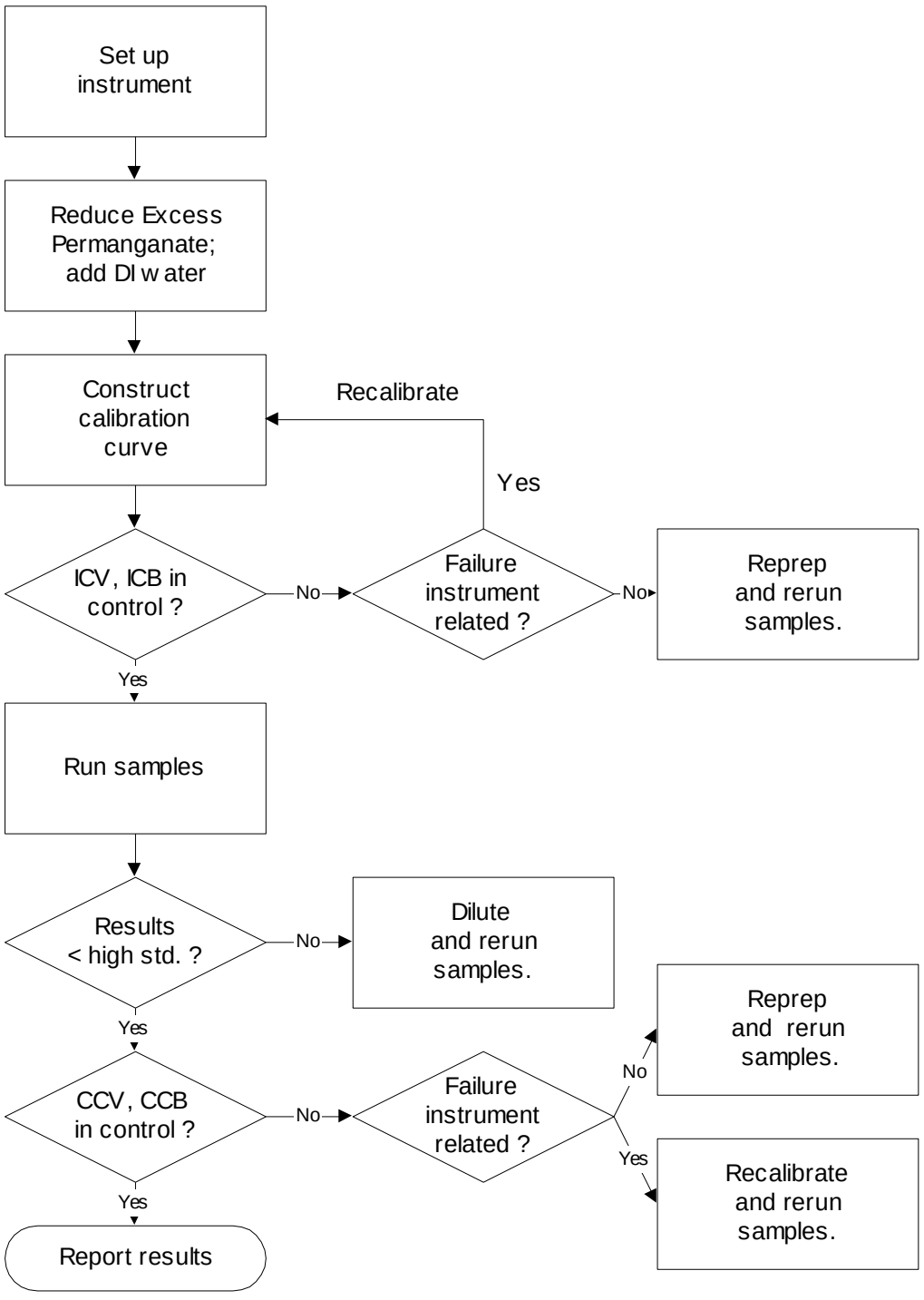
19.9.2 Formatting changes throughout, particularly section 7.9, 7.10, and 11

19.9.3 Removed references to Client Requirement Sheet

19.9.4 Added Hydra II to Equipment section.

19.9.5 Removed exception to MSA in Section 18.

CVAA Mercury Analysis



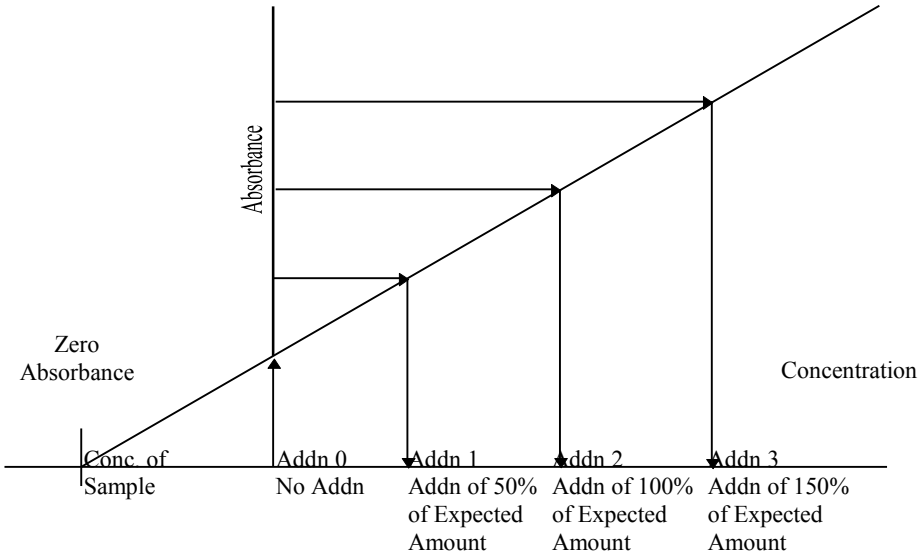
**MSA GUIDANCE**

**Method of Standard Addition**

Four equal volume aliquots of sample are measured and known amounts of standards are added to three aliquots. The fourth aliquot is the unknown and no standard is added to it. The concentration of standard added to the first aliquot should be 50% of the expected concentration. The concentration of standard added to the second aliquot should be 100% of the expected concentration and the concentration of standard added to the third aliquot should be 150% of the expected concentration. The volume of the unspiked and spiked aliquots should be the same (i.e., the volume of the spike added should be negligible in relation to the volume of sample).

To determine the concentration of analyte in the sample, the absorbance (or response) of each solution is determined and a linear regression performed. On the vertical axis the absorbance (or response) is plotted versus the concentrations of the standards on the horizontal axis using 0 as the concentration of the unspiked aliquot. An example plot is shown in Figure 1. When the resulting line is extrapolated back to zero absorbance, the point of interception of the horizontal axis is the concentration of the unknown. Calculate the correlation coefficient (r) and the x-intercept (where y=0) of the curve. The concentration in the digestate is equal to the negative x-intercept.

Figure




- For the method of standard additions to be correctly applied, the following limitations must be taken into consideration.
- The plot of the sample and standards must be linear over the concentration range of concern. For best results, the slope of the curve should be similar to that of a plot of the aqueous standard curve.
- The effect of the interference should not vary as the ratio of the standard added to the sample matrix changes.

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# STANDARD OPERATING PROCEDURE

# ANALYSIS OF VOLATILE ORGANIC COMPOUNDS BY GC/MS

| | |
|---|---|
| **Analyte:** | **Volatile Organic Compounds (Various)** |
| **SOP #:** | **8260C_121613_R8.1** |
| **Method Reference:** | **EPA SW846/5030B/5035/8260C**<br>**EPA 624** |
| **Issue Date:** | **February 7, 2002** |
| **Revision No.:** | **8.1** |
| **Revision Date:** | **August 11, 2014** |
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**Reviewed and Approved August 11, 2014 by:**

Director, Environmental Services: Yemane Yohannes

Director, Quality Management: Charles O'Bryan

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# STANDARD OPERATING PROCEDURE
# ANALYSIS OF VOLATILE ORGANIC COMPOUNDS
# BY GC/MS

## SOP#: 8260C_121613_R8.1

## TABLE OF CONTENTS

# 1.0 Scope and Application

## 1.1 Introduction

RTI Laboratories, Inc. has prepared this document to detail the Standard Operating Procedure (SOP) for the analysis of soil and water samples by Purge and Trap/Gas Chromatography/Mass Spectrometry. Analytes targeted for this method are listed in Appendix B and include Purgable Hydrocarbons listed in EPA SW-846 Method 8260. Specific compound lists are contained in the test codes resident in the Omega LIMS.

A detailed description of the instrumentation, calibration, run parameters and quality control procedures is included in this SOP. For definition of terms not specifically defined in this document refer to RTI QAP Section 16.

## 1.2 Summary of Method

Volatile analytes present in water or soil samples are analyzed by the purge and trap method of sample introduction followed by gas chromatography/mass spectrometry. The mass spectrometer is tuned to meet method requirements, calibration curves are established, and system performance and continuing calibration standards verify acceptable instrument operation prior to sample analysis. Once all calibration and quality control parameters have been successfully analyzed, samples are placed in appropriate purge and trap vessels where an inert gas purges the volatile components from the sample and delivers the analytes to a solid sorbent trap. The trap is heated to release the analytes and swept into a gas chromatograph where compound separation occurs. Compounds eluting from the GC column are introduced into a mass spectrometer where compounds are identified by the characteristic mass spectra and quantified using the primary characteristic ion.

# 2.0 Safety Precautions

2.1 Compounds applicable to this method are known or suspected carcinogens. Proper personal protective procedures should be employed when handling standard materials and samples that may contain potentially toxic compounds.

# 3.0 Sample Requirements and Sample Handling Procedures

3.1 Samples are received in accordance with the RTI Standard Operating Procedure for Sample Receipt and Custody (SRC001-A). Appropriate U. S. Environmental Protection Agency (EPA) sample handling procedures and sample preservation recommendations are followed.

3.2 Water samples and TCLP ZHE extracts are collected in commercially obtained 40 ml pre-cleaned vials containing HCl preservative with Teflon lined screw caps. All samples are stored at 4 degrees C and have a maximum 14-day holding time. Samples collected in unpreserved vials have a maximum holding time of 7 days. The pH of each water sample is checked following analysis to ensure the presence of preservative. Samples should be received with no overt bubbles or headspace in the vial. If a problem occurs with the sample the sampler is contacted and noted in the LIMS

3.3 Soil sample collection using methanol preservation - High level Method 5035.

3.3.1 RTI supplies 40 ml weighed vials containing 10ml methanol. Samples should be collected by weighing (or estimating from the soil density) 10 gm of soil directly into the vial containing methanol.

3.3.2 Vials are weighed prior to analysis at the laboratory to determine the amount of soil added. Samples containing <9 gm are flagged and samples containing >20 gm are rejected (Refer to section 11.6). Samples are additionally flagged if the soil is not completely submerged in the methanol.

3.3.3 Samples must be stored on ice or at 4$^{o}$C and delivered to the laboratory within 4 days. Sample holding time is 14 days from collection to analysis.

3.3.4 A separate bulk soil sample must be collected for percent solids determination.

3.4 Soil sample collection - Low level using Method 5035.

3.4.1 RTI supplies 40 ml weighed vials containing 5ml sodium bisulfate or unpreserved. Samples should be collected by weighing (or estimating from the soil density) 5 gm of soil directly into the vial containing matrix modifier.

3.4.2 Vials are weighed prior to analysis at the laboratory to determine the amount of soil added.

3.4.3 Samples must be stored on ice or at 4$^{o}$C and delivered to the laboratory within 4 days. Sample holding time is 14 days from collection to analysis.

3.5 Soil sample collection – Encore devices.

3.5.1 Samples collected in these devices have a 48 hr holding time from collection to receipt at the laboratory and transfer to methanol.

3.5.2 Upon arrival at the laboratory, 10 grams of sample will be transferred from the device to a vial containing 10 ml of methanol (if a 10 g Encore is used for collection the entire volume of soil will be transferred to the vial). The date and time of transfer is noted on the chain of custody. Record the weight in the sample logbook.

3.5.3 Encore samples may also be processed using the low level method with aqueous sodium bisulfate. RTI maintains 40 ml weighed vials containing 5ml sodium bisulfate. Upon arrival at the laboratory, 5 grams of sample will be transferred from the device to a 40 ml weighed vial containing 5ml sodium bisulfate. The date and time of transfer is noted on the chain of custody Record the weight in the sample logbook.

3.6 Bulk soil sample collection – Method 5035.

3.6.1 Samples should be collected in a pre-cleaned, wide mouth 4 or 8 oz jar filled completely with minimal headspace. It is recommended that a separate container be used for the sampling of volatile organic compounds (VOC's). In the case of a single container submitted with other requests in conjunction with VOC analysis, two five gram samples will be removed from the container and placed in separate VOC vials immediately following sample logging.

3.7 Soil Sample Collection – State of Alaska. Volatile organic compounds (i.e. BTEX) collected in conjunction with GRO analysis will follow the sample collection procedures specified in the GRO SOP (25 g soil preserved with 25 ml methanol collected in 4 oz containers).

## 4.0 MDL, Linear Range, Accuracy and Precision

4.1 The method detection limit (MDL) is statistically defined at the 99% confidence level according to 40 CFR Part 136 App. B. Seven replicates containing all of the analytes of interest at a concentration level of 1-5 times the estimated D.L. are analyzed and the standard deviation is calculated. The Student's T Value for the 7 replicates (3.143) is multiplied by the standard deviation of the analyte to calculate the MDL. MDLs are updated on major instrument changes and are kept on file in the Laboratory. MDLs and reporting limits are incorporated into the applicable test code in the Omega LIMS.

4.2 The LOD (limit of detection) is determined by spiking reagent water at 1-4 times the MDL and prepared using the same procedure as samples. Analytes must be present at levels 3 times or greater than the blank response (greater than 3 times the signal to noise ratio). The concentration used is the LOD for that analyte. LOD determinations must be performed quarterly.

4.3 The LOQ (limit of quantification) is determined by spiking reagent water at the reporting limit (RL/CRQL) and prepared in the same manner as samples. Analyte recovery must be within 20% of the expected concentration. The concentration used and successfully recovered is the LOQ for that analyte. LOQ determinations must be performed quarterly.

4.4 Initially accuracy and precision at the LOQ is determined by spiking 4 aliquots of reagent water at the reporting limit (RL/CRQL) and prepared using the same procedure used for samples. The average recovery must be within 20% of the expected value and the %RSD must be less than 15%.

4.5 LOD/LOQ determinations that do not meet the specifications above require repeat analysis, adjustment to the spiking levels and/or reporting limits, repeating the MDL determination at adjusted concentrations if required and repeat LOD/LOQ determinations.

4.6 The range used by RTI for methanol extracted samples is 30 ug/KG to 10000 ug/KG for most compounds. For aqueous samples the linear range is 1 ug/L to 200 ug/L for most compounds. Low level soils, the linear range is 1ug/KG to 200 ug/KG for most compounds. The linear range for some of compounds may be established at a lower upper limit. If an analyte concentration is above the linear range, a dilution of that sample that results in a concentration in the linear range will be analyzed.

4.7 The accuracy and precision for this method are determined by analyzing four LCS samples at a concentration of 10 ug/L of each compound (m/p-Xylenes – 20 ug/L). The average percent recovery, standard deviation, and the relative standard deviation are calculated for each analyte. Quality control limits, mean recovery values and RPD results are incorporated in the Omega LIMS.

## 5.0 Interferences

5.1 The major source of interference is associated with contamination. Specific areas of concern are discussed below.

5.1.1 Impurities in the purge gas and sorbent trap may introduce volatile compounds into the system. Using high purity purge gas and baking of the trap minimizes this problem. Routine analysis of method/reagent blanks is performed to ensure the system is free from contamination.

5.1.2 Contamination may arise when a low level or target analyte free sample is analyzed immediately following a sample containing high concentration of compounds. These situations should be investigated and suspect samples repeated following a blank analysis.

5.1.3 Samples containing high concentrations of non-target compounds or high levels of target analytes will require dilutions and will raise the minimum detectable limits for some or all compounds. Little can be done to avoid this problem other than to attempt to use the lowest possible dilution volume.

5.2 Methylene chloride as a common laboratory solvent can present potential contamination problems. Samples must be stored and processed in areas where methylene chloride is not used since this compound will diffuse through the septa and caps of sample vials. Attention to trip blanks and method blanks will identify possible problems with methylene chloride contamination. All steps to clean the system and prevent system and/or sample exposure must be undertaken when contamination is identified.

5.3 Trip blanks are prepared for each sampling event to accompany the samples through the entire process. These will assist in identifying potential sources of contamination resulting from diffusion of volatile organics through the septa of sample vials.

5.3.1 RTI supplies 40 ml weighed vials containing 5ml sodium bisulfate or unpreserved for low level soil samples. No other preparatory steps are required.

5.3.2 RTI supplies 40 ml weighed vials containing 10ml methanol for high level soil samples. No other preparatory steps are required.

5.3.3 Water samples trip blanks are prepared by filling with ASTM type II DI water from the volatile laboratory, a 40 ml pre-cleaned vials containing HCl preservative with Teflon lined screw cap.

5.4 For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds, or high concentrations of compounds being determined, it may be necessary to wash the purging device with a soap solution, rinse it with organic-free reagent water, and then dry the purging device in an oven at 105 °C. In extreme situations where contamination occurs, the entire purge-and-trap device may require dismantling and cleaning.

## 6.0 Apparatus and Materials

6.1 Agilent 5890 GC gas chromatograph in split injection mode, Agilent 5972 Quadrapole MS, Windows based computer workstation with HP ChemPC and Enviroquant software – Version B (VOA 7).

6.2 Agilent 6890 GC gas chromatograph in split injection mode, Agilent 5973 Quadrapole MS, Windows based computer workstation with HP ChemPC and Enviroquant software – Version D (VOA 11).

6.3 Agilent 6890 GC gas chromatograph in split injection mode, Agilent 5973 Quadrapole MS, Windows based computer workstation with HP ChemPC and Enviroquant software – Version D (VOA 12).

6.4 Agilent 6890 GC gas chromatograph in split injection mode, Agilent 5973 Quadrapole MS, Windows based computer workstation with HP ChemPC and Enviroquant software – Version E (VOA 10).

6.5 Restek Rtx-624 (30m, 0.25mm, 1.4µm plate) capillary column and JW DB-624 (60m, 0.25mm, 1.4µm plate) capillary column.

6.6 EST Centurion Auto sampler (2) with external heated soil cup for low level soil analysis, and EST ENCON purge and trap with external sparge unit and Supelco Vocarb 3000 thermal trap. The heated transfer line is connected directly to the Electronic Pressure Control (EPC) inlet on the GC.

6.7 EST Centurion Auto sampler and EST ENCON purge and trap with external sparge unit and Supelco Vocarb 3000 thermal trap. The heated transfer line is connected directly to the Electronic Pressure Control (EPC) inlet on the GC.

6.8 Encon Purge and Trap (6).

6.9 Top Loading Balance capable of weighing to 0.1g.

6.10 EPA Protocol B cleaned 40mL VOA vials with Teflon Septa.

6.11 Hamilton gas tight micro syringes – 1.0, 10-, 25-, 50-, 100-, 250-, 1000µL.

6.12 Wheaton target vial crimper and de-capper.

6.13 National Scientific 11mm Teflon lined aluminum caps.

6.14 National Scientific 2mL amber target vials.

6.15 Class A volumetric flasks with stoppers – 10-, 50-, 100-mL.

6.16 Disposable Pasteur pipettes.

6.17 Branson Sonicator 3510.

## 7.0 Reagents

7.1 ASTM type II DI water.

7.2 Methanol, $CH_3OH$ – Purge and Trap quality or equivalent, demonstrated to be free of analytes. Store apart from other solvents. Record reagent in Omega Chemical Inventory. Methanol expires 1 year after opening.

7.3 Stock Standards: NOTE: Two different vendors numbers are maintained. One for preparing the calibration standards and the second for preparing Calibration Check Standards (CCV), Laboratory Control Samples (LCS) and Matrix Spikes (MS)/Matrix Spike Duplicates (MSD). Store with minimal headspace and protect from light at -10°C or less in Freezer 01 located in the VOA Lab. Prior to initial use, the analyst should review the Certificate of Analysis for statement of conformance, traceability of the standard, and uncertainty of certified values. All certificate are maintained in the volatiles laboratory. Stock Standards are to be recorded in OMEGA Spike/Standard Inventory Unopened standards should be replaced as recommended by the manufacturer or sooner if standard degradation is apparent. Opened Stock Standards expire 6 months after opening. Table 1 lists the standards currently in use for this method.

7.4 Intermediate Standard Solutions - Using Stock standards prepare solution in methanol containing the compounds of interest, either singly or mixed together. Store with minimal headspace and protect from light at -10°C or less in Freezer 01 in the VOA Lab. Standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. Replace after one week. Calibration standard preparation procedures are listed in Section 8, Table 2.

7.5 All Stock and Intermediate Standards are to be recorded in OMEGA Spike/Standard Inventory. The analyst will include the source, part number, lot number, description, and initial volume of all standards and solvents used to make the standard. Each standard will be given a unique identification number. This number begins with the department abbreviation followed by a six-digit date and a letter (e.g. VOA122100A, VOA122100B, etc…). Affix a label to each stock standard vial. Write the identification number, standard description, and expiration date on the label.

7.6 Surrogate and internal standards - The surrogates are Toluene-$d_8$, 4-Bromofluorobenzene, and Dibromofluoromethane. The internal standards are Chlorobenzene-$d_5$, 1,4 - Dichlorobenzene-$d_4$, Pentafluorobenzene, and 1,4-Difluorobenzene. A 50 µg/mL surrogate/internal standard solution should be prepared as described in Section 8. Each sample undergoing GC/MS analysis must be spiked with the surrogate/internal standard stock solution prior to analysis. The Centurion will automatically deliver 5 µL of the 50 µg/mL intermediate IS/SS resulting in a 50 µg/L spike.

7.7 Helium - Ultra pure - Cryogenic Gases

7.8 40mL vials containing sodium bisulfate - Reagent Grade

7.9 40Ml vials containing hydrochloric acid (1:1 v/v)

**Table 1**
**Stock Standard Solutions**

| Source | Part # | Description |
|---|---|---|
| Absolute Standards | 33003 | 2000 µg/ml Method 8260B 78 Analyte Volatiles Mixtu |
| Absolute Standards | 30058 | 2000 µg/ml Method 8260B 6 Analyte VOC Gas Mixtu |
| Restek | 30462 | 2000 µg/ml Freon 113 |
| Absolute Standards | 70074 | 1000 µg/ml 2-Chloroethyl vinyl ether |
| Absolute Standards | 70214 | 1000 µg/ml 2-Methylnaphthalene |
| Absolute Standards | 70944 | 1000 µg/ml 1,2,3-Trimethylbenzene |
| Absolute Standards | 92746 | Various Concentrations Oxygenates |
| Absolute Standards | 70409 | 1000 µg/ml 1,3.5- Trichlorobenzene |
| Absolute Standards | 71627 | 1000 µg/ml Methylcyclohexane |
| Absolute Standards | 71023 | 1000 µg/ml Cyclohexane |
| Absolute Standards | 71031 | 1000 µg/ml Methyl Acetate |
| Ultra Scientific | DWM-544 | 2000 µg/ml Method 8260B 6 Analyte VOC Gas Mixtu |
| Ultra Scientific | DWM-589N-1 | 2000 µg/ml Method 8260B 54 Analyte Volatiles Mixtu |
| Ultra Scientific | DWM-592-1 | 2000 µg/ml Method 524.2 24 Analyte Volatiles Mixtur |
| Ultra Scientific | EPA-1016 | 5000 µg/ml 2-Chloroethyl vinyl ether |
| Restek | 30619 | 2000 µg/ml Oxygenates |
| Ultra Scientific | CUS-3598 | 1000 µg/ml 2-Methynaphtalene |
| AccuStandard | MREF1410X | 2000 µg/ml Freon 113 |
| Ultra Scientific | STM-341N-1 | 2000 µg/ml 4 Component Internal Standard |

| | | |
|---|---|---|
| Ultra Scientific | STM-330N-1 | 2000 µg/ml 3 Component Surrogate Standard |

| 1000 mg/ml Acrolein Stock Solution | | |
|---|---|---|
| **Volume (mL** | **Part #** | **Part Description** |
| 6 | RCC-15( | 97.2% Acrolein – Ultra Scientific |
| 5000 | 232-1 | Purge and Trap Grade Methanol |

| 1000 mg/ml 1,2,3-Trimethylbenzene Stock Solution | | |
|---|---|---|
| **Volume (mL** | **Part #** | **Part Description** |
| 6.2 | T73202-5m | 90% 1,2,3-Trimethylbenzene |
| 5000 | 232-1 | Purge and Trap Grade Methanol |

| 2000 mg/ml 1,3,5-Trichlorobenzene Stock Solution | | |
|---|---|---|
| **Amount** | **Part #** | **Part Description** |
| 0.02g | T54607-5( | 99% 1,3,5-Trichlorobenzene |
| 10mL | 232-1 | Purge and Trap Grade Methanol |

| 1000 mg/ml 3 Additional Analytes | | |
|---|---|---|
| **Volume (mL)** | **Part #** | **Part Description** |
| 13 | 442531 | Cyclohexane, neat 99.9% pure |
| 11 | FLSA-016 | Ethanoic Acid Methyl Ester, neat 99.9% pure |
| 13 | 66294 | Methylcyclohexane, 99.5% pure |
| 10mL | 232-1 | Purge and Trap Grade Methanol |

| 1000 mg/ml Vinyl Acetate | | |
|---|---|---|
| **Volume (mL** | **Part #** | **Part Description** |
| 11 | A16247 | 99% Vinyl Acetate, pure |
| 10000 | 232-1 | Purge and Trap Grade Methanol |

| 50 mg/mL VOA Internal Standard and Surrogate Intermediate f Centurion | | |
|---|---|---|
| **Volume (mL** | **Part #** | **Part Description** |
| 250 | STM-341N | 2000 µg/mL 4 Analyte Internal Standard Mix |
| 250 | STM-330N | 2000 µg/mL 3 Analyte Surrogate Standard Mix |
| 950 | 232-1 | Purge-&-Trap Grade Methanol |
| 10000 to | | |

## 8.0 Preparation of Standards and Calibration Procedure

8.1 Instrument tune check – 50 ng of BFB is injected into the GC/MS and evaluated against the criteria specified in Method 8260. These parameters are incorporated into the data system and appear on the tune report.

8.1.1 The BFB tune check must be performed prior to analyzing samples and every 12 hours of continuous instrument run time. The resultant mass spectra for the BFB must meet the criteria given below before sample analysis begins.

| m/z | Required Intensity (relative abundance) |
|---|---|
| 50 | 15 to 40% of m/z 95 |
| 75 | 30 to 60% of m/z 95 |
| 95 Base peak | 100% relative abundance |
| 95 | 5 to 9% of m/z 95 |
| 173 | Less than 2% of m/z 174 |
| 174 | Greater than 50% of m/z 95 |
| 175 | 5 to 9% of m/z 174 |
| 176 | Greater than 95% but less than 101% of m/z 174 |
| 177 | 5 to 9% of m/z 176 |

8.1.2 Preparation of BFB solution.

| Preparation of 50 mg/ml BFB Stock Solution | | |
|---|---|---|
| **Volume (mL)** | **Part #** | **Part Description** |
| 125 | STS-110N | 2000 µg/mL 4-Bromofluorobenzene Solution |
| 4875 | 232-1 | Purge and Trap Grade Methanol |
| 5000 total | | |

8.1.3 For aqueous and methanol preserved soil samples the working 12 hour solution is prepared by adding 10 ul of the of the 50 ug/ml BFB stock (Section 8.1.2) to a final volume of 50 ml DI water. When analyzing low level soil samples the BFB solution is prepared by adding 1 ul of the stock to a final volume of 5 ml DI water.

8.2 Initial and continuing calibration intermediate standards are prepared from the stock standards (Section 7, Table 1) and neat materials for Acrolein, 1,2,3-Trimethylbenzene, 1,3,5-Trichlorobenzene, 1000µg/mL 3 additional compounds, and Vinyl Acetate according to the tables below and labeled with a 7 day expiration date from the date of preparation

| 50 mg/ml VOA Initial Calibration Intermediate Standard | | |
|---|---|---|
| **Volume (mL)** | **Part #** | **Part Description** |
| 40 | STM330N1 | 2000 µg/ml Surrogates |
| 80 | Various | 1000 µg/ml Acrolein |
| 40 | 70474 | 2000 µg/ml Freon 113 |
| 80 | 70944 | 1000 µg/ml 1,2,3-Trimethylbenzene |
| 40 | 92746 | Various Concentration Oxygenates |
| 40 | 33003 | 2000 µg/ml Method 8260B 78 Analyte Volatile Mixture |
| 40 | 30058 | 2000 µg/ml Method 8260B 6 Analyte VOC Ga Mixture |
| 80 | 70074 | 1000 µg/ml 2-Chloroethyl vinyl ether |
| 80 | 70409 | 1000 µg/ml 1,3,5-Trichlorobenzene |

| | | |
|---|---|---|
| 80 | 70214 | 1000 µg/ml 2-Methylnaphthalene |
| 80 | 71627 | 1000 µg/ml Methylcyclohexane |
| 80 | 71023 | 1000 µg/ml Cyclohexane |
| 80 | 71031 | 1000 µg/ml Methyl Acetate |
| 80 | Various | 1000 µg/ml Vinyl Acetate |
| 680 | 232-1 | Purge-&-Trap Grade Methanol |
| 1600 total | | |

**50 mg/ml VOA Initial/Continuing Calibration Verification Intermediate Standard**

| Volume (mL | Part # | Part Description |
|---|---|---|
| 40 | DWM-589N | 2000 µg/ml Method 524.2 54 Analyte Volatiles M |
| 40 | DWM-544-1 | 2000 µg/ml Method 524.2 6 Analyte Gas Mixture |
| 40 | DWM-592-1 | 2000 µg/ml Method 524.2 24 Analyte Volatiles M |
| 16 | EPA-1016 | 5000 µg/ml 2-Chloroethyl vinyl ether |
| 40 | CUS5037 | 2000 µg/ml Freon 113 |
| 80 | CUS3598 | 1000 µg/ml 2-Methynaphtalene |
| 80 | Various | 1000 µg/ml 1,2,3-Trimethylbenzene |
| 40 | OGAD001 | Various Concentration Oxygenates |
| 40 | Various | 2000 µg/ml 1,3,5-Trichlorobenzene |
| 80 | Various | 1000 µg/ml Acrolein |
| 80 | Various | 1000 µg/ml Vinyl Acetate |
| 80 | Various | 1000 µg/ml 3 Additional Analytes |
| 940 | 232-1 | Purge-&-Trap Grade Methanol |
| 1600 total | | |

8.2.1 Working initial calibration standards are prepared according to the table below. These standards are prepared fresh for each use. In some cases the lowest standard or the highest standard might not be used to construct the calibration curve (e.g. The 0.3ug/L standard is used to calibrate benzene only) A minimum of 5 continuous calibration standards is required for initial calibration. The lowest calibration standard must be equal to or less than the laboratory reporting limit for that compound. Refer to Appendix B for routine quantification ranges.

**Centurion Calibration Standards (Water Method/Methanol Soils*)**

| Level (ng/mL) | Conc. of Intermed Std. | µL of Intermediate Added | Final Vol. (mL) |
|---|---|---|---|
| 0.6 | 50 µg/mL | 0.6 | 50 |
| 1.0 | 50 µg/mL | 1.0 | 50 |
| 5.0 | 50 µg/mL | 5.0 | 50 |
| 10 | 50 µg/mL | 10 | 50 |
| 25 | 50 µg/mL | 25 | 50 |
| 50 | 50 µg/mL | 50 | 50 |
| 100 | 50 µg/mL | 100 | 50 |
| 200 | 50 µg/mL | 200 | 50 |

**Centurion Calibration Standards (Low level soil Method)**

| Level (ng/mL) | Conc. of Intermed Std. | µL of Intermediate Added | Final Vol. (mL) |
|---|---|---|---|
| 1.0 | 50 µg/mL | 0.1 | 5 |
| 5.0 | 50 µg/mL | 0.5 | 5 |
| 10 | 50 µg/mL | 1.0 | 5 |
| 25 | 50 µg/mL | 2.5 | 5 |
| 50 | 50 µg/mL | 5.0 | 5 |
| 100 | 50 µg/mL | 10 | 5 |
| 200 | 50 µg/mL | 20 | 5 |

*Calibration standards for quantifying methanol preserved soils samples will contain 1 ml of purge and trap grade methanol (Section 7.2) per 50 ml of standard to simulate sample conditions.

8.2.2 Working continuing calibration standards are prepared by adding 50 ul of the of the 50 ug/ml intermediate standard to a final volume of 50 ml DI water. Calibration standards for quantifying methanol preserved soils samples will contain 1 ml of purge and trap grade methanol (Section 7.2) per 50 ml of standard to simulate sample conditions. When analyzing low-level soil samples the CCV solution is prepared by adding 5 ul of the intermediate to a final volume of 5 ml DI water. This standard is prepared for a single use and re-prepared as needed.

8.3 A minimum of 5 continuous calibration standards is required for initial calibration. The lowest calibration standard must be equal to or less than the laboratory reporting limit for that compound. The initial calibration must meet the criteria below.

8.3.1 The %RSD of the response factor for each compound must be <20% or the linear regression correlation coefficient must be >0.99 for successful calibration. If more than 10% of the compounds exceed 20% or do not meet the minimum correlation coefficient the initial calibration is not considered acceptable. The system must be evaluated for leaks or active sites (Refer also to Section 13.2 for guidelines in isolating potential problems) and a new initial calibration performed. Decisions and evaluation of compounds will rely on the experience or the analyst.

8.3.2 For compounds that exceed 20% RSD the linear regression function of the data system can be used for analyte quantification. For proper use of the linear regression function, the correlation coefficient must be greater than 0.99 with at least 5 standards used in the calibration. The force through zero option may be used based on the response of the curve relative to the intercept (intercept not significantly different than zero) or with evaluation of the impact on results at the lower end of the calibration curve. Quantification of results at or slightly above the lowest standard may be more accurate when using the force through zero option of the data system. Since the data system does not include zero in the calculation of the regression equation and merely pivots the line through zero, this procedure is consistent with

the guidelines in Method 8000C.

8.3.3 If the %RSD of an analyte is >20% and the linear regression correlation is <0.99 a non-linear model can be used for calibration/quantification. This applies only to situations where the analysts has experience with a compound that does not respond according to a linear model over a sufficiently wide working range or when other approaches have not met the acceptance criteria. When using quadratic regression for the calibration model there must be at least 3 statistical degrees of freedom. Therefore, a minimum of 6 standards must be included in the calibration. The minimum cc must be >0.99. Analyst experience specific to the analyte in question is critical in selecting this option. Non-linear calibration cannot be used to compensate for detector saturation or to avoid proper instrument maintenance. In addition quadratic fitting cannot be used for calibration of more than 10% of the target compounds.

8.3.4 When linear regression is used for calibration the lowest calibration standard must be evaluated by quantifying the standard against the established calibration curve. The low standard is re-calculated using the established calibration curve - the standard does not have to be re-analyzed. The resulting calculated concentration must be within 30% of the standard concentration. If the concentration exceeds 30% the result is compared to the LCS control limits. If the concentration falls within the control limits the calibration is considered acceptable. If the result does not meet either of the criteria above the reporting limit for the compound must be modified to level that yields acceptable quantification for that level or results at or within 30% of the lowest calibration standard must be reported as estimated.

8.3.5 All reported compounds must have an acceptable calibration evaluation using one of the options above.

8.3.6 The response factors for the average RRF and the lowest calibration standard are compared to the minimum RRF in the table in Appendix B. In addition each calibration standard may be compared to the minimum RRF to ensure compounds are responding as expected. If the minimum response factor for the average or low standard is not met the system must be assessed to determine the cause for the decrease in sensitivity for the affected compounds and corrected prior to sample analysis.

8.3.7 For identification of a compound all of the spectral ions evaluated for each compound must have a signal to noise ratio of at least 3:1 at the lowest calibration standard. This is based on visual estimation by the analyst during data review. Compounds that contain spectral evaluation ions where the signal to noise ratio is less than 3:1 will require the reporting limit to be set at a concentration where all ions can be adequately identified. The signal to noise ratio for the primary quantification ions should be at least 5:1 and preferably 10:1.

8.3.8 The RRT of each target analyte in each calibration standard should agree within +/- 0.06 RRT units.

8.4 GC/MS calibration verification – Initial calibration verification (ICV) is performed immediately after calibration by analysis of the second source standard. Continuing calibration verification (CCV)is performed at the beginning of each 12-hour analytical shift. The second source standard is used for both the ICC and CCV

8.4.1 The BFB tune check must be performed prior to analyzing samples and every 12 hours of continuous instrument run time (See 8.1).

8.4.2 The initial calibration curve (Sec. 8.2) for each compound of interest should be verified immediately after initial calibration and once every 12 hours prior to sample analysis. The results from the calibration verification (Sec. 8.2.2) analysis must meet the following criteria.

8.4.2.1 Each compound must meet the minimum RRF in the table in Appendix B before reporting sample results. If the minimum RRF is not achieved corrective action is required prior to reporting the affected compounds in samples. Individual compounds that do not meet the minimum RRF must be re-analyzed with acceptable RRF results. Compounds meeting the minimum RRF can be reported. In cases where several compounds fail to meet the minimum RRF criteria the analyst in conjunction with the Laboratory Director or QA Director will determine the suitability of reporting any data.

8.4.2.2 The percent difference for compounds calibrated using average response factors or percent drift for other calibration methods must be <20% for each target compound.

8.4.2.2.1 If more that 20% of the target compounds exceed the 20% criteria corrective action must be taken prior to sample analyses. In cases of less than 20% unacceptable results the compounds that exceed 20% D or drift can be reported under the following guidelines.

8.4.2.2.1.1 Non-detect compounds may be reported without qualification if the calibration verification result exhibits elevated non-compliant results and adequate sensitivity for the compound.

8.4.2.2.1.2 If the calibration verification result is low or the compound is detected in the sample analyte data is qualified as estimated.

8.4.2.2.2 For or samples requiring compliance with DoD QSM criteria all target compounds must meet the 20% criteria. In instances where an analyte(s) exceeds 20% and sample re-analysis cannot be performed the compound(s) is noted in the case narrative and sample results are qualified.

8.4.3 The retention times of the internal standards in the calibration verification standard must be within 10 seconds of the retention time of the internal standards in the mid-point standard for the associated initial calibration.

8.4.4 The responses of the internal standards in the calibration verification standard must be with 50% - 100% of the mid-point standard for associated initial calibration.

8.4.5 A method blank or calibration blank must be analyzed and demonstrate the analytical system is free of contamination that would impact sample results. Non-target compounds that do not interfere with target compounds or target compound results less than the LOD may be ignored.

8.4.6 An ending CCV must be analyzed at the end of the analytical sequence. Results for all target compounds must be within 50% D or drift. The evaluation criteria in Sec. 8.4.2.2 are applied to this CCV.

## 9.0 Sample Preparation

9.1 Allow samples to warm to ambient temperature prior to analyzing.

## 10.0 Diagram/Table

10.1 Reserved

## 11.0 Analytical Procedure

11.1 Recommended purge and trap and GC/MS conditions. Individual settings for each instrument configuration are maintained in the instrument methods and may vary from the table parameters listed below.

| Parameter | Encon |
|---|---|
| Purge gas | He |
| Purge time (min) | 11 |
| Purge temperature ($^{o}$C) | Ambient |
| Dry purge time ($^{o}$C) | 1 |
| Desorb temperature ($^{o}$C) | 260 |
| Desorb time (min) | 2 |
| Bake temperature ($^{o}$C) | 270 |
| Bake time (min) | 8 |
| Transfer line temperature ($^{o}$C) | 130 |
| Valve temperature ($^{o}$C) | 130 |
| Cycle timer (min) | NA |

| HP GC Parameters | |
|---|---|
| | With Encon |
| Injector temperature (°C) | 150 |
| Detector temperature (°C) | 280 |
| Carrier gas (He) flow rate (mL/min) | 1.0 |
| Velocity (cm/sec) | 35.9 |
| Split flow (mL/min) | 20 |
| Split ratio | 20:1 |
| Initial oven temperature (°C) | 40 for 2 min |
| Temperature program | 13°C/min to 220°C, hold for 1.5 min. |
| Run time (min) | 17 |
| Oven equlibrium time (min) | 0.5 |

| HP Quadrapole MS Parameters | |
|---|---|
| Start time (min) | Varies |
| Low mass | 35 |
| High mass | 260 |
| Threshold | 200 |
| Sampling | 3 |
| Scans/sec | 2.01 |
| EM voltage | 200+ relative |

11.2 Sample Preparation

11.2.1 Centurion unpreserved soil sample: Verify and record the calibration of the VOA laboratory top loading balance in the balance log. Transfer 5.0 g of sample to a 40 ml VOA vial. Record the sample weight. Add approximately 10 ml de-ionized water. **DO NOT** add the IS/SS stock standard. The Centurion unit will dispense 5 µL of the 50 µg/ml IS/SS stock automatically. Seal the vial. **Note**: this is not a dilution when compared to the initial calibration.

11.2.2 Centurion methanol preserved soil sample: Weigh the vial and record the weight of the sample collected (weigh to 0.1 g). Methanol preserved soils are generally collected in standard 40 ml pre-cleaned glass screw-cap VOA vials with Teflon lined silicone septa. Verify the 10gsample/10mL methanol ratio in the Methanol Preserved Sample Logbook. Add additional methanol by injecting with a syringe through the septa if the sample weight exceeds 10 gm and is less than 20 gm. (REJECT SAMPLE IF SAMPLE WEIGHT EXCEEDS 20 gm). Flag the sample if the weight is less than 9 gm as <10% Methanol:Soil Ratio. Sonicate for 20 minutes. After sonication, allow sample sediment to settle. Using a 1000 µL syringe, transfer a 1mL aliquot sample to a 50 ml volumetric flask. Bring to volume with de-ionized water. Invert the volumetric 2-3 times, then transfer sample to a 40mL VOA vial. Rinse the syringe 3 times with fresh methanol before transferring the next sample. **Note**: this is a 50 times dilution when compared to the initial calibration curve.

11.2.3 Centurion low-level soil sample: Weigh the vial and record the weight of the sample collected. Make sure any paper labels are properly affixed to the vial. Hanging labels can interfere with gripper arm's ability to transfer vials to different positions. Place the unopened vial in the Centurion and set up instrument in the soil mode.

11.2.4 Centurion water sample: Allow water samples to equilibrate to room temperature. No other preparatory steps are necessary. Post analysis, the analyst is to check and record in the Aqueous Preservation Logbook, sample pH to ensure proper sample preservation. Flag the sample if the pH >2.

11.3 Run sequence set up using Chemstation software. Methods are set up within the system according to the manufacturers' instructions and applicable method reference.

11.3.1 From the Top View, select **Sequence/Edit Sample Log Table**. Each line in the table contains information for the analysis of one sample.

11.3.2 Click on a blank line in the table. Then click the arrow under the box labeled Type and select the type of sample to be run.

11.3.3 Use the tab key or mouse to move to the Vial box and enter the vial number.

11.3.4 Move to Method and enter the name of the method to be used for the current sample (For a list of methods, type ? in this field).

11.3.5 Supply the Data File name, Sample Name, and any Miscellaneous Information. Sample name will contain the laboratory sample ID and must correspond exactly with the LIMS designation. The miscellaneous information will contain the LIMS sample type (SAMP, MBLK, LCS, CCV, MS, etc) and the test code.

11.3.6 Use the **Repeat, Cut, Copy,** and **Paste** buttons as appropriate to add sample to the table. **Repeat** copies the highlighted line, increments the vial number, and places the new line immediately after the highlighted one. **Copy** copies the highlighted line without change. Use **Paste** to position that line where you wish. When finished, click **OK**.

11.3.7 To download the sequence to the GC/MS, select **Sequence/Run** from the Top View. Enter the date of analysis for Sequence Comment (e.g. 01/17/01). Enter the analyst's name for Operator Name. Use the analysis date for Data File Directory (e.g. D:\DATA\011701\). When ready click **Run Sequence**.

11.4 Centurion auto sampler setup.

11.4.1 Use the Centurion software to program the auto sampler. For more instruction on how to utilize the program, refer to the Centurion Operation Manual, Chapter 3.

11.5 Compound identification and quantification

11.5.1 Compound identification is based on relative retention time (RRT) and characteristic mass spectrum.

11.5.2 Initial identification is a compound that elutes with +/- 0.06 RRT units of the RRT of the standard compound. The 0.06 criteria is programmed into the data system method.

11.5.3 The mass spectrum of compounds within the RRT range is compared to the spectrum of the standard compound. Relative intensities of the characteristic ions should be within 30% of the expected relative intensities for the reference spectrum.

11.5.4 Co-eluting structural isomers that cannot be resolved by retention time and that have similar mass spectra are reported as the sum of the isomers (i.e. m,p-xylenes).

11.5.5 Analyst experience in evaluating mass spectra and identifying compounds in the presence of interfering components is important in final compound identification.

11.5.6 Identified compounds are quantified from the average response factor of the initial calibration or other calibration model employed when required.

11.5.7 Compounds exhibiting concentrations above the upper calibration level are diluted into the calibration range. If insufficient sample is available for dilution (i.e. both water sample vials already used) the concentration is flagged as estimated (E).

11.5.8 Compound concentrations that are below the laboratory reporting limit or lowest calibration point but positively identified above the MDL are flagged as estimated (J).

11.6 Manual integration guidelines and procedures

11.6.1 Situation may arise whereby the quantification provided by the data system is inappropriate. This can occur due to co-elution, baseline noise or matrix interference.

11.6.2 When manual integration of a compound is necessary the following guidelines must be followed.

11.6.2.1 Manual quantification is performed by integrating the area of the quant ion for the compound.

11.6.2.2 The integration will only include the area attributable to the compound of interest.

11.6.2.3 The area integrated shall not include baseline background noise.

11.6.2.4 The area integrated shall not extend beyond the point where the sides of the peak intersect with the baseline.

11.6.2.5 Manual integration must not be used solely to meet quality control criteria.

11.6.2.6 Manual integration must not be used as a substitute for corrective action on the GC/MS system.

11.6.3 Instances of manual integration are flagged with a "m" by the data system. Cases of manual integrations require review and approval by the Laboratory Manager or QA Director and are documented in the corresponding instrument Excel file or in the LIMS analytical sequence Linked Files.

## 12.0 Details of Calibration and Calculations

12.1 Response Factor: $Rf = (Ax * Cis)/(Ais * Cx)$

Where: Ax = Area of the characteristic ion for the compound being measured.
Ais = Area of the characteristic ion for the specific internal standard.
Cis = Amount of the specific internal standard (ng).
Cx = Concentration amount of the compound being measured (ng).

12.2 Concentration: $$(ug/L \text{ or } ug/kg) = \frac{(Ax)(Is)}{(Ais)(Rf)(Vo)} * Df$$

Where: Ax = Area of characteristic ion for compound being measured.
Is = Amount of internal standard injected (ng).
Ais = Area of characteristic ion for the internal standard.
R.F = Response factor for compound being measured.
Df = Dilution factor (where applicable)
Vo = Sample volume in gm or ml.

12.3 Percent Relative Standard Deviation: $$\%RSD = \frac{SD}{X} * 100$$

Where: RSD = Relative Standard Deviation.
X = Mean of the 3-5 initial R.F for a compound.
SD = Standard Deviation of average R.F for a compound.

12.4 Percent Drift: $$\% \text{ Drift} = \frac{Ce - Ca}{Ce} * 100$$

Where: Ce = Expected concentration.
Ca = Actual concentration.

12.5 Percent difference: $\% D = \frac{RF - Avg.\ RF}{Avg.\ RF} * 100$

Where: RF = Relative response factor.
Avg. RF = Average RRF from the ICAL.

12.6 Linear Regression: $y = ax + b$

Where: y = Instrument response (peak area)
a = Slope of the line
x = Concentration of the calibration standard
b = The intercept

12.7 Quadratic Regression: $y = ax^2 + bx + c$

## 13.0 Quality Assurance/Quality Control (QA/QC) Requirements

13.1 Tune Check – 50 ng of BFB is injected into the GC/MS and evaluated against the criteria specified in Method 8260. These parameters are incorporated into the data system and appear on the tune report.

13.1.1 The BFB tune check must be performed prior to analyzing samples and every 12 hours of continuous instrument run time. Tune parameters must be within established limits.

13.1.2 Corrective Action – Repeat tune check. If problem persists re-tune the instrument using either manual or auto-tune procedures. If this fails to correct the problem clean the source.

13.2 Following successful tuning the ICV/CCV sample must be analyzed and must pass the method criteria (Section 8.4). This sample must be analyzed every 12 hours of continuous instrument run time and at the end of each analytical sequence.

13.2.1 Corrective Action – Repeat ICV/CCV sample. If acceptable results are not obtained, check the standard for degradation, assess the system for leaks, ensure that the injection port and column inlet are free from contamination and that active sites within the system are not causing the problem. Repeat the initial calibration procedure once the problem has been identified and corrected.

13.2.2 Check to be sure that there are no errors in integration of internal standards and target compounds. Examine chromatograms for interfering peaks and integrated peak areas. If errors are found, recalculate the data accordingly.

13.2.3 Make sure certified solutions and calibration standards are not expired. Expired solutions and standards may exhibit analyte degradation. Replace all expired standards and remake all calibration standards. Recalibrate the instrument.

13.2.4 Check the purge flow. Chloromethane is the most likely compound to be lost if the purge flow is too fast. Bromoform is one of the compounds most likely to be purged very poorly if the purge flow is too slow. The purge flow should be 40 mL/min. Adjust flow accordingly and recalibrate.

13.2.5 Cold spots and active sites may adversely affect response. Tetrachloroethene and 1,1-dichloroethane are degraded by contaminated transfer lines. Check all heated zones. Bake the trap for 20 minutes to remove any contamination. If response does not improve, the analyst may wish purge methanol at 70 $^{O}$C for 20 minutes to try to remove contamination. Replacement of trap, transfer line, and nickel tubing may be necessary. The instrument must be recalibrated after performing any of these steps.

13.2.6 High variability may indicate a system leak or reactive sites on the column. Leaks are noted if base line levels are high and atmospheric masses are predominant in the tune (18, 28,32, and 44). Check connections for leaks. A column that has developed active sites may need to be replaced. Typical column life expectancy is 2 years. The instrument must be recalibrated after performing these checks.

13.3 The CCV is evaluated for all target analytes in the batch. Percent D or drift for each should be within 80 – 120 % (+/-20%) beginning and 50 – 150% (+/-50%) ending. All compounds must meet the minimum RRF criteria.

13.3.1 Corrective Action – Repeat CCV and steps above (section 13.1 & 13.2) if necessary bake the trap and check for sources of contamination. All samples associated with an unacceptable CCV must be re-analyzed for the affected compounds. The analytical sequence must be re-analyzed in cases where more than 20% of the compounds do not meet the acceptance criteria.

13.3.2 Corrective Action – Immediately analyze two consecutive CCVs (within one hour of the last instrument injection). If both CCV samples meet the acceptance criteria associated samples may be reported – re-analysis is not required. If either CCV does not meet the criteria corrective actions and sample re-analysis are required.

13.4 For each 12 hour or less analytical event a Method Blank is analyzed. This is prepared for water samples by filling a 40 ml vial with deionized water containing HCl preservative, for soils 10 g (methanol preserved) or 5 g (low level) of clean sand is added to a 40 ml VOA vial containing 10 ml of methanol or 5 ml of sodium bisulfite and process as a soil sample. Surrogates and internal standards are added to each method blank.

13.4.1 Acceptance Criteria: Result less than one half the reporting limit for all target analytes

13.4.2 Corrective Action: Clean system, bake the trap and check for sources of contamination.

13.5 For each batch of samples a Laboratory Control Sample (LCS) is prepared by adding 10 ul of CCV standard to 50 ml DI water in a volumetric flask and then transferring to a 40ml vial. The concentration of the LSC is 10 ug/L. Methanol soil LCS samples are prepared by spiking 100 ul of the CCV standard to 10 g of clean sand in a 40 ml VOA vial and adding 10 ml of methanol. The LCS is then sonicated of 20 min and analyzed as a soil sample. For low-level soil analysis 1 ul of the CCV solution is added to 5 g of clean sand in a 40 ml VOA vial and adding 5 ml sodium bisulfite.

13.5.1 Acceptance Criteria: 70 – 130 % recovery, or statistically calculated or according to project (i.e. QSM) guidelines. Current LCS control limits are set to values cited in the DoD QSM version 5.0.

13.5.2 Corrective Action: Repeat LCS, re-prepare CCV solution and repeat LSC and repeat calibration procedure if necessary. See also Sec. 14.6.

13.6 For each matrix batch of 20 or less samples a MS/MSD is included that contains all of the components of interest. Control limits for each compound are statistically derived and the batch MS/MSD is evaluated against these limits. Spikes for water samples are prepared by adding 8.0 ul of the CCV solution to an undiluted sample, or by performing an appropriate dilution in a 50mL volumetric flask and introducing 10.0 ul of CCV standard to the sample. Methanol preserved soil sample spikes are prepared in the same manner as water samples with the exception that 1000 ul of methanol is added to each and 10uL of the CCV solution is added. Low level soil sample spikes are prepared by adding 1 ul of the CCV standard and to a 5 g sample.

13.6.1 Acceptance Criteria: Within statistically derived control limits (default limits - 70 130%). MSD RDP - 25%. For some projects and all projects submitted under the DoD QSM the MS/MSD recovery limits are set to the LCS control limits. The current LIMS test codes specify MS/MSD recovery limits set to the LCS control limits

13.6.2 Corrective Action –Evaluate the sample spiked for matrix interference and flag the data as necessary.

13.7 Surrogate Control Limits

13.7.1 For each sample matrix the first 30 surrogate recoveries are used to establish control limits based on the Mean recovery +/- 3 times the standard deviation. This procedure is performed annually.

13.7.2 For samples (including QC samples) in which the surrogate recovery falls outside the established control limits, the following is required.

13.7.2.1 Check calculations for errors

13.7.2.2 Check instrument performance

13.7.2.3 Re-prep and re-analyze the samples if the above show no problems or

flag the data if sample matrix interference is present.

13.8 Internal standard responses.

13.8.1 The response for each internal standard must be within –50% to +100% of the mid-level calibration standard.

13.8.2 Failure to achieve the above criteria requires inspection of system operation and any necessary corrective actions. Any sample associated with the CCV must be re-analyzed.

13.9 The retention times of the internal standards in the calibration verification standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the that in the mid-point standard level of the most recent initial calibration sequence, then the chromatographic system must be inspected for malfunctions and corrections must be made, as required. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

13.10 Initial demonstrations of proficiency are performed by all analysts for all instruments and methods. IDP records are kept on file in the laboratory and referenced in analyst training files. Demonstrations of proficiency are re-performed in instances of new staff or major changes in methodology or equipment.

13.11 Storage Blanks.

13.11.1 Several VOC vials (3-5) are filled with DI water, capped with no headspace and stored in the VOC sample refrigerator.

13.11.2 At a frequency of every 14 days or less one of the storage blanks is removed and included in a sample analytical sequence. Analysis will proceed by the same procedures used for sample analysis and storage blank data will be imported into the associated LIMS analytical sequence.

13.11.3 Storage blanks exhibiting results less than the LOD for all target compounds and absence of non-target compounds are considered acceptable.

13.11.4 Presence of methylene chloride or other known laboratory artifacts consistent with levels found in method blanks and samples will be considered as laboratory contamination unrelated to storage conditions. Narration of the occurrence will follow standard laboratory practice for these occurrences.

13.11.5 If target or non-target compounds are detected in a storage blank proceed as follows:

13.11.5.1 Assess the associated method blank, QC samples and field samples in the analytical sequence for presence and levels of the compounds identified in the storage blank.

13.11.5.2 Evaluate previous analytical events for presence and levels of the compounds detected in the storage blanks.

13.11.5.3 Evaluate sample chromatography data for anomalies associated with the compounds detected (presence of compounds in otherwise clean samples or inconsistencies with expected sample data).

13.11.5.4 Immediately analyze a second storage blank and assess for presence and levels of contaminating compounds.

13.11.5.5 Investigate the storage refrigerator for broken, leaking or loosely capped samples and attempt to identify the source of contamination.

13.11.5.6 Clean the storage refrigerator when necessary and analyze storage blanks daily until the blank results are acceptable.

13.11.5.7 Qualify and narrate data for all impacted samples with regard to the nature and extent of the contamination.

## 14.0 Data Reporting Requirements

14.1 Sample concentrations are read directly from the DATA SYSTEM.

14.2 Aqueous sample are routinely reported as ug/L (mg/L for TCLP extracts and when requested).

14.3 Soil samples are reported as ug/kg on a dry weight basis where:

ug/kg = concentration x 100/percent solids.

Methanol extracted (preserved) soils:
ug/kg = ug/L x DF x MD x MC

DF = (ml DI water/amt. MeOH added) x ratio of MeOH to soil
MD = (ml of methanol in sample + (sample wt. g x percent moisture))/10
MC = 100/%solids

DF is the dilution factor determined by both the factor for the amount of methanol added to an amount of DI water (typically 1 ml methanol in 50 ml DI water) and the amount of methanol divided by the weight in g of soil sampled (target 10 g of soil to 10 ml of methanol = 1).

MD is the dilution of the water miscible solvent by the water content of the sample for samples with greater than 10% moisture.

MC is the dry weight conversion.

14.4 Raw instrument results, laboratory sample identification, date and time of analysis, analyte type and test code are entered directly into the Omega LIMS by direct importing of the data system files into Omega. All calculations to derive final result (including dry weight conversions) are performed automatically by the LIMS. Sample weights, preparation information and percent moisture results are entered into the appropriate section of the LIMS prior to instrument data and are automatically factored into the final results.

14.5 After calculation of the imported sequence verify that there are no QC flags or qualifier requiring additional actions. If present investigate and repeat or re-analyze as needed.

14.6 Due to the large number of compounds that may be included in some target compound lists all analytes may not meet all of the QC criteria specified in Sections 8 and 13. In addition there is generally limited sample volume for multiple repeat analyses. The following guidelines are used for data reporting.

14.6.1 Compound data cannot be reported without an acceptable initial calibration using average response factors, linear regression or quadratic (non-linear least squares regression).

14.6.2 Compounds that do meet all of the ICV/CCV criteria are evaluated according to the protocol in Sec. 8. In addition assess whether the affected compound is a critical project analyte. Compounds that are not critical to the objectives of the project may be reported with adequate qualification, narration and data qualifiers.

14.6.3 Compounds in the LCS that exceed control limits may be reported with adequate qualification, narration and data qualifiers. LCS data is deemed acceptable if no more than 4 compounds exceed control limits. Elevated LCS data for non-detected analytes may be reported with adequate qualifiers and narration.

## 15.0 Preventative Maintenance and Routine Cleaning

15.1 To ensure the system is kept free of any contamination, steps must be taken to keep the system clean.

15.2 All routine maintenance and trouble shooting to the Analytical System will be recorded in the Maintenance Log for that instrument in Omega.

15.3 Source cleaning will be performed whenever the tune criteria for BFB cannot be met or when instrument performance warrants source cleaning

15.4 Check helium purge flows as needed (typically during troubleshooting activities). Flow should be within 39-41 ml/min.

15.5 Gradually declining response factors for all parameters is evidence for trap replacement. Follow the manufacturer's instructions on how to disassemble the trap. The new trap should be conditioned at 280°C for 1 hour. A typical Supelco Vocarb 3000 trap will last from 3 to 6 months, depending on frequency of use and sample VOC concentration.

15.6 If trap replacement does not result in improved response factors, the soil and or water probe assemblies should be disassembled and cleaned. Follow the manufacturer's instructions on how to disassemble the soil and water probe. Sonicate the probe in methanol and dry with a high velocity air purge. Probes should be cleaned routinely every 6 months.

15.7 If trap replacement and probe cleanings do not improve repose factors, all nickel heated transfer lines should be replaced

15.8 Depending on the frequency of direct injections, every 2 to 3 months replace the injector septum and liner. Bring all heated zones (oven, detector, and injector) to ambient temperature and vent the MS via the software prior to all GC maintenance.

15.9 Approximately every two years the column will need replacement due to residual oxidation of the polysiloxane stationary phase. If poor chromatographic resolution is noted before this time, cut off 1 meter of the column at the injection port and reinstall. Bring all heated zones (oven, detector, and injector) to ambient temperature and vent the MS via the software prior to all GC maintenance.

15.10 Leaks are very common in the MSD interface and should be checked with the procedure given by Hewlett Packard in the hardware reference manual. Leaks are noted if base line levels are high and atmospheric masses are predominant in the tune (18, 28,32, and 44).

15.11 Common MSD maintenance tasks are listed in Table 2. Performing these tasks on a regular basis can reduce operating problems and prolong system life.

15.12 Replace fore line pump fluid every six months.

15.13 Replace diffusion pump fluid annually.

## 16.0 Waste Management and Pollution Prevention

16.1 Pollution Prevention

16.1.1 Reagents are purchased and quantities used to reflect anticipated usage and minimize disposal of expired or unused chemicals.

16.1.2 Chemicals are handled in a manner that minimizes the potential for release or spill of the material.

16.2 Waste Management

16.2.1 Organic materials are treated as hazardous waste and placed in the appropriate waste drum for disposal.

16.2.2 Soil samples are composited in a drum designated for disposal.

16.2.3 Disposal of materials is addressed in the laboratory QAP (Section 5.6).

## 17.0 References

17.1 EPA Test Methods for Evaluating Solid Waste. Laboratory Manual Physical/Chemical Methods, Method 8260C, Revision 2, 1996.

17.2 EPA Test Methods for Evaluating Solid Waste. Laboratory Manual Physical/Chemical Methods, Method 5030B, Revision 2, 1996.

17.3 EPA Test Methods for Evaluating Solid Waste. Laboratory Manual Physical/Chemical Methods, Method 5035, Revision 0, 1996.

17.4 40 CFR Part 136 – App. A Meth.624: Purgeables. App. B: Appendix B to Part 136-Definition and Procedure for the Determination of the Method Detection Limit-Revision 1.11.

17.5 RTI Laboratories, Inc. Quality Assurance Plan.

17.6 RTI Laboratories, Inc. Chemical Hygiene Plan.

17.7 RTI Laboratories, Inc. SOP: SRC001-A, Sample Receipt and Custody SOP.

17.8 RTI Laboratories, Inc. Employee Handbook.

17.9 Centurion Operation Manual

## 18.0 Revisions

18.1 Section 13.11 Storage Blanks added to SOP.

## Appendix A - Instructions for the Analysis Using Selective Ion Monitoring (SIM)

The MDEQ RRD Operational Memorandum No. 2 and other programs require reporting limits for specific analytes at levels below those routinely assayed. For example the MDEQ analytical target detection limit for 1,2-dibromoethane (EDB) has been established at 0.05ug/L for waters and 20ug/Kg for soils. Single/selected ion monitoring (SIM) will increase instrument sensitivity in order meet the required reporting limit for EDB and other compounds. Prior to running a SIM analysis, it may be required to run a full scan using low-level methods (e.g. as done for the EPA Contract Laboratory Program).

Operation in the SIM mode requires preparation of standards at lower concentration levels than specified in Sec. 8.

Working initial calibration standards are prepared from the stock standard referenced in Sec. 8 according to the table below. These standards are prepared fresh for each use.

**Centurion Calibration Standards (Water Method/Methanol Soils*)**

| Level (ug/L) | Conc. Of Stock Std | UL of Stock Added | Final Vol (mL) |
|---|---|---|---|
| 0.05 | 50 | 0.1 | 100 |
| 0.4 | 50 | 0.2 | 100 |
| 1 | 50 | 1 | 50 |
| 5 | 50 | 5 | 50 |
| 10 | 50 | 10 | 50 |
| 25 | 50 | 25 | 50 |

*Calibration standards for quantifying methanol preserved soils samples will contain 1 ml of purge and trap grade methanol (Section 7.2) per 50 ml of standard to simulate sample conditions.

Working continuing calibration standards are prepared by adding 10 □l of the of the 50 □g/ml intermediate standard (Sec. 8) to a final volume of 50 ml DI water. This standard is prepared for a single use and re-prepared as needed.

Internal standardization is employed in this technique and are the same as that used for a full scan (Section 8.5). The %RSD of the response factors for compounds should be <15 % or evaluated according to the guidelines in Section 8.

Continuing calibration standards must have %D values <20%. SPCC/CCC compounds are not utilized in this technique.

The instrument is set up to operate in the SIM mode according to the manufacturer's instructions. The applicable ions for the compound of interest are selected by choosing the three ions with the highest abundance from the spectra of the scan mode analysis. The following table represents the settings for the analysis of EDB.

5972 Quadropole MS Parameters SIM

| | |
|---|---|
| Ion 1 m/z | 107 |
| Ion 2 m/z | 109 |
| Ion 3 m/z | 188 |
| Dwell | 50 |
| Resolution | Low |

## Appendix B - 8260 Analytes, Internal Standards, Surrogates

| | Target Ion | Q1 | Q2 | Expected Retention Time (min) | Min. RRF | Routine Quant Range Aqueous | Routine Quant Range Soils |
|---|---|---|---|---|---|---|---|
| Pentafluorobenzene (Internal Std) | 168 | 169 | | 4.57 | | | |
| Dichlorodifluoromethane | 85 | 87 | 100 | 1.27 | 0.100 | 1-200 | 1-200 |
| Chloromethane | 50 | 52 | 49 | 1.42 | 0.100 | 1-200 | 1-200 |
| Vinyl chloride | 62 | 64 | 47 | 1.5 | 0.100 | 1-200 | 0.6-200 |
| Bromomethane | 94 | 96 | 79 | 1.74 | 0.100 | 1-100 | 15200 |
| Chloroethane | 64 | 66 | 49 | 1.83 | 0.100 | 5-200 | 1-200 |
| Trichlorofluoromethane | 101 | 103 | 66 | 2.01 | 0.100 | 1-200 | 1-200 |
| Diethyl ether | 59 | 74 | 45 | 2.28 | | 5-200 | 5-200 |
| 1,1-Dichloroethene | 61 | 63 | 96 | 2.48 | 0.100 | 1-200 | 1-200 |
| Freon113 | 101 | 151 | 85 | 2.45 | 0.100 | 1-200 | 1-200 |
| Acrolein | 56 | 55 | 53 | 2.45 | | 10-200 | 10-200 |
| Acetone | 43 | 58 | 39 | 2.59 | 0.100 | 10-200 | 10-200 |
| Iodomethane | 142 | 127 | 141 | 2.62 | | 5-200 | 5-200 |
| Carbon disulfide | 76 | 78 | 64 | 2.65 | 0.100 | 5-200 | 5-200 |
| Allyl chloride | 41 | 76 | | 2.81 | 0.100 | 1-200 | 1-200 |
| Methylene Chloride | 49 | 84 | 86 | 2.95 | 0.100 | 5-200 | 5-200 |
| 2-Methyl-2-propanol | 59 | 41 | 43 | 3.08 | | 1-200 | 1-200 |
| Acrylonitrile | 53 | 52 | 50 | 3.23 | | 5-200 | 1-200 |
| trans-1,2-Dichloroethene | 61 | 96 | 98 | 3.14 | 0.100 | 1-200 | 1-200 |
| tert-Butyl Methyl Ether | 73 | 57 | 41 | 3.14 | 0.100 | 5-200 | 5-200 |
| Methyl Acetate | 43 | 74 | 59 | 3.30 | 0.100 | 1-200 | 1-200 |
| Isopropyl ether | 45 | 63 | 87 | 3.57 | | 5-200 | 5-200 |
| 1,1-Dichloroethane | 63 | 65 | 83 | 3.56 | 0.200 | 1-200 | 1-200 |
| tert-Butyl Ethyl Ether | 59 | 87 | 57 | 3.89 | | 5-200 | 5-200 |
| Vinyl Acetate | 43 | 86 | 42 | 3.57 | | 1-200 | 1-200 |
| 2-butanone | 43 | 72 | 57 | 4.13 | 0.100 | 5-200 | 5-200 |
| cis-1,2-Dichloroethene | 61 | 96 | 63 | 4.08 | 0.100 | 1-200 | 1-200 |
| 2,2-Dichloropropane | 77 | 79 | 97 | 4.05 | | 1-200 | 1-200 |
| Vinyl Acetate | 43 | 86 | 42 | 4.09 | | 1-200 | 1-200 |
| Propionitrile | 54 | 53 | | 4.24 | | 5-200 | 10-200 |
| Methyl acrylate | 55 | 85 | 58 | 4.18 | | 1-200 | 1-200 |
| Methacrylonitrile | 41 | 67 | 52 | 4.34 | | 1-200 | 1-200 |
| Bromochloromethane | 130 | 128 | 93 | 4.3 | | 1-200 | 1-200 |
| Tetrahydrofuran | 42 | 72 | 71 | 4.32 | | 10-200 | 10-200 |
| Chloroform | 83 | 85 | 87 | 4.37 | 0.200 | 1-200 | 1-200 |
| Dibromofluoromethane (Surrogate) | 113 | 111 | | 4.52 | | 1-50 | 1-50 |
| 1,1,1-Trichloroethane | 97 | 101 | 61 | 4.49 | 0.100 | 1-200 | 1-200 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 1-Chlorobutane | 56 | 41 | 43 | 4.6 | | 1-200 | 1-200 |
| 1,1-Dichloropropene | 75 | 110 | 39 | 4.64 | | 1-200 | 1-200 |
| Carbon tetrachloride | 119 | 117 | 121 | 4.6 | 0.100 | 1-200 | 1-200 |
| tert-Amyl Methyl Ether | 73 | 87 | 55 | 4.92 | | 1-200 | 1-200 |
| 1,2-Dichloroethane | 62 | 64 | 63 | 4.91 | 0.100 | 1-200 | 1-200 |
| Benzene | 78 | 52 | 77 | 4.82 | 0.500 | 1-200 | 0.3-200 |
| Cyclohexane | 56 | 84 | 41 | 5.01 | 0.100 | 1-200 | 1-200 |
| | | | | | | | |
| 1,4-Difluorobenzene (Internal Std) | 114 | 88 | 63 | 5.22 | | | |
| Trichloroethene | 130 | 132 | 97 | 5.42 | 0.200 | 1-200 | 1-200 |
| 1,2-Dichloropropane | 63 | 65 | 76 | 5.68 | 0.100 | 1-200 | 1-200 |
| Methyl methacrylate | 41 | 69 | 100 | 5.78 | | 1-200 | 1-200 |
| Dibromomethane | 174 | 172 | 176 | 5.79 | | 1-200 | 1-200 |
| Bromodichloromethane | 83 | 85 | 129 | 5.93 | 0.200 | 1-200 | 1-200 |
| Methyl Cyclohexane | 83 | 55 | 98 | 6.11 | 0.100 | 1-200 | 1-200 |
| 2-Nitropropane | 41 | 39 | | 6.23 | | 5-200 | 1-200 |
| 2-Chloroethyl vinyl ether | 63 | 65 | 107 | 6.24 | | 10-200 | 1-200 |
| cis-1,3-Dichloropropene | 75 | 77 | 110 | 6.37 | 0.200 | 1-200 | 1-200 |
| 4-Methyl-2-pentanone | 43 | 58 | 100 | 6.53 | 0.100 | 10-200 | 10-200 |
| Toluene-d8 (Surrogate) | 98 | 100 | 99 | 6.58 | | 1-50 | 1-50 |
| Toluene | 91 | 92 | 65 | 6.65 | 0.400 | 1-200 | 1-200 |
| trans-1,3-Dichloropropene | 75 | 110 | 77 | 6.94 | 0.100 | 1-200 | 1-200 |
| Ethyl methacrylate | 69 | 41 | 99 | 6.99 | | 1-200 | 1-200 |
| 1,1,2-Trichloroethane | 97 | 83 | 99 | 7.12 | 0.100 | 1-200 | 1-200 |
| 1,3-Dichloropropane | 76 | 78 | 41 | 7.29 | | 1-200 | 1-200 |
| Tetrachloroethene | 166 | 164 | 168 | 7.16 | 0.200 | 1-200 | 1-200 |
| 2-Hexanone | 43 | 58 | 57 | 7.36 | 0.100 | 10-200 | 10-200 |
| Chlorodibromomethane | 129 | 127 | 131 | 7.48 | 0.100 | 1-200 | 1-200 |
| 1,2-Dibromoethane | 107 | 109 | 188 | 7.6 | 0.100 | 1-200 | 1-200 |
| | | | | | | | |
| Chlorobenzene-d5 (Internal Std) | 117 | 82 | 52 | 8.06 | | | |
| Chlorobenzene | 112 | 114 | 77 | 8.08 | 0.500 | 1-200 | 1-200 |
| 1,1,1,2-Tetrachloroethane | 131 | 133 | | 8.18 | | 1-200 | 1-200 |
| Ethylbenzene | 91 | 106 | 51 | 8.17 | 0.100 | 1-200 | 1-200 |
| m,p-xylene | 91 | 106 | 51 | 8.3 | 0.100 | 1-200 | 1-200 |
| OXYL | 91 | 106 | 51 | 8.72 | 0.300 | 1-200 | 1-200 |
| Styrene | 104 | 78 | 103 | 8.76 | 0.300 | 1-200 | 1-200 |
| Bromoform | 173 | 171 | 252 | 8.96 | 0.100 | 1-200 | 1-200 |
| Cumene | 105 | 120 | 77 | 9.11 | 0.100 | 1-200 | 1-200 |
| 4-Bromofluorobenzene (Surrogate) | 95 | 174 | 176 | 9.31 | | 1-50 | 1-200 |
| 1,1,2,2-Tetrachloroethane | 83 | 85 | 168 | 9.52 | 0.300 | 1-200 | 1-200 |
| TDCB | 53 | 88 | | 9.59 | | 1-200 | 1-200 |
| 1,2,3-Trichloropropane | 75 | 110 | 112 | 9.56 | | 1-200 | 1-200 |
| Bromobenzene | 77 | 156 | 158 | 9.46 | | 1-200 | 1-200 |
| n-Propylbenzene | 91 | 120 | 105 | 9.55 | | 1-200 | 1-200 |
| 2-Chlorotoluene | 91 | 126 | 128 | 9.66 | | 1-200 | 1-200 |
| 1,3,5-Trimethylbenzene | 105 | 120 | 91 | 9.76 | | 1-200 | 1-200 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 4-Chlorotoluene | 91 | 126 | 128 | 9.79 | | 1-200 | 1-200 |
| 4-Isopropyltoluene | 119 | 134 | | 10.51 | | 1-200 | 1-200 |
| tert-Butylbenzene | 119 | 91 | 134 | 10.1 | | 1-200 | 1-200 |
| 1,2,4-Trimethylbenzene | 105 | 120 | 91 | 10.17 | | 1-200 | 1-200 |
| sec-Butylbenzene | 105 | 134 | 91 | 10.34 | | 1-200 | 1-200 |
| 1,3-Dichlorobenzene | 146 | 148 | 111 | 10.49 | 0.600 | 1-200 | 1-200 |
| | | | | | | | |
| 1,4-Dichlorobenzene-d4 (Internal Std) | 152 | 115 | | 10.57 | | | |
| 1,4-Dichlorobenzene | 146 | 148 | 75 | 10.6 | 0.500 | 1-200 | 1-200 |
| 123TMB | 105 | 120 | 91 | 10.63 | | 1-200 | 1-200 |
| Benzyl Chloride | 91 | 126 | 65 | 10.63 | | 1-200 | |
| n-Butylbenzene | 91 | 92 | 134 | 10.97 | | 1-200 | 1-200 |
| 1,2-Dichlorobenzene | 146 | 148 | 75 | 11.01 | 0.400 | 1-200 | 1-200 |
| Hexachloroethane | 117 | 201 | 166 | 11.23 | | 1-200 | 1-200 |
| DBCP | 75 | 155 | 157 | 11.9 | 0.050 | 5-200 | 5-200 |
| 1,2,4-Trichlorobenzene | 180 | 182 | 109 | 12.8 | 0.200 | 1-200 | 1-200 |
| 1,2,3-Trichlorobenzene | 180 | 182 | 145 | 13.36 | | 1-200 | 1-200 |
| Hexachlorobutadiene | 225 | 223 | 227 | 12.95 | | 5-200 | 5-200 |
| Naphthalene | 128 | 129 | 102 | 13.08 | | 5-200 | 5-200 |
| 2MN | 142 | 141 | 115 | 14.36 | | 5-200 | 5-200 |

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# STANDARD OPERATING PROCEDURE

# ANALYSIS OF PESTICIDES AND POLYCHLORINATED BIPHENYLS (PCBs)

| | |
|---|---|
| **Analyte:** | **Pesticides and PCBs** |
| **SOP #:** | **8081_8082_072312_R9** |
| **Method Reference:** | **EPA SW846/8081B/8082A**<br>**40 CFR Part 136 App. A Meth. 608** |
| **Issue Date:** | **December 7, 2005** |
| **Revision No.:** | **9** |
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| **Reviewed Date:** | **July 23, 2012** |

**Reviewed and Approved by: July 23, 2012**

Director, Quality Management: Charles O'Bryan

Supervisor, Environmental Services: James Wuokila

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**ANALYSIS OF PESTICIDES AND PCBs**

**SOP#: 8081_8082_072312_R9**

**TABLE OF CONTENTS**

## 1.0 Scope and Application:

1.1 Introduction

RTI Laboratories, Inc, has prepared this document to detail the Standard Operating Procedure (SOP) for the analysis of PCB and pesticide compounds by gas chromatography/ECD. This SOP applies to analytical procedures according to EPA Methods 8081A, 8082 & 608. Modifications to these methods are specified throughout this SOP.

A detailed description of the instrumentation, calibration, run parameters and quality control procedures where applicable is included in this SOP. For definition of terms not specifically defined in this document refer to RTI QAP Section 16.

1.2 Summary of Method

1.2.1 A measured volume of sample is extracted according to the applicable preparation method (SOPs – 3510, 3545, 3550). The prepared extract is separated by gas chromatography using split dual capillary columns. Analytes are then measured with dual electron capture detectors. If the extract requires further cleanup to eliminate interferences, this method provides for a florisil column cleanup procedure, an acid cleanup procedure and an elemental sulfur removal procedure (3610B, 3611A, 3620B, 3630C, 3650B, 3660B).

## 2.0 Safety Precautions

2.1 Compounds applicable to this method are known or suspected carcinogens. Standard preparation is conducted in fume hoods designated for organic use.

2.2 Extraction solvents are flammable and/or toxic and must be handled with caution. All extractions are performed in a manner designed to minimize exposure to these chemicals using appropriate hoods and personal protection.

## 3.0 Sample Requirements and Sample Handling Procedures

3.1 Samples are received in accordance with RTI Laboratories, Inc Standard Operating Procedure for sample login. Appropriate U. S. Environmental Protection Agency (EPA) sample handling procedures and sample preservation recommendations are followed. Water samples are collected in 1L pre-cleaned amber bottles with Teflon lined screw caps. Soil samples are received in pre-cleaned wide mouth jars with Teflon lined lids ranging from 2 oz. to 9 oz. in size.

3.1.1 The holding time for water samples is 7 days from collection to extraction and 40 days from extraction to analysis except for PCBs – 1 yr. from collection to extraction and 1 yr. from extraction to analysis.

3.1.2 The holding time for solid samples for pesticides is 14 days from collection to extraction and 40 days from extraction to analysis. The holding time for PCBs is 1 year from collection to extraction and 1 year from extraction to analysis.

3.1.3 All samples are stored at $4^{o}$ C.

3.1.4 All extracts are stored refrigerated at $<6^{o}$ C, extract holding time is 40 days.

3.1.5 For other sample handling protocols, see sample receiving SOP.

## 4.0 MDL, Linear Range, Accuracy and Precision

4.1 The method detection limit (MDL) is statistically defined at the 99% confidence level according to 40 CFR Part 136 App. B. Seven replicates containing all of the analytes of interest at a concentration level of 1-5 times the estimated D.L. are analyzed and the standard deviation is calculated. The Student's T Value for the 7 replicates (3.143) is multiplied by the standard deviation of the analyte to calculate the MDL. MDLs are updated annually (or as needed) and are kept on file in the Laboratory. MDLs and reporting limits are incorporated into the applicable test code in the Omega LIMS.

4.2 The LOD (limit of detection) is determined by spiking reagent water at 1-4 times the MDL and prepared using the same procedure as samples. Analytes must be present at levels 3 times or greater than the blank response (greater than 3 times the signal to noise ratio). The concentration used is the LOD for that analyte. LOD determinations must be performed quarterly.

4.3 The LOQ (limit of quantification) is determined by spiking reagent water at the reporting limit (RL/CRQL) and prepared in the same manner as samples. Analyte recovery must be within 30% of the expected concentration. The concentration used and successfully recovered is the LOQ for that analyte. LOQ determinations must be performed quarterly.

4.4 Initially accuracy and precision at the LOQ is determined by spiking 4 aliquots of reagent water at the reporting limit (RL/CRQL) and prepared using the same procedure used for samples. The average recovery must be within 30% of the expected value and the %RSD must be less than 15%.

4.5 LOD/LOQ determinations that do not meet the specifications above require repeat analysis, adjustment to the spiking levels and/or reporting limits, repeating the MDL determination at adjusted concentrations if required and repeat LOD/LOQ determinations.

4.6 The accuracy and precision for this method are determined by analyzing four aliquots from a Laboratory Control Sample containing the element(s) of interest at the mid-level of the calculated range (diluted if above this range). Percent recovery, standard deviation, and the relative standard deviation are calculated for each analyte and documents are kept on file in the laboratory.

4.7 The range used by RTI Laboratories, Inc is 5 to 80ng/ml for most of the pesticides and 50 to 2000ng/ml for the PCB's. The linear range for some of compounds may be established at a lower upper limit, see Section 8 for details. If an analyte concentration is above the linear range, a dilution of that sample that results in a concentration in the linear range will be analyzed.

## 5.0 Interferences

5.1 Interferences can arise from carry over due to high sample concentrations or contamination from reagents and/or glassware. Blanks are analyzed to ensure system cleanliness in both instances. All glassware must be scrupulously cleaned before use. Glassware-cleaning procedures are specified in the QAP. Glassware should be heated in a muffle furnace at 400 degrees C for 15 to 30 minutes, or solvent rinsed prior to use. High purity solvents are used for preparation and analysis.

5.2 Samples containing high concentrations of non-target analytes or extremely high levels of select target analytes can result in elevated detection limits for other target analytes. Dilution of the extract may improve the resolution and quantification of some analytes but will generally cause an elevation in the RDL.

5.3 Interferences caused by phthalate esters result in non-target interfering peaks on the chromatogram. Common flexible plastics contain varying amounts of these phthalates. Take caution not to use soft plastic funnels, separatory funnels, bottles, pipettes or syringes in any of the preparation or sample cleanup steps.

5.4 Interferences caused by co-extracted non-target peaks such as oils, chlorinated solvents and other petroleum-based products can either mask or intensify the peaks from the PCB congeners. Many of these interfering compounds can be eliminated using sample cleanup techniques such as mercury cleanup, acid washing, florisil cleanup, silica gel cleanup or GPC cleanup.

5.5 Compounds that have the same retention time under the conditions employed can cause a positive interference. Analysis on a second dissimilar column is necessary when analytes of interest are detected.

5.6 MS/MSD recoveries often are affected by samples containing PCBs other than the spiked 1016/1260 Aroclors.

## 6.0 Apparatus and Materials

6.1 Glass Funnels

6.2 pH indicator paper

6.3 Graduated cylinders.

6.4 Glass beakers

6.5 Class A Microliter syringes, 50ul, 10 ul, 25ul, 1000µl, 500µl.

6.6 Volumetric glassware Class A, 1.0,2.0,5.0,10.0,25.0,50.0, and 100.0 ml volumes

6.7 Glass vials – 2ml with Teflon lined screw caps, 10ml with Teflon lined screw caps.

6.8 Pyrex glass wool

6.9 Pasteur pipettes

6.10 Analytical balance capable of weighing to 0.0001gm.

6.11 GC-ECD 1 Varian 3400 with dual ECD and dual columns. Equipped with a Varian 8100 auto sampler

6.12 GC-ECD 2. Varian 3400 with dual ECD and dual columns. Equipped with a Varian 8100 auto sampler

6.13 GC-ECD 3. Hewlett Packard 5890 GC with two electron capture detectors, HP 7673 auto sampler and HP Data System.

6.14 GC-ECD 4. Hewlett Packard 6890 GC with two electron capture detectors, HP auto sampler and HP Data System.

6.15 GC-ECD 5. Hewlett Packard 6890N GC with two electron capture detectors, HP auto sampler and HP Data System.

6.16 RTX CLP Pesticides I - 30m x 0.53 mm primary column (or equivalent)

6.17 RTX CLP Pesticides II - 30m x 0.53 mm – confirmatory column (or equivalent)

6.18 Carrier gas- He 99.999% purity with a flow near 5.0ml/min.

6.19 Make up gas- $N_2$ 99.999% purity with a flow near 60ml/min.

6.20 PC with Microsoft Windows, Varian Star Data System 5.3, EnviroQuant Chemstation G1701BA Version B 01.00 and Omega LIMS.

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## 7.0 Reagents

7.1 Anhydrous Sodium sulfate- purify by heating at 450C for 4 hours/dry in desiccator.

7.2 Methylene chloride – pesticide grade

7.3 Surrogate solution – refer to section 8.0

7.4 LCS/MS/MSD spike mix (PCB's) – refer to 3550, 3545 and 3510 SOPs

7.5 LCS/MS/MSD spike mix (Pesticides) – refer to 3550, 3545 and 3510 SOPs

7.6 Degradation check standard mix- refer to section 8.0

7.7 Acetone – pesticide grade.

7.8 Sulfuric acid – conc.

7.9 Reagent water, ASTM Type II

7.10 Hexane – pesticide grade.

7.11 Calibration standard mixes – refer to section 8.0.

7.12 All reagents and standards prepared must be labeled with a minimum:

7.12.1 Identity of the material
7.12.2 Concentration of the solution
7.12.3 Date prepared
7.12.4 Initials of analyst preparing the solution
7.12.5 Expiration date determined by:
Manufacturer expiration date for stock standards
Standards: 6 months or the date of the soonest expiring standard
Reagents: Vendor expiration date or 1 yr. not to exceed any vendor expiration date

## 8.0 Preparation of Standards and Calibration Procedure

8.1 A five to six point calibration curve is prepared by diluting stock standards as below.

8.1.1 Standards are stored in a refrigerator/freezer dedicated to standards. The manufacture's expiration date is to be followed for all unopened standards. All stock standard solutions must be replaced after one year or sooner if routine QC tests indicate a problem. All other standard solutions must be replaced after six months or sooner if routine QC indicates a problem.

8.1.2 Refer QAP Section 6 for general calibration procedures.

8.1.3 Stock Standard Mixes

8.1.3.1 PCB - Ultra EPA-1282 –Aroclor 1016, 1000ppm
8.1.3.2 PCB - Ultra EPA-1362 –Aroclor 1260, 1000ppm.
8.1.3.3 Ultra PPM 8082 - Aroclor 1016/1260, 1000ppm each.
8.1.3.4 Aroclor 1016, 1000ppm, Absolute Standards, 90123.
8.1.3.5 Aroclor 1221, 1000ppm, Absolute Standards, 79403
8.1.3.6 Aroclor 1232, 1000ppm, Absolute Standards, 79097
8.1.3.7 Aroclor 1242, 1000ppm Absolute Standards, 79098
8.1.3.8 Aroclor 1248, 1000ppm, Absolute Standards, 79099
8.1.3.9 Aroclor 1254, 1000ppm Absolute Standards, 79100
8.1.3.10 Aroclor 1260, 1000ppm, Absolute Standards, 90129
8.1.3.11 Aroclor 1262, 1000ppm, Absolute Standards, 79102
8.1.3.12 Aroclor 1268, 1000ppm Absolute Standards, 90166
8.1.3.13 Aroclor 1016, 1000ppm Ultra, EPA-1282
8.1.3.14 Aroclor 1221, 1000ppm Ultra, EPA-1292
8.1.3.15 Aroclor 1232, 1000ppm Ultra, EPA-1302
8.1.3.16 Aroclor 1242, 1000ppm Ultra, EPA-1312
8.1.3.17 Aroclor 1248, 1000ppm Ultra, EPA-1342
8.1.3.18 Aroclor 1254, 1000ppm Ultra, EPA-1352
8.1.3.19 Aroclor 1260, 1000ppm Ultra, EPA-1362
8.1.3.20 Aroclor 1262, 1000ppm Ultra, EPA-1372
8.1.3.21 Aroclor 1268, 1000ppm Ultra, EPA-1382
8.1.3.22 Pesticide – Ultra PPM 8008C - each pesticide, 1000ppm
8.1.3.23 Pesticide – AccuStandard Z-014C-R- each pesticide, 2000ppm
8.1.3.23.1 Alternate Second source Cerilliant ERS-013, 2000ppm
8.1.3.24 Toxaphene – Absolute - Toxaphene, 1000ppm
8.1.3.25 Toxaphene- Ultra-PP-271-Toxaphene, 100ppm.
8.1.3.25.1 Alternate Second source AccuStandard p-093s-h, 1000ppm
8.1.3.26 Chlordane- Absolute -Chlordane, 1000ppm
8.1.3.27 Chlordane-Ultra –PP-151 – Chlordane, 100ppm.
8.1.3.27.1 Alternate Second source AccuStandard p-017s-10x, 1000ppm
8.1.3.28 Surrogate- Ultra ISM-320-1 - TCMX/DCB each, 200ppm.
8.1.3.29 Degradation check mix- Supelco-4-8282- DDT/Endrin each, 500ppm.

8.1.2 Intermediate working standards:

8.1.2.1 Surrogate 20ppm std.- prepared by adding 0.1ml of Ultra ISM 320-1 (200ppm) to 900ul of pesticide grade Hexane.

8.1.2.2 PCB calibration std. 10ppm PCB/ 0.5ppm Surrogate- prepared by adding 100µl of Ultra PPM 8082 (1000ppm) and 25µl of Surrogate 200ppm std to a 10ml class A volumetric flask and dilute to 10ml with pest grade Hexane.

8.1.2.3 PCB ICCV/CCV std 10ppm- prepared by adding 100µl of PCB - Ultra EPA-1282 and 100µl of Ultra EPA-1362 and 25µl of Surrogate 200ppm std to a 10ml class A volumetric flask and dilute to 10ml with pest grade Hexane.

8.1.2.4 PCB ICV/CCV std 1.0ppm- prepared by adding 1000µl of PCB ICV/CCV std 10ppm to a 10ml class A volumetric flask and dilute to 10ml with pest grade Hexane.

8.1.2.5 Pesticides calibration std 10ppm– prepared by adding 250µl of Surrogate 200ppm std and 50µl of Ultra PPM 808C to a 5ml class A volumetric flask and dilute to 5ml with pesticide grade Hexane.

8.1.2.6 Pesticide ICV/CCV/Spike intermediate standard 10ppm- prepared by adding 50µl of AccuStandard Z-014C-R to a 10 ml class A volumetric flask and dilute to 5 ml with pest grade Hexane.

8.1.2.7 Pesticide ICV/CCV 40 ppb – Prepared by adding 40µl of 8.1.2.6 and 20µl of 8.1.2.1 to 10 ml final volume with hexane in a volumetric flask.

8.1.2.8 Toxaphene calibration standard 10ppm-prepared by adding 100µl of the Absolute standard to a 10ml class A volumetric flask and dilute to 10ml with pest grade Hexane.

8.1.2.9 Toxaphene ICV/CCV std 1.0 ppm- prepared by adding 100µl of the Ultra PP271 a 10ml class A volumetric flask and dilute to 10ml with pest grade Hexane. Add 20 µl of the 20-ppm surrogate (Sec. 8.1.2.1).

8.1.2.10 Chlordane calibration standard 1.0 ppm- prepared by adding 10 µl of the Absolute standard to a 10ml class A volumetric flask and dilute to 10ml with pest grade Hexane. Add 5 µl of the Ultra ISM 320-1 standard.

8.1.2.11 Chlordane ICV/CCV standard 0.5 ppm- - prepared by adding 50 µl of Ultra PP-151 standard to a 10ml class A volumetric flask and dilute to 10ml with pest grade Hexane. Add 20 µl of the 20 ppm surrogate (Sec. 8.1.2.1).

8.1.2.12 Pesticide 0.1 ppm calibration standard – Prepared by diluting 100µl of 8.1.2.5 to 10ml final volume with hexane in a volumetric flask.

8.1.2.13 Degradation check mix 5ppm- prepared by adding 10µl of Supelco-4-8282 to 990µl of pesticide grade hexane..

8.1.2.14 Expiration dates of the diluted standards are the same as the expiration dates of the stock standards

8.1.3 Calibration standards: PCB's and Toxaphene/chlordane - Six Calibration standards are prepared according to Table 3. Calibration standards: Pesticides mix calibration standards are prepared according to Table 3.

**Table 3**

| Calibration Standard | Source | Source Conc. | | Amount added | | Final volume | | Final Conc. | |
|---|---|---|---|---|---|---|---|---|---|
| C1 | Chlordane calibration std 1.0ppm | 10 | ng/µl | 1000 | µl | 1.0 | ml | 1000 | ng/ml |
| C2 | Chlordane calibration std 1.0ppm | 10 | ng/µl | 800 | µl | 1.0 | ml | 800 | ng/ml |
| C3 | Chlordane calibration std 1.0ppm | 10 | ng/µl | 600 | µl | 1.0 | ml | 600 | ng/ml |
| C4 | Chlordane calibration std 1.0ppm | 10 | ng/µl | 400 | µl | 1.0 | ml | 400 | ng/ml |
| C5 | Chlordane calibration std 1.0ppm | 10 | ng/µl | 200 | µl | 1.0 | ml | 200 | ng/ml |
| C6 | Chlordane calibration std 1.0ppm | 10 | ng/µl | 100 | µl | 1.0 | ml | 100 | ng/ml |
| ICV/CCV | Chlordane icv/ccv std 0.5ppm | | | | | | | | |
| | | | | | | | | | |
| C1 | Toxaphene calibration std 10ppm | 10 | ng/µl | 500 | µl | 1.0 | ml | 5000 | ng/ml |
| C2 | Toxaphene calibration std 10ppm | 10 | ng/µl | 200 | µl | 1.0 | ml | 2000 | ng/ml |
| C3 | Toxaphene calibration std 10ppm | 10 | ng/µl | 100 | µl | 1.0 | ml | 1000 | ng/ml |
| C4 | Toxaphene calibration std 10ppm | 10 | ng/µl | 50 | µl | 1.0 | ml | 500 | ng/ml |
| C5 | Toxaphene calibration std 10ppm | 10 | ng/µl | 20 | µl | 1.0 | ml | 200 | ng/ml |
| C6 | Toxaphene calibration std 10ppm | 10 | ng/µl | 10 | µl | 1.0 | ml | 100 | ng/ml |
| ICV/CCV | Toxaphene icv/ccv std 1.0 ppm | | | | | | | | |
| | | | | | | | | | |
| C1 | Pesticides calibration std 0.1ppm | 0.1 | ng/µl | 1000 | µl | 1.0 | ml | 100 | ng/ml |
| C2 | Pesticides calibration std 0.1ppm | 0.1 | ng/µl | 800 | µl | 1.0 | ml | 80 | ng/ml |
| C3 | Pesticides calibration std 0.1ppm | 0.1 | ng/µl | 600 | µl | 1.0 | ml | 60 | ng/ml |
| C4 | Pesticides calibration std 0.1ppm | 0.1 | ng/µl | 400 | µl | 1.0 | ml | 40 | ng/ml |
| C5 | Pesticides calibration std 0.1ppm | 0.1 | ng/µl | 200 | µl | 1.0 | ml | 20 | ng/ml |
| C6 | Pesticides calibration std 0.1ppm | 0.1 | ng/µl | 100 | µl | 1.0 | ml | 10 | ng/ml |
| C7 | Pesticides calibration std 0.1ppm | 0.1 | ng/µl | 50 | µl | 1.0 | ml | 5 | ng/ml |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| ICV/CCV | Pesticide icv/ccv std 40ppb + 20□ surrogate | | | | | | | | |
| C1 | PCB calibration std 10ppm | 10 | ng/µl | 400 | µl | 1.0 | ml | 4000 | ng/ml |
| C2 | PCB calibration std 10ppm | 10 | ng/µl | 200 | µl | 1.0 | ml | 2000 | ng/ml |
| C3 | PCB calibration std 10ppm | 10 | ng/µl | 100 | µl | 1.0 | ml | 1000 | ng/ml |
| C4 | PCB calibration std 10ppm | 10 | ng/µl | 50 | µl | 1.0 | ml | 500 | ng/ml |
| C5 | PCB calibration std 10ppm | 10 | ng/µl | 20 | µl | 1.0 | ml | 200 | ng/ml |
| C6 | PCB calibration std 10ppm | 10 | ng/µl | 10 | µl | 1.0 | ml | 100 | ng/ml |
| C7 | PCB calibration std 10ppm | 10 | ng/µl | 5 | µl | 1.0 | ml | 50 | ng/ml |
| ICV/CCV | PCB icv/ccv std 1.0ppm | 1.0 | ng/µl | 1000 | µl | 1.0 | ml | 1000 | ng/ml |

8.1.4 Degradation check standard 40 ppb: prepared by adding 12µl to 1.5ml final volume with pesticide grade hexane.

8.1.5 PCB analyses are calibrated using Aroclors 1016 and 1260 for initial and continuing calibration. At least five peaks from each Aroclor are calibrated using at least five levels preferably six. For Aroclors other than 1016 and 1260 identified in samples a one-point calibration for the individual Aroclor is performed. The level will correspond to the mid-point of the calibration range.

8.1.6 Five peaks are chosen for each Aroclor. The peaks chosen will be representative of the Aroclor and each of the 5 peaks will be at least 25% of the height of the largest Aroclor. At least one of the five peaks for the individual Aroclor should be unique to that Aroclor

8.2. Calibration Verification Standards (CCV) standards are prepared according to Table 3.

8.3. Initial calibration is performed by analyzing at least five calibration standards (the lowest calibration standard used for the curve must be at or below the RL).

8.3.1 The linear regression function of the data system will be used for analyte quantification provided the correlation coefficient is greater than 0.99.

8.3.2 Alternatively the average response factor (RF) can be used for quantification and/or verifying linear calibration. Acceptable use of linear calibration using average RF is determined if the RSD for all compounds is < 20%. For Method 608 the % RSD must by <10.

8.3.1. Initial calibration is performed at method start up and upon failure of a continuing calibration standard (CCV). The criteria noted in Sec. 8.3.1 and 8.3.2 must be met for both columns.

8.3.2. If the initial calibration curve fails the calibration criteria above, the following corrective action must take place, Repeat the calibration curve, if the curve still fails, replace the curve standards. Repeat the calibration curve, if the curve still fails, clean or replace the injection port liner, remove a portion of the inlet end of the column or troubleshoot the detector as necessary.

8.4 Continuing Calibration.

8.4.1 The degradation check standard and CCV are analyzed at the start of each batch and after every 10 field samples. An ending CCV must be analyzed at the end of each analytical run or 12-hour time period. All compounds must be within 15% of the expected concentration and the degradation compounds must exhibit breakdown of less than 15%. The CCV standards bracketing the samples must both be acceptable before

reporting the samples analyzed in between the two CCV standards. Acceptance criteria must be demonstrated on both columns.

8.4.2 If the degradation is greater than 15% then the following corrective action must be performed. Clean or replace the injection port liner, and remove the first 12-18 inches of the column. Repeat the degradation check, if the check still fails, replace the column.

8.4.3 If the CCV standard fails the 15% criteria then the following corrective action must be taken. Replace and reanalyze the CCV standard, if this still fails, generate a new initial calibration curve.

8.4.4 For quantifying PCB Aroclors the approach specified in Method 8082 is preferred (quantifying individual peaks instead of the entire Aroclor pattern). However, Method 608 requires quantification based on the total response for the Aroclor. Calibration is performed to satisfy both Method 608 and 8082 requirements.

## 9.0 Sample Preparation

9.1 Allow samples to warm to ambient temperature and proceed with extraction procedures as specified in SOP# 3510C, 3545 and 3550B.

9.2 All samples extracts are stored in a refrigerator/freezer dedicated to samples only.

9.3 Sample extract cleanup procedures

9.3.1 Allow the 2mL extracts to warm to ambient temperature.

9.3.2 For SW-8081 extracts (low level pesticides).

9.3.2.1 Place a a Phenomenex STRATA FLPR Florasil column onto a 10mL vial. Wet with 1-2mL of a 9:1 Hexane/Acetone.

9.3.2.2 Using a 1mL syringe, transfer 1mL of the hexane extract to the column.

9.3.2.3 Wash the column with 2mL aliquots of the 9:1 Hexane/Acetone. Repeat until approximately 10mL of wash has been collected.

9.3.2.4 Transfer the washed extract to a TurboVap concentrator tube and re-concentrate to 1mL.

9.3.4 PCBs

9.3.4.1 Add 5mL concentrated Sulfuric Acid to the 1 or 2mL hexane extract. Shake for 1 minute.

9.3.4.2 Let the sample rest for 5 minutes to allow the phases to completely separate. Using a Pasteur pipette, transfer the hexane layer to a 2mL auto sampler vial. Add approximately 0.05 - 0.10g of florasil and 0.25 - 0.50g of copper.

## 10.0 Diagram/Table

10.1 Reserved.

## 11.0 Analytical Procedure

11.1 Set GC conditions as follows:

11.1.1 Injector Temp. - 250 $^{o}$C
11.1.2 Detector Temp. - 300 $^{o}$C
11.1.3 Initial Oven Temp/Time - 150 $^{o}$C for 1 min
11.1.4 Rate 10$^{o}$/min to 280$^{o}$ C
11.1.5 Oven Temp/Time final - 280 $^{o}$C for 8 min (Total Time – 20 minutes)
11.1.5.1 Oven programs vary on instruments due to differing types of flow controls. ECD#1 (Method 2012gc1pcb - 20minute run time), ECD#2 (Method 2012gc2-20min - 20minute run time), ECD#3 (Method PESTPCB – 35minute runtime), ECD#4 (Method 2012ecd – 25minute runtime), ECD#5 (Method ECD5 20 minute runtime)
11.1.6 Auto sampler – inject 1 or 2 ul of sample extract/standards using solvent flush technique (Star method 2010gc1).

11.2 Activate current method file.

11.3 Activate Sample List File (File/New Sample List) and enter samples according to LIMS type LCS, MS, MSD, MBLK, CCV, CCB and SAMP with the corresponding batch or Omega sample ID. Enter initials of the analyst. Analytical date and time will be set by the computer data system.

11.3.1 The sample list is the run log and a typical run sequence should follow as below:

11.3.1.1 Primer (usually 5x highest calibration standard)
11.3.1.2 Reagent Blank
11.3.1.3 Degradation check standard (for pesticide analysis only)
11.3.1.4 Initial calibration curve when required.
11.3.1.5 Calibration Verification Standard
11.3.1.6 LCS (for each target list)
11.3.1.7 Method Blank
11.3.1.8 10 samples
11.3.1.9 Reagent Blank
11.3.1.10 Degradation check standard (optional)
11.3.1.11 CCV (must be analyzed once every 10 samples.)
11.3.1.12 Repeat 11.3.1.5 and 11.3.1.10 for the remainder of the samples including any additional QC samples (MS, MSD, LCS).

**NOTE:** Method blank, MS, MSD, LCS should be analyzed at or near the beginning of the sequence.

11.4 Load samples on the auto sampler tray in order with the run log above.

11.5 Begin sample list.

11.6 If the response of any compound or Aroclor exceeds the working range of the system, dilute/cleanup the extract and reanalyze.

11.7 Compound identification and quantification

11.7.1 For pesticides compound identification is based on the retention time (RT) of the eluting peak in comparison to calibration standard.

11.7.2 Initial identification is a compound that elutes within 0.05 min. of the RT of the standard compound. The 0.05 criteria is programmed into the data system method.

11.7.3 All compound identification must be confirmed by the results for the second column. The compound must be within the RT window on both compounds for positive identification

11.7.4 Co-eluting compounds must be resolved on one of the columns.

11.7.5 Aroclor identification is performed by overlaying standard Aroclor chromatographic response patterns on the sample chromatogram.

11.7.6 Analyst experience in evaluating chromatographic data and identifying compounds in the presence of interfering components is important in final compound identification.

11.7.7 Identified compounds are quantified from the linear regression curve generated by the data system during initial calibration.

11.7.8 Sample results are reported from the primary analytical column (CLP I, Sec. 6.13) unless the RPD result from values obtained on each column exceeds 40% in the absence of overlapping peaks causing an erroneously high result on one column. In these instances the higher result is reported and the disparity is note in the comments field in the LIMS analytical sequence table for inclusion on the report case narrative.

11.7.9 Compounds exhibiting concentrations above the upper calibration level are diluted into the calibration range. If insufficient sample is available for dilution (i.e. both water sample vials already used) the concentration is flagged as estimated (“E”).

11.7.10 Compound concentrations that are below the laboratory reporting limit or lowest calibration point but positively identified above the MDL are flagged as estimated (“J”).

11.8 Manual integration guidelines and procedures

11.8.1 Situation may arise whereby the quantification provided by the data system is inappropriate. This can occur due to co-elution, baseline noise or matrix interference.

11.8.2 When manual integration of a compound is necessary the following guidelines must be followed.

11.8.2.1 Manual quantification is performed by integrating the area of the peak for the compound.

11.8.2.2 The integration will only include the area attributable to the compound of interest.

11.8.2.3 The area integrated shall not include baseline background noise.

11.8.2.4 The area integrated shall not extend beyond the point where the sides of the peak intersect with the baseline.

11.8.2.5 Manual integration must not be used solely to meet quality control criteria.

11.8.2.6 Manual integration must not be used as a substitute for corrective action on the GC system.

11.8.3 Instances of manual integration are flagged with a "U or m" by the data system. Cases of manual integrations require review and approval by the Laboratory Manager or QA Director and are documented in the corresponding instrument Excel file or in the LIMS analytical sequence Linked Files.

## 12.0 Details of Calibration and Calculations

12.1 Analyze the degradation check standard before the calibration standards. Match the retention times of the peaks in the standards with the sample peaks. For PCB quantification using Method 608 quantify every identifiable peak unless interference with non-target peaks occurs. Add peak area of each identifiable peak and calculate as total response in sample versus total response in the standard. When using Method 8082 compare and quantify at least 5 PCB peaks and average the individual results. Record results in Omega as µg/ml in extract. Omega will combine prep data, dilutions and instrument results and perform final calculations including dry weight calculations for reporting soil results.

12.2 Response Factor:

Rf = Peak Area/Std. Conc.

12.3 Degradation check:

$$\%\ \text{breakdown of DDT} = \frac{\text{sum of degradation peak areas (DDD + DDE)}}{\text{sum of all peak areas (DDT + DDD + DDE)}} \times 100$$

$$\%\ \text{breakdown of Endrin} = \frac{\text{sum of degradation peak areas ( Aldehyde + Ketone)}}{\text{sum of all peak areas (Endrin + Aldehyde + Ketone)}} \times 100$$

12.4 % RSD:

Average Rf = (Rf1+Rf2+Rf3+Rf4+Rf5)/5

Std. Dev. = SQRT $[(\text{sum}x^2 - \text{sum}(x)^2/n)/(n-1)]$

%RSD = Std. Dev./Average Rf x 100

12.5 Percent Difference:

$$\% \text{ Diff} = \frac{C_e - C_f}{C_e} \times 100$$

Where: $C_e$ = Expected concentration
$C_f$ = Concentration found

12.6 Relative Percent Difference (RPD)

$$RPD = (| R1 - R2 | / ((R1 + R2)/2)) * 100$$

Where: R1 = First result
R2 = Second result

12.7 Linear Regression: $y = ax + b$

Where: y = Instrument response (peak area)
a = Slope of the line
x = Concentration of the calibration standard
b = The intercept

## 13.0 Quality Assurance/Quality Control (QA/QC) Requirements

13.1 Daily Setup of Blanks, Standards and Degradation check standard:

13.1.1 A continuing calibration verification standard (CCV) must be analyzed for all applicable analytes to assure the working curve is still valid. The % Difference or (% drift) must be less than 15%.

13.1.2 This value is calculated for each compound and can be no greater than 15% in order to continue. If the check standard is found to exceed 15% difference for any of the components then an additional check standard may be analyzed and compared to the curve as above. If this second check standard is still out of control, initial calibration must be performed and a new 5-point curve generated. If the second check standard is within the allowable 15% difference samples may be analyzed using the average Cf from the curve to quantify detected compounds. The daily continuing calibration verification standard must be run after every 10 samples.

13.1.3 A reagent/method blank must be run at the beginning of each day to guarantee the system is free of contamination. If any target compound or interfering non target compounds are found in the blank at levels greater than one half the LOQ (reporting limit), then the source of contamination must be identified and corrective action taken before sample analysis can proceed. Corrective actions include reanalysis of the method blank, analysis of reagent blanks, baking systems components (column, detector) and checks on sample preparation

procedure. Contamination which does not interfere with target compounds may be ignored.

13.1.4 An injection port degradation check sample must be run prior to analyzing pesticide samples. This is separate standard containing DDT and Endrin and involves checking for Endrin aldehyde/Endrin ketone and DDD/DDE as breakdown products. The breakdown products cannot exceed 15% of the total for DDT or Endrin.

13.2 LCS, Matrix Spike/Matrix Spike Duplicate

13.2.1 In each batch of samples a Laboratory Control Sample (LCS), matrix spike, and matrix spike duplicate (MSD) must be analyzed. For water samples, preparation of batch MS/MSD is dependent upon the availability of extra sample provided by the client. Rotation among client samples is required when amount of sample volume is available. In the absence of sufficient sample volume a LCS duplicate is prepared. Statistical control limits are calculated for the recoveries and duplicate percent differences to determine warning and control limits. These limits will be compared to the applicable project limits (i.e. QSM Tables) and the narrower of the limits will be used to establish control limits provide the data sets are reasonably comparable. In cases where the calculated control limits are significantly greater than the QSM (or other) limits corrective actions will be instituted to achieve control limits consistent with the requirements of the project. If a sample falls outside of these limits action will be taken to determine if the cause was due to matrix interference or method deficiencies including re-preparation of these QC samples when appropriate. In the absence of statistical limits due to the lack of sufficient data points (i.e. water MS/MSD due to lack of sufficient volumes) interim limits based on the four LCS samples from the IDMP will be used to evaluate the batch QC data.

13.2.1.1 Acceptance Criteria MS/MSD – within laboratory statistical limits. For QSM compliance these limits are set to the LCS control limits.

13.2.1.2 Acceptance Criteria RPD – within laboratory statistical limits.

13.2.1.3 Acceptance Criteria LCS – within laboratory statistical limits or project limits as described above.

13.3 Retention Time Windows

13.3.1 Retention time windows will be established and maintained for all components. For Aroclors, at least 3-5 characteristic peaks should be used to determine the RT window.

13.3.2 RT windows are determined by analyzing three control samples over a 72 hour time frame.

13.3.3 The average and standard deviation of the three determinations are calculated and the window is defined as the Mean (average) +/- 3 times the standard deviation.

13.3.4 The retention time windows are re-calculated whenever a new column is installed.

13.3.5 The GC data system does not allow for compound specific RT windows. The widest window (0.05 min.) is programmed into the applicable method and applied to all compounds.

13.4 Surrogate Control Limits

13.4.1 For each sample matrix the first 30 surrogate recoveries are used to establish control limits based on the Mean recovery +/- 3 times the standard deviation. These limits are updated annually or sooner if the control chart reveals a bias trend.

13.4.2 For samples and QC samples in which the surrogate recovery falls outside the established control limits, the following is required.

13.4.3 Check calculations for errors

13.4.4 Check instrument performance

13.4.5 Re-analyze extract- if acceptable than no other actions are required

13.4.6 Re-extract and re-analyze the samples if the above show no problems or flag the data as estimated concentration if sample cannot be re-analyzed or if matrix interferences are obvious and cannot be cleaned up using the methods defined in the appropriate cleanup SOP's.

## 14.0 Data Reporting Requirements

14.1 If any compound is detected at a level above the MDL it must be confirmed on a second column before reporting the data with the results agreeing within 40%. If the conformation is positive, report the higher of the two calculated values. If the difference exceeds 40% then the data is qualified. If a compound is found to co-elute with another compound on one column and not the conformation column, results are reported from the column that does not co-elute the compound of interest.

14.2 If any compound is found in a sample at a concentration greater than that of the highest standard the sample must be re-analyzed after dilution. No data shall be reported with concentrations greater than the highest calibration standard. The sample should be diluted until all compounds of interest are within the working range of the standard curve.

14.3 The instrument data files produced by this method include the laboratory sample id, the date and time of analysis, the analysis type and the analyst's initials.

14.4 Sample concentrations are reported in µg/ml from the Star data system.

14.5 Raw results are entered into Omega. Prep factors are automatically imported from sample prep logs. Dilutions are entered in the analytical sequence.

14.6 Sample results are reported as ug/L for water and ug/kg for soil as dry weight.

14.7 Raw instruments results are entered directly into the Omega LIMS system using excel spreadsheets, direct instrument interface (routinely used for this procedure) or manually. All calculations to derive final result (including dry weight conversions) are performed automatically by the LIMS. Sample preparation information and percent moisture results are entered into the appropriate section of the LIMS prior to instrument data and are automatically factored into the final results.

14.8 Confirm that there are no QC flags or qualifiers in this sequence. If present, investigate and repeat or reanalyze as necessary.

## 15.0 Preventative Maintenance and Routine Cleaning

15.1. Change septum weekly or as needed. (100 injections max.)

15.2. Check carrier gas and make up gas daily

15.3. Change carrier and make up gas traps every 6 months or sooner as needed.

15.4. Bake out column as needed at 270 $^{0}$C for 1 hour .

15.5. Clean ECD as needed thermally at 330-350$^{0}$C.

## 16.0 Waste Management and Pollution Prevention

16.1 Pollution Prevention

16.1.1 Reagents are purchased and quantities used to reflect anticipated usage and minimize disposal of expired or unused chemicals.

16.1.2 Chemicals are handled in a manner, which minimizes the potential for release or spill of the material.

16.2 Waste Management

16.2.1 Organic solvents are treated as hazardous waste and placed in the appropriate waste drum for disposal.

16.2.2 Soil samples are composited in a drum designated for incineration.

16.2.3 Disposal of materials is addressed in the laboratory QAP (Section 5.6).

## 17.0 References

17.1 SW-846-EPA Test Methods for Evaluating Solid Waste. Laboratory Manual Physical/Chemical Methods, Nov, 1986, Revision 1 Sept, 1994, Method 3510C, 3545, 3550B, 3610B, 3611A, 3620B, 3630C, 3650B, 3660B, 8081B, and 8082A.

17.2 40 CFR Part 136, App. A, Meth. 608.

17.3 RTI Laboratories, Inc SOP#'s 3510C, 3545, and 3550B.

17.4 RTI Laboratories, Inc. Quality Assurance Plan.

17.5 RTI Laboratories, Inc. SOP SRC001-A, Sample Receipt and Custody.

17.6 RTI Laboratories, Inc. Chemical Hygiene Plan.

17.7 RTI Laboratories, Inc. Employee Handbook.

Table 4 Target Analytes

| | | |
|---|---|---|
| 4,4´-DDD | Aroclor (unspecified) | AROCLOR-1242-4 |
| 4,4´-DDE | Aroclor 1016 | AROCLOR-1242-5 |
| 4,4´-DDT | Aroclor 1221 | AROCLOR-1248-1 |
| Aldrin | Aroclor 1232 | AROCLOR-1248-2 |
| alpha-BHC | Aroclor 1242 | AROCLOR-1248-3 |
| alpha-Chlordane | Aroclor 1248 | AROCLOR-1248-4 |
| beta-BHC | Aroclor 1254 | AROCLOR-1248-5 |
| Chlordane, total | Aroclor 1260 | AROCLOR-1254-1 |
| delta-BHC | Aroclor 1262 | AROCLOR-1254-2 |
| Dieldrin | Total PCBs | AROCLOR-1254-3 |
| Endosulfan I | AROCLOR-1016-4 | AROCLOR-1254-4 |
| Endosulfan II | AROCLOR-1016-5 | AROCLOR-1254-5 |
| Endosulfan sulfate | AROCLOR-1221-1 | AROCLOR-1260-1 |
| Endrin | AROCLOR-1221-2 | AROCLOR-1260-2 |
| Endrin aldehyde | AROCLOR-1221-3 | AROCLOR-1260-3 |
| Endrin ketone | AROCLOR-1221-4 | AROCLOR-1260-4 |
| gamma-BHC | AROCLOR-1221-5 | AROCLOR-1260-5 |
| gamma-Chlordane | AROCLOR-1232-1 | AROCLOR-1262-1 |
| Heptachlor | AROCLOR-1232-2 | AROCLOR-1262-2 |
| Heptachlor epoxide | AROCLOR-1232-3 | AROCLOR-1262-3 |
| Methoxychlor | AROCLOR-1232-4 | AROCLOR-1262-4 |
| Toxaphene | AROCLOR-1232-5 | AROCLOR-1262-5 |
| Hexachlorobenzene | AROCLOR-1242-1 | |
| Decachlorobiphenyl | AROCLOR-1242-2 | |
| Tetrachloro-m-xylene | AROCLOR-1242-3 | |

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# STANDARD OPERATING PROCEDURE

# SONICATION EXTRACTION PROCEDURE FOR SEMI – VOLATILE ORGANICS

| | |
|---|---|
| **Analyte:** | **Semi-volatile organic compounds** |
| **SOP #:** | **3550B_070912_R7** |
| **Method Reference:** | **EPA SW-846 3550** |
| **Issue Date:** | **December 2, 2005** |
| **Revision No.:** | **7** |
| **Revision Date:** | **July 9, 2012** |

**Reviewed and Approved July 9, 2012 by:**

| | |
|---|---|
| Director Quality Management: | Charles O'Bryan |
| Supervisor, Environmental Services: | James Wuokila |

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**SONICATION EXTRACTION PROCEDURE FOR**
**SEMI – VOLATILE ORGANICS**

**SOP#: 3550B_070912_R7**

**TABLE OF CONTENTS**

## 1.0 Scope and Application

### 1.1 Introduction

RTI Laboratories, Inc, has prepared this document to detail the Standard Operating Procedure (SOP) for the preparation of the preparation of solid samples for analysis of semi-volatile compounds by gas chromatography/mass spectrometry, pesticides and PCB's by GC/ECD, PNAs by HPLC and DRO by GC/FID. This SOP contains the procedures for sonication extraction (Method 3550B) for solid samples. Wipe samples (particularly for PCB's) are prepared using this procedure.

A detailed description of the instrumentation, calibration, run parameters and quality control procedures used for analysis are not included in this SOP. For definition of terms not specifically defined in this document refer to RTI QAP Section 16.

### 1.2 Summary of Method

1.2.1 A 25 to 30 g aliquot of sample is weighed and dried with anhydrous sodium sulfate. The solvent appropriate to the analysis, surrogates and spikes (where applicable) are added to the solid sample or wipe and sonicated for 3 minute at full power. The solvent extract is removed and filtered through anhydrous sodium sulfate. The procedure is repeated three times and the final extract is concentrated to the desired volume. This method has been modified to use 50ml aliquots instead of 100ml aliquots of extraction solvent.

## 2.0 Safety Precautions

2.1 Compounds applicable to this method are known or suspected carcinogens. Standard preparation is conducted in fume hoods designated for organic use.

2.2 Extraction solvents are flammable and/or toxic and must be handled with caution. All extractions are performed in a manner designed to minimize exposure to these chemicals using appropriate hoods and personal protection (such as, gloves, lab coat, and safety glasses.

## 3.0 Sample Requirements and Sample Handling Procedures

3.1 Samples are received in accordance with RTI's Standard Operating Procedure for Sample Receipt and Custody (SRC001-A). Appropriate U. S. Environmental Protection Agency (EPA) sample handling procedures and sample preservation recommendations are followed. Soil samples are collected in 2 to 9 oz. pre-cleaned wide mouth jars with Teflon lined lids.

3.2 The holding time for soil samples is 14 days from collection to extraction and 40 days from extraction to analysis.

3.3 All samples are stored at 4° C in the walk-in cooler.

3.4 Minimum sample size – 30 g.

## 4.0 MDL, Linear Range, Accuracy and Precision

4.1 Not applicable to this SOP. See the appropriate analytical SOP for details

## 5.0 Interferences

5.1 Interferences can arise from carry over due to high sample concentrations or contamination from reagents and/or glassware. Method blanks are prepared to ensure system cleanliness in both instances. All glassware must be scrupulously cleaned before use. Phthalates are common lab contaminants and will leach from any soft plastic material used during sampling or during prep.

5.2 Samples containing high concentrations of non-target analytes or extremely high levels of select target analytes can result in elevated detection limits for some or all compounds. Dilution of the extract may improve the resolution and quantification of some analytes but will generally cause an elevation in the RDL. Interferences from high molecular weight organics such as oils will cause an elevated baseline. If this background is at a high concentration it will interfere with analyte identification as well as quantification.

5.3 Sample extract interferences can be cleaned up using techniques described in the SOP for sample extract cleanup (florisil cleanup, acid cleanup, sulfur cleanup or dilution (3610B, 3611A, 3620B, 3630C, 3650B, 3660B)). Dilution of the extract can also be used to minimize interferences.

## 6.0 Apparatus and Materials

6.1 Analytical Balance capable of weighing to 0.1 gm.

6.2 Glass or Teflon Funnels

6.3 pH indicator paper

6.4 Residual chlorine test strips

6.4 Graduated cylinders. 1000ml and 100ml

6.5 Glass beakers, 250 ml size.

6.6 Sonicator – Ultrasonic Processor XL or Heat Systems Virsonic 300 or equivalent.

6.7 Class A Microliter syringes, 50ul, 10 ul, 25ul, 1000µl, 5000µl.

6.8 Volumetric glassware

6.9 Glass vials – 2ml with Teflon lined screw caps.

6.10 Pyrex glass wool

6.11 Filter paper, Whatman #41 or equivalent.

6.12 Pasteur pipettes

6.13 10ml Glass graduated pipettes

6.14 TurboVap II evaporator – Zymark

6.15 200ml concentrators tubes with a 1.0ml graduated tip- available through Caliper

6.16 4" x 4" gauze pads – for wipe collection.

6.17 PC with BalanceLink software, Microsoft Excel and Omega.

## ~~7.0 Reagents~~

7.1 Anhydrous Sodium sulfate- cleaned by muffle furnace for 4 hours at 400 degrees C

7.2 Methylene chloride – pesticide grade

7.3 Hexane – pesticide grade

7.4 Acetone – pesticide grade

7.5 Acetonitrile – HPLC grade or better.

7.6 Sulfuric acid – 1:1 in DI water

7.7 ASTM Type II DI.

7.8 Clean soil for Method Blank and LCS, this may be sand heated in a muffle furnace for 4 hours at 400 degrees C.

7.9 Dry Nitrogen – for TurboVap.

7.10 Stock Standards

7.10.1 Pesticide Mix 2000ug/mL, Absolute, Part No. 10013

7.10.2 TCMX/DCB Surrogate 200ug/mL, Ultra, Part No. ISM-320
7.10.3 PCB 1016/1260 1000ug/mL, Ultra, Part No. PPM-8082
7.10.4 8270 LCS Mix 200ug/mL, Cerrilliant, Part No. ERS-077

7.10.5 8270 Surrogate Mix 4000ug/mL, Ultra, Part No. ISM-331
7.10.6 n-Eicosane 99%, Ultra, Part No. RNA-011
7.10.7 SAE 30W Motor Oil 20mg/mL, Accustandard, Part No. FU-018-D-40X
7.10.8 Diesel #2 Fuel Oil 20mg/mL, Accustandard, Part No. FU-002-D-40X
7.10.9 Surrogate p-Terphenyl d14 2000ppm solution, Ultra , Part No. ATS-160
7.10.10 PNA spike mix – 500ppm each analyte, Ultra, Part No. PM-831-1
7.10.11 2-Methylnapthalene – Solid Stock Material Ultra, Part No. RAH-045
7.10.12 Acenaphthalene 5000ppm standard, Ultra, Part # EPA-1064
7.10.13 Acenaphthylene 5000ppm standard, Ultra, Part No. EPA-1065
7.10.14 Napthalene 5000ppm standard, Ultra, Part EPA-1134

7.11 SVOC working standards. All solutions have a 6-month expiration date.

7.11.1 BNAE Surrogate spiking solution 250ppm–

7.11.1.1 Working surrogate solution 25 ppm - prepared by adding 1.56ml of 8270 Surrogate Mix (7.10.5) to a 25ml class A volumetric flask and dilute to the mark with pesticide grade acetone. Add 0.1ml to each sample (25ug/extract).

7.11.2 BNA MS/MSD/LCS spike mix 200ppm –

7.11.2.1 The 8270 LCS Mix (7.10.4) is ready for use. Add 0.1ml to each LCS, MS, and MSD samples (20ug/extract).

7.12 PCB/Pesticide standards:

7.12.1 Pesticide ICV/CCV Intermediate standard 10ppm - prepared by adding 50µl of Absolute-10013 (7.10.1) to a 10ml class A volumetric flask and dilute to 10ml with pest grade Hexane

7.12.2 Working TCMX/DCB Surrogate 0.2ug/mL – prepared by adding 100µl TCMX/DCB Surrogate 200ug/mL (7.10.2) to a 100ml Class A volumetric flask and diluting to mark with pesticide grade acetone.

7.12.3 PCB MS/MSD/LCS spike mix 2ug/mL - prepared by adding 50µl of the PCB 1016/1260 1000ug/mL (7.10.3) to a 25ml Class A volumetric flask and diluting to mark with pesticide grade acetone. Add 1.0ml per MS/MSD/LCS.

7.12.4 Pesticide MS/MSD/LCS Working Spike 2ug/mL - prepared by adding 250µl of Pesticide ICV/CCV standard 10ppm (7.12.1), add 1.0ml per pesticide MS/MSD/LCS (100ng per extract).

7.12.5 Technical chlordane and toxaphene are not routinely part of the pesticide spike mixes.

7.13 PNA method 8310:

7.13.1 Surrogate spiking solution- 5ppm p-terphenyl d14 (250ul of 2000 ppm stock (7.10.9) diluted to 100ml with pesticide grade acetonitrile. Add 1mL to every sample.

7.13.2 2-Methylnapthalene 10,000ug/mL - prepare by dissolving 0.1g 2-Methylnapthalene (7.10.11) in a 10mL volumetric flask and dilute to the mark with pesticide grade methylene chloride.

7.13.3 MS/MSD/LCS Spike Mix

7.13.3.1 100ul PAH Mix 500ppm each section 7.7
7.13.3.2 90ul Acenapthalene 5000ppm section 7.10
7.13.3.3 90ul Acenapthylene 5000ppm section 7.11
7.13.3.4 90ul Napthalene 5000ppm section 7.12
7.13.3.5 27.5ul 2-methlnapthalene 10,000ppm section 7.9
7.13.3.6 Final volume 20mL Acetonitrile.
7.13.3.7 Add one ml of the working spike (7.13.2) to 30g ottowa sand to prepare LCS and 30g sample to prepare MS/MSD.

7.14 DRO/ORO.

7.14.1 DRO/ORO Surrogate Intermediate 5000ug/mL – weigh 0.05g of n-Eicosane (7.10.6) in a 10mL volumetric flask and dilute to the mark with pesticide grade methylene chloride.

7.14.2 DRO/ORO Working Surrogate 150ug/mL – prepare by adding 300uL of the DRO/ORO Surrogate Intermediate (7.14.1) to a 10mL volumetric flask and dilute to the mark with pesticide grade acetone. Add 100uL to each sample.

7.14.3 DRO/ORO MS/MSD/LCS Spike Mix 5000/10000ug/mL - add 500 ul SAE 30W Motor Oil (7.10.7) and 250uL Diesel #2 Fuel Oil (7.10.7) to a final volume of 1mL with pesticide grade acetone. Add 10uL to each MS/MSD/LCS.

7.15 All reagents and standards prepared must be labeled with a minimum:

7.15.1 Identity of the material
7.15.2 Concentration of the solution
7.15.3 Date prepared

7.15.4 Initials of analyst preparing the solution
7.15.5 Expiration date.

## 8.0 Preparation of Standards and Calibration Procedure

8.1 Ultra sonic processor tuning procedure – Heat System Model SL2015. Tune each use.

8.1.1 The probe should not be in contact with or immersed in liquid during tuning.

8.1.2 Turn the output control knob counter clockwise to zero and turn the pulsar duty cycle to off.

8.1.3 Press the power switch to the ON position. The switch will illuminate.

8.1.4 Press and hold the tune switch.

8.1.5 Turn the output control knob towards setting 3 and note the position of the needle on the % output power meter. Do not exceed 70%.

8.1.6 Rotate the tuning knob clockwise or counter clockwise until a minimum reading is obtained (usually less than 20%).

8.1.7 Turn the output control knob towards setting 7 and note the position of the needle on the % output power meter. Do not exceed 70%.

8.1.8 Rotate the tuning knob as above (8.1.6) until a minimum output power reading is obtained (usually less that 20%).

8.1.9 Repeat above steps (8.1.7 and 8.1.8) with the output control knob turned towards setting 10.

8.1.10 Release the tune switch.

8.2 Ultra sonic processor tuning procedure – Tekmar Model TM 502. Tune each use.

8.2.1 The probe should not be in contact with or immersed in liquid during the tuning procedure.

8.2.2 Set the timer to HOLD.

8.2.3 Set the output control to 10.

8.2.4 Momentarily hold down the on/off/tune switch to tune and rotate the tuning control clockwise or counter clockwise until a minimum reading (usually less that 20%) is obtained on the power monitor. If a minimum reading cannot be obtained the probe or tip may be loose or out of resonance or the power supply or converter requires servicing. A loose probe will usually generate a loud piercing sound.

8.2.5 Set the output control to 4.

8.2.6 Release the on/off/tune switch.

## 9.0 Sample Preparation

9.1 Allow samples to warm to ambient temperature.

9.2 With each batch of samples prepare a method blank, LCS and LCS duplicate (LCSD) by adding spiking solution specified for analytical request (section 7). If sufficient volume is supplied a MS/MSD (spiked according to section 7) is prepared with the batch of samples.

9.3 Verify the calibration of the balance used and record the calibration in the logbook daily.

9.4 Measure 30 gm of well-mixed soil discarding any water layer and eliminating foreign objects such as sticks, rocks, etc. and capture the weight into the “SampAmt” column of the Omega Prep Batch using the BalanceLink software. If the sample is a wipe, place the entire wipe sample into a 250 ml beaker.

9.4 Add minimum amount of sodium sulfate and mix until the sample is free flowing like sand. If needed for a wet sample, add additional sodium sulfate. If sample is dry, less sodium sulfate may be used.

9.5 Add 1.0ml of the appropriate surrogate mix (section 7.12 through 7.15) then immediately add 50 ml of methylene chloride.

9.6 Place the cleaned sonicator horn approximately 3-8 mm below the surface of the solvent but not in contact with the soil and sonicate for 3 min at full power with the pulse duty set to 50%.

9.7 Decant the extracts through a funnel containing filter paper and approximately ½ inch of sodium sulfate and collect in a 200 ml TurboVap vessel. Be careful not to fill the TurboVap vessel more than 2/3 full, too much solvent in the vessel will spray out the top.

9.8 Add 50ml methylene chloride to the beaker and repeat 9.6 and 9.7 two additional times combining the extracts.

9.9 Transfer the container to the TurboVap concentrator. Set the TurboVap according to the manufacturer's instructions (use the manual setting and tank pressure at 20psi). Concentrate to 1.0 ml at 44 degrees C( for methylene chloride).

9.10 PCB and Pesticide extracts require a solvent exchange to hexane. When the methylene chloride solvent extract reaches about 1 to 2 ml add 10 ml of hexane, set the TurboVap temperature to 46-50 degrees C and re-concentrate to 2 ml using the graduated tip of the concentrator tube. Add an additional 4.0ml of Hexane (using the 5.0ml syringe) to the concentrator tube.

9.11 PNA extracts require a solvent exchange to acetonitrile. When the methylene chloride solvent extract reaches about 1 to 2 ml add 10 ml of acetonitrile, set the TurboVap to 55 degrees C and re-concentrate to 1 ml using the graduated tip of the concentrator tube. Add an additional 1.0ml of acetonitrile (using the 1.0ml syringe) to the concentrator tube.

9.12 Transfer the concentrate to a 2-ml vial auto sampler vial. If the sample will not concentrate to 1 to 2 ml (oily waste) collect the extract in a 10 ml vial (or 40 ml vial if necessary) and record the final volume.

9.13 The analyst will decide what cleanup technique, if any will be required.

9.14 In the sample preparation log in the LIMS enter initial the sample volume in ml (1000 ml is the default), final extract volume (1 ml is the default) and sample matrix. Additionally enter the amount of surrogate and spike solutions added in ml.

9.15 The preparation analyst must also enter date and time of start and completion as well as analyst ID and method I

9.16 Enter all applicable Reagents/Chemicals and Spikes/Standard information in the preparation form.

## 10.0 Diagram/Table

10.1 Reserved

## 11.0 Analytical Procedure

11.1 This section is not applicable to this SOP.

## 12.0 Details of Calibration and Calculations

12.1 This section is not applicable to this SOP.

## 13.0 Quality Assurance/Quality Control (QA/QC) Requirements

13.1 Prepare a method blank for each batch of twenty or less samples by extracting cleaned sand.

13.2 Prepare a laboratory control sample (LCS) for each batch of twenty or less samples per matrix, by adding the appropriate amount of the spike mix to 30 g of cleaned sand.

13.3 Prepare a matrix spike (MS) and matrix spike duplicate (MSD) for each batch of twenty or less samples per matrix, if sufficient volume is available by adding the appropriate amount of the spike mix to a representative sample.

13.4 Corrective action procedures are specified in the applicable SOP's.

## 14.0 Data Reporting Requirements

14.1 Refer to applicable analytical SOP.

## 15.0 Preventative Maintenance and Routine Cleaning

15.1 The sonicators are tuned according to the manufacturers instructions daily or with each use. Record tuning in the maintenance log.

15.2 At the end of the work shift, the glassware is to be cleaned and put away. The counters are to be cleaned and wiped down.

15.3 Daily: Balance must be checked prior to use with the certified weights and recorded.

15.4 TurboVap: Ensure that the water bath reservoir is filled to at least above the bottom of the cutout circle on the vertical portion of the interior wall. Check to make sure that the N2 tank is not empty and that the nitrogen is flowing to the sample tube at the proper pressures..

15.5 Check the TurboVap displayed temperature with a calibrated thermometer on each day of use.

## 16.0 Pollution Prevention and Waste Management

16.1 Pollution Prevention

16.1.1 Reagents are purchased and quantities used to reflect anticipated usage and minimize disposal of expired or unused chemicals.

16.1.2 Chemicals are handled in a manner, which minimizes the potential for release or spill of the material.

16.2 Waste Management

16.2.1 Organic solvents are treated as hazardous waste and placed in the appropriate waste drum for disposal.

16.2.2 Disposal of materials is addressed in the laboratory QAP (Section 5.6).

## 17.0 References

17.1 EPA Test Methods for Evaluating Solid Waste. Laboratory Manual Physical/Chemical Methods, Nov, 1986, Revision 1 Sept, 1994. Method 3550, 3610B, 3611A, 3620B, 3630C, 3650B, 3660B.

17.2 RTI Laboratories, Inc. Quality Assurance Plan.

17.3 RTI Laboratories, Inc. SOP SRC001-A, Sample Receipt and Custody.

17.4 RTI Laboratories, Inc. Chemical Hygiene Plan.

17.5 RTI Laboratories, Inc. Employee Handbook.

**VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE**

# STANDARD OPERATING PROCEDURE

# FOR

# THE ANALYSIS OF POLYCHLORINATED DIBENZO-p-DIOXINS AND POLYCHLORINATED DIBENZOFURANS (PCDDs/PCDFs)

# BY

# HIGH-RESOLUTION GAS CHROMATOGRAPHY/HIGH-RESOLUTION MASS SPECTROMETRY (HRGC/HRMS)

## (CF-OA-E-002)

APPLICABLE TO METHODS:
EPA SW-846 Method 8290A, EPA Method 1613B, EPA SW-846 Method 0023A, EPA Method TO-9a

PROPRIETARY INFORMATION



CFA

**CFA's Document Control Officer certifies this document to be a true copy of the fully executed original.**

W. M. Larkins

# TABLE OF CONTENTS

## 1.0 STANDARD OPERATING PROCEDURE FOR THE ANALYSIS OF POLYCHLORINATED DIBENZO-P-DIOXINS AND POLYCHLORINATED DIBENZOFURANS (PCDD/PCDF) BY HIGH-RESOLUTION GAS CHROMATOGRAPHY/HIGH-RESOLUTION MASS SPECTROMETRY (HRGC/HRMS)

## 2.0 METHOD OBJECTIVE, PURPOSE, CODE, AND SUMMARY

This standard operating procedure (SOP) covers the analytical determination of PCDD/PCDFs according to the following methods:

2.1 SW-846 Method 8290A

2.2 EPA Method 1613B

2.3 SW-846 Method 0023A

2.4 EPA Method TO-9a (Jan 99)

## 3.0 APPLICABLE MATRICES

Applicable matrices for methods 8290A and 1613B include groundwater, wastewater, surface water, leachate, soil, sediment, sludge, oil, and tissue. The applicable matrix for method 0023A is an air sampling train, which may contain XAD resin (a hydrophobic crosslinked polystyrene copolymer resin, supplied as 20-60 mesh size white insoluble beads), filters, impinger water and solvent rinses. TO-9a is an ambient air sampling train which may contain polyurethane foam (PUF, a polyurethane foam, supplied as 1-3 inch cylinders approximately 3 inches long), XAD resin, filters, and solvent rinses.

## 4.0 METHOD SCOPE, APPLICABILITY, AND DETECTION LIMIT

4.1 Methods 8290A, 1613B and 0023A may be used to quantify PCDD/PCDFs that are soluble in methylene chloride and/or toluene. The compounds are separated using a gas chromatograph (GC) and detected using a high-resolution double focusing mass spectrometer (HRMS). Appendix 1 lists the analytes currently analyzed using these methods and their practical quantitation limits.

4.2 The practical quantitation limit (PQL) is the lowest level in the calibration curve. The PQL is the lowest level at which compounds may be accurately quantitated and is compound dependent. The calibration curve typically ranges from 1.0 ng/mL to 1000 ng/mL for methods 8290A, 0023A, and TO-9a, and from 0.5 ng/mL to 2000 ng/mL for method 1613B. These ranges reflect instrument readings, which are in ng/mL (ppb). It should be noted that the calibration range may vary between calibrations and instruments.

4.3 Method detection limit studies (MDLs) are performed and/or verified on an annual basis. MDLs are done for aqueous, solid, tissue and XAD matrices. For more information regarding MDLs, refer to The Determination of Method Detection Limits, CF-LB-E-001.

4.4 Qualified analysts must demonstrate proficiency initially and annually thereafter with an IDOC, CDOC, or PT study. Acceptability criteria may be found in the applicable analytical method.

4.4.1 To establish the ability to generate acceptable accuracy and precision, the analyst should perform an "analyst validation study" or Initial Demonstration of Capability. Four LCS standards are extracted and analyzed. Calculate the average recovery and the standard deviation of the recovery for each analyte of interest using the four results. Then compare the average and the standard

deviation with the corresponding criteria found in Table 6 of method 1613B, or with the determined limits for methods 8290A and 0023A. If the average and the standard deviation for all analytes of interest meet the acceptance criteria, then the analyst may begin work on actual samples. If the validation study fails for one or more of the compounds, then the study must be repeated for those compounds which failed.

## 5.0 METHOD VARIATIONS

5.1 Cape Fear Analytical analyzes a calibration point at 0.25 ng/mL, which is below the method required low point.

5.2 Standards and sample extracts are stored at room temperature to avoid analyte loss. Many of the target analytes in these methods form a strong cohesive bond with solids such as glass in cold temperatures; this type of analyte loss is not addressed in the method. (This is a variance from the following method recommendations: ≤6° per method 8290A; < -10°C per 1613B; -10° to -20° C per DoD QSM.)

5.3 Cape Fear Analytical utilizes the DB-5MS GC column, which is capable of better resolution of the TCDF isomers. This column exhibits a different elution pattern than the DB-5 column referenced in the analytical methods. Relative retention time limits have been determined for this column for use with method 1613B, and are listed in Table 9.

5.4 Method 1613B does not address the reporting of EDL and EMPC. These values are reported for this method only when requested by the client.

## 6.0 DEFINITIONS

6.1 Accuracy: The degree of agreement between an observed value and an accepted reference value.

6.2 AlphaLIMS: The Laboratory Information Management System used at CFA, LLC.

6.3 Blank: An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and standard additions that are used with other samples. The LMB (Lab Method Blank) is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus. Contamination may be derived during sampling, transportation, storage or analysis. The blank may be used to establish a background value.

6.4 Calibration Standard (CAL): An aliquot of a primary standard solution or stock standard solution. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

6.5 Calibration Verification Standard (CVS, CCAL, CS3WT): A solution of target analytes with a concentration near the mid-point of the calibration range. It should be obtained from a second source vendor and is used to verify the initial calibration on a basis described in the determinative method. This solution may also contain the window defining analytes and the column performance mix.

6.6 Cleanup Standards: Isotopes added prior to cleanup that are used to measure the efficiency of the fractionation step alone. Method 1613B uses one compound (37Cl4-2378-TCDD) as the Cleanup Standard. Method 8290A does not address the use of cleanup standards.

6.7 Duplicate Analysis: The analysis or measurement of the variable of interest performed identically on two field subsamples of the same sample. The results from duplicate analyses are used to evaluate analytical or measurement precision of sample, preservation, or storage internal to the laboratory.

6.8 Estimated Detection Limit (EDL): A calculation of the concentration of a given analyte required to produce a signal with a peak height of at least 2.5 times the background signal level. The EDL is calculated for each 2378-substituted congener that is not identified.

6.9 Estimated Maximum Possible Concentration (EMPC): A calculation for a peak characterized by a response with a signal-to-noise ratio of at least 2.5 for both the quantitation ions, and meeting all identification criteria except ion ratio. EMPC is a worst-case estimate of the concentration.

6.10 Extraction Standards: Isotopes added prior to extraction that serve as internal standards for many 2,3,7,8 substituted congeners. In addition, to measure the overall extraction and fractionation efficiencies. Method 8290A names them Internal Standards while Method 1613B uses the Labeled Compounds terminology.

6.11 Injection Standards: Isotopes added prior to injection to determine the recoveries of the Extraction and Cleanup Standards. Method 8290A names them Recovery Standards while Method 1613B calls them Internal Standards.

6.12 Internal Standard (ISTD): A known amount of standard added to a test portion of a sample as a reference for evaluating the retention time and concentration of dependent analytes and controlling the precision and bias of the applied analytical method.

6.13 Laboratory Control Standard (LCS): An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The LCS is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

6.14 Laboratory Duplicate (DUP): Aliquots of a sample taken from the same container and processed in the same manner under identical laboratory conditions. The aliquot is analyzed independently from the parent sample and the results are compared to measure precision and accuracy.

6.15 Matrix Spike and Matrix Spike Duplicate (MS and MSD): Two separate aliquots of an environmental sample to which known quantities of the method analytes are added in the laboratory. The MS and MSD are analyzed exactly like a sample, and their purpose is to determine whether the sample matrix contributes bias to the analytical results. The concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS/MSD adjusted. Percent recovery is calculated for both aliquots, and RPD is calculated between the two.

6.16 Method Detection Limit (MDL): The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero.

6.17 Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves, a data quality

indicator. Precision is usually expressed as standard deviation, variance or range in either absolute or relative terms.

6.18 Quantitation Limits (also PQL, RL): The value at which an instrument can accurately measure an analyte at a specific concentration (i.e., a specific numeric concentration can be quantified). These points are established by the upper and lower limits of the linear calibration range.

6.19 Sampling Standards: Isotopes added prior to field sampling for Method 0023A and Method TO-9a that are used to measure the efficiency of the sampling step alone.

## 7.0 INTERFERENCES/LIMITATIONS

7.1 Contaminants found in extraction glassware, solvents, and other sample processing hardware may jeopardize the integrity of this method.

7.2 Glassware must be scrupulously cleaned as soon as possible after extraction.

7.3 Contamination may also occur in the GC/MS system. High boiling materials tend to build up in the injection port and the front end of the column. The analyst should maintain a thorough working knowledge of keeping the injection port free of contamination, including changing out the septum, injection port liner, O-ring, ferrule, and gold seal.

7.4 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed with solvent between samples. If carryover is suspected, potentially impacted samples must be re-analyzed after any needed maintenance, solvent replacement, and/or cleaning has been done.

7.5 Upon review of a completed sequence, if one is required to perform a 200x or greater dilution because of a sample's target concentrations, that the rinse vials on the instrument that determined this dilution need must have it's solvent replaced. This action should be documented in the maintenance log.

## 8.0 SAFETY PRECAUTIONS AND WARNINGS

METHYLENE CHLORIDE IS A SUSPECTED CARCINOGEN AND A KNOWN SKIN IRRITANT.

NO OCCUPATIONAL EXPOSURE LIMIT FOR DIOXIN HAS BEEN ESTABLISHED. IT IS A KNOWN AND PROBABLE HUMAN CARCINOGEN.

CONTACT WITH OXIDIZERS MAY GENERATE EXPLOSIVE MIXTURES.

PREVENT SKIN AND EYE CONTACT BY USING SPECIFIED PERSONAL PROTECTIVE EQUIPMENT WHEN MAKING STOCK REAGENTS.

WORK UNDER A HOOD TO PREVENT INHALATION WHEN USING METHYLENE CHLORIDE.

8.1 Eye protection should be worn when handling samples, reagents, or standards. NOTE: Contact lenses pose a special problem; soft lenses may absorb irritants and all lenses concentrate them. DO NOT wear contact lenses in the laboratory.

8.2 Treat all chemicals and samples as potential health hazards and reduce exposure to these chemicals to the lowest level possible. CFA maintains a current reference file of Material Safety Data Sheets (MSDS). These documents and individual sample MSDS provided by clients are maintained in the laboratory.

8.3 Personal Protective Equipment (PPE)

8.3.1 Gloves and eye protection should be worn when handling reagents, solvents, standards and samples.

8.3.2 Analysts should prepare samples and standards under the hood.

8.4 All samples, chemicals, extracts, and extraction residues must be transferred, delivered, and disposed of safely according to all related SOPs.

8.5 Never leave gas cylinders unchained or untied.

8.6 In the event of an accident or medical emergency, call for help immediately. When time and safety permit, management should be notified of all accidents.

8.7 Fire escape routes are posted in the lab, and all personnel should be familiar with them. In addition, fire safety equipment such as fire extinguishers and fire blankets are located in the lab. Training is available on the proper operation of this equipment.

8.8 The analyst must use care when assembling and operating instrumentation. Check to see that the gas chromatograph equipment is properly assembled and hooked up to the proper gas cylinder and power, referencing the appropriate manual. Analytical equipment must only be operated by qualified personnel.

8.9 For further safety instructions, consult the Safety Manual, CF-LB-N-001.

## 9.0 APPARATUS, EQUIPMENT AND INSTRUMENTATION

9.1 Equipment associated with this method includes:

9.1.1 Gas tight syringes

9.1.2 2 mL high recovery (conical) autosampler vials and storage racks

9.1.3 Teflon crimp tops

9.1.4 Crimper/De-crimper

9.1.5 GC Columns

9.1.5.1 Agilent DB5-MS or equivalent; 60 m, 0.25 mm, 0.25 um

9.1.5.2 Agilent DB-225 or equivalent; 30 m, 0.25 mm, 0.25 um

9.1.6 Quartz/Glass injection port liners

9.1.7 Injection port liner O-ring seals

9.1.8 Gold seals

9.1.9 Ferrules

9.1.10 Column cleaving tool

9.1.11 Septa (thermogreen)

9.1.12 10-100 uL adjustable air displacement pipette with disposable tips

9.2 Instrumentation

9.2.1 Waters Autospec Premier high resolution mass spectrometer

9.2.2 Agilent 7890 Gas Chromatograph

9.2.2.1 A suggested temperature program for primary analysis follows:

| | |
|---|---|
| Initial Temp. | 140° C |
| Hold Time | 1.0 min. |
| Rate 1 | 20° C/min. |
| Temperature 2 | 180° C |
| Time 2 | 2°/min |
| Temperature 3 | 235° C |

| | |
|---|---|
| Rate 3 | 30° C/min. |
| Final Temp. | 290° C |
| Hold Time | 13 min. |
| Run Time: | 45 minutes (may vary due to column length or flow rate) |
| Solvent Delay: | 18.0 min. |
| Splitless Valve Time: | 1.5 min. |
| Flow: | 1.8 mL/min. |
| Mass Range: | See descriptor definitions (Table 2) |

**NOTE:** These instrument conditions and rates are guidelines which may change.

9.2.3 LEAP Technologies GC PAL Autosampler

9.2.3.1 Suggested parameters:

Sample volume – 1 µL

Air volume – 0.5 µL

Solvent push volume – 1 µL

Number of sample washes - 0

Solvent washes - 30

Sample viscosity wait – 1 second

Number of sample pumps - 0

Injection mode - Fast

## 10.0 REAGENTS AND STANDARDS

10.1 Reagents and standards

10.1.1 Nonane

10.1.2 Source Standards: Source Standards are purchased directly from vendors and may be diluted to make stock, intermediate, or working standards. These may include extraction standard, matrix spiking standard, cleanup standard, injection standard, as well as others. Source standards expire per the vendor expiration date or after five years from the date opened, whichever is shorter. Please reference CF-LB-E-007 and CF-OA-E-002 for further information regarding standards and their preparation.

10.1.3 Initial Calibration (ICAL) Standards: Certified calibration standards are purchased from commercial vendors at a minimum of five concentration levels. One of the calibration standards is at a concentration near, but above, the method detection limit; the others should correspond to the expected range of compounds found in samples. Calibration standards expire after a maximum of five years and should be monitored frequently for signs of degradation.

10.1.4 Calibration Verification Standards (CVS, CCAL, CS3WT): A certified CVS is purchased from a second source commercial vendor at a concentration that is near to the midpoint of the calibration curve.

10.1.5 Window Defining Mix and Column Performance Mix (WDM and CPM): A standard containing the first and last eluters for each homolog group, as well as the dioxin and furan isomers used to demonstrate isomer specificity on the GC column in use. These may be contained in the same standard as the calibration verification (known as CS3WT).

## 11.0 SAMPLE HANDLING AND PRESERVATION

11.1 Sample extracts have a 45-day holding time from the date of extraction by methods 8290A and 0023A, and a 365 day holding time from the date of extraction by 1613B. Note that per method 8290A, tissue extracts must be completely analyzed by 45 days from collection. TO-9a cartridges are considered clean for 30 days from preparation, samples must be extracted 7 days from collection and analyzed 40 days from extraction. See Table 13.

11.2 Sample extracts are delivered from the prep lab to the instrument lab and are stored in a darkened hood at room temperature. The extracts are usually grouped according to preparation batches and are accompanied by the batch pull sheet and other pertinent paperwork.

11.3 Custody of samples is monitored using the AlphaLIMS sample tracking system. Each analyst should scan the samples planned to run into their custody prior to analysis.

11.4 All sample extracts should be treated with caution as potential health hazards. Refer to Section 8.0 on safety.

## 12.0 SAMPLE PREPARATION

12.1 Before extracts can be analyzed on the instrument, they must first be evaporated to dryness under nitrogen and then spiked with injection standard to set the final volume nominally at 20 µL. A determination must also be made as to whether the extract should be diluted. The decision to dilute a sample extract is based on a number of factors: sample screening, historical data about the sample or sample site, the appearance of the extract (color, viscosity, incidental odor, turbidity, etc.), or regulatory considerations. The experience of the analyst is invaluable in making this determination.

**NOTE:** Sample extracts may contain multiple layers or sediment. Samples that contain sediment are returned to cleanup. Multiple layers are treated on a case-by-case basis. If the extract can be homogenized, then a uniform sample is achieved. If the extract remains bi-phasic, the PM and client are contacted for further guidance.

12.2 If a sample is to be analyzed without dilution ('neat'), 2 nanograms of injection standard solution is added to the extract using a pipette (20 µL of a 0.1 ng/µL = 100 pg/µL extract concentration). A cap is then placed on the vial and secured by crimping before vortexing the sample to ensure complete mixing and vial wall washing.

12.3 If samples require dilution, the dilution is made using nonane or appropriate solvent. If not previously added, 2 nanograms of JS is added to the autosampler vial. Dilution prep may involve the addition of supplemental extraction standard (ES) and is documented in the injection prep logbook.

12.4 Once samples are prepped, they are ready to be injected onto the instrument. An autosampler is used to inject standards and sample extracts on the instrument.

12.5 The need for dilution may also be determined after analysis is performed, and may still be performed as above. Under normal circumstances, a sample would be diluted if any chromatographic peaks saturate the detector.

## 13.0 QUALITY CONTROL REQUIREMENTS

Typically a blank (LMB), laboratory control sample (LCS) and laboratory control sample duplicate (LCSD) are extracted and analyzed with each prep batch. Other client requirements may include a matrix spike (MS) and matrix spike duplicate (MSD) or sample duplicate (DUP).

13.1 Blanks

13.1.1 A blank is extracted with each batch of 20 or fewer samples to demonstrate that interferences from glassware, reagents and the analytical system are under control. Blanks are carried through all stages of sample preparation and analysis. For Method 1613B, an acceptable blank must be below the minimum levels listed in Table 2 of the method for all analytes. For Methods 8290A, 0023A, and TO-9a, all analytes must be below the Lower Method Calibration Limits.

13.1.2 The percent recovery of each labeled standard (extraction and cleanup) is calculated as shown in Sec. 17.4.5. Recoveries must be within the limits in Table 7 for method 1613B. For methods 8290A and 0023A, extraction standard recoveries must be within 40-135%. Sampling standards for Method 0023A must be within 70-130%. For method TO-9a, extraction standards must be within 50-120% for tetra- through hexa- and within 40-120% for hepta- and OCDD. Sampling standards for Method TO-9a must be within 70-130%.

13.2 Laboratory Control Samples and Matrix Spikes

13.2.1 The spiking standard for LCS/LCSDs and MS/MSDs contains all analytes listed in Table 5. For each LCS, LCSD, MS and MSD, the concentration of each analyte and its percent recovery are calculated as shown in Sec.17.4.1 and 17.4.5. For methods 8290A and 0023A, percent recoveries should be within 70-130%. For method 1613B, recovered concentrations should be within the limits in Table 6.

13.2.2 If recovery is not within these limits, the data may need to be re-checked for errors, or the samples and QC may need to be re-analyzed. In addition, the instrumentation may need to be checked for performance problems. If the LCS fails to meet acceptance criteria due to low recovery, the associated samples may have to be re-extracted and re-analyzed when possible. If one or more recoveries are high in the LCS and these analytes are not detected in the samples, the event should be documented and data may be reported. If the MS and MSD both fail due to matrix interference and/or dilution, data may be reported provided the associated LCS passes acceptance criteria.

**NOTE:** Many clients have contract specific criteria that must be considered when evaluating recovery of the Quality Control samples.

13.2.3 The percent recovery of each labeled standard (extraction and cleanup) is calculated as shown in Sec. 17.4.5. Recoveries must be within the limits in Table 6 for method 1613B. For methods 8290A and 0023A, extraction standard recoveries must be within 40-135%. Sampling standards for Method 0023A must be within 70-130%. For method TO-9a, extraction standards must be within 50-120% for tetra- through hexa- and within 40-120% for

hepta- and OCDD. Sampling standards for Method TO-9a must be within 70-130%.

13.3 Samples

13.3.1 The percent recovery of each labeled standard (as listed in SOP CF-OA-E-001) is calculated as shown in Sec. 17.4.5. Recoveries must be within the limits in Table 7 for method 1613B or 40-135% for method 8290A. For method TO-9a, extraction standards must be within 50-120% for tetra- through hexa- and within 40-120% for hepta- and OCDD. Sampling standards for Method TO-9a must be within 70-130%.

13.3.2 Calculated EDLs should be below the PQLs in Table 1. Any reported EDLs above the PQLs should be noted in the case narrative.

## 14.0 INSTRUMENT CALIBRATION, STANDARDIZATION, AND PERFORMANCE

14.1 Mass spectrometer performance

14.1.1 The mass spectrometer is operated in electron ionization mode. A static resolving power of at least 10,000 (10 percent valley definition) must be demonstrated at appropriate masses before any analysis is performed. Static resolving power checks must be performed at the beginning and at the end of each 12-hr period of operation. Corrective action must be implemented whenever the resolving power does not meet the requirement.

14.1.1.1 Chromatography time for PCDDs and PCDFs exceeds the long term mass stability of the mass spectrometer. Because the instrument is operated in the high-resolution mode, mass drifts of a few ppm (e.g., 5 ppm in mass) can have serious adverse effects on instrument performance. Therefore, a mass drift correction is mandatory. A lock-mass ion from the reference compound PFK is used for tuning the mass spectrometer. The selection of the lock-mass ion is dependent on the masses of the ions monitored within each descriptor. Lock mass ions may be found in the descriptor table, Table 2. The level of the reference compound (PFK) metered into the ion chamber during HRGC/HRMS analyses should be adjusted so that the amplitude of the most intense selected lock-mass ion signal (regardless of the descriptor number) does not exceed 10 percent of the full scale deflection for a given set of detector parameters. Under these conditions, sensitivity changes that might occur during the analysis can be more effectively monitored. NOTE: Excessive PFK (or any other reference substance) may cause noise problems and contamination of the ion source resulting in an increase in downtime for source cleaning.

14.1.2 Documentation of the instrument resolving power must be accomplished by recording the peak profile of the high-mass reference signal (m/z 380.9760) obtained during the above peak matching experiment by using the low mass PFK ion at m/z 304.9824 as a reference. The minimum resolving power of 10,000 must be demonstrated on the high-mass ion while it is transmitted at a lower accelerating voltage than the low-mass reference ion, which is transmitted at full sensitivity. The format of the peak profile representation (Figure 2) must allow manual determination of the resolution, i.e., the

horizontal axis must be a calibrated mass scale (amu or ppm per division). The result of the peak width measurement (performed at 5 percent of the maximum, which corresponds to the 10 percent valley definition) must appear on the hard copy and cannot exceed 100 ppm at m/z 380.9760 (or 0.038 amu at that particular mass).

14.2 System Performance

System performance criteria are presented below. The laboratory may use the recommended GC column described in Sec. 9.1. The laboratory must document that all applicable system performance criteria are met before sample analysis begins. Sec. 9.2.2 provides recommended GC conditions that may be used to satisfy the required criteria. Mass spectrometer resolving power checks must be performed at the beginning and the end of each 12-hr period of operation. A GC column performance check is required at the beginning of each 12-hr period during which samples are analyzed. For Method 1613B, a continuing calibration must be performed at the beginning of the sequence, while for Methods 0023A and 8290A, continuing calibrations must be performed at both the beginning and the end of a sequence. An ending continuing calibration may also serve as the beginning check for the next sequence.

14.2.1 GC Column performance check

14.2.1.1 Inject 1 µL of an aliquot of the column performance check solution (Sec. 10.1.5) and acquire selected ion monitoring (SIM) data within a total cycle time of $\leq$ 1 second. The chromatographic separation between 2,3,7,8-TCDD and the peaks representing any other unlabeled TCDD isomers must be resolved with a valley of $\leq$ 25 percent (Figure 1), where:

Valley percent = $(x/y) \times 100$

x = measured as in Figure 1 from the 2,3,7,8-closest TCDD eluting isomer

y = the peak height of 2,3,7,8-TCDD

For 2378-TCDF confirmatory analysis, the chromatographic separation between 2378-TCDF and its closest eluters must be resolved with a valley of $\leq$ 25 percent.

14.2.1.2 It is the responsibility of the laboratory to verify the conditions suitable for the appropriate resolution of 2,3,7,8-TCDD from all other TCDD isomers. The GC column performance check solution also contains the known first and last PCDD/PCDF eluters under the conditions described in this SOP. Their retention times are used to determine the five homologue retention time windows that are used for qualitative (Sec. 15.3.1.1) and quantitative purposes. All peaks (including 13C12-2,3,7,8-TCDD) should be labeled and identified on the chromatograms. All first eluters of a homologous series should be labeled with the letter "F," and all last eluters of a homologous series should be labeled with the letter "L". Any individual selected ion current profile (SICP) or the reconstructed homologue ion current constitutes an acceptable form of data presentation. A SICP for the labeled compounds is also required.

14.2.1.3 Particular caution should be exercised for the switching time between the last tetra-chlorinated congener (1,2,8,9-TCDF) and the first penta-chlorinated congener (1,3,4,6,8-PeCDF), as these two compounds elute within 15 sec of each other on the 60-m DB-5 column, and overlap on the 60-m DB-5ms column. Both congeners must be acquired within one analysis.

14.2.1.4 The absolute retention time of $^{13}C_{12}$-1,2,3,4-TCDD must exceed 25.0 minutes on the primary GC column in use, and 15.0 minutes on the confirmatory GC column.

14.3 Initial Calibration

14.3.1 Prior to running a multi-level calibration, take precautions to ensure that the instrument meets system performance criteria. The analyst must document that all system performance criteria are met before analyzing an initial calibration.

14.3.2 Initial calibration is required before any samples are analyzed for PCDDs and PCDFs and must meet the acceptance criteria listed below. Initial calibration is also required if any routine calibration does not meet the required criteria listed in Sec. 15.2, and at a minimum, annually.

14.3.3 At a minimum, all five high-resolution concentration calibration solutions listed in Table 5 must be used for the initial calibration.

14.3.4 Tune the instrument with PFK to meet the above-specified system performance criteria.

14.3.5 Inject the GC column performance check solution and acquire SIM mass spectral data. The total cycle time for each descriptor must be < 1 second. The laboratory must not perform any further analysis until it is demonstrated and documented that the criteria listed in Sec. 15.1.1.1 are met.

14.3.6 By using the same conditions (GC and MS) that produced acceptable results with the column performance check solution, analyze each of the five concentration calibration solutions. Each injection must meet the following ion ratio and signal-to-noise (S/N) requirements:

14.3.6.1 The ratio of the areas of the integrated ion current for the ions appearing in Table 2 (homologous series quantitation ions) must be within the indicated control limits (set for each homologous series) in Table 3. These ion ratio requirements must be within the specified control limits simultaneously in one run. It is the analyst's responsibility to take corrective action if the ion abundance ratios are outside the limits.

14.3.6.2 For each selected ion current profile (SICP) and for each GC signal corresponding to the elution of a target analyte and of its labeled standards, the S/N ratio must be better than or equal to 10. Manual measurement of S/N is required for any GC peak that has an apparent S/N of less than 15:1. The result of the calculation must appear on the SICP above the GC peak in question.

14.3.7 Calculate the 17 relative response factors (RF) for unlabeled target analytes relative to their appropriate internal standards (see Table 10). Also calculate

the RFs for the ESs and CSs relative to the appropriate injection standards according to the following formula:

$$RF = \frac{A_x C_{is}}{A_{is} C_x}$$

Where:

Ax = Sum of the Areas of the two characteristic ions for the compound being measured.

Ais = Sum of the Areas of the two characteristic ions for the specific internal standard.

Cis = Concentration of the specific internal standard.

Cx = Concentration of the compound being measured.

The RF is a dimensionless quantity; the units used to express Cis and Cx must be the same.

14.3.8 The RF for other isomers within a homolog group shall be determined from the average RF of the 2,3,7,8-substituted isomers. For example, the RF for non-2,3,7,8-substituted HxCDD isomers (totals peaks) is the average of the three 2,3,7,8-substituted isomers. NOTE: If only one 2,3,7,8-substituted isomer is present in the calibration then use that isomer's RF for all isomers within its homolog group.

14.3.9 Because more than five calibration levels may be analyzed, the analyst may choose to deactivate one or more levels globally. If a level is not used, it will be deactivated in the method for all analytes in that calibration mixture. In some cases the upper level(s) of the calibration may be deactivated in order to meet method criteria for single compounds. This practice results in a narrower calibration range. The low standard representing the PQL cannot dropped. Please note that this practice does not represent "cherry picking," which is acknowledged as an unacceptable laboratory practice.

14.3.10 The average RF must be calculated for each compound as follows:

$$RF_{avg} = \frac{\sum_{i=1}^{n} X}{n}$$

Where:

$N$ = number of calibration levels

$X_i$; i=1 to n, are the compounds RF values for each calibration point

14.3.11 Criteria for acceptable initial calibration

The criteria listed below for acceptable calibration must be met before sample analyses are performed.

14.3.11.1 Per method 8290A, the percent relative standard deviations for the mean response factors from the 17 unlabeled standards must not exceed ± 20 percent, and those for the nine labeled reference compounds must not exceed ± 20 percent. These limits also apply to Method 0023A. Per method 1613B, the percent relative standard deviations for the mean response factors from the 17

unlabeled standards must not exceed ± 20 percent, and those for the fifteen labeled reference compounds must not exceed ± 35 percent. See Table 12 for method TO-9a minimum requirements.

$$\%RSD = \frac{SD}{\bar{x}} \times 100$$

Where:

RSD = relative standard deviation

$\bar{x}$ = mean of 5 or more initial RFs for a compound

SD = standard deviation of average RFs for a compound

$$SD = \sqrt[2]{\frac{\sum_{i=1}^{n}(X - A)}{n-1}}$$

where:

$n$ = number of calibration levels

$X_i$; i=1 to n, are the compounds RF values for each calibration point

$A$ = average of the RFs from above

## 15.0 PROCEDURE FOR ANALYSIS AND INSTRUMENT OPERATION

### 15.1 Resolution check

15.1.1 At the beginning and end of each 12-hour window, mass resolution must be tuned and/or verified. A static resolving power of at least 10,000 must be demonstrated at appropriate masses before analysis is performed.

15.1.2 Using a PFK molecular leak, tune the instrument to the minimum required resolving power of 10,000 at m/z 330.9792 (for day to day operations, the instrument may be tuned to approximately 11,000). Verify that the exact mass of m/z 380.9760 is within 5 ppm of the required value.

### 15.2 Column Performance/Window Defining/Continuing Calibration Check (CS3WT)

15.2.1 Inject 1 uL of the CS3WT or CPM. Verify that all column performance and window defining criteria in Section 14.2.1 have been met.

15.2.2 The CS3WT also contains the analytes for continuing calibration. The initial calibration curve for each compound of interest must be verified once every 12 hours.

Calculate the percent difference using:

$$\%\ \text{Difference} = \frac{\left|\overline{RF}_i - RF_c\right|}{\overline{RF}_i} \times 100$$

Where:

$\overline{RF}_i$ = average response factor from initial calibration

$RF_C$ = response factor from current CS3WT

Calculate analyte concentrations using:

$$\left[PCDD/PCDF\right] = \frac{\left(A_{unk}^{ion1} + A_{unk}^{ion2}\right)}{\left(A_{ES}^{ion1} + A_{ES}^{ion2}\right)} \times \frac{Q_{ES}}{\overline{RF}}$$

Where:

$A_{unk}$ and $A_{ES}$ = the integrated area for each ion monitored.
$Q_{ES}$ = the amount of extraction standard in pg/uL
RF = Average RF from the ICAL for the compound

15.2.2.1 For methods 0023A and 8290A, if the percent difference for each native analyte in the CS3WT is $\leq$ 20%, and for each labeled analyte is $\leq$ 30%, the initial calibration is assumed to be valid. For method 1613B, analyte concentrations must fall within the limits in Table 8. If the criteria are not met, corrective action should be taken. If no source of the problem can be determined after corrective action has been taken, a new calibration may need to be generated. For Method TO-9a See Table 12 for minimum requirements.

15.2.2.2 All ion ratios must be within the limits in Table 3.

15.2.2.3 For methods 0023A and 8290A, if no more than two unrelated compounds in the continuing calibration check performed at the end of a 12-hour period fail by no more than $\pm$25% for the 17 unlabeled compounds and $\pm$35% for the 9 labeled compounds, the average RF values from the beginning and ending continuing calibration checks should be used to compute the analyte concentrations, instead of the RF values obtained from the initial calibration. No further sample analyses should be performed until an acceptable calibration is achieved.

15.3 Sample Analysis

15.3.1 Data Interpretation

15.3.1.1 Qualitative Determination

For a peak to be identified as a PCDD or PCDF, it must meet all of the criteria listed below.

15.3.1.1.1 The signals for the two m/z's being monitored must be present and maximize within ±2 seconds of each other.

15.3.1.1.2 The signal-to-noise ratio between the two m/z's must be $\geq$ 2.5 for native compounds and $\geq$ 10 for labeled compounds.

15.3.1.1.3 Ion ratios must be within the limits in Table 3.

15.3.1.1.4 Relative Retention Times

15.3.1.1.4.1 For Methods 0023A and 8290A, congeners which have an isotopically labeled compound must fall within -1 to +3 seconds of the labeled compound. Congeners with no labeled compound must be within 0.005 retention time units of the RRT measured in the continuing calibration. (See Table 11.) For method TO-9a, congeners which have an

isotopically labeled compound must fall within -3 to +3 seconds of the labeled compound. Congeners with no labeled compound must be within 0.005 retention time units of the RRT measured in the continuing calibration.

15.3.1.1.4.2 For Method 1613B, relative retention times must be within the RRT limits found in Table 9.

15.3.1.1.4.3 For non-2378 peaks, retention times must be within the retention time windows established by the analysis of the window defining mixture (Sec. 14.2.1.2).

15.3.1.1.5 For PCDFs, no peak may be present in the associated PCDPE channel at the same retention time. If a PCDPE peak is present, the PCDF peak should be reported with a flag denoting the interference.

15.3.1.1.6 Any sample in which 2378-TCDF has been identified at or above the method reporting limit must be confirmed on a second column (DB-225 or equivalent).

15.3.1.2 Calibration Limit Exceedance

15.3.1.2.1 If a compound in a sample exceeds the upper calibration limit, all subsequent samples must be checked for carryover contamination.

15.3.1.2.2 When a subsequent sample is non-detect for the compound in question, the sequence is again considered acceptable for reporting.

15.3.1.2.3 All affected samples between the exceeding sample and the non-detect sample must be re-analyzed.

## 16.0 EQUIPMENT AND INSTRUMENT MAINTENANCE

16.1 Preventive maintenance on a HRGC/HRMS system involves the following basic areas:

16.1.1 Vacuum pumps for the inlets, source, and analyzer need a change of oil about every year or when system performance indicates it is needed.

16.1.2 The GC injection port is cleaned as needed, approximately once a week. It is recommended that the septum and injection port liner be replaced at the time of cleaning. Additionally, the gold plated seal should be cleaned or replaced.

16.1.3 Ion source maintenance is usage dependent. The type and quantity of samples that have been injected determine the frequency of ion source cleaning and filament replacement.

16.1.4 Autosampler maintenance is primarily that of cleanliness. Most autosamplers need their moving parts to be clean and lightly lubricated. The

most frequent corrective maintenance is that of changing the syringe, usually about once per month.

16.1.5 Instrument maintenance logs are kept with each instrument and serve as a record of all the maintenance that has been done on the instrument.

16.2 Non-Routine Maintenance Procedures (Special, Operational or Failure Mode Maintenance)

16.2.1 Service is provided to the instrument via the analyst, the in-house instrument service engineer, or a technical support specialist from the manufacturer. When instrument failure occurs, different parts of the instrument are isolated to determine the root cause. For example, the injection port may be capped off if a leak is suspected to prove the leak is/is not coming from that source. Instrument maintenance logbooks are kept for each instrument detailing the type of maintenance performed on the instrument and when it was performed. Preventive maintenance visits are scheduled annually for the mass spectrometers.

16.2.2 Analytical GC columns are clipped or replaced when the existing column shows signs of excessive degradation or the inability to properly resolve chromatographic peaks. Excessive peak tailing, poor responses, and baseline disturbances may also indicate that the column needs to be replaced.

## 17.0 DATA RECORDING, CALCULATION AND REDUCTION METHODS

17.1 Data are evaluated qualitatively and quantitatively using a software program such as Waters MassLynx, or equivalent data system.

17.2 Data are reviewed, and a hard copy is generated. If manual integrations are made, a hard copy of the manual integration is printed and initialed by the analyst and included with the raw data.

17.3 Additional supporting documentation, such as totals pages generated by the software may be included with the data.

17.4 Quantitative Analysis

17.4.1 The concentration (ng/L for aqueous, ng/g for solids) of each identified compound in the sample is calculated as follows:

$$\left[PCDD/PCDF\right] = \frac{\left(A_{unk}^{ion1} + A_{unk}^{ion2}\right)}{\left(A_{ES}^{ion1} + A_{ES}^{ion2}\right)} \times \frac{Q_{ES}}{W_{unk} \times D \times \overline{RF}}$$

Where:

$A_{unk}$ and $A_{ES}$ = the integrated area for each ion monitored.
$Q_{ES}$ = the amount of extraction standard added to the sample in nanograms
$W_{unk}$ = the initial sample aliquot size, in liters for waters and in grams for solids.
$D$ = (% moisture in sample)/100, or 1 for waters
$\overline{RF}$ = Average RF from the ICAL for the compound

17.4.2 The estimated detection limit (EDL) is calculated as follows:

$$\left[EDL_{ppt}\right] = 2.5 \times \frac{\left(H_{unk}^{ion1} + H_{unk}^{ion2}\right)}{\left(H_{ES}^{ion1} + H_{ES}^{ion2}\right)} \times \frac{Q_{ES}}{W_{unk} \times \overline{RF}}$$

Where:

$H_{unk}$ = the height of the noise present in each ion monitored.
$H_{ES}$ = the height of the extraction standard peak in each ion monitored.
2.5 = signal-to-noise factor for minimum height of peak.

17.4.3 The estimated maximum possible concentration (EMPC) is calculated in the same manner as a concentration (Section 17.4.1).

17.4.4 The concentration of each extraction and cleanup standard is calculated as follows:

$$\left[ES_{ng}\right] = \frac{\left(A_{ES}^{ion1} + A_{ES}^{ion2}\right)}{\left(A_{JS}^{ion1} + A_{JS}^{ion2}\right)} \times \frac{Q_{JS}}{\overline{RF}}$$

Where:

$A_{ES}$ and $A_{JS}$ = the integrated area for each ion monitored.
$Q_{JS}$ = the amount of injection standard added to the sample in nanograms
$\overline{RF}$ = Average RF from the ICAL for the compound

The cleanup standard concentration is calculated as above, substituting the area of the individual cleanup standard ions for the extraction standard ions.

17.4.5 Percent recovery is calculated as follows:

$$\%R = \frac{R_{ng}}{S_{ng}} \times 100$$

Where:

$R_{ng}$ = the amount of standard recovered in nanograms.
$S_{ng}$ = the amount of standard spiked in nanograms.

## 18.0 POLLUTION/CONTAMINATION

18.1 Work area should be maintained free of dust and dirt accumulations.

18.2 Fume hoods are utilized to remove fumes and reduce the risk of airborne contaminants to ensure personnel safety. Hoods are monitored in accordance with CF-FC-E-003 for Fume Hood Face Velocity Performance Checks.

18.3 The laboratory area is restricted to authorized personnel.

## 19.0 DATA REVIEW, APPROVAL AND TRANSMITTAL

19.1 A review process is used to insure the quality of the data. Raw data are reviewed first by the analyst, then by a second (peer) analyst or a data validator. When the analyst is satisfied that the data have been correctly processed and uploaded to the LIMS, a data report is generated from AlphaLIMS. The AlphaLIMS report along with the raw data and supporting documentation, such as a run log and case narrative, are submitted for review to the data validator or another experienced analyst. The reviewer goes through the raw data as if he/she was working it up for the first time and verifies that they are correct. In addition, he/she must make sure that the data have been correctly entered into AlphaLIMS. AlphaLIMS reports may be self-reviewed. If errors are discovered in either the raw data or the AlphaLIMS report, then the two analysts should discuss the differences and how best to resolve them. In some cases, the peer review process may uncover errors that lead to a sample being re-extracted or re-run. In cases such as these, a nonconformance report (NCR) should be completed and submitted to the Quality

department. It is recommended that a copy of the NCR be given to the prep analyst if it involves a re-extraction and that a copy be kept with the original data.

19.2 Once the data review has been completed by the reviewer, the batch is returned to the analyst for corrections (if applicable) and the status is updated from REVW to DONE in AlphaLIMS.

19.3 Data may be transmitted automatically to AlphaLIMS. This automatic "upload" procedure may be activated prior to data review or after data review is complete. In either case, the data recorded in AlphaLIMS are checked by the analyst for accuracy and completeness.

## 20.0 CORRECTIVE ACTION FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

Corrective action for out-of-control data may require instrument maintenance, re-analysis, re-extraction, or a more complex set of actions. When troubleshooting measures fail to bring an analytical process or data into control, a nonconformance report and/or corrective action should be initiated in accordance with CF-QS-E-004 for the Documentation of Nonconformance Reporting and Dispositioning and Control of Nonconforming Items, and CF-QS-E-002 for Conducting Corrective Action.

## 21.0 CONTINGENCIES FOR HANDLING THESE SITUATIONS

Troubleshooting is used to determine the appropriate action to take when an initial or continuing calibration, blank and/or laboratory control sample fails to meet the acceptance criteria defined for the method. Troubleshooting may involve one or more of the following actions:

21.1 If analytes in a multi-point calibration fail to meet specified criteria, additional standards for the failing compounds may need to be reanalyzed. If they still do not meet specifications, instrument maintenance or new standards may be required before work is continued.

21.2 If a continuing calibration fails to meet specified criteria, instrument tuning or inlet maintenance may be required. If routine maintenance procedures fail to produce a second consecutive calibration verification within acceptance criteria, then the laboratory must demonstrate acceptable performance after further corrective action with two consecutive calibration verifications, or a new initial calibration must be analyzed.

21.3 If a method blank fails to meet defined criteria, the source of contamination should be found and eliminated before proceeding with analysis.

21.4 If normal equipment and software operating procedures do not resolve trouble-shooting efforts, the manuals for software, hardware and other equipment discussed in this SOP are available for consultation and resolution. On-line support may be available from software and instrument manufacturers, as well. Any revisions, repairs or corrective actions required must be documented in accordance with the laboratory's Quality System as described in CF-QS-B-001.

## 22.0 RECORDS MANAGEMENT

22.1 Run logs are generated for each instrument each day that the instrument is run. These run logs serve as records of what is run on the instrument, including samples, QC, calibrations, tunes, etc. Additional information is provided in the run log, including the analyst's initials, run date and time, and file name.

22.2 Raw data are stored in the lab in filing cabinets and/or boxes as long as there is space available. When space runs out, the data are boxed and sent to storage.

22.3 All records generated as a result of this procedure are maintained as quality documents in accordance with CF-QS-E-008 for Quality Records Management and Disposition.

## 23.0 LABORATORY WASTE HANDLING AND DISPOSAL

Sample extracts that have been run are temporarily stored in case they have to be reanalyzed. Once space is no longer available to keep them in the lab, they are moved to Waste Disposal where they are handled and disposed in accordance with the Laboratory Waste Management Plan, CF-LB-G-001.

## 24.0 REFERENCES

24.1 Test Methods for Evaluating Solid Waste: Laboratory Manual Physical/ Chemical Methods, Volume 1B, SW-846, 3rd Edition, Feb. 2007. Method 8290A, "Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High Resolution Gas Chromatorgraphy/ High Resolution Mass Spectrometry (HRGC/HRMS)," Rev. 1, Feb. 2007. USEPA, Office of Solid Waste and Emergency Response, Washington, DC 20460.

24.2 Method 1613, "Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS," Rev. B, Oct. 1994. USEPA, Office of Water, Engineering and Analysis Division, 401 M Street SW, Washington, D.C. 20460.

24.3 Test Methods for Evaluating Solid Waste: Laboratory Manual Physical/ Chemical Methods, Volume 1B, SW-846, 3rd Edition, Feb. 2007. Method 0023A, "Sampling Method for Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofuran Emissions From Stationary Sources," Rev. 1, Dec. 1996. USEPA, Office of Solid Waste and Emergency Response, Washington, DC 20460.

24.4 Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition. "Compendium Method TO-9A, Determination of Polychlorinated, Polybrominated and Brominated/Chlorinated Dibenzo-p-Dioxins and Dibenzofurans in Ambient Air." January 1999. Center for Environmental Research Information, Office of Research and Development, USEPA, Cincinatti, OH 45268.

24.5 The NELAC Institute, (TNI) 2009 Standard, EL-V1-2009.

## 25.0 HISTORY

Revision 1: Section 15.3.1.2 added.

Revision 2: Absolute RT information added in 14.2.1.4; Calibration limit exceedance information added in section 15.3.1.2; Table 8 footnote describing RRT window adjustment to column used.

Revision 3: Method 0023A requirements added.

Revision 4: 2378-TCDF confirmation procedure and requirements added.

Revision 5: Injection standard changed from Tridecane to nonane. Discussion of equipment use and operation instructions was added, per DoD ELAP gray box 22.

Revision 6: Added TO-9a support and additional Tables for Method 8290.

Revision 7: Removed references to 8290 cleanup standard. Added TO-9a reference.

Revision 8: RRT limits for 1613 adjusted to method limits, except for three which have methods widths but db-5ms centers.

Revision 9: Added air matrix descriptions.

Revision 10: Table 9 updated. Maintenance rule for highly contaminated samples. TNI reference updated.

Revision 11: Changed EDL signal to noise value to 2.5. Updated Table references.

Revision 12: Added Table 13, Method Holding Times.

## TABLE 1: METHOD ANALYTES AND PQLs

| Analyte | Solid/Tissues (pg/g) | Aqueous (pg/L) | Air (pg) | CAS Number* |
|---|---|---|---|---|
| 2378-TCDD | 1 | 10 | 10 | 1746-01-6 |
| 12378-PeCDD | 5 | 50 | 50 | 40321-76-4 |
| 123478-HxCDD | 5 | 50 | 50 | 39227-28-6 |
| 123678-HxCDD | 5 | 50 | 50 | 57653-85-7 |
| 123789-HxCDD | 5 | 50 | 50 | 19408-74-3 |
| 1234678-HpCDD | 5 | 50 | 50 | 35822-39-4 |
| OCDD | 10 | 100 | 100 | 3268-87-9 |
| | | | | |
| 2378-TCDF | 1 | 10 | 10 | 51207-31-9 |
| 12378-PeCDF | 5 | 50 | 50 | 57117-41-6 |
| 23478-PeCDF | 5 | 50 | 50 | 57117-31-4 |
| 123478-HxCDF | 5 | 50 | 50 | 70648-26-9 |
| 123678-HxCDF | 5 | 50 | 50 | 57117-44-9 |
| 234678-HxCDF | 5 | 50 | 50 | 60851-34-5 |
| 123789-HxCDF | 5 | 50 | 50 | 72918-21-9 |
| 1234678-HpCDF | 5 | 50 | 50 | 67562-39-4 |
| 1234789-HpCDF | 5 | 50 | 50 | 55673-89-7 |
| OCDF | 10 | 100 | 100 | 39001-02-0 |

* Chemical Abstract Services number

# TABLE 2: MASS DESCRIPTORS

| Function (#) | Channel (#) | Mass (amu) | Dwell Time (ms) | I.C. Delay (ms) |
|---|---|---|---|---|
| 1 | 1 | 303.9016 | 50 | 10 |
| 1 | 2 | 305.8987 | 50 | 10 |
| 1 | 3 | 315.9419 | 50 | 10 |
| 1 | 4 | 304.9824 | 50 | 10 |
| 1 | 5 | 304.9824 | (Lock) | 10 |
| 1 | 6 | 317.9389 | 50 | 10 |
| 1 | 7 | 319.8965 | 50 | 10 |
| 1 | 8 | 321.8936 | 50 | 10 |
| 1 | 9 | 327.8847 | 50 | 10 |
| 1 | 10 | 331.9368 | 50 | 10 |
| 1 | 11 | 333.9339 | 50 | 10 |
| 1 | 12 | 339.8597 | 50 | 10 |
| 1 | 13 | 341.8568 | 50 | 10 |
| 1 | 14 | 375.8364 | 50 | 10 |
| 2 | 1 | 339.8597 | 50 | 10 |
| 2 | 2 | 341.8568 | 50 | 10 |
| 2 | 3 | 351.9 | 50 | 10 |
| 2 | 4 | 353.897 | 50 | 10 |
| 2 | 5 | 355.8546 | 50 | 10 |
| 2 | 6 | 357.8517 | 50 | 10 |
| 2 | 7 | 366.9792 | 50 | 10 |
| 2 | 8 | 366.9792 | (Lock) | 10 |
| 2 | 9 | 367.8949 | 50 | 10 |
| 2 | 10 | 369.8919 | 50 | 10 |
| 2 | 11 | 409.7974 | 50 | 10 |
| 3 | 1 | 373.8207 | 50 | 10 |
| 3 | 2 | 375.8178 | 50 | 10 |
| 3 | 3 | 380.976 | 50 | 10 |
| 3 | 4 | 380.976 | (Lock) | 10 |
| 3 | 5 | 383.8639 | 50 | 10 |
| 3 | 6 | 385.861 | 50 | 10 |
| 3 | 7 | 389.8156 | 50 | 10 |
| 3 | 8 | 391.8127 | 50 | 10 |
| 3 | 9 | 401.8559 | 50 | 10 |
| 3 | 10 | 403.853 | 50 | 10 |
| 3 | 11 | 445.7555 | 50 | 10 |
| 4 | 1 | 407.7818 | 50 | 10 |
| 4 | 2 | 409.7788 | 50 | 10 |
| 4 | 3 | 417.8253 | 50 | 10 |
| 4 | 4 | 419.822 | 50 | 10 |
| 4 | 5 | 423.7767 | 50 | 10 |
| 4 | 6 | 425.7737 | 50 | 10 |
| 4 | 7 | 430.9728 | 50 | 10 |
| 4 | 8 | 430.9728 | (Lock) | 10 |
| 4 | 9 | 435.8169 | 50 | 10 |
| 4 | 10 | 437.814 | 50 | 10 |
| 4 | 11 | 479.7165 | 50 | 10 |
| 5 | 1 | 441.7427 | 50 | 10 |
| 5 | 2 | 443.7398 | 50 | 10 |
| 5 | 3 | 454.9728 | 50 | 10 |
| 5 | 4 | 454.9728 | (Lock) | 10 |
| 5 | 5 | 457.7377 | 50 | 10 |
| 5 | 6 | 459.7348 | 50 | 10 |
| 5 | 7 | 469.778 | 50 | 10 |
| 5 | 8 | 471.775 | 50 | 10 |
| 5 | 9 | 513.6775 | 50 | 10 |

## TABLE 3: THEORETICAL ION RATIOS AND CONTROL LIMITS

| Level of Chlorination | Theoretical Ratio | Control Limits | |
|---|---|---|---|
| | | Lower | Upper |
| 4 | 0.77 | 0.65 | 0.89 |
| 5 | 1.55 | 1.32 | 1.78 |
| 6 | 1.24 | 1.05 | 1.43 |
| 6[a] | 0.51 | 0.43 | 0.59 |
| 7 | 1.05 | 0.88 | 1.20 |
| 7[b] | 0.44 | 0.37 | 0.51 |
| 8 | 0.89 | 0.76 | 1.02 |

[a] Used only for $^{13}$C-HxCDF
[b] Used only for $^{13}$C-HpCDF

## TABLE 4: 1613B LIMITS FOR TETRA ONLY TESTS

| Compound Name | Test Conc. (pg/µL) | CCAL Limits (pg/µL) | OPR Limits (pg/µL) | Sample Limits (pg/µL) |
|---|---|---|---|---|
| 2,3,7,8-TCDD | 10 | 8.2 - 12.3 | 7.3 - 14.6 | - |
| 2,3,7,8-TCDF | 10 | 8.6 - 11.6 | 8.0 - 14.7 | - |
| $^{13}C_{12}$-2,3,7,8-TCDD | 100 | 85 - 117 | 25 - 141 | 31 - 137 |
| $^{13}C_{12}$-2,3,7,8-TCDF | 100 | 76 - 131 | 26 - 126 | 29 - 140 |
| $^{37}Cl_4$-2,3,7,8-TCDD | 10 | 8.3 - 12.1 | 3.7 - 15.8 | 4.2 - 16.4 |

TABLE 5: INITIAL CALIBRATION CONCENTRATIONS

| | Concentration (pg/uL) | | | | |
|---|---|---|---|---|---|
| Analyte | CS-0.5 | CS-2 | CS-3 | CS-4 | CS-5 |
| 2378-TCDD | 0.25 | 2 | 10 | 40 | 200 |
| 2378-TCDF | 0.25 | 2 | 10 | 40 | 200 |
| 12378-PeCDD | 1.25 | 10 | 50 | 200 | 1000 |
| 12378-PeCDF | 1.25 | 10 | 50 | 200 | 1000 |
| 23478-PeCDF | 1.25 | 10 | 50 | 200 | 1000 |
| 123478-HxCDD | 1.25 | 10 | 50 | 200 | 1000 |
| 123678-HxCDD | 1.25 | 10 | 50 | 200 | 1000 |
| 123789-HxCDD | 1.25 | 10 | 50 | 200 | 1000 |
| 123478-HxCDF | 1.25 | 10 | 50 | 200 | 1000 |
| 123678-HxCDF | 1.25 | 10 | 50 | 200 | 1000 |
| 123789-HxCDF | 1.25 | 10 | 50 | 200 | 1000 |
| 234678-HxCDF | 1.25 | 10 | 50 | 200 | 1000 |
| 1234678-HpCDD | 1.25 | 10 | 50 | 200 | 1000 |
| 1234678-HpCDF | 1.25 | 10 | 50 | 200 | 1000 |
| 1234789-HpCDF | 1.25 | 10 | 50 | 200 | 1000 |
| OCDD | 2.5 | 20 | 100 | 400 | 2000 |
| OCDF | 2.5 | 20 | 100 | 400 | 2000 |
| Extraction Standards | | | | | |
| $^{13}$C-2378-TCDD | 100 | 100 | 100 | 100 | 100 |
| $^{13}$C-2378-TCDF | 100 | 100 | 100 | 100 | 100 |
| $^{13}$C-12378-PeCDD | 100 | 100 | 100 | 100 | 100 |
| $^{13}$C-12378-PeCDF | 100 | 100 | 100 | 100 | 100 |
| $^{13}$C-23478-PeCDF | 100 | 100 | 100 | 100 | 100 |
| $^{13}$C-123678-HxCDD | 100 | 100 | 100 | 100 | 100 |
| $^{13}$C-123478-HxCDD | 100 | 100 | 100 | 100 | 100 |
| $^{13}$C-123478-HxCDF | 100 | 100 | 100 | 100 | 100 |
| $^{13}$C-123678-HxCDF | 100 | 100 | 100 | 100 | 100 |
| $^{13}$C-123789-HxCDF | 100 | 100 | 100 | 100 | 100 |
| $^{13}$C-234678-HxCDF | 100 | 100 | 100 | 100 | 100 |
| $^{13}$C-1234678-HpCDD | 100 | 100 | 100 | 100 | 100 |
| $^{13}$C-1234678-HpCDF | 100 | 100 | 100 | 100 | 100 |
| $^{13}$C-1234789-HpCDF | 100 | 100 | 100 | 100 | 100 |
| $^{13}$C-OCDD | 200 | 200 | 200 | 200 | 200 |
| Cleanup Standards | | | | | |
| $^{37}$Cl-2378-TCDD | 0.25 | 2 | 10 | 40 | 200 |
| Injection Standards | | | | | |
| $^{13}$C-1234-TCDD | 100 | 100 | 100 | 100 | 100 |
| $^{13}$C-123789-HxCDD | 100 | 100 | 100 | 100 | 100 |

# TABLE 6: METHOD 1613B LCS LIMITS

| LCS Recovery Limits | | |
|---|---|---|
| **Analyte** | **Amount Spiked** | **Limit** |
| | **(pg/uL)** | **(pg/uL)** |
| 2378-TCDD | 10 | 6.7-15.8 |
| 12378-PeCDD | 50 | 35-71 |
| 123478-HxCDD | 50 | 35-82 |
| 123678-HxCDD | 50 | 38-67 |
| 123789-HxCDD | 50 | 32-81 |
| 1234678-HpCDD | 50 | 35-70 |
| OCDD | 100 | 78-144 |
| | | |
| 2378-TCDF | 10 | 7.5-15.8 |
| 12378-PeCDF | 50 | 40-67 |
| 23478-PeCDF | 50 | 34-80 |
| 123478-HxCDF | 50 | 36-67 |
| 123678-HxCDF | 50 | 42-65 |
| 123789-HxCDF | 50 | 39-65 |
| 234678-HxCDF | 50 | 35-78 |
| 1234678-HpCDF | 50 | 41-61 |
| 1234789-HpCDF | 50 | 39-69 |
| OCDF | 100 | 63-170 |
| | | |
| $^{13}$C-2378-TCDD | 100 | 20-175 |
| $^{13}$C-12378-PeCDD | 100 | 21-227 |
| $^{13}$C-123478-HxCDD | 100 | 21-193 |
| $^{13}$C-123678-HxCDD | 100 | 25-163 |
| $^{13}$C-1234678-HpCDD | 100 | 26-166 |
| $^{13}$C-OCDD | 200 | 26-397 |
| | | |
| $^{13}$C-2378-TCDF | 100 | 22-152 |
| $^{13}$C-12378-PeCDF | 100 | 21-192 |
| $^{13}$C-23478-PeCDF | 100 | 13-328 |
| $^{13}$C-123478-HxCDF | 100 | 19-202 |
| $^{13}$C-123678-HxCDF | 100 | 21-159 |
| $^{13}$C-123789-HxCDF | 100 | 17-205 |
| $^{13}$C-234678-HxCDF | 100 | 22-176 |
| $^{13}$C-1234678-HpCDF | 100 | 21-158 |
| $^{13}$C-1234789-HpCDF | 100 | 20-186 |
| | | |
| $^{37}$Cl-2378-TCDD | 10 | 3.1-19.1 |

## TABLE 7: METHOD 1613B ES (SAMPLES & LMB) RECOVERY LIMITS

| Compound Name | Amount Spiked (pg/µL) | Limits % |
|---|---|---|
| $^{13}C_{12}$-2,3,7,8-TCDD | 100 | 25 - 164 |
| $^{13}C_{12}$-1,2,3,7,8-PeCDD | 100 | 25 - 181 |
| $^{13}C_{12}$-1,2,3,4,7,8-HxCDD | 100 | 32 - 141 |
| $^{13}C_{12}$-1,2,3,6,7,8-HxCDD | 100 | 28 - 130 |
| $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD | 100 | 23 - 140 |
| $^{13}C_{12}$-OCDD | 200 | 17 - 157 |
| $^{13}C_{12}$-2,3,7,8-TCDF | 100 | 24 - 169 |
| $^{13}C_{12}$-1,2,3,7,8-PeCDF | 100 | 24 - 185 |
| $^{13}C_{12}$-2,3,4,7,8-PeCDF | 100 | 21 - 178 |
| $^{13}C_{12}$-1,2,3,4,7,8-HxCDF | 100 | 26 - 152 |
| $^{13}C_{12}$-1,2,3,6,7,8-HxCDF | 100 | 26 - 123 |
| $^{13}C_{12}$-2,3,4,6,7,8-HxCDF | 100 | 28 - 136 |
| $^{13}C_{12}$-1,2,3,7,8,9-HxCDF | 100 | 29 - 147 |
| $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF | 100 | 28 - 143 |
| $^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF | 100 | 26 - 138 |
| $^{37}Cl_4$-2,3,7,8-TCDD | 10 | 35 - 197 |

## TABLE 8: METHOD 1613B CONTINUING CALIBRATION LIMITS

| Compound Name | CCAL (pg/µL) | Limits (pg/µL) | Compound Name | CCAL (pg/µL) | Limits (pg/µL) |
|---|---|---|---|---|---|
| 2,3,7,8-TCDD | 10 | 7.8 - 12.9 | $^{13}C_{12}$-2,3,7,8-TCDD | 100 | 82 - 121 |
| 1,2,3,7,8-PeCDD | 50 | 39 - 65 | $^{13}C_{12}$-1,2,3,7,8-PeCDD | 100 | 62 - 160 |
| 1,2,3,4,7,8-HxCDD | 50 | 39 - 64 | $^{13}C_{12}$-1,2,3,4,7,8-HxCDD | 100 | 85 - 117 |
| 1,2,3,6,7,8-HxCDD | 50 | 39 - 64 | $^{13}C_{12}$-1,2,3,6,7,8-HxCDD | 100 | 85 - 118 |
| 1,2,3,7,8,9-HxCDD | 50 | 41 - 61 | $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD | 100 | 72 - 138 |
| 1,2,3,4,6,7,8-HpCDD | 50 | 43 - 58 | $^{13}C_{12}$-OCDD | 200 | 96 - 415 |
| OCDD | 100 | 79 - 126 | $^{13}C_{12}$-2,3,7,8-TCDF | 100 | 71 - 140 |
| 2,3,7,8-TCDF | 10 | 8.4 - 12 | $^{13}C_{12}$-1,2,3,7,8-PeCDF | 100 | 76 - 130 |
| 1,2,3,7,8-PeCDF | 50 | 41 - 60 | $^{13}C_{12}$-2,3,4,7,8-PeCDF | 100 | 77 - 130 |
| 2,3,4,7,8-PeCDF | 50 | 41 - 61 | $^{13}C_{12}$-1,2,3,4,7,8-HxCDF | 100 | 76 - 131 |
| 1,2,3,4,7,8-HxCDF | 50 | 45 - 56 | $^{13}C_{12}$-1,2,3,6,7,8-HxCDF | 100 | 70 - 143 |
| 1,2,3,6,7,8-HxCDF | 50 | 44 - 57 | $^{13}C_{12}$-2,3,4,6,7,8-HxCDF | 100 | 73 - 137 |
| 2,3,4,6,7,8-HxCDF | 50 | 44 - 57 | $^{13}C_{12}$-1,2,3,7,8,9-HxCDF | 100 | 74 - 135 |
| 1,2,3,7,8,9-HxCDF | 50 | 45 - 56 | $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF | 100 | 78 - 129 |
| 1,2,3,4,6,7,8-HpCDF | 50 | 45 - 55 | $^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF | 100 | 77 - 129 |
| 1,2,3,4,7,8,9-HpCDF | 50 | 43 - 58 | $^{37}Cl_4$-2,3,7,8-TCDD | 10 | 7.9 - 12.7 |
| OCDF | 100 | 63 - 159 | | | |

## TABLE 9: METHOD 1613B RELATIVE RETENTION TIME LIMITS

| Compound | RRT Reference | RRT Limits |
|---|---|---|
| 2,3,7,8-TCDD | 13C -2,3,7,8-TCDD | 0.999 - 1.002 |
| 1,2,3,7,8-PeCDD | 13C -1,2,3,7,8-PeCDD | 0.999 - 1.002 |
| 1,2,3,4,7,8-HxCDD | 13C -1,2,3,4,7,8-HxCDD | 0.999 - 1.001 |
| 1,2,3,6,7,8-HxCDD | 13C -1,2,3,6,7,8,-HxCDD | 0.997 - 1.003 |
| 1,2,3,7,8,9-HxCDD | 13C -1,2,3,6,7,8,-HxCDD | 0.997 - 1.016 |
| 1,2,3,4,6,7,8-HpCDD | 13C -1,2,3,4,6,7,8-HpCDD | 0.999 - 1.001 |
| OCDD | 13C –OCDD | 0.999 - 1.001 |
| 2,3,7,8-TCDF | 13C -2,3,7,8-TCDF | 0.999 - 1.003 |
| 1,2,3,7,8-PeCDF | 13C -1,2,3,7,8-PeCDF | 0.999 - 1.002 |
| 2,3,4,7,8-PeCDF | 13C -2,3,4,7,8-PeCDF | 0.999 - 1.002 |
| 1,2,3,4,7,8-HxCDF | 13C -1,2,3,4,7,8-HxCDF | 0.999 - 1.001 |
| 1,2,3,6,7,8-HxCDF | 13C -1,2,3,6,7,8-HxCDF | 0.996 - 1.004 |
| 2,3,4,6,7,8-HxCDF | 13C -2,3,4,6,7,8,-HxCDF | 0.999 - 1.001 |
| 1,2,3,7,8,9-HxCDF | 13C -1,2,3,7,8,9-HxCDF | 0.999 - 1.001 |
| 1,2,3,4,6,7,8-HpCDF | 13C -1,2,3,4,6,7,8-HpCDF | 0.999 - 1.001 |
| 1,2,3,4,7,8,9-HpCDF | 13C -1,2,3,4,7,8,9-HpCDF | 0.999 - 1.001 |
| OCDF | 13C –OCDD | 1.002 - 1.011 |
| 13C -2,3,7,8-TCDD | 13C -1,2,3,4-TCDD | 0.986 - 1.053 |
| 13C -1,2,3,7,8-PeCDD | 13C -1,2,3,4-TCDD | 0.849 - 1.416 |
| 13C -1,2,3,4,7,8-HxCDD | 13C -1,2,3,7,8,9-HxCDD | 0.980 - 1.003 |
| 13C -1,2,3,6,7,8-HxCDD | 13C -1,2,3,7,8,9-HxCDD | 0.983 - 1.005 |
| 13C -1,2,3,4,6,7,8-HpCDD | 13C -1,2,3,7,8,9-HxCDD | 1.068 - 1.092 |
| 13C –OCDD | 13C -1,2,3,7,8,9-HxCDD | 1.050 - 1.329 |
| 13C -2,3,7,8-TCDF | 13C -1,2,3,4-TCDD | 0.904 - 1.084 |
| 13C -1,2,3,7,8-PeCDF | 13C -1,2,3,4-TCDD | 0.893 - 1.318 |
| 13C -2,3,4,7,8-PeCDF | 13C -1,2,3,4-TCDD | 0.869 - 1.384 |
| 13C -1,2,3,4,7,8-HxCDF | 13C -1,2,3,7,8,9-HxCDD | 0.960 - 0.986 |
| 13C -1,2,3,6,7,8-HxCDF | 13C -1,2,3,7,8,9-HxCDD | 0.962 - 0.988 |
| 13C -2,3,4,6,7,8,-HxCDF | 13C -1,2,3,7,8,9-HxCDD | 0.957 - 1.019 |
| 13C -1,2,3,7,8,9-HxCDF | 13C -1,2,3,7,8,9-HxCDD | 0.973 - 1.043 |
| 13C -1,2,3,4,6,7,8-HpCDF | 13C -1,2,3,7,8,9-HxCDD | 1.026 - 1.068 |
| 13C -1,2,3,4,7,8,9-HpCDF | 13C -1,2,3,7,8,9-HxCDD | 1.050 - 1.144 |
| 37Cl -2,3,7,8-TCDD | 13C -1,2,3,4-TCDD | 0.988 - 1.051 |

**Due to the use of the DB-5MS column, some compounds exhibit slightly different elution times, resulting in RRT limits which vary from the method. The widths of the limits are the same as the method, only the center of the window has been adjusted to the DB-5MS's elution times.**

## TABLE 10: Method 8290 IS assignments

**Internal Standard References**
**Method 8290**

| Analytes | Internal Standards |
|---|---|
| 2378-TCDD | $^{13}$C-2378-TCDD |
| 12378-PeCDD | $^{13}$C-12378-PeCDD |
| 123478-HxCDD | $^{13}$C-123678-HxCDD |
| 123678-HxCDD | $^{13}$C-123678-HxCDD |
| 123789-HxCDD | $^{13}$C-123678-HxCDD |
| 1234678-HpCDD | $^{13}$C-1234678-HpCDD |
| OCDD | $^{13}$C-OCDD |
| 2378-TCDF | $^{13}$C-2378-TCDF |
| 12378-PeCDF | $^{13}$C-12378-PeCDF |
| 23478-PeCDF | $^{13}$C-12378-PeCDF |
| 123478-HxCDF | $^{13}$C-123678-HxCDF |
| 123678-HxCDF | $^{13}$C-123678-HxCDF |
| 123789-HxCDF | $^{13}$C-123678-HxCDF |
| 234678-HxCDF | $^{13}$C-123678-HxCDF |
| 1234678-HpCDF | $^{13}$C-1234678-HpCDF |
| 1234789-HpCDF | $^{13}$C-1234678-HpCDF |
| OCDF | $^{13}$C-OCDD |
| **Extraction Standards** | **Injection Standards** |
| $^{13}$C-2378-TCDD | $^{13}$C-1234-TCDD |
| $^{13}$C-12378-PeCDD | $^{13}$C-1234-TCDD |
| $^{13}$C-123678-HxCDD | $^{13}$C-123789-HxCDD |
| $^{13}$C-1234678-HpCDD | $^{13}$C-123789-HxCDD |
| $^{13}$C-OCDD | $^{13}$C-123789-HxCDD |
| $^{13}$C-2378-TCDF | $^{13}$C-1234-TCDD |
| $^{13}$C-12378-PeCDF | $^{13}$C-1234-TCDD |
| $^{13}$C-123678-HxCDF | $^{13}$C-123789-HxCDD |
| $^{13}$C-1234678-HpCDF | $^{13}$C-123789-HxCDD |
| **Injection Standards** | |
| $^{13}$C-1234-TCDD | NA |
| $^{13}$C-123789-HxCDD | NA |

## TABLE 11: 8290 Retention time limits

**Retention Time Limits**
***Method 8290***

| Analytes | Description | Limits |
|---|---|---|
| 2378-TCDD | 2,3,7,8-substituted congeners, which have an isotopically-labeled standard present in the sample extract | must be within -1 to +3 seconds of the isotopically-labeled standard |
| 12378-PeCDD | | |
| 123678-HxCDD | | |
| 123789-HxCDD | | |
| 1234678-HpCDD | | |
| OCDD | | |
| 2378-TCDF | | |
| 12378-PeCDF | | |
| 123678-HxCDF | | |
| 123789-HxCDF | | |
| 1234678-HpCDF | | |
| 123478-HxCDD | 2,3,7,8-substituted compounds that do not have an isotopically-labeled standard present in the sample extract | must fall within 0.005 retention time units of the relative retention time as determined from the daily routine calibration |
| 23478-PeCDF | | |
| 123478-HxCDF | | |
| 234678-HxCDF | | |
| 1234789-HpCDF | | |
| OCDF | | |
| Total TCDDs | Non-2,3,7,8-substituted target compounds | must be within the corresponding homologous retention time windows established by analyzing the column performance check solution, relative to an isotopically-labeled standard in the sample |
| Total PeCDDs | | |
| Total HxCDDs | | |
| Total HpCDDs | | |
| Total TCDFs | | |
| Total PeCDFs | | |
| Total HxCDFs | | |
| Total HpCDFs | | |
| $^{13}$C-2378-TCDD | Isotopically-labeled standards | No method limits: allowed to shift as long as the predicted RT of the native window defining isomers established by analyzing the column performance check solution remain within the descriptor switching time |
| $^{13}$C-12378-PeCDD | | |
| $^{13}$C-123678-HxCDD | | |
| $^{13}$C-1234678-HpCDD | | |
| $^{13}$C-OCDD | | |
| $^{13}$C-2378-TCDF | | |
| $^{13}$C-12378-PeCDF | | |
| $^{13}$C-123678-HxCDF | | |
| $^{13}$C-1234678-HpCDF | | |
| $^{13}$C-1234-TCDD | | |
| $^{13}$C-123789-HxCDD | | |

# TABLE 12: METHOD TO-9A MINIMUM REQUIREMENTS FOR INITIAL AND DAILY CALIBRATION

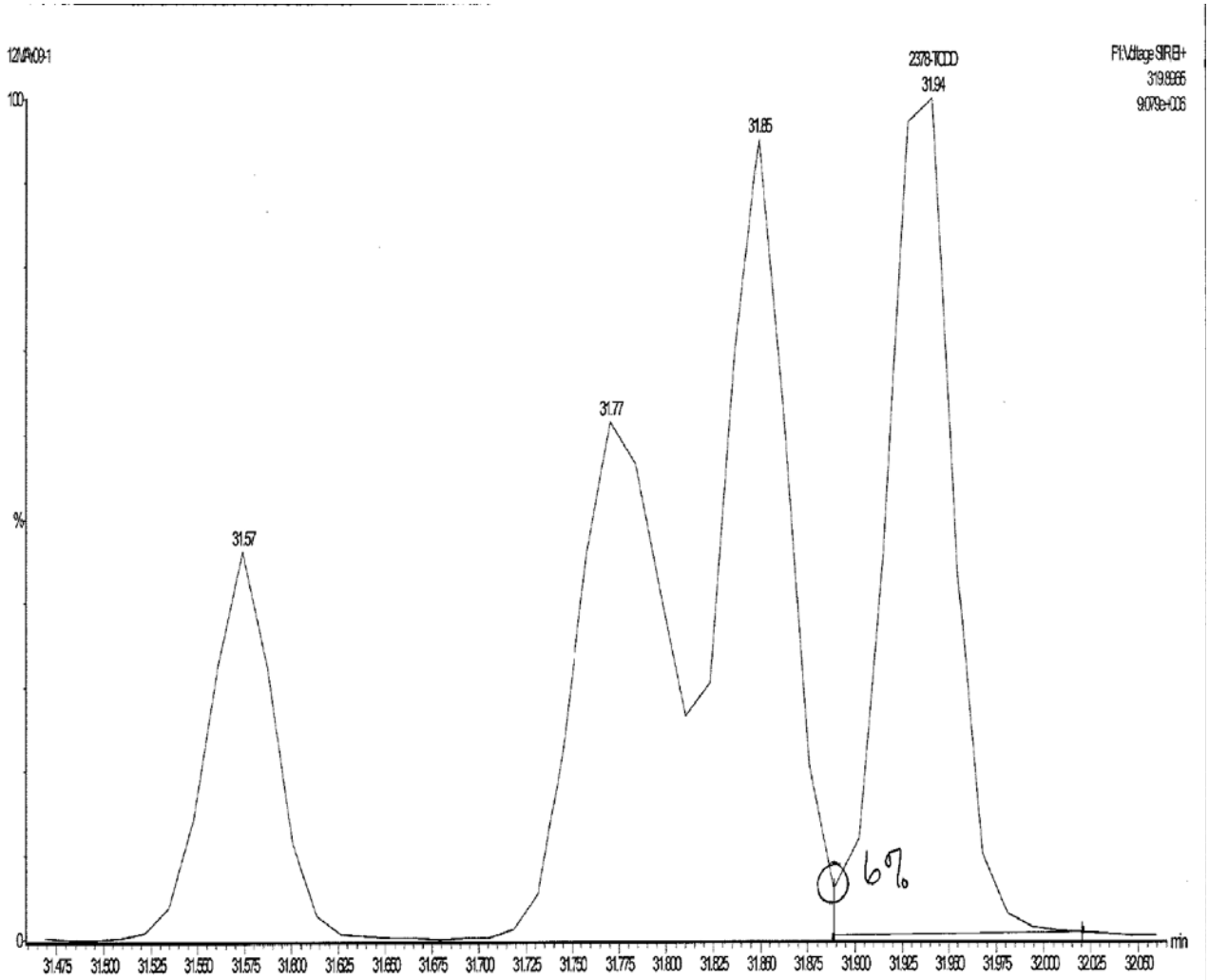
| Unlabeled Analytes | ICAL (RSD) | CVS (%D) |
|---|---|---|
| 2,3,7,8-TCDD | 25 | 25 |
| 2,3,7,8-TCDF | 25 | 25 |
| 1,2,3,7,8-PeCDD | 25 | 25 |
| 1,2,3,7,8-PeCDF | 25 | 25 |
| 2,3,4,7,8-PeCDF | 25 | 25 |
| 1,2,4,5,7,8-HxCDD | 25 | 25 |
| 1,2,3,6,7,8-HxCDD | 25 | 25 |
| 1,2,3,7,8,9-HxCDD | 25 | 25 |
| 1,2,3,4,7,8-HxCDF | 25 | 25 |
| 1,2,3,6,7,8-HxCDF | 25 | 25 |
| 1,2,3,7,8,9-HxCDF | 25 | 25 |
| 2,3,4,6,7,8-HxCDF | 25 | 25 |
| 1,2,3,4,6,7,8-HpCDD | 25 | 25 |
| 1,2,3,4,6,7,8-HpCDF | 25 | 25 |
| OCDD | 25 | 25 |
| OCDF | 30 | 30 |
| **Internal Standards** | | |
| 13C-2,3,7,8-TCDD | 25 | 25 |
| 13C-1,2,3,7,8-PeCDD | 30 | 30 |
| 13C-1,2,3,6,7,8-HxCDD | 25 | 25 |
| 13C-1,2,3,4,6,7,8-HpCDD | 30 | 30 |
| 13C-OCDD | 30 | 30 |
| 13C-2,3,7,8-TCDF | 30 | 30 |
| 13C-1,2,3,7,8-PeCDF | 30 | 30 |
| 13C-1,2,3,4,7,8-HxCDF | 30 | 30 |
| 13C-1,2,3,4,6,7,8-HpCDF | 30 | 30 |
| **Surrogate Standards** | | |
| 37Cl-2,3,7,8-TCDD | 25 | 25 |
| 13C-2,3,4,7,8-PeCDF | 25 | 25 |
| 13C-1,2,3,4,7,8-HxCDD | 25 | 25 |
| 13C-1,2,3,4,7,8-HxCDF | 25 | 25 |
| 13C-1,2,3,4,7,8,9-HpCDF | 25 | 25 |

## TABLE 13: METHOD HOLDING TIMES

| Method | Collection to Extraction | Extraction to Analysis |
|---|---|---|
| 8290A * | 30 days | 45 days |
| 1613B | 365 days | 365 days |
| DLM02.2 | 365 days | 365 days |
| M23 | 30 days | 45 days |
| TO-9a | 7 days | 40 days |
| CBC01.2 | 35 days collect to analysis | |
| 1668A/C | 365 days | 365 days |

* NOTE: The holding times listed in method 8290 are recommendations. PCDDs and PCDFs are very stable in a variety of matrices, and holding times under the conditions listed in this section may be as long as a year for certain matrices.

## FIGURE 1: 2378-TCDD CHROMATOGRAPHIC SEPARATION



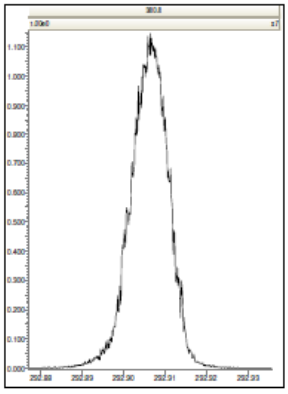
## FIGURE 2: INSTRUMENT RESOLVING POWER (EXAMPLE)

**Experiment Calibration Report** **MassLynx 4.1** Page 1 of 1

File: Experiment: dioxin_db5ms.exp Reference: pfk.ref Function: 1 @ 200 (ppm)

Printed: Saturday, June 09, 2012 10:43:58 Eastern Standard Time

M 292.9824 R 14455



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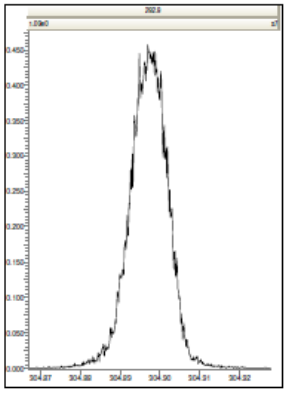
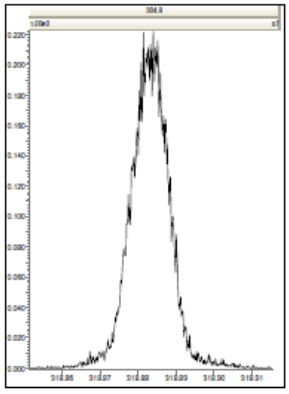


M 318.9792 R 14043



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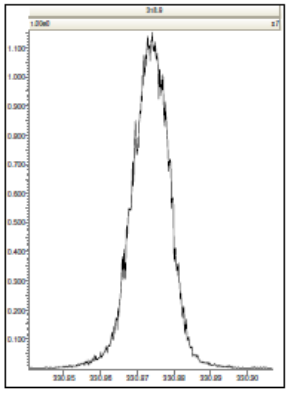

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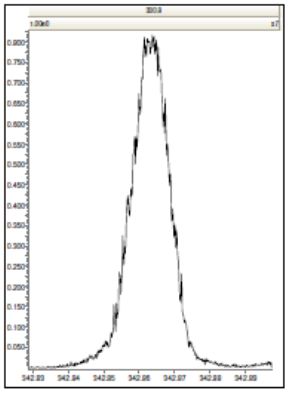
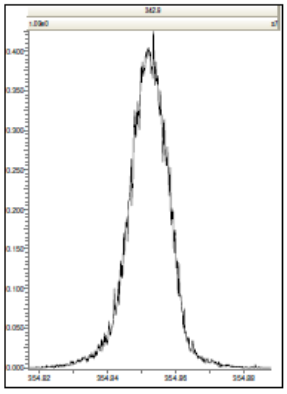


M 354.9792 R 12502



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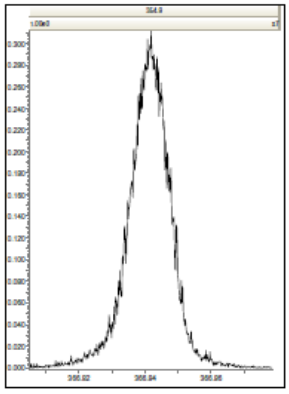
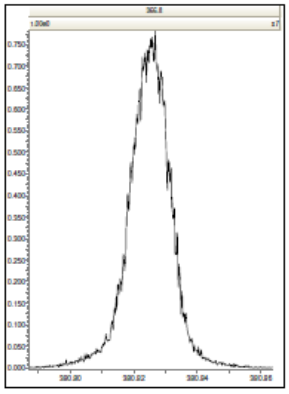


M 380.9760 R 13093



**RTI Laboratories, Inc.**
**31628 Glendale**
**Livonia, Michigan 48150**

# ANALYTICAL STANDARD OPERATING PROCEDURE

# SAMPLE PREPARATION FOR THE ANALYSIS OF CYANIDE

| | |
|---|---|
| **Analyte:** | **Cyanide** |
| **SOP#:** | **4500-CN_102213_R9** |
| **Method Reference:** | **Standard Methods 4500-CN C&E, SW-846 9012/9010** |
| **Issue Date:** | **February 28, 2005** |
| **Revision No.:** | **8** |
| **Revision Date:** | **October 21, 2013** |

**Reviewed and Approved: October 21, 2013**

Director, Quality Management: Charles O'Bryan

Director, Environmental Services: Yemane Yohannes

**STANDARD OPERATING PROCEDURE**

**ANALYSIS OF CYANIDE**

**SOP#: 4500-CN_102113_R9**

## TABLE OF CONTENTS

## 1.0 Scope and Application:

1.1 Introduction

RTI Laboratories, Inc. has prepared this document to detail the Standard Operating Procedure (SOP) for the preparation of samples for the analysis of cyanide in drinking, surface and saline waters, domestic and industrial waste and solid samples.

A detailed description of the instrumentation, calibration, run parameters and quality control procedures is included in this SOP. For definition of terms not specifically defined in this document refer to RTI QAP Section 16.

1.2 Summary of Method

1.2.1 Cyanide is distilled from water samples for 90 minutes. The distillate is reacted with a pyridine/barbituric acid solution, in the presence of Chloramine T to give a pink/red colored complex with an absorbance measured at 575nm. Analysis is performed according to the procedures detailed in the Kone analyzer SOP and is based on Standard Methods 4500-CN E.

## 2.0 Safety Precautions

2.1 Waste materials submitted for analyses may contain hazardous components. Uncharacterized waste samples should be handled in a manner that minimizes exposure and personal contact. Analysis should be performed in a fume hood.

2.2 Cyanide is an established toxic substance and other chemicals used should be regarded as a potential health risk. Sample preparation and analysis is performed in a manner designed to minimize exposure using routine good laboratory practices.

## 3.0 Sample Requirements and Sample Handling Procedures

3.1 Samples are received in accordance with RTI Laboratories, Inc. Standard Operating Procedure for Sample Receipt and Custody (SRC001-A). Appropriate U. S. Environmental Protection Agency (EPA) sample handling procedures and sample preservation recommendations are followed.

3.1.1 Samples are collected in pre-preserved (with sodium hydroxide) clean 250 – 1000 mL plastic bottles and maintained on ice at 4 degrees C following collection. Samples requiring analysis for amenable cyanide are collected in amber bottles and preserved the same as the total cyanide.

3.1.2 Soil, sludge and solid samples are collected in pre cleaned wide mouth glass jars and stored at 4 degree C.

3.1.3 Sample volume minimum requirements: 50 mL, aqueous – 10 g, solids.

3.1.4 Maximum sample holding time is 14 days.

## 4.0 MDL, LOD, LOQ, Linear Range, Accuracy and Precision

4.1 The method detection limit (MDL) is statistically defined at the 99% confidence level according to 40 CFR Part 136 App. B. Seven replicates containing all of the analytes of interest at a concentration level of 1-5 times the estimated D.L. are analyzed and the standard deviation is calculated. The Student's T Value for the 7 replicates (3.143) is multiplied by the standard deviation of the analyte to calculate the MDL. MDLs are performed on instrument set up and following significant changes to the instrument, method or personnel. MDLs are kept on file in the Laboratory. MDLs and reporting limits are incorporated into the applicable test code in the Omega LIMS.

4.2 The LOD (limit of detection) is determined by spiking reagent water at 1-4 times the MDL and prepared using the same procedure as samples. Analytes must be present at levels 3 times or greater than the blank response (greater than 3 times the signal to noise ratio). The concentration used is the LOD for that analyte. LOD determinations must be performed quarterly.

4.3 The LOQ (limit of quantification) is determined by spiking reagent water at the reporting limit (RL/CRQL) and prepared in the same manner as samples. Analyte recovery must be within 20% of the expected concentration. The concentration used and successfully recovered is the LOQ for that analyte. LOQ determinations must be performed quarterly.

4.4 Initially accuracy and precision at the LOQ is determined by spiking 4 aliquots of reagent water at the reporting limit (RL/CRQL) and prepared using the same procedure used for samples. The average recovery must be within 20% of the expected value and the %RSD must be less than 15%.

4.5 LOD/LOQ determinations that do not meet the specifications above require repeat analysis, adjustment to the spiking levels and/or reporting limits, repeating the MDL determination at adjusted concentrations if required and repeat LOD/LOQ determinations.

4.6 The accuracy and precision for this method are determined by analyzing four aliquots from a Laboratory Control Sample containing the element(s) of interest at the mid-level of the calibration range. Percent recovery, standard deviation, and the relative standard deviation are calculated for each analyte and documents are kept on file in the laboratory.

4.7 Reporting Limit = 0.01 mg/L, aqueous – 1 mg/Kg, solids. The linear range for the procedure is 0.01 – 0.5 mg/L.

## 5.0 Interferences

5.1 Known interferences are aldehydes, nitrate-nitrite, oxidizing agents such as chlorine, thiocyante, thiosulfate, and sulfide. Chlorine decomposes most of the cyanide. To eliminate the chlorine treat the sample with sodium thiosulfate, use only 0.1 gram per 100mL of sample.

5.2 Nitrate and nitrite present in sample will results in a positive interference. To remove nitrate-nitrite 2 grams of sulfamic acid in added per 50mL of sample.

5.3 Sulfides will interfere with the analytical procedure and can be remove by the addition of lead carbonate.

## 6.0 Apparatus and Materials

6.1 Midi-Stil Cyanide distillation unit

6.2 Cyanide glassware

6.3 Konelab Analyzer.

6.4 Volumetric Flasks, 100mL; 250mL; 500mL; and 1 Liter – Class A.

6.5 Borosilicate Glass Boiling Beads - WR 26396-630

6.6 50 mL plastic centrifuge tubes.

6.7 Vacuum Pump

6.8 Disposable cups - Gordon Food Service

6.9 Potassium Iodide-starch test paper.

6.10 Amber safe light for amenable cyanide

6.11 Stir plate

## 7.0 Reagents

7.1 Sodium Hydroxide

7.2 Cyanide Primary and Second Source Standard 1000 mg/L (two different vendors). Prepare a 50mg/L working solutions by diluting 2.5 mL of the standard to 50 mL DI water. Prepared fresh each use.

7.3 Sodium thiosulfate

7.4 Pyridine

7.5 Barbituric acid

7.6 Chloramine-T

7.7 Chloramine-T solution – (1.0g chloramine-T in 100 mL DI water). Commercially obtained. Prepare weekly and store refrigerated.

7.8 Pyridine Barbituric acid solution – (6.0g barbituric acid, 30mL pyridine, 6mL concentrated HCl diluted to 100mL with water). Store at 4 deg. C in dark. Discard after 1 week.

7.9 Sodium dihydrogenphosphate 13.8g of $NaH_2PO_4.H_2O$ in 100mL DI water. Store refrigerated.

7.10 Sulfuric Acid - VWR JT9673-33

7.11 Magnesium chloride Solution 51% - Commercially obtained. Store at 4 deg. C.

7.12 Reagent Grade DI water.

7.13 10N NaOH solution: Dissolve 400g of NaOH in 1 Liter of DI water, caution, solution will be very hot, do not handle until cooled.

7.14 1.25N NaOH solution: 125mL of 10N NaOH in 1 Liter of DI water.

7.15 0.25N NaOH solution: 25mL of 10N NaOH in 1 Liter of DI water.

7.16 Sulfuric Acid Solution (1:1) In 500mL volumetric flask, add 250mL of concentrated Sulfuric acid to 250mL of DI water, Stir until cool.

7.17 Calcium hypochlorite (0.35M) 5g calcium hypochlorite in 100mL DI water.

7.18 Sulfamic acid (0.4N) dissolve 4g in 1L water

7.19 Acsorbic acid

7.20 Acetic acid buffer, pH 4.0: Dissolve 243 g of sodium acetate in 400 ml DI water, add 480 g concentrated acetic acid and dilute to 1 liter final volume with DI water.

7.21 All reagents and standards prepared must be logged in the appropriate standards/reagents log labeled with a minimum:

7.21.1 Identity of the material
7.21.2 Concentration of the solution
7.21.3 Date prepared
7.21.4 Initials of analyst preparing the solution
7.21.5 Expiration date.

## 8.0 Preparation of Standards and Calibration Procedure

8.1 The correlation coefficient of the calibration curve must be >0.995 to continue with the analysis of samples. If this criterion is not met the calibration standards must be re-analyzed or new standards prepared and analyzed until an acceptable cc is obtained.

8.2.1 From the 50-mg/L working standard (Sec. 7.2), pipette 0.5 mL into a 50 mL volumetric flask and dilute to volume. The concentration of this standard is 0.5 mg/L. Program the instrument to prepare calibration standards at 0.5, 0.25, 0.1, 0.05, 0.025, 0.02 and 0.1.

8.2 A continuing calibration verification standard is prepared with each batch of samples. From the 50-mg/L working standard (Sec. 7.2), pipette 0.25 mL into a 50 mL volumetric flask and dilute to volume. The concentration of this standard is 0.25 mg/L. Process the CCV with the samples according to the procedure in Sec. 9.

8.2.1 The CCV is analyzed following calibration, at the beginning of each analytical sequence for continuing calibration verification, after every 10 samples and at the end of the analytical sequence.

8.2.2 The percent recovery for each CCV must be within 90-110%. Samples that are not bracketed by acceptable CCVs must be re-analyzed.

8.3 Reporting limit verification standard (CRQL) is prepared with each batch of samples. From the 0.5 mg/L working standard (Sec. 7.2), pipette 100 µL into a 50 mL volumetric flask and dilute to volume. The concentration of this standard is 0.01 mg/L. Process the CRQL with the samples according to the procedure in Sec. 9.

8.3.1 The CRQL is analyzed at the beginning and end of each analytical sequence.

8.3.2 The percent recovery for each CRQL must be within 80-120%.

8.4 Prepare a laboratory control sample (LCS) for each batch of twenty or less samples by adding 0.1 mL of the second source working standard solution (Section 7.2) to 50 mL DI water. Expected concentration is 0.1 mg/L.

## 9.0 Sample Preparation-Distillation

9.1 Allow samples to warm to room temperature.

9.2 Test all samples with starch iodide paper to determine if chlorine is present. If the paper turns blue add ascorbic acid until the paper no longer turns.

9.3 Test all samples for sulfide content by placing a drop of sample on lead acetate paper moistened with acetic acid buffer solution (Sec. 7.20). Darkening of the paper indicates a positive result. Add lead acetate or lead carbonate to the sample and re-test. Repeat procedure until there is no darkening of the acidified lead acetate test paper.

9.4 For amenable cyanide all steps through the treatment are done under amber light to avoid the exposure of the sample to fluorescent or sunlight. To one aliquot of the sample in a beaker with stirring, add hypochlorite (7.14) drop wise until an excess of chlorine is indicated using starch iodide paper. Stir the sample continuously for one hour, maintaining the pH between 11 and 12 using sodium hydroxide (7.12). After 1 hour, add sodium thiosulfate until the KI-starch indicator paper indicates the no residual chlorine remains. Distill both the treated and an untreated aliquot.

9.5 Prepare samples for distillation by adding 50mL or an aliquot diluted to 50mL for aqueous samples to the glass cyanide tube in the rear of the mini-still.

9.6 For soil/solid materials add 2.5 g of sample to the glass cyanide tube in the rear of the mini-still and then add 50mL of water.

9.7 Add a few glass-boiling beads to the tubes containing samples and quality control samples.

9.8 To the absorption tubes in the front of the mini-still, add 50mL of 0.25N NaOH.

9.9 For the CCV (0.25mg/L) add 0.25 mL of the second source standard (Section 7.2). For the LCS 0.1 mg/L) and MS/MSD (0.25mg/L) add 0.1mL and 0.25mL of the primary solution respectively.

9.10 Assemble glassware. First, attach the distillation heads to the sample tubes in the rear of the still. Next, attach the condensers to the distillation heads. Next, connect the absorption tube heads to the absorption tubes. Finally, connect the tubing that runs from the absorption tube heads to the vacuum and distillation heads. The top tube should connect to the distillation tube head and the lower

tube connects to the vacuum source located at the front of the mini-still. Make sure all fittings are seated firmly before turning on the vacuum.

9.11 Turn on the vacuum and cooling water. The cooling water should be set at 1.3 mL/min using the meter located on the left of the mini-still. Adjust the airflow through each of the samples using the adjustment knobs on the front. The flow should be approximately the same through all. If it appears that the sample will foam out of the sample cylinder and into the collection cylinder, try lowering the airflow. Is the sample still foams over it is necessary to use a smaller aliquot of the sample.

9.12 Add 5 mL of sulfamic acid through the air intake tube.

9.13 Add 5mL of 1:1 $H_2SO_4$ and 2mL $MgCl_2$ to the air inlet tube.

9.14 Turn on unit and bring the sample to boiling and maintain that temperature for at least 60 min.

9.15 Discontinue heating but continue airflow for 15 min.

9.16 After the distillation is complete, let the samples cool to room temperature.

9.17 When cool the distillates are quantitatively transferred to a 50 ml plastic centrifuge tube and brought to a final volume of 50 ml with DI water.

## 10.0 Diagram/Table

10.1 Reserved.

## 11.0 Analytical Procedure

11.1 The KONE analyzer is turned on and the cyanide program is selected. Samples are added to the sample cups and loaded into the racks. The first spot in the racks must have the CCV followed by the method blank, LCS and the samples with required MS/MSD. The KONE analyzer will run the CCV after each ten analysis and at the end of the batch. This program allows for the automatic addition and mixing of reagents, incubation and analysis of the sample.

11.2 Daily Start Up.

11.2.1 Fill the reagent water jug located in the lower purple drawer of the Konelab analyzer with DI water, being careful not to introduce any contamination to the jug or the nozzle that goes into the jug.

11.2.2 Replace the reagent water jug.

11.2.3 Discard the used cuvettes located in the top purple drawer of the Konelab analyzer.

11.2.4 Replace the discarded cuvette holder, being careful to position it correctly.

11.2.5 Turn on computer before the Konelab instrument.

11.2.6 After the Konelab software starts, turn on the Konelab unit at the rear right of the unit.

11.2.7 After the software connects the Konelab analyzer to the computer, a message should appear in yellow to the top left of the screen stating, “startup needed.”

11.2.8 To perform startup press the button on the lower left of the screen labeled ”Startup (f1)”.

11.3 Calibration.

11.3.1 Load calibration standards (see Loading Sample Segments section of this document).

11.3.2 From the main menu, select” Calibr./QC Selection (F6)”.

11.3.3 From the next screen, select the method or test you wish to calibrate by left clicking on the method name so that the name is highlighted.

11.3.4 Select, “Calibrate (F1)”.

11.3.5 Return to the main menu. To start the analysis press the green button on the keyboard where the “page up” button would normally be.

11.3.6 When the calibration is complete a message will appear

11.4 Loading Sample Segments.

11.4.1 From the main menu, select “Samples” from the top of the screen.

11.4.2 From the bottom of the screen, select “More (F8)”, this will give you the next page of menu options.

11.4.3 From the bottom of the screen, select “Sample Segment (F5)”.

11.4.4 The screen will now show 14 spaces (in the order and spacing of a sample segment).

11.4.5 Choose the correct sample segment from the menu at the top left of the screen. It is important that correct one is used because the segments have a bar coding that the instrument uses to distinguish the individual segments. The segments above the dashed line are in the instrument; those below are not in the instrument.

11.4.6 For a calibration std or a CCV std, use down arrow to the left of each sample location, the named std to use will appear in a dropdown menu. The standards above the dashed line are for calibration curves; the standards below the dashed lines are control std (CCV). For CCV standards use a 13mm x 100mm glass test tube because each method has a CCV std analyzed every 10 samples and a 2ml sample cup will not be enough for an average batch of samples. Also for the 13mm x 100mm glass test tubes, a sharpie marker must be used to darken the area on the test tube near the bar code on the segment so that the instrument reads the size of the test tube correctly.

11.4.7 After typing a sample name into the correct position on the segment press enter or tab to advance to the next position.

11.4.8 After naming and correctly filling the sample cups in the segment, the samples must have an analysis request assigned. To assign a request, use the mouse and left click on the first sample (not std), this will take you to another screen.

11.4.9 Notice the information in the grey area in the middle of the screen. The segment number is there, samples 1 to 14 are also there with little orange test tubes for each position that was given a sample name.

11.4.10 Left click the mouse on the first sample position and then left click on the test requested on the right window. The request should now appear on the left window with the samples name appearing at the top in a white box. It is very important to take the time and ensure the correct test is selected. IF THE WRONG TEST IS CHOSEN AND THE REAGENT VIALS FOR THE INCORRECT TEST ARE CLOSED THE SAMPLE PROBE NEEDLE COULD BREAK AND REQUIRE AN EXTENSIVE REPAIR.

11.4.11 At the bottom of this screen choose “insert segment (F2)”.

11.4.12 Follow the instructions on screen.

11.4.13 Go to the main menu by choosing main from the top right of the screen.

11.4.14 Then back to the main menu, to start the analysis press the green button on the keyboard where the “page up” button would normally be.

11.5 Loading Reagents.

11.5.1 Place the reagent tray in the reagent loading rack before starting analysis. Make sure tray is tight in the position on the rack.

11.5.2 Select method to be analyzed.

11.5.3 From the main menu, select “Reagent” from the top of the screen. Reagent box appears on the screen. This page shows all the reagents required for each method.

11.5.4 Uncap reagent vials for that particular method.

11.5.5 At the end of the day when analysis is complete all the reagents are stored in the refrigerator next to the walk in cooler.

11.6 Loading Cuvettes: Cuvettes should be loaded very carefully in the cuvette compartment (following the instructions on the cuvette wrapper). Note: Don’t touch the cuvette with your fingers.

11.7 On completion of analysis, from main menu, select results. Print results.

11.8 Accept page.

11.9 From the main menu, select F4 from the bottom of the screen.

11.10 Select test.

11.11 Then click F2 for selected report or F3 for all reports.

11.12 Daily Shutdown.

11.12.1 From the main menu, select the button at the lower left labeled “ standby (f2)”.

11.12.2 The instrument will prompt you to insert the wash solution into the stat position labeled “wash”. The wash solution is 4.5%NaOCl + NaOH <1%.

11.12.3 After completing the standby command, you will be prompted to remove the wash solution.

11.12.4 To close the Konelab software. From the main menu choose “more (f8)”.

11.12.5 From the next list of menu items at the bottom of the screen choose “ Management (f3)”.

11.12.6 From the next list of menu items at the bottom of the screen choose " more (f8)"

11.12.7 From the next list of menu items at the bottom of the screen choose " exit (f3)". This will close the Konelab software.

11.12.8 From the Win NT desktop screen , press the" start" button and choose " shutdown" and choose shutdown and then pres ok.It is now all right to shut off the power to the Konelab analyzer at the rear of the analyzer.

11.13 Test Flow

11.13.1 Sample and dilution:

Volume(µL):100
Disp. with: Extra
Volume(µL): 20
Dilution with: Special dil. (0.25N NaOH)
Wash reagent: [None]
Raw sample disp. with: Extra
Volume(µL): 20
Special diluent: 0.25N NaOH
Diluent disp. with: Extra
Volume(µL): 20

11.13.2 Reagent

Reagent: CN Buffer (sodium dihydrogenphosphate)
Volume(µL): 30
Disp with: Extra
Volume(µL): 20
Wash reagent: [None]

11.13.3 Reagent

Reagent: CN Chlor T (Choramine T)
Volume(µL): 4
Disp. with: Extra
Volume(µL): 20
Wash reagent: [None]

11.13.4 Incubation

Time(sec.): 90

11.13.5 Endpoint

Blank
Resp. min (A): *
Resp. max (A): *

11.13.6 Reagent

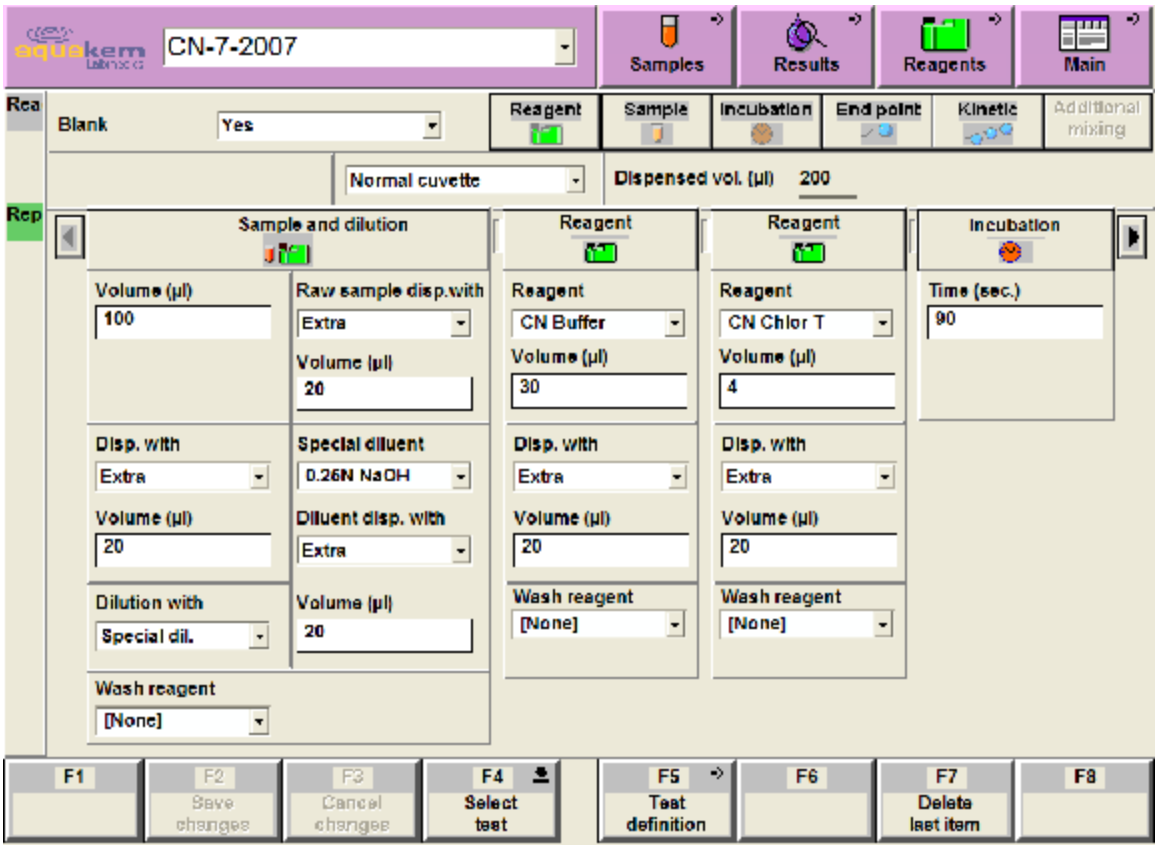
Reagent: CN Pyr Bar (Pyridine/barbituic acid solution)
Volume(µL): 10
Disp. with: Water
Volume(µL): 56
Wash reagent: [None]

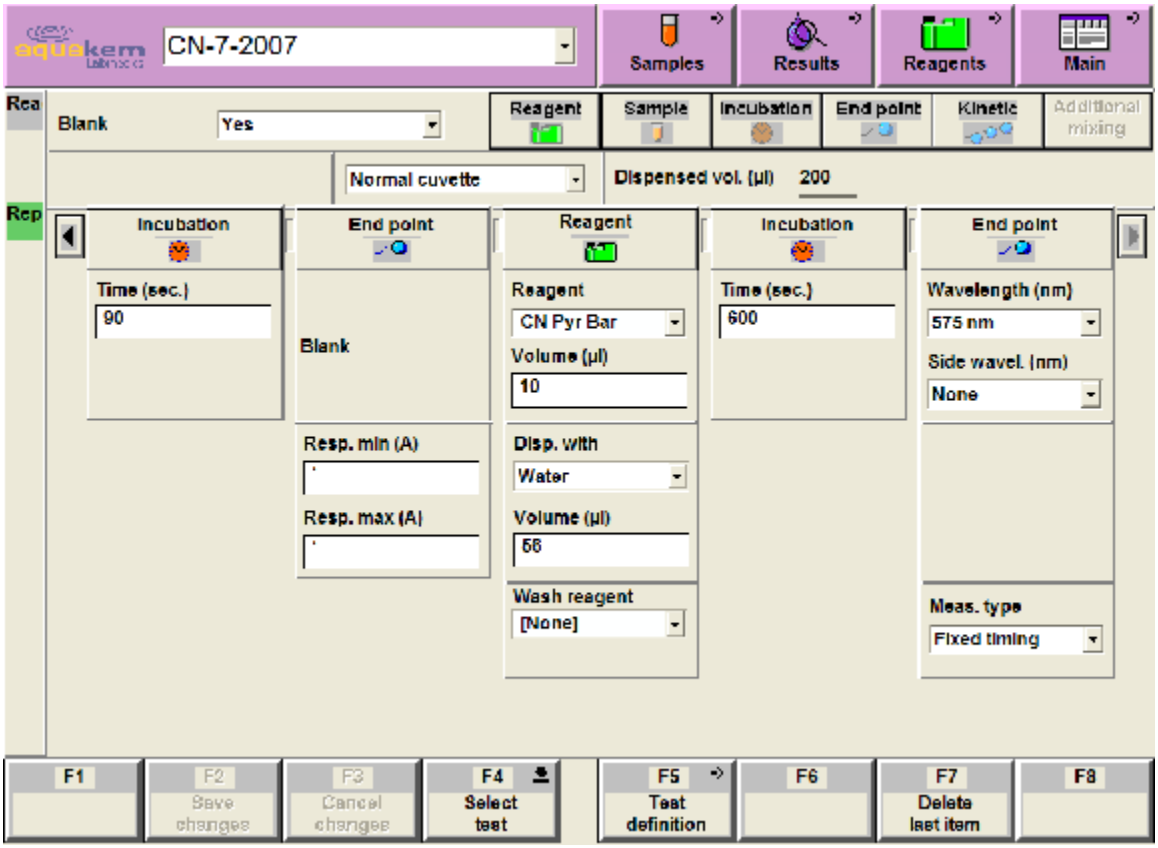
11.13.7 Incubation

Time(sec.): 600

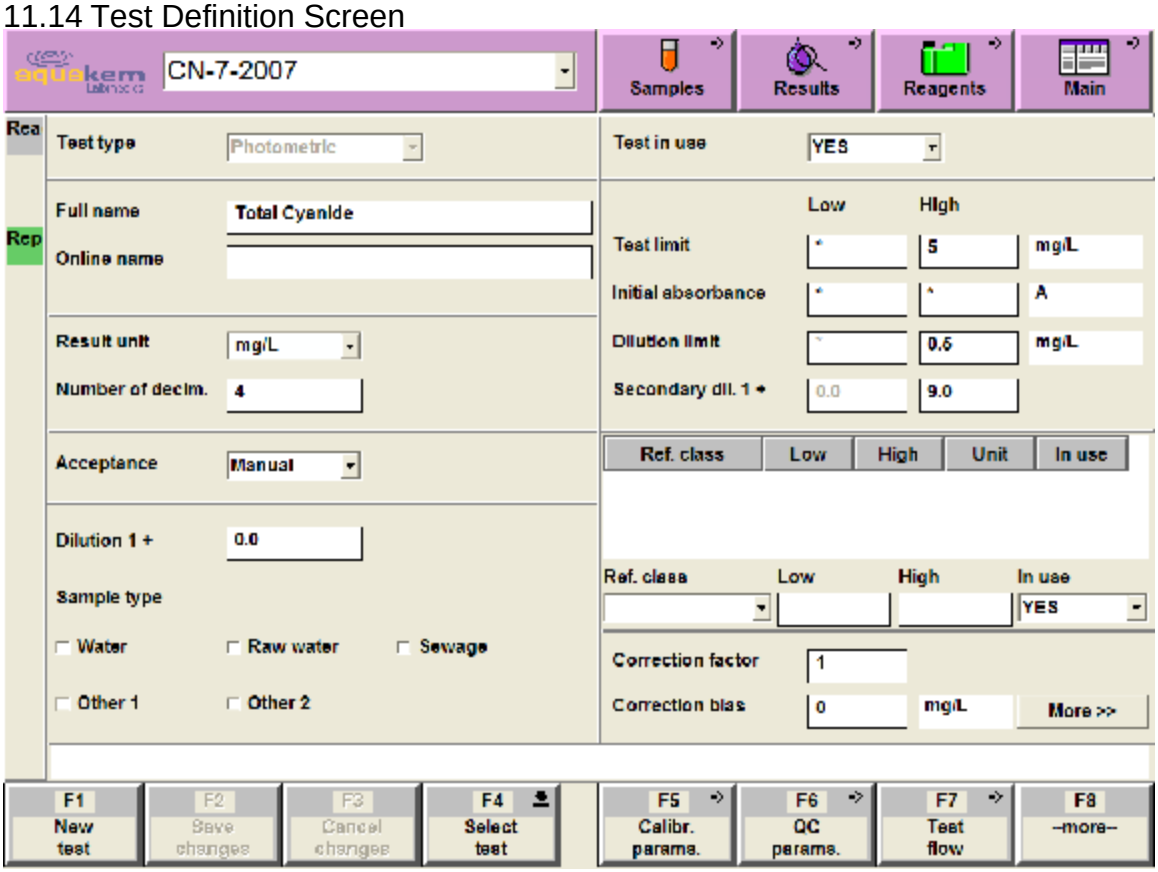
11.13.8 End point

Wavelength(nm): 540
Side wavel.(nm): None
Meas. Type: Fixed timing

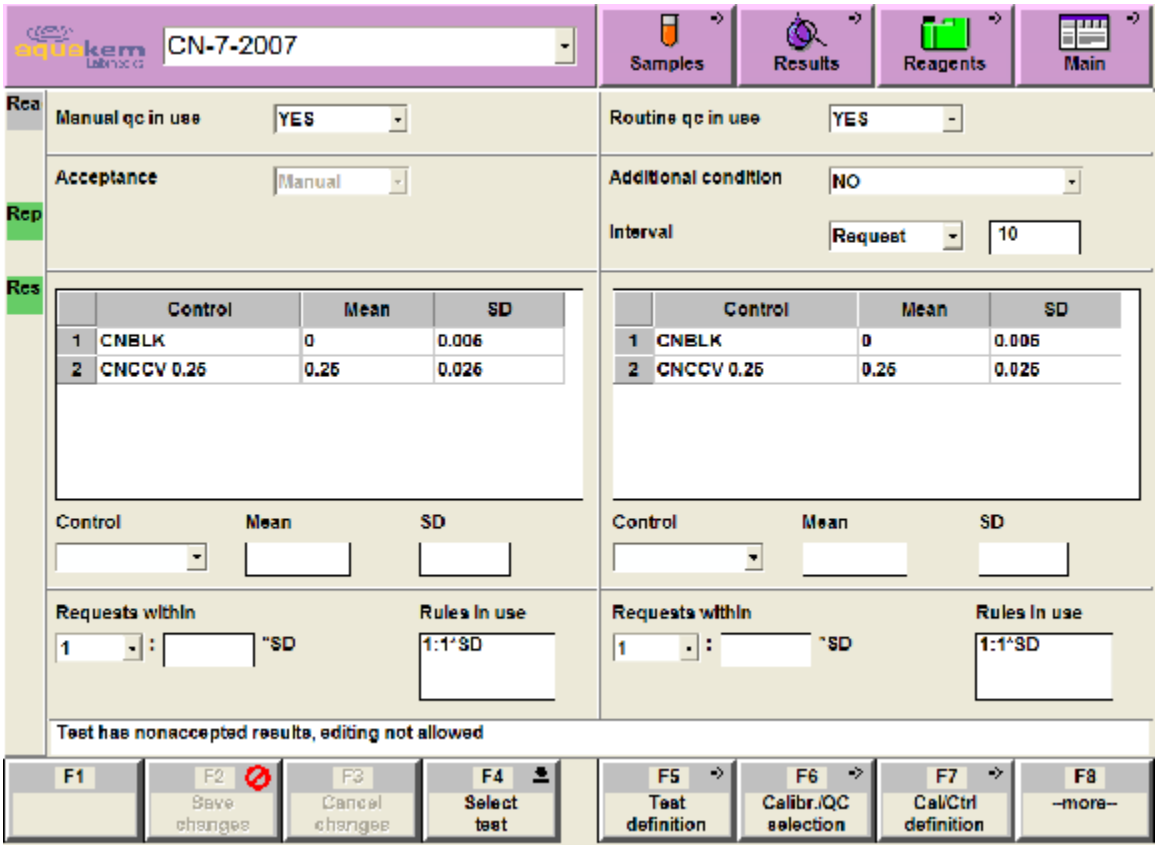




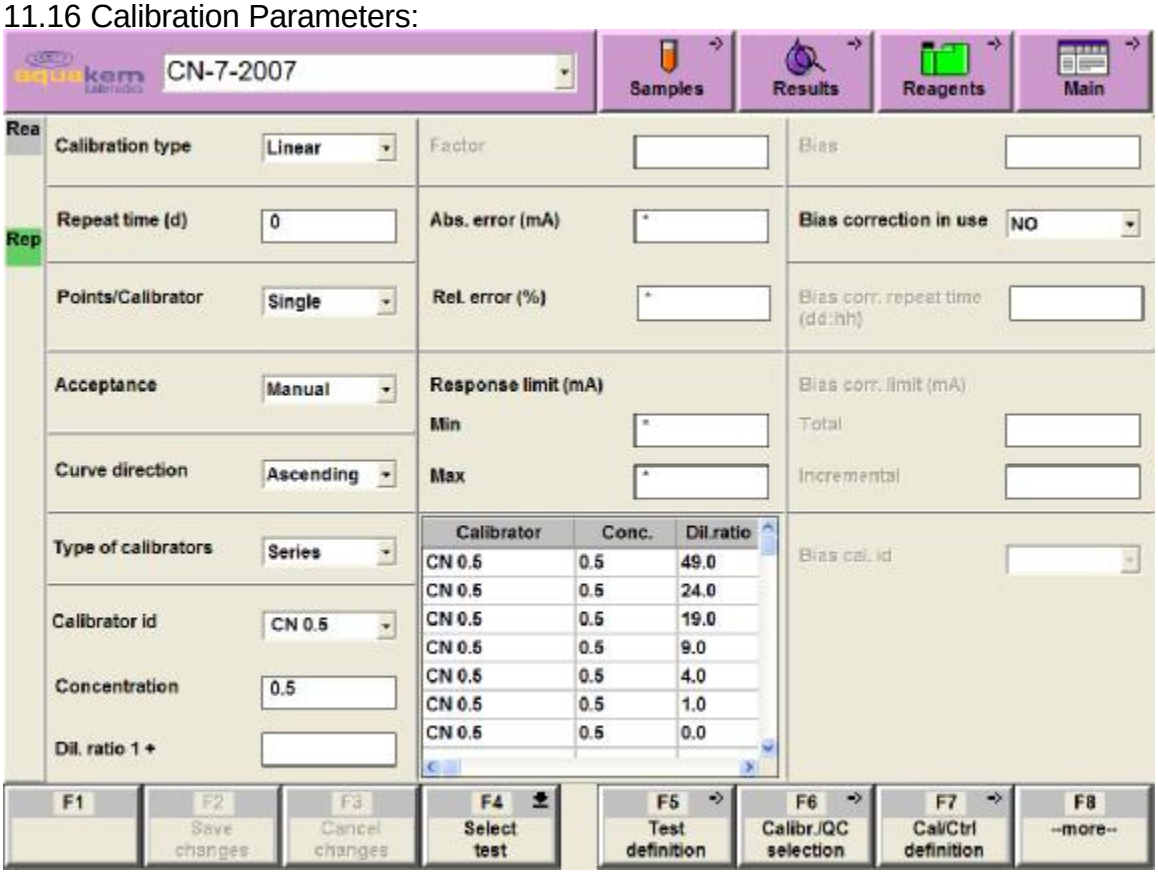

## 11.14 Test Definition Screen



## 11.15 QC Parameters:



11.16 Calibration Parameters:




## 12.0 Details of Calibration and Calculations

12.0 Final results are calculated as specified in section 14.

12.1 The CCV must be analyzed at the frequency specified in Section 13 and the concentration must be within 10% of the known value for confirmation of instrument calibration.

12.3 Continuing calibration standards are evaluated by:

% Recovery = actual conc./expected conc. * 100

12.4 Percent recovery - LCS

% Recovery = conc. recovered/conc. expected * 100

12.5 Relative Percent Difference – Duplicate samples

RPD = [result 1 - result 2]/average result1.result2) * 100

12.6 Initial Calibration Equation.

$y = mx + b$

y = sample absorbance
m = slope
x = sample concentration
b = intercept

## 13.0 Quality Assurance/Quality Control (QA/QC) Requirements

13.1 Prepare a method blank for each batch of samples using DI water.

13.1.1 Acceptance Criteria: < **½ RL (LOQ)**

13.1.2 Corrective Action: Determine the source and eliminate (see interferences). Re-analyze samples as necessary.

13.2 Prepare a laboratory control sample (LCS) for each batch of twenty or less samples by adding 0.1 mL of the second source working standard solution (Section 7.2) to 50 mL DI water. Expected concentration is 0.1 mg/L.

13.2.1 Acceptance Criteria: **80 - 120 % recovery.**

13.2.2 Corrective Action: For results outside of acceptance limits determine source of the problem. Re-analyze LCS and samples.

13.3 Prepare a matrix spike (MS) and matrix spike duplicate (MSD) for each batch of twenty or less samples by adding 0.1 mL of the working standard (Section 7.2) to 50 mL final volume of a representative sample. The expected concentration is 0.1 mg/L.

13.4.1 Acceptance Criteria: **80 – 120 % recovery (acceptance ranges are set to LCS limits).**

13.4.2 Corrective Action: For results outside of lab established control limits attempt to determine source of the problem (matrix interferences/poor injection/instrument problems). Re-analyze and/or flag data.

13.4 Duplicate Sample (DUP) – Optionally prepared with each batch of samples in place of or in addition to the MSD (required if no MSD is prepared)

13.4.1 Acceptance Criteria (RPD) **<20 %** or within laboratory established statistical control limits.

13.4.2 Corrective Action: Evaluate sample homogeneity and flag data if necessary.

## 14.0 Data Reporting Requirements

14.1 Sample results are reported as mg/L (aqueous samples) and mg/kg (solid samples).

14.2 Raw results are entered into Omega. Prep factors are automatically imported from sample prep logs. Dilutions are entered in the analytical sequence.

14.3 Sample results are reported as mg/kg for soil as dry weight.

mg/kg dry wt. = mg/kg wet wt.*100/percent solids

14.3 Raw instruments results are entered directly into the Omega LIMS system using excel spreadsheets, direct instrument interface or manually. All calculations to derive final result (including dry weight conversions) are performed automatically by the LIMS. Sample preparation information and percent moisture results are entered into the appropriate section of the LIMS prior to instrument data and are automatically factored into the final results.

14.4 Confirm that there are no QC flags or qualifiers in this sequence. If present, investigate and repeat or reanalyze as necessary. See section 9.2 of the QAP for more detail on qualifiers.

## 15.0 Preventative Maintenance and Routine Cleaning

15.1 Maintain distillation apparatus and all glassware in clean condition.

15.2 Refer to the Kone Analyzer for instrument maintenance procedures.

## 16.0 Waste Management and Pollution Prevention

16.1 Pollution Prevention

16.1.1 Reagents are purchased and quantities used to reflect anticipated usage and minimize disposal of expired or unused chemicals.

16.1.2 Chemicals are handled in a manner that minimizes the potential for release or spill of the material.

16.2 Waste Management

16.2.1 Acidic materials (pH<2) are treated as hazardous waste and placed in the appropriate waste drum for disposal.

16.2.2 Soil samples are composited in a drum designated for incineration.

16.2.3 Disposal of materials is addressed in the laboratory QAP (Section 5.6).

## 17.0 References

17.1 Standard Methods for the Examination of Water and Wastewater, On-line 4500-CN C&E.

17.2 EPA Test Methods for Evaluating Solid Waste. Laboratory Manual Physical/Chemical Methods, Nov 1986, Revision 2 December 1996. Method 9012, 9010B.

17.3 RTI Laboratories, Inc. Quality Assurance Plan.

17.4 RTI Laboratories, Inc. SOP SRC001-A, Sample Receipt and Custody.

17.5 RTI Laboratories, Inc. Chemical Hygiene Plan.

17.6 RTI Laboratories, Inc. Employee Handbook.

**RTI Laboratories, Inc.**
**31628 Glendale**
**Livonia, Michigan 48150**

# ANALYTICAL STANDARD OPERATING PROCEDURE

## ANALYSIS OF INORGANIC ANIONS

| | |
|---|---|
| **Analyte:** | **F, Cl, Br, $NO_3$, $NO_2$, $PO_4$, $SO_4$** |
| **SOP#:** | **300.0_080813_R7** |
| **Method Reference:** | **EPA 300.0, SW-9056** |
| **Issue Date:** | **February 28, 2001** |
| **Revision No.:** | **7** |
| **Revision Date:** | **August 8, 2013** |

**Reviewed and Approved: August 13, 2013**

| | |
|---|---|
| Director, Quality Management: | Charles O'Bryan |
| Director, Environmental Services: | Yemane Yohannes |

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**STANDARD OPERATING PROCEDURE**

**ANALYSIS OF INORGANIC ANIONS**

**SOP#: 300.0_080813_R7**

**TABLE OF CONTENTS**

## 1.0 Scope and Application

1.1 Introduction

RTI Laboratories, Inc., has prepared this document to detail the Standard Operating Procedure (SOP) for the preparation and analysis of water, soil and bomb combustion solutions samples for inorganic anions listed in the U.S. EPA Method 300.0 by Ion Chromatography (IC). This SOP incorporates the procedures for preparation and analysis of potable and non-potable waters, solids (after extraction), and neutral leachate as well as the analytical operating criteria found in EPA Methods 300.0 and SW-846 9056. Other anions such as sulfite may also be determined using ion chromatographic techniques following the general procedures specified in this SOP

A detailed description of the instrumentation, calibration, run parameters and quality control procedures where applicable is included in this SOP. For definition of terms not specifically defined in this document refer to RTI Laboratories, Inc. QAP Section 16.

1.2 Summary of Method:

1.2.1 Aliquots of the water sampled are filtered and placed in auto sampler vials. Soil samples are extracted using deionized water, filtered, and placed in auto sampler vials. The samples are analyzed using ion chromatography and quantification is based on the peak area response from a conductivity detector.

## 2.0 Safety Precautions

2.1 Materials applicable to this method are not known carcinogens, however chemicals should be regarded potential health risks. Sample preparation and analysis is performed in a manner designed to minimize exposure using routine good laboratory practices.

## 3.0 Sample Requirements and Sample Handling Procedures

3.1 Samples are received in accordance with RTI's Standard Operating Procedure for Sample Receipt and Custody (SRC001-A). Appropriate U. S. Environmental Protection Agency (EPA), sample handling procedures and sample preservation recommendations are followed. Water samples are collected in glass or polyethylene bottles. No preservative is added to the sample containers for standard anion analyses. Nitrate-nitrite analysis is performed on sample containers preserved with 1 ml of 1:1 sulfuric acid. Soil and waste samples are received in wide mouth glass jars ranging from 2 oz. to 9 oz. in size.

3.2 All samples are stored at $4^{o}$ C. Oil and Solvent samples for industrial chemistry testing may be stored at room temperature.

3.3 Solid extracts are extracted within 14 days and analyzed within the holding time for aqueous samples (Sec. 3.4).

3.4 Maximum recommended aqueous sample holding time:

3.4.1 28 days – Chloride, Fluoride, Bromide and Sulfate. Nitrate-Nitrite collected in sulfuric acid preserved container.

3.4.2 48 hours – Nitrate, Nitrite and ortho-Phosphate.

## 4.0 MDL, Linear Range, Accuracy and Precision

4.1 The method detection limit (MDL) is statistically defined at the 99% confidence level according to 40 CFR Part 136 App. B. Seven replicates containing all of the analytes of interest at a concentration level of 1-5 times the estimated D.L. are analyzed and the standard deviation is calculated. The Student's T Value for the 7 replicates (3.143) is multiplied by the standard deviation of the analyte to calculate the MDL. MDLs are performed on instrument set up and following significant changes to the instrument, method or personnel. MDLs are kept on file in the Laboratory. MDLs and reporting limits are incorporated into the applicable test code in the Omega LIMS.

4.2 The LOD (limit of detection) is determined by spiking reagent water at 1-4 times the MDL and prepared using the same procedure as samples. Analytes must be present at levels 3 times or greater than the blank response (greater than 3 times the signal to noise ratio). The concentration used is the LOD for that analyte. LOD determinations must be performed quarterly.

4.3 The LOQ (limit of quantification) is determined by spiking reagent water at the reporting limit (RL/CRQL) and prepared in the same manner as samples. Analyte recovery must be within 20% of the expected concentration. The concentration used and successfully recovered is the LOQ for that analyte. LOQ determinations must be performed quarterly.

4.4 Initially accuracy and precision at the LOQ is determined by spiking 4 aliquots of reagent water at the reporting limit (RL/CRQL) and prepared using the same procedure used for samples. The average recovery must be within 20% of the expected value and the %RSD must be less than 15%.

4.5 LOD/LOQ determinations that do not meet the specifications above require repeat analysis, adjustment to the spiking levels and/or reporting limits, repeating the MDL determination at adjusted concentrations if required and repeat LOD/LOQ determinations.

4.6 The accuracy and precision for this method are determined by analyzing four aliquots from a Laboratory Control Sample containing the element(s) of interest at the mid-level of the calibration range. Percent recovery, standard deviation, and the relative standard deviation are calculated for each analyte and documents are kept on file in the laboratory.

4.7 The linear range is 0.05 – 10 mg/L for all Fluoride, Chloride, Nitrite, Bromide, and Nitrate. The linear range for o-Phosphate and Sulfate is 0.05-15 mg/L.

## 5.0 Interferences

5.1 Interferences can arise from carry over due to high sample concentrations or contamination from reagents and/or glassware. Blanks are injected to ensure system cleanliness in both instances. All glassware must be scrupulously cleaned before use.

5.2 Samples containing high concentrations of non-target analytes or extremely high levels of select target analytes can result in elevated detection limits for other target analytes. Dilution of the sample may improve the resolution and quantification of some analytes but will generally cause an elevation in the RDL.

5.3 Any species with a retention time similar to that of the desired ion will interfere. Large quantities of ions eluting close to the ion of interest will also result in interference. Separation can be improved by adjusting the eluent concentration and/or flow rate. Sample dilution and/or the use of standard additions can also be used (Sec. 11.9). For example, high levels of organic acids may be present in industrial wastes, which may interfere with inorganic anion analysis. Two common species, formate and acetate, elute between fluoride and chloride.

5.4 Samples that contain particles larger than 0.45 µm and reagent solutions that contain particles larger than 0.20 µm require filtration to prevent damage to instrument columns and flow systems.

5.5 If a packed bed suppressor column is used, it will be slowly consumed during analysis and, therefore, will need to be regenerated. Use of either an anion fiber suppressor or an anion micro-membrane suppressor eliminates the time-consuming regeneration step through the use of a continuous flow.

5.6 Bromide and nitrate elute very close together and are potential mutual interferences. The Br /$N0_3$ ratio should not be higher than 1:10 or 10:1 if both anions are to be quantified.

## 6.0 Apparatus and Materials

6.1 Primary Instrument

6.1.1 Dionex ICS-1000
6.1.2 AS40 Auto sampler
6.1.3 ASRS300 Suppressor 4mm
6.1.4 AS9-HC IonPac Analytical Column 4 x 250mm
6.1.5 AG9-HC IonPac Guard Column 4 x 50mm
6.1.6 Chromeleon Software v. 6.80

6.2 Backup Instrument - Ion Chromatography system consisting of:

6.2.1 Pump
6.2.2 Dionex Conductivity detector
6.2.3 Dionex AS40 Automated sampler.
6.2.4 PeakNet- D4YYMC11_IOC Chromatography Data System
6.2.5 Dionex AMMS 111 4-mm suppressor
6.2.6 Analytical column Dionex Ion-Pac AS9-HC PN#051786.
6.2.7 Guard column Dionex Ion-Pac AG9-11C PN#051791

6.3 Vials with filter caps.

6.4 Class A volumetric flasks.

6.5 Eppendorf 10-100 µL size

6.6 Eppendorf 100-1000 µL size

6.7 Eppendorf 500-5000 µL size

6.8 Whatman Filter paper

6.9 3ml sterile disposable syringes

6.10 2000 mL Class “A” volumetric flask

## 7.0 Reagents

7.1 Deionized Water with specific conductance of <1 µmho/cm (type II water).

7.2 1000mg/l Stock Analytical Standard Mixture EPA 300.0 Anions mix A- 7 components (Fluoride, chloride, bromide, nitrite, nitrate, phosphate & sulfate), Absolute Standards, Part No. 52118. Store refrigerated at 4 deg. C.

7.3 Second source stock: Various Concentrations Stock Analytical Standard Anions mix 7 components (Fluoride 100 ppm, chloride 200 ppm, bromide 200 ppm, nitrate 200 ppm, nitrite 200 ppm, phosphate 300 ppm and sulfate 300 ppm), Absolute Standards, Part No. 59011. Store refrigerated at 4 deg. C.

7.4 Sodium Carbonate Anhydrous, ACS Reagent Grade

7.5 Eluent: Add 4g sodium carbonate (7.4) to 3780 mL DI water.

7.6 All reagents and standards prepared must be labeled with a minimum:

7.6.1 Identity of the material
7.6.2 Concentration of the solution
7.6.3 Date prepared
7.6.4 Initials of analyst preparing the solution
7.6.5 Expiration date.

## 8.0 Preparation of Standards and Calibration Procedure

8.1 Initial Calibration – A successful curve is established when all analytes have a correlation coefficient of >0.995. The %RSD should be less than 15%.

8.1.1 Initial Calibration Standards prepared at: 0.05 mg/L, 0.1 mg/L 0.5mg/L, 1 mg/L, 5 mg/L, 7.5 mg/L 10 mg/L, and 15 mg/L from the 1000 mg/L stock analytical standard (7.2) as specified below. Prepare fresh each use.

8.1.1.1 0.05ppm: Pipette 500 µL of 8.1.1.5 (5ppm) in a 50ml volumetric flask and dilute to 50ml with DI water.
8.1.1.2 0.1ppm: Pipette 1000 µL of 8.1.1.5 (5ppm) in a 50ml volumetric flask and dilute to 50ml with DI water.
8.1.1.3 0.5ppm: Pipette 25 µL of 1000ppm in a 50ml volumetric flask and dilute to 50ml with DI water.
8.1.1.4 1ppm: Pipette 50 µL of 1000ppm in a 50ml volumetric flask and dilute to 50ml with DI water.
8.1.1.5 5ppm: Pipette 250 µL of 1000ppm in a 50ml volumetric flask and dilute to 50ml with DI water.
8.1.1.6 7.5ppm: Pipette 375 µL of 1000ppm in a 50ml volumetric flask and dilute to 50ml with DI water.
8.1.1.7 10ppm: Pipette 500 of 1000ppm in a 50ml volumetric flask and dilute to 50ml with DI water.
8.1.1.8 15ppm: Pipette 750 µL of 1000ppm in a 50ml volumetric flask and dilute to 50ml with DI water.

8.2 Following analysis of the calibration standards the instrument data system plots the linear calibration curve and calculates the correlation coefficient. The correlation coefficient must be >0.995. If any analyte does not meet the calibration criteria initial calibration must be repeated with successful correlation coefficients for all analytes prior to analysis of samples.

8.3 The calibration curve is verified by the analysis of an Initial Calibration Verification (ICV) standard. This standard is prepared from the second source standard (Sec. 7.3) by diluting 1.25 ml of the stock standard to a final volume of 50 ml DI water in a volumetric flask. Analyte concentrations in the ICV are F - 2.5 ppm, Cl - 5.0 ppm, NO2 - 5.0 ppm, Br - 5.0 ppm, NO3 - 5.0 ppm, PO4 - 7.5 ppm, SO4 - 7.5 ppm.

8.4 The response of the ICV must be 90 – 110% of the expected concentration for each analyte prior to analyzing samples. If a successful response is not achieved re-preparation/re-analysis of the ICV or re-calibration is required until the response is within acceptance criteria

8.5 Continuing calibration verification (CCV) standard 5 mg/L: Pipette 250 µl of the 1000ppm standard (Sec 7.2) in a 50ml volumetric flask and dilute to 50ml with DI water. Standards are filtered using Whatman filter paper. Prepare fresh each use.

8.6 Continuing Calibration Verification (CCV) is analyzed every 10 samples and at the end of the analytical sequence. The response must be within 10% of the expected concentration. All samples must be bracketed by acceptable CCVs. Failure to meet the CCV criteria requires re-analysis of the associated samples following any necessary corrective actions required including repeating/re-preparing the CCV, instrument re-calibrations or other measures as needed.

8.7 Reporting limit verification standards (CRQL/CRQL2) are prepared daily and analyzed at a minimum at the beginning and end of each analytical batch. The first standard is prepared by diluting 0.5 ml of the CCV standard (Sec. 8.5) to a final volume of 50 ml DI water in a volumetric flask. The second standard is prepared by diluting 1mL of the CCV standard (Sec. 8.5) to a final volume of 50 ml DI water in a volumetric flask. The response must be within 20% of the expected concentration. All samples must be bracketed by acceptable CRQLs. Failure to meet the CRQL criteria requires re-analysis of the associated samples following any necessary corrective actions required including repeating/re-preparing the CRQL, instrument re-calibrations or other measures as needed.

## 9.0 Sample Preparation

9.1 Aqueous samples Preparation – Aqueous samples are filtered using Whatman filter paper if there are solids present. Samples are diluted 1:10 in DI water.

9.2 Solid/Soil samples Preparation

9.2.1 Measure 10 gm of well-mixed soil eliminating foreign objects such as sticks, rocks, etc. using a balance and place in a 250 ml plastic bottle.

9.2.2 Add 200 mL deionized water and tumble at 28 rev./min for 18 +/- 2 hours.

9.2.3 Filter a portion using a Whatman filter paper.

9.3 Solid waste samples for chloride, sulfur (as sulfate), nitrogen (as nitrate), phosphorus (as phosphate), fluoride and bromide are prepared according to SOP 5050 – Bomb Preparation.

## 10.0 Diagram/Table

10.1 Reserved.

## 11.0 Analytical Procedure

11.1 Method, run, and integration parameters are stored in the respective instrumentation according to manufacturers procedures.

11.2 A new sequence file is created for each batch of samples.

11.3 Run sequence follows as below:

11.3.1 Initial Calibration (when required)
11.3.2 ICV/CCV
11.3.3 CRQLs
11.3.4 Method Blank/CCB
11.3.5 LCS
11.3.6 10 samples
11.3.7 CCV
11.3.8 CCB
11.3.9 10 samples
11.3.10 MS and MSD (Every batch of 20)
11.3.11 DUP (Every batch of 20)
11.3.12 CCV
11.3.13 CCB
11.3.14 CRQLs

NOTE: Method blanks and LCS samples referencing soil samples will contain the analytical batch ID.

11.4 Instrument conditions:

11.4.1 Eluent Flow – 1.2mL/min, Isocratic
11.4.2 Sample Injection - 100µL sample loop
11.4.3 Runtime – 20min
11.4.4 Suppressor Current – 52mA

11.5 Load auto sampler according to sequence file.

11.6 Begin sample analysis.

11.7 During data interpretation a qualitative identification is made when sample peak falls within the established retention time ($R_t$) window.

11.8 Positive results must be manually evaluated and all integrations confirmed. Baseline adjustments are often necessary due to sample matrix interferences.

11.9 If the resulting chromatogram for a particular sample fails to produce adequate resolution such that the identification of the anion of interest is questionable, prepare a new sample spiked with a known amount of the anion under question and reanalyze in order to confirm the presence or absence of analyte.

11.10 Manual integration guidelines and procedures

11.10.1 Situation may arise whereby the quantification provided by the data system is inappropriate. This can occur due to co-elution, baseline noise or matrix interference.

11.10.2 When manual integration of a compound is necessary the following guidelines must be followed.

11.10.3 Manual quantification is performed by integrating the area of the peak for the compound.

11.10.4 The integration will only include the area attributable to the compound of interest.

11.10.5 The area integrated shall not include baseline background noise.

11.10.6 The area integrated shall not extend beyond the point where the sides of the peak intersect with the baseline.

11.10.7 Manual integration must not be used solely to meet quality control criteria.

11.10.8 Manual integration must not be used as a substitute for corrective action on the IC system.

11.10.9 Instances of manual integration are flagged with a "*" by the data system. All manual integrations are imported into the associated Omega analytical sequence with the analyst rationale for the integration. Integration files are reviewed during data validation and approved by the data reviewer prior to data acceptance.

## 12.0 Details of Calibration and Calculations

12.1 Calibration is performed using least squares linear regression from the equation.

$y = mx + b$
y = sample absorbance
m = slope
x = sample concentration
b = intercept

12.2 Daily, Initial, and Continuing calibration verification is determined by the response of the standard where:

%D (percent difference)=((True Value-Calculated Value)/True Value)*100

12.3 Percent recovery - matrix spikes, post digestion spikes and LCS

% Recovery = conc. recovered/ conc. expected * 100

12.4 Relative Percent Difference

RPD = [result 1 - result 2]/average result1..result2) * 100

## 13.0 Quality Assurance/Quality Control (QA/QC) Requirements

13.1 Retention Time Windows will be established and maintained for each analyte.

13.1.1 Determined by analyzing three control samples over a 72-hour period.

13.1.2 Defined as the Mean +/– (3 times the standard deviation)

13.1.3 Re-calculated whenever a new column or new guard column is installed.

13.1.4 Retention time and tolerances are programmed into data analysis method and all standards are checked to ensure analytes fall within the $R_t$ window.

13.2 The acceptance criteria for the initial calibration curve must be a correlation coefficient of 0.995 or higher for each individual analyte. The force through zero option may be used based on the response of the curve relative to the intercept (intercept not significantly different than zero) and with evaluation of the impact on results at the lower end of the calibration curve. Quantification of results at or slightly above the lowest standard may be more accurate when using the force through zero option of the data system. Since the data system does not include zero in the calculation of the regression equation and merely pivots the line through zero, this procedure is consistent with the guidelines in Method 8000C. Repeat initial calibration if acceptance criteria is not met.

13.3 The ICV is analyzed immediately following initial calibration.

13.2.1 Acceptance Criteria: **<10%D**

13.2.2 Corrective Action: Repeat ICV. If repeat fails acceptance criteria repeat initial calibration.

13.4 CCV's are analyzed following every 10 samples and at the end of the batch.

13.3.1 Acceptance Criteria: **<10%D**

13.3.2 Corrective Action: All samples analyzed after a passing CCV and prior to failing CCV must be re-analyzed. Determine the cause of the failure, perform any necessary maintenance and re-analyze the CCV. If acceptable results are produced, repeat samples. In instances of continuing failure of the CCV, correct the problem and repeat the initial calibration before proceeding with sample analysis.

13.5 Reporting Limit Verification (RLV/CRQL) standard: The 0.05 and 0.1 ppm standard are analyzed at the beginning and end of each analytical sequence.

13.4.1 Acceptance Criteria: **All analytes <20% D**

13.4.2 Corrective Action: Repeat RLV and re-calibrate if repeat fails.

13.6 Prepare a method blank for each batch of samples using DI water for aqueous samples and clean sand (if available) for solid samples.

13.5.1 Acceptance Criteria: **All analytes below 1/2 RL**

13.5.2 Corrective Action: Determine the source and eliminate (see interferences). Re-analyze samples.

13.7 Analyze a laboratory control sample (LCS) for each batch of 20 or fewer samples. This standard is the ICV standard prepared from the second source standard (Sec. 7.3) by diluting 1.25 ml of the stock standard to a final volume of 50 ml DI water in a volumetric flask. Analyte concentrations in the LCS are F - 2.5 ppm, Cl - 5.0 ppm, NO2 - 5.0 ppm, Br - 5.0 ppm, NO3 - 5.0 ppm, PO4 - 7.5 ppm, SO4 - 7.5 ppm. This standard is analyzed and designated as the batch LCS.

13.7.1 Acceptance Criteria: **80 – 120 % Recovery** (Limits also apply to soils as a suitable clean matrix for soils is not available)

13.7.2 Corrective Action: Investigate cause. Repeat analyses of the batch. Re-prep samples and re-analyze as necessary.

13.8 Prepare a matrix spike (MS) and matrix spike duplicate (MSD) for each batch of 20 or less samples use 25 µL of the 1000 mg/L stock standard (7.2) in a 5 ml vial and bring to volume with the designated sample. If statistical control limits are established for the LCS, those limits will apply to the MS and MSD.

13.7.1 Acceptance Criteria: **80-120% Recovery**
**RPD £ 20%**

13.7.2 Corrective Action: For any compound outside of lab-established control limits attempt to determine source of the problem (matrix interferences/poor injection/instrument problems). Re-analyze and/or flag data.

13.9 Prepare a sample duplicate with each batch of samples.

13.9.1 Acceptance Criteria: **<20%D between sample and duplicate**

13.9.2 Corrective Action: Investigate cause. Repeat analyses of the batch. Re-prep samples and re-analyze as necessary

## 14.0 Data Reporting Requirements

14.1 Samples exhibiting results above the highest calibration standard must be diluted within the calibration range.

14.2 Unfamiliar Matrixes: For positive identification the sample is spiked with a known quantity of all analytes in question.

14.3 Soil Samples are reported as µg/Kg on a dry weight basis where:

µg/Kg = [(C x Ve x Df) / Vi] x [100 / %solid]
C = concentration found in sample (µg/mL)
Ve = volume of water used to extract soil (mL)
Df = dilution factor
Vi = initial weight of sample (Kg)

14.4 Water calculations are reported as µg/L where:

µg/L = (C x Df) * 1000
C = concentration found in sample (µg/ml)
Df = dilution factor

14.5 Raw instruments results are entered directly into the Omega LIMS system using excel spreadsheets, direct instrument interface or manually. All calculations to derive final result (including dry weight conversions) are performed automatically by the LIMS. Sample preparation information and percent moisture results are entered into the appropriate section of the LIMS prior to instrument data and are automatically factored into the final results.

14.6 Confirm that there are no QC flags or qualifiers in this sequence. If present, investigate and repeat, re-analyze as necessary or flag data according to LIMS protocol.

## 15.0 Preventative Maintenance and Routine Cleaning

15.1 Daily: monitor system pressure for any large increases or decreases.

15.2 Increase in system pressure requires changing of the column.

15.3 A decrease in pressure necessitates a system check for leaks.

## 16.0 Pollution Prevention and Waste Management

16.1 Pollution Prevention

16.1.1 Reagents are purchased and quantities used to reflect anticipated usage and minimize disposal of expired or unused chemicals.

16.1.2 Chemicals are handled in a manner that minimizes the potential for release or spill of the material.

16.2 Waste Management

16.2.1 Acidic materials (pH<2) are treated as hazardous waste and placed in the appropriate waste drum for disposal.

16.2.2 Soil samples are composited in a drum designated for incineration.

16.2.3 Disposal of materials is addressed in the laboratory QAP (Section 5.6).

## 17.0 References

17.1 EPA Methods for Chemical Analysis of Water and Wastewater, 600/4/70/200 Method 300.0R2.1.

17.2 USEPA Test Methods for Evaluating Solid Waste, Physical Chemical Method. SW-846 Method 9056 – Determination of Inorganic Anions by Ion Chromatography. Revision 0, September 1994.

17.3 Standard Test Method for Shake Extraction of Solid Waste with Water, ASTM D 3987

17.3 RTI Laboratories, Inc. Quality Assurance Plan.

17.4 RTI Laboratories, Inc. SOP SRC001-A, Sample Receipt and Custody.

17.5 RTI Laboratories, Inc. Chemical Hygiene Plan.

17.6 RTI Laboratories, Inc. Employee Handbook.