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Comprehensive Long-term Environmental Action Navy

CONTRACT NUMBER N62467-04-D-0055

Resource Conservation and Recovery Act Addendum No. 4 to the Quality Assurance Project Plan for

SWMUs 8, 15, 18, 19, 20 and the Old Gun Tub Storage Lot for Interim Measures at SWMU 7 (Old Rifle Range), SWMU 8 (Building 106 Pond), SWMU 13 (Mine Fill B), SWMU 17 (PCB Burial/Pole Yard), and SWMU 9 (Pesticide Control Area)

Naval Surface Warfare Center Crane Division Crane, Indiana

Contract Task Order 0467

September 2008

NAVFAC
Naval Facilities Engineering Command
Midwest
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Great Lakes, Illinois 60088

TETRA TECH NUS, Inc.

REVISION 0
SEPTEMBER 2008

RESOURCE CONSERVATION AND RECOVERY ACT ADDENDUM NO. 4 TO THE QUALITY ASSURANCE PROJECT PLAN FOR SWMUs 8, 15, 18, 19, 20, AND THE OLD GUN TUB STORAGE LOT FOR INTERIM MEASURES AT SWMU 7 (OLD RIFLE RANGE), SWMU 8 (BUILDING 106 POND), SWMU 13, (MINE FILL B), SWMU 17 (PCB BURIAL/POLE YARD), AND SWMU 9 (PESTICIDE CONTROL AREA)

NAVAL SURFACE WARFARE CENTER
CRANE DIVISION
CRANE, INDIANA

COMPREHENSIVE LONG-TERM
ENVIRONMENTAL ACTION NAVY (CLEAN) CONTRACT

Submitted to:
Naval Facilities Engineering Command
Midwest
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Building IA, Code EV
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CONTRACT NUMBER N62467-04-D-0055
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SEPTEMBER 2008

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ACRONYMS

%R	percent recovery
bgs	below ground surface
CAAA	Crane Army Ammunition Activity
CFR	Code of Federal Regulations
CLEAN IV	Comprehensive Long-Term Environmental Action Navy
COC	chemical of concern
CTO	Contract Task Order
cy	cubic yard
DQI	data quality indicator
DQO	Data Quality Objective
DRO	Diesel Range Organics
EDD	Electronic Data Deliverable
EDE	Electronic Data Exchange
EI	Environmental Indicator
EMAC	Environmental Multi-Award Contractor
ERSM	Environmental Restoration Site Manager
FOL	Field Operations Leader
FTMR	Field Task Modification Request
GRO	Gasoline Range Organics
HASP	Health and Safety Plan
HI	hazard index
HSM	Health and Safety Manager
ICP	inductively coupled plasma
IDEM	Indiana Department of Environmental Management
IDW	investigation-derived waste
IM	Interim Measure
IMWP	Interim Measures Work Plan
LDR	Land Disposal Restriction
MCS	media cleanup standard
MDL	method detection limit
mg/kg	milligram per kilogram
MS	matrix spike
MSD	matrix spike duplicate

NAFVAC MW	Naval Facilities Engineering Command Midwest
Navy	United States Navy
NFESC	Naval Facilities Engineering Services Command
NSWC	Naval Surface Warfare Center
NWRS	North Wind Remediation Services, Inc.
OGTSL	Old Gun Tub Storage Lot
OICC	Officer in Charge of Construction
OPR	Old Pistol Range
ORR	Old Rifle Range
OSHA	Occupational Safety and Health Administration
PCB	Polychlorinated Biphenyl
PM	Project Manager
ppb	part per billion
PPE	Personal protective equipment
ppm	parts per million
ProgMan	Program Manager
PTA	Pyrotechnic Test Area
QA	Quality Assurance
QAM	Quality Assurance Manager
QAO	QA Officer
QAPP	Quality Assurance Project Plan
QC	Quality Control
RCRA	Resource Conservation and Recovery Act
RCRIS	Resource Conservation and Recovery Information System
RFI	Facility Investigation
RPD	Relative Percent Difference
RPM	Remedial Project Manager
sf	square feet
SI	Site Investigation
SOP	Standard Operating Procedure
SOW	statement of work
SSO	Site Safety Officer
SWMU	Solid Waste Management Unit
Tetra Tech	Tetra Tech NUS, Inc.
TPH	Total Petroleum Hydrocarbons
TSCA	Toxic Substances Control Act

TV	target value
U.S. EPA	United States Environmental Protection Agency

1.0 PROJECT DESCRIPTION

The Naval Surface Warfare Center (NSWC) Crane prepared a Quality Assurance Project Plan (QAPP) [Tetra Tech NUS, Inc. (Tetra Tech), 2004] for a Phase III Resource Conservation and Recovery Act (RCRA) Facility Investigation (RFI) at the following Solid Waste Management Units (SWMUs):

- SWMU 8, Building 106 Pond
- SWMU 15, Roads and Grounds Area

That QAPP also governed data collection for completion of the United States Environmental Protection Agency (U.S. EPA) Region 5 Resource Conservation and Recovery Information System (RCRIS) code Environmental Indicator (EI) Form (Form CA725) for the following sites:

- SWMU 18, Load and Fill Area Buildings
- SWMU 19, Pyrotechnic Test Area (PTA)
- SWMU 20, Crane Army Ammunition Activity (CAAA) Quality Assurance (QA) / Quality Control (QC) Test Area
- Old Gun Tub Storage Lot (OGTSL)

That QAPP was approved by U.S. EPA Region 5, and the required field work was conducted in accordance with the QAPP.

QAPP Addendum No. 1, dated November 2006, was approved by U.S. EPA Region 5. QAPP Addendum No. 1 was developed to include Interim Measures (IMs) Work Plans (IMWPs) to govern IMs conducted at the following Crane sites:

- Old Pistol Range (OPR) and Old Rifle Range (ORR) at SWMU 7
- SWMU 8, Building 106 Pond Area
- SMWU 13, Mine Fill B
- SWMU 17, PCB Pole Yard

The focus of the IMWPs was excavation of contaminated soil and sediment and other IMs that were designed to reduce or eliminate the extent and magnitude of contamination at each of these four sites.

QAPP Addendum No. 2 was developed to govern the sampling and analyses of surface soils to provide data on potentially site-related organic and inorganic chemical concentrations at UXO 5 and UXO 7. QAPP Addendum No. 2, dated August 2007 has been submitted to U.S. EPA Region 5, and is awaiting approval.

QAPP Addendum No. 3 was developed for the collection and analysis of surface and subsurface soil samples at SWMU 9 (Pesticide Control Area) to complete delineation of pesticide contamination and to determine whether herbicide contamination is present. The information collected will be provided in a report and will be used as follows:

- Refine the extent of pesticide contamination requiring remediation.
- Establish whether herbicide contamination is present at concentrations requiring remediation.
- Provide data for determining whether the soils contain listed hazardous wastes.
- Provide data for determining whether the RCRA Land Disposal Restriction (LDR) requirements are met.

1.1 DESCRIPTION OF QAPP ADDENDUM NO. 4

This QAPP Addendum No. 4 governs sampling and analyses for the purposes of remediation and waste disposal of materials removed from SWMU 9. Specifically, the following objectives will be achieved:

- Confirming that cleanup goals have been met.
- Provide data on residual contaminant concentrations in soils.

It is a supplement to the approved IMWP (Tetra Tech, 2007).

This Addendum was prepared for the NSWC Crane facility, located in Crane, Indiana, through the Naval Facilities Engineering Command Midwest (NAFVAC MW) under Contract Task Order (CTO) 0467 for the Comprehensive Long-Term Environmental Action Navy (CLEAN) IV, Contract Number N62467-04-D-0055. For any work to be conducted under this Addendum that is unique to this project, the appropriate information is presented in this document or references are provided to other documents containing the required information.

Site physical conditions are summarized in the IMWP (Tetra Tech, 2007) for SWMU 9. Descriptions of the IM to be conducted, except details of confirmation sampling and analyses and waste disposal sampling and analyses, are described in Section 3.0 of the IMWP. Additional details of the IM are

provided in the remaining sections of the IMWP. Therefore, only very brief descriptions of the sites are provided below.

1.2 SCOPES OF WORK

1.2.1 Surface Soil Excavations

SWMU 9 planned surface soil excavation [0 to 2 feet below ground surface (bgs)] areas are identified on Figures 1-1 and 1-2. The surface soil excavation area located at the former fire training area (south of former Building 55) includes approximately 30 cubic yards (cy) of Toxic Substance Control Act (TSCA) regulated soil and approximately 193 cy of non-TSCA regulated soil (volumes based on in place contaminant concentrations). The surface excavation area located south and west of the former Building 55 includes approximately 666 cy of hazardous soil (based on in place contaminant concentrations and historic process knowledge). The surface soil excavation area located south of Building 150 includes approximately 26 cy of non-hazardous soil (based on in place contaminant concentrations).

Northing and Easting coordinates for the surface soil excavation area vertices are provided in Table 3-2 of the IMWP. The volume of soil removed from each excavation area is based on the area of each excavation and the 2-foot excavation depth, with no sloping of the excavation sides. Volume calculations are provided in Appendix B of the IMWP and summarized below:

Excavation Area	Depth of Excavation	Volume	Weight
Fire Training Area	2 feet bgs	184 cy	274 tons
Fire Training Area*	2 feet bgs	39 cy	58 tons
Former Building 55 Area**	2 feet bgs	673 cy	999 tons
Building 150 Area	2 feet bgs	26 cy	39 tons
Total Surface Soil to be Excavated		922 cy	1,370 tons

* TSCA regulated material
** Hazardous material

Physical features will not be removed during the excavation of surface soils. Physical features include, but are not limited to, steam lines, monitoring wells, buildings, concrete pads, railroad track, and bituminous concrete paved roads. The volume estimates presented in the IMWP assume that these physical features remain in place.

Sediment that accumulates in the erosion and sediment control devices (see Section 4.0 of the IMWP) prior to verification that all contaminated soil has been removed from the associated surface soil excavation areas will be disposed off-site along with the excavated contaminated surface soil. Following verification of contaminant removal, sediment that accumulates in the erosion and sediment control devices will be placed in the excavation as backfill material or spread across the disturbed ground surface of the associated soil excavation area.

The amount of soil to be excavated at Former Building 55 may change based on the recent sampling event under QAPP Addendum No. 3.

The following is a listing of the chemicals of concern (COCs) that are present at each of the three excavation areas.

Excavation Area	Applicable COCs
Former Fire Training Area	Polychlorinated Biphenyls (PCBs)
Former Building 55 Area	Pesticides and Diesel Range Organics (DRO)
Building 150 Area	DRO

Confirmation Sampling

Sample collection and analysis, handling of confirmation sampling derived waste, and decontamination procedures will be consistent with those described in the approved QAPP for SWMUs 8, 15, 18, 19, and 20 and the Old Gun Tub Storage Lot (Tetra Tech, 2004). The rationale for using this QAPP as the source QAPP is that it was prepared for similar field activities and analytical methods at NSWC Crane and was approved by EPA Region 5, which is also the lead regulatory agency for the SWMU 9 activities.

Following soil excavation, samples will be collected from the soil remaining on the excavation floors and sidewalls to verify that residual PCB, pesticide, and DRO concentrations in the exposed soils are acceptable. The COC media cleanup goals for achieving acceptable human health risks in soil at SWMU 9 are listed in the following table:

Contaminant Group	COCs	Media Cleanup Standards
PCBs	Total PCBs (surface soil)	1 ppm(1)
	Total PCBs (subsurface soil)	25 ppm(1)
DRO	DRO	1,600 ppm(2)
Pesticides	4,4'-DDD	24,300 ppb(4)
	4,4'-DDE	17,150 ppb(4)
	4,4'-DDT	3,600 ppb(3)
	Dieldrin	300 ppb(4)
	Heptaclor	1,050 ppb(4)
Pesticides (Continued)	Alpha-chlordane	3,500 ppb(3)
	Gamma-chlordane	3,500 ppb(3)

1 Toxic Substances Control Act (TSCA) high occupancy areas standard of 1 part per million (ppm) [40 Code of Federal Regulations (CFR) 761.61(a)(4)(i)(A)] and low occupancy areas standard of 25 ppm [40 CFR 761.61(a)(4)(i)(A)].
2 Indiana Department of Environmental Management (IDEM) Default Closure Level for direct contact to soil under a residential scenario.
3 Risk-based concentration for residential exposures to soil based on a target hazard index (HI) of 0.1.
4 Risk based concentration for residential exposure to soil based on a 1E-05 cancer risk level.

2,4-D - dichlorophenoxyacetic acid
2,4,5,-T - trichlorophenoxyatetic acid
2,4,5-TP - trichlorophenoxypropionic acid
DDD - dichlorodiphenyldichloroethane
DDE - dichlorodiphenyldichloroethylene
DDT - dichlorodiphenyltrichloroethane
ppb - parts per billion
ppm - parts per million

Following completion of soil removal, Tetra Tech will also collect samples from beneath Environmental Multi-Award Contractor (EMAC) North Wind Remediation Services, Inc. (NWRS) support facilities (decontamination pads, materials storage areas, and temporary access roads), if needed, to verify that surface soils below these facilities were not inadvertently contaminated during remediation activities. Details on the samples to be collected by Tetra Tech, including descriptions of the sampling plan designs, are provided in Section 3.0 of this QAPP.

Waste Characterization

In addition to the samples collected by Tetra Tech, NWRS will collect waste characterization samples to satisfy the selected disposal facility permit requirements. Details about the samples to be collected, including descriptions of the sampling plan designs, are provided in Section 3.0 of this QAPP.

1.2.2 Subsurface Soil Excavation

All SWMU 9 subsurface soils identified as having COCs at concentrations that result in unacceptable risks to ecological and human receptors will be removed, characterized, and disposed at approved off-site hazardous and non-hazardous waste disposal facilities. NWRS intends to use in-situ samples for characterization purposes. However, site conditions may require that some soils be excavated and stockpiled or containerized for characterization sampling. All excavated soil will remain on site until waste characterization has been completed.

The planned subsurface soil excavation areas are identified on Figures 1-1 and 1-2. The subsurface excavation area located at the former fire training area (south of former Building 55) includes approximately 395 cy of non-TSCA regulated soil and 39 cy of TSCA regulated soil (based on in place contaminant concentrations). The subsurface excavation area located south and west of former Building 55 measures includes approximately 111 cy of hazardous soil (based on in place contaminant concentration and known historic process).

Northing and Easting coordinates for the subsurface soil excavation area vertices are provided in Table 3-2 of the IMWP. Due to the depth of this excavation, the excavation requires sidewalls that are sloped to provide for a stable excavation. This layback of side slopes requires the removal of an additional 312 cy of soil from the Former Fire Training area excavation and an additional 84 cy of soil from the area south and west of former Building 55. This soil will be disposed off-site with the other excavated soils but should be kept separate from identified hazardous materials to the extent possible for disposal characterization purposes. It is expected that the sidewall excavation soil at the Former Fire Training Area will be characterized as non-TSCA regulated soil and the sidewall excavation soil from the area south and west of former Building 150 will be characterized as hazardous waste.

Excavation Area	Depth of Excavation	Volume	Weight
Fire Training Area	5 feet bgs	434 cy	644 tons
Fire Training Area Side Slopes	5 feet bgs	312 cy	463 tons
Former Building 55**	4 feet bgs	111 cy	165 tons
Former Building 55 Side Slopes**	4 feet bgs	84 cy	125 tons
Total Subsurface Soil to be Excavated		**941 cy**	**1,397 tons**

* TSCA regulated material
** Hazardous material

Confirmation Sampling

Following soil excavation, samples will be collected from the soil remaining on the excavation floors and sidewalls to verify that residual concentrations in the exposed soils are acceptable.

The COC media cleanup goals for achieving acceptable human health risks in soil at SWMU 9 are listed in the following table:

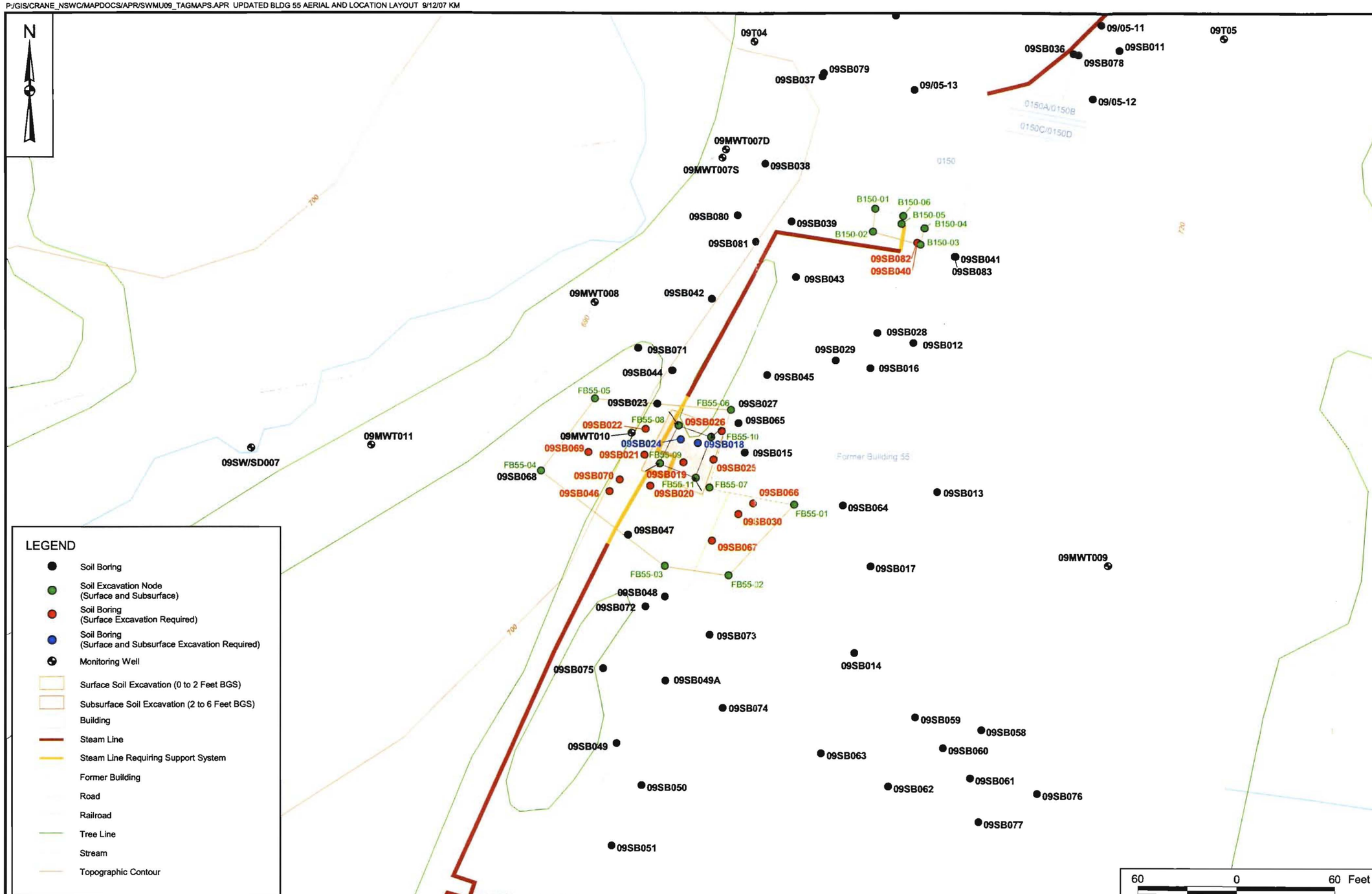
Contaminant Group	COCs	Media Cleanup Standards
PCBs	Total PCBs (surface soil)	1 ppm(1)
	Total PCBs (subsurface soil)	25 ppm(1)
DRO	DRO	1,600 ppm(2)
Pesticides	4,4'-DDD	24,300 ppb(4)
	4,4'-DDE	17,150 ppb(4)
	4,4'-DDT	3,600 ppb(3)
	Dieldrin	300 ppb(4)
	Heptaclor	1,050 ppb(4)
	Alpha-chlordane	3,500 ppb(3)
	Gamma-chlordane	3,500 ppb(3)

1 TSCA high occupancy areas standard of 1 ppm [40 CFR 761.61(a)(4)(i)(A)] and low occupancy areas standard of 25 ppm [40 CFR 761.61(a)(4)(i)(A)].
2 IDEM Default Closure Level for direct contact to soil under a residential scenario.
3 Risk-based concentration for residential exposures to soil based on a target HI of 0.1.
4 Risk based concentration for residential exposure to soil based on a 1E-05 cancer risk level.

Waste Characterization

In addition to the samples collected by Tetra Tech, NWRS will collect waste characterization samples to satisfy the selected disposal facility permit requirements. Details about the samples to be collected, including descriptions of the sampling plan designs, are provided in Section 3.0 of this QAPP.

P:/GIS/CRANE_NSWC/MAPDOCS/APR/SWMU09_TAGMAPS.APR UPDATED BLDG 55 AERIAL AND LOCATION LAYOUT 9/12/07 KM



CONTRACT NO. CTO 0467

APPROVED BY ___ DATE ___

APPROVED BY ___ DATE ___

DRAWING NO. FIGURE 1 - 1

REV 1

ORGANIC CONTAMINANTS IN SOIL
EXCEEDING HUMAN HEALTH SCREENING LEVELS
FORMER BUILDING 55 EXCAVATION AREA
SWMU 9 QAPP ADDENDUM NO. 4
NSWC CRANE
CRANE, INDIANA

NAVFAC

DRAWN BY S. STROZ DATE 3/29/07

CHECKED BY V. PLACHY DATE 9/12/07

COST/SCHED-AREA

SCALE: AS NOTED

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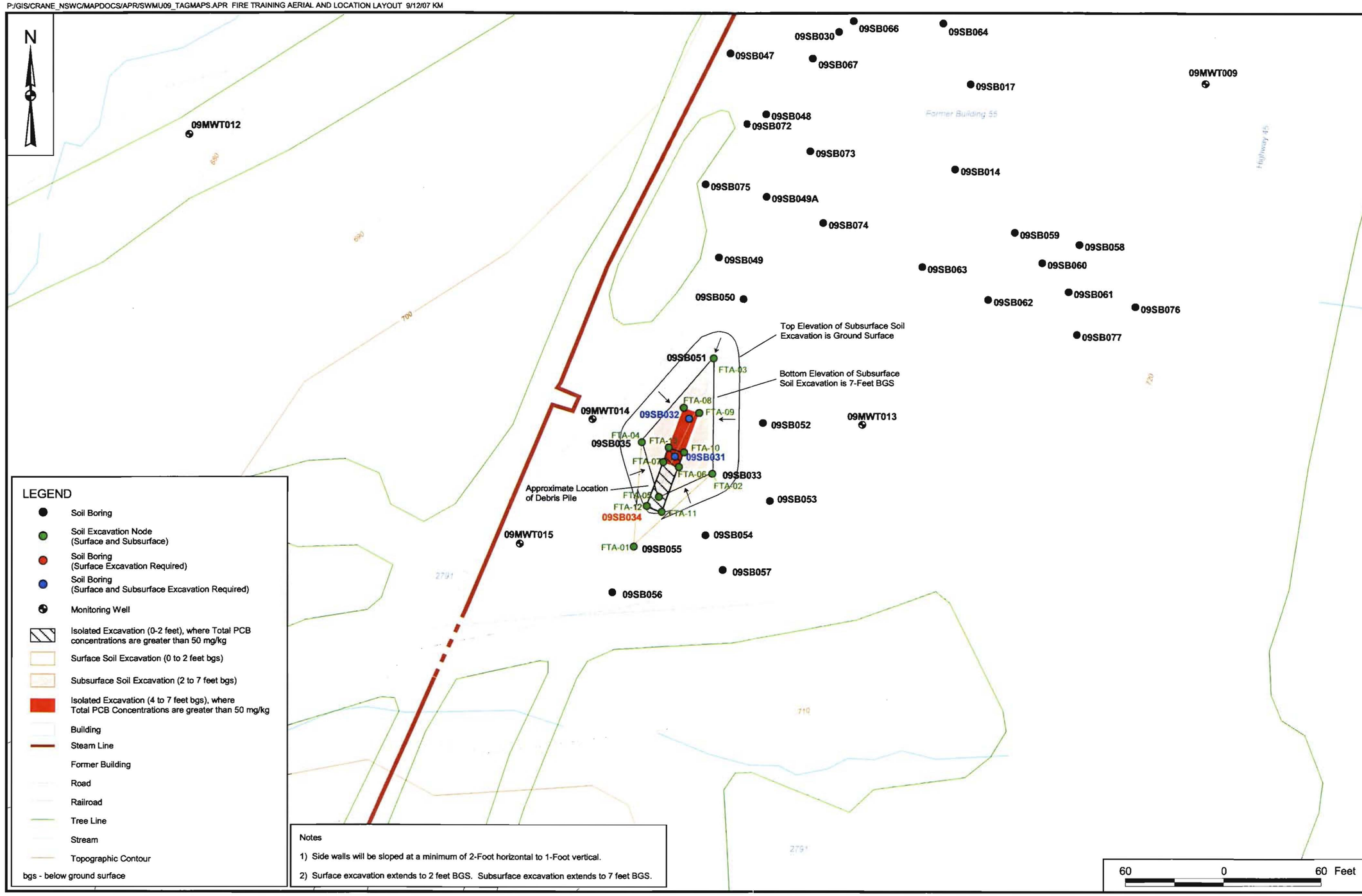


CONTRACT NO. CTO 0042

APPROVED BY ___ DATE ___

APPROVED BY ___ DATE ___

DRAWING NO. FIGURE 1 - 2

REV 1

FORMER FIRE FIGHTING TRAINING AREA EXCAVATION
SWMU 9 QAPP ADDENDUM NO. 4
NSWC CRANE
CRANE, INDIANA

NAVFAC

DRAWN BY S. STROZ DATE 3/29/07

CHECKED BY V. PLACHY DATE 9/12/07

COST/SCHED-AREA

SCALE AS NOTED

2.0 PROJECT ORGANIZATION AND RESPONSIBILITIES

This section describes the project management, organization, and responsibilities of key personnel for IMs designed to remove contamination described in Section 1.0 at NSWC Crane SWMU 9.

Tetra Tech, on behalf of the United States Navy (Navy), is responsible for the preparation for this document and for confirmation sampling and analyses. The remedial contractor is responsible for implementing the IMs for the contamination removal and associated waste disposal. This will include waste sampling and analyses.

The subcontracted laboratory for SMWU 9 is responsible for analyzing all confirmation samples in accordance with the analytical methods and additional requirements specified in this document. It also will be the responsibility of the analytical laboratory to properly dispose of unused sample aliquots.

2.1 MANAGEMENT

The roles and responsibilities described in this section are identified separately for Tetra Tech and NWRS. Individual key persons responsible for work to be conducted under this QAPP Addendum No. 4 are identified in Figure 2-1. Corresponding addresses and telephone numbers of key personnel are listed by organization in Table 2-1.

Tetra Tech and NWRS will report directly to Naval Facilities Engineering Command, Midwest (NAVFAC MW). Tetra Tech and NWRS will maintain open channels of communication during field activities to facilitate resolution of problems as efficiently as possible. Personnel from the Navy will be actively involved and will coordinate with Tetra Tech and NWRS personnel as necessary. Responsibilities for program management, project management, field operations, and laboratory operations are discussed in the following sections, as appropriate. It is intended that the individuals named will assume the designated responsibilities to the extent that the specific person is available to perform the stated activities.

2.1.1 U.S. EPA Oversight

The U.S. EPA Region 5 Project Manager (PM), Peter Ramanauskas, will oversee the implementation of corrective measures at SWMU 9. He will also represent U.S. EPA's interests and will provide input from this perspective and lend general historical and technical assistance to NSWC Crane field activities.

2.1.2 Navy Project Manager

The Navy Remedial Project Manager (RPM), Mr. Howard Hickey, acts as the focal representative for the United States Navy, providing management, technical direction, and oversight for all NSWC Crane project activities performed by contractors (e.g., Tetra Tech and NWRS) and their subcontractors. The Navy RPM is responsible for ensuring that NWRS and their subcontractors receive a copy of this QAPP Addendum No. 4. In matters such as facilitation of site access, oversight, etc., the Navy RPM is assisted by the NSWC Environmental Restoration Site Manager (ERSM), Mr. Tom Brent.

2.1.3 Tetra Tech Program and Project Management

Tetra Tech Program Manager

The Tetra Tech CLEAN Program Manager (ProgMan), Mr. John Trepanowski, provides operations, technical, and administrative leadership and oversees and supports quality policies. The ProgMan assigns project PMs and oversees their performance. The ProgMan also ensures the availability of technical and support resources for program operations, and maintains consistency in procedures and projects among CTO assignments. In these matters, the ProgMan is assisted by the PM.

Tetra Tech Project Manager

The Tetra Tech PM, Mr. Ralph Basinski, has overall responsibility for ensuring that the project meets U.S. EPA objectives and Navy and Tetra Tech quality standards associated with IM oversight, sample collection, sample analyses, and data interpretation to determine whether IMs are completed satisfactorily. The PM is responsible for the preparation and distribution of this QAPP Addendum, at the direction of the Navy RPM, to all parties (except NWRS and their subcontractors) connected with the project. The Navy RPM is responsible for distributing the QAPP Addendum to NWRS and NWRS subcontractors. The PM will report to the Navy RPM and is responsible for technical QC and project oversight. Additional responsibilities of the PM are as follows:

- Ensuring timely resolution of project-related technical, quality, and safety questions associated with Tetra Tech operations.

- Functioning as the primary Tetra Tech interface with the Navy RPM, the NSWC Crane ERSM, Tetra Tech field and office personnel, and laboratory and NWRS points-of-contact.

- Ensuring that Tetra Tech health and safety issues related to this project are communicated effectively to all personnel and off-site laboratories.

- Monitoring and evaluating all Tetra Tech subcontractor performance.

- Coordinating and overseeing work performed by Tetra Tech field and office technical staff (including data validation, data interpretation, and report preparation).

- Coordinating and overseeing maintenance of all Tetra Tech project records.

- Coordinating and overseeing review of Tetra Tech project deliverables.

- Preparing and issuing final Tetra Tech deliverables to the Navy.

- Approving the implementation of corrective actions associated with the Tetra Tech portion of project quality.

Tetra Tech Project Chemist

The Tetra Tech Project Chemist, Mr. Edward Sedlmyer, has overall responsibility for ensuring that the project meets objectives from the standpoint of laboratory performance. The Project Chemist is responsible for the technical preparation of laboratory statements of work (SOWs) and work releases. PMs of all subcontractor laboratories conducting confirmation sample analyses will report to the Tetra Tech Project Chemist. The Project Chemist will report to the Tetra Tech PM. Additional responsibilities of the Project Chemist are as follows:

- Providing technical advice to the Tetra Tech team on matters of project chemistry.
- Monitoring and evaluating subcontractor laboratory performance.
- Ensuring timely resolution of laboratory-related technical, quality, or other issues effecting project goals.
- Functioning as the primary interface with all subcontracted laboratories and the PM.
- Coordinating and overseeing work performed by all subcontracted laboratories.
- Coordinating and overseeing review of laboratory deliverables.
- Recommending appropriate laboratory corrective actions.

Tetra Tech Health and Safety Manager

The Tetra Tech Health and Safety Manager (HSM), Mr. Matt Soltis, is responsible for the following:

- Providing technical advice to the PM on matters of health and safety
- Overseeing the development and review of the Health and Safety Plan (HASP)
- Conducting health and safety audits
- Preparing health and safety reports for management

Each field event will have the support of a health and safety officer that will be assigned by the HSM.

2.1.4 EMAC Project Management

NWRS Project Manager

NWRS has overall responsibility for ensuring that the SWMU 9 project meets U.S. EPA objectives and Navy and NWRS quality standards to ensure that the remediation is completed satisfactorily. The NWRS PM, Mr. Todd Carmichael, will report to the Navy RPM and is responsible for technical QC and project oversight. Additional responsibilities of the NWRS PM are as follows:

- Ensuring timely resolution of project-related technical, quality, and safety associated with NWRS operations.

- Functioning as the primary NWRS interface with the Navy RPM, the NSWC Crane ERSM, Tetra Tech field personnel, and waste disposal facility points of contact.

- Ensuring that NWRS health and safety issues related to this project are communicated effectively to all personnel and off-site laboratories.

- Monitoring and evaluating all NWRS subcontractor performance.

- Coordinating and overseeing work performed by NWRS field staff (including excavation, waste segregation, sludge dewatering, and sampling to determine hazardous status of wastes prior to disposal).

- Coordinating and overseeing maintenance of all NWRS project records.

- Coordinating and overseeing review of NWRS project deliverables.
- Preparing and issuing final NWRS deliverables to the Navy.
- Approving the implementation of corrective actions associated with the SWMU-specific NWRS portion of project quality.

NWRS Field Operations Leaders

The NWRS Field Operations Leader (FOL), Mr. Tim Walls, has overall responsibility for ensuring that the SWMU 9 IM meet objectives from the standpoint of adequate removal of contaminated media and appropriate disposal of wastes. The NWRS FOL will have autonomy with regard to deciding how best to implement the field portion of the IM, but completion of the IM will be determined by Tetra Tech on behalf of the Navy through confirmation sampling and analysis. The NWRS FOL will report to the NWRS PM. Additional responsibilities of the NWRS FOL are as follows:

- Providing technical advice to the field team on matters of remediation goals and implementation of IMWP.
- Ensuring that wastes are sampled representatively to determine their status for waste disposal.
- Ensuring timely resolution of technical, quality, or other issues effecting project goals.
- Functioning as the primary interface with all SWMU-specific NWRS subcontractors and the NWRS PM.
- Recommending appropriate field corrective actions.

NWRS Health and Safety Manager

The NWRS HSM is responsible for the following:

- Providing technical advice to the NWRS PM on matters of health and safety.
- Overseeing the development and review of the HASP.

- Conducting health and safety audits.
- Preparing health and safety reports for management.

2.2 QUALITY ASSURANCE

This section identifies the QA responsibilities for the QAPP Addendum No. 4. Responsibilities of U.S. EPA, Tetra Tech, NWRS, and the analytical laboratories are discussed.

2.2.1 U.S. EPA

The U.S. EPA chemist, Mr. Allen Debus, has the responsibility to review and approve chemistry aspects of the QAPP Addendum No. 4 and to provide overall QA support and review. Additional responsibilities may include the following:

- Coordinating external performance and system audits of the contracted laboratory
- Reviewing and evaluating analytical field and laboratory procedures

2.2.2 Tetra Tech QA Manager

The Tetra Tech Quality Assurance Manager (QAM), Dr. Tom Johnston, is responsible for overall QA for the Tetra Tech portion of the project. He reports directly to the Tetra Tech ProgMan. He acts on behalf of the United States Navy for project QA. The QAM is responsible for the following:

- Developing, maintaining, and monitoring QA policies and procedures.
- Providing training to Tetra Tech staff in QA/QC policies and procedures.
- Conducting systems and performance audits to monitor compliance with environmental regulations, contractual requirements, QAPP requirements, and corporate policies and procedures.
- Auditing project records.
- Monitoring subcontractor quality controls and records.
- Assisting in the development of corrective action plans and ensuring correction of nonconformances reported in internal or external audits.

- Ensuring that this QAPP Addendum meets Tetra Tech, Navy, and U.S. EPA requirements.
- Overseeing the responsibilities of the Tetra Tech Project QA/QC Advisor.
- Preparing QA reports for management.

2.2.3 Tetra Tech Project QA Advisor

The Tetra Tech Project QA Advisor, Ms. Kelly Carper, supports the PM in preparing and reviewing the QAPP and in conducting data assessments. The Project QA Advisor communicates directly with the QAM on matters of QA/QC.

2.2.4 Waste Characterization and Confirmation Sample Laboratory Responsibilities

The subcontracted laboratories are responsible for analyzing all samples in accordance with the analytical methods and additional requirements specified in this QAPP Addendum No. 4. It will also be the analytical laboratories' responsibilities to properly dispose of unused sample aliquots. Responsibilities of key laboratory personnel are outlined in the following paragraphs.

Laboratory Project Manager

The Laboratory PM (confirmation samples) will interface directly with the Tetra Tech Project Chemist and Tetra Tech PM, and the Laboratory PM (waste characterization samples) will interface directly with the NWRS PM. The Laboratory PMs will perform the following tasks:

- Ensure that method and project-specific requirements are properly communicated and understood by laboratory personnel.
- Ensure that all laboratory resources are available on an as-required basis.
- Ensure compliance with analytical and project QA requirements.
- Review data packages for completeness, clarity, and compliance with project requirements.

- Inform the Tetra Tech PM or NWRS PM, as applicable, of project status and any sample receipt or analytical problems.

- Oversee the preparation of and approving final analytical reports before submittal to Tetra Tech.

Laboratory Quality Assurance Officer

The Laboratory QA Officer (QAO) will report directly to the Laboratory Operations Manager. The Laboratory QAO will be independent of laboratory production management to ensure that laboratory quality performance is assessed without schedule and cost considerations. Responsibilities of the Laboratory QAO include the following:

- Defining appropriate laboratory QA procedures and monitoring overall laboratory QA.

- Stopping work if a condition adverse to the quality of work is encountered, if QA or QC procedures are not followed, or if analytical out-of-control events are encountered that have not been corrected.

- Approving and maintaining document control of all QA documents and SOPs.

- Performing and/or implementing internal system and performance audits and verifying completion of corrective actions cited in audits.

- Directing laboratory participation in laboratory accreditation and certification programs.

Laboratory Sample Custodian

The Laboratory Sample Custodian will report to the Laboratory Operations Manager. Responsibilities of the Laboratory Sample Custodian include the following:

- Receiving and inspecting the incoming sample containers.
- Recording the conditions of the incoming sample containers.
- Signing appropriate documents.
- Verifying chain-of-custody records.
- Notifying the Laboratory PM of sample receipt and inspection.
- Assigning a unique identification number and customer number and entering each into the sample receiving log.

- With the help of the Laboratory PM, initiating transfer of the samples to appropriate lab sections.
- Controlling and monitoring access/storage of samples and extracts.

Laboratory Technical Staff

The laboratory technical staff will be responsible for sample analyses based on the analytical methods and requirements specified in this QAPP Addendum No. 4.

2.3 FIELD INVESTIGATION

Tetra Tech will be responsible for all field sampling and analysis activities related to confirming that the IM is completed satisfactorily. NWRS will be responsible for all field sampling and analysis activities directly related to characterization of the remediation wastes for disposal. The Tetra Tech and NWRS field teams will be organized according to the activities planned. Field team members will be selected based on the type and extent of effort required. All team members will be appropriately skilled and trained for the tasks they are assigned to perform

2.3.1 Field Operations Leaders

The Tetra Tech and NWRS FOLs are responsible for coordinating all on-site personnel and for providing technical assistance, when required. The NWRS FOL, or designee, will coordinate and lead all excavation and waste removal operations. The NWRS FOL has authority to complete the field work in the most efficient manner while adhering to the requirements of this QAPP Addendum No. 4 and the HASP. The Tetra Tech FOL will conduct confirmation sampling activities. The Tetra Tech and NWRS FOLs will ensure the availability and maintenance of all sampling materials and equipment pertinent to their function. The Tetra Tech FOL is responsible for completing all sampling, field, and chain-of-custody documentation, will assume custody of all samples sent to the confirmation sampling laboratory, and will ensure the proper handling and shipping of samples. The Tetra Tech FOL will report directly to the Tetra Tech PM but will have authority to guide field operations to efficiently conclude the scheduled work. Specific Tetra Tech and NWRS FOL responsibilities include the following:

- Ensuring that all health and safety requirements unique to the SWMU 9 IM is implemented.

- Functioning as the on-site communications link between field staff members, Site Safety Officer (SSO), the NSWC Crane ERSM, and the Tetra Tech PM or NWRS PM.

- Alerting off-site analytical laboratories of any special health and safety hazards associated with environmental samples.

- Overseeing the mobilization and demobilization of all field equipment and subcontractors.

- Coordinating and managing the field technical staff.

- Adhering to the work schedules provided by the Tetra Tech PM and NWRS PM, as applicable.

- Ensuring the proper maintenance of site logbooks, field logbooks, and field recordkeeping.

- Initiating field task modification requests (field change orders) when necessary.

- Identifying and resolving problems in the field, resolving difficulties via consultation with the NSWC Crane ERSM, implementing and documenting corrective action procedures, and providing communication between the field team and project management.

2.3.2 Site QA/QC Advisor

The FOLs (or designees) will act as the Site QA/QC Advisors and will be responsible for ensuring adherence to all QA/QC requirements as defined in this QAPP Addendum No. 4. Strict adherence to these procedures is critical to the collection of acceptable and representative data. The following is a summary of the Site QA/QC Advisor's responsibilities:

- Ensuring that field QC samples are collected at the proper frequencies.

- Ensuring that additional volumes of sample are supplied to the analytical laboratories with the proper frequency to accommodate laboratory QA/QC analyses.

- Ensuring that measuring and test equipment are calibrated, used, and maintained in accordance with applicable procedures and technical standards.

- Acting as liaison between site personnel, laboratory personnel, and the QAM.

- Managing bottleware shipments and overseeing field preservation.

2.3.3 Site Safety Officer

The FOL (or designee) will also serve as the SSO. The duties of the Tetra Tech SSO are detailed in the Tetra Tech HASP; the duties of the NWRS SSO are detailed in the applicable NWRS HASP. The SSOs have stop-work authority, which can be executed upon the determination of an imminent safety hazard.

2.3.4 Technical Staff

The technical staff for this project will be drawn from pools of qualified personnel. All of the designated team members will be experienced professionals who possess the degree of specialization and technical competence required to effectively and efficiently perform the required work.

Field staff members are responsible for complying with field-related requirements as presented in this QAPP Addendum and the HASP.

2.4 SPECIAL TRAINING REQUIREMENTS AND CERTIFICATIONS

All field personnel will have appropriate training to conduct the field activities to which they are assigned. Additionally, each site worker will be required to have completed a 40-hour course (and 8-hour refresher, if applicable) in Health and Safety Training as described under Occupational Safety and Health Administration (OSHA), 29 CFR 1910.120(b)(4).

TABLE 2-1

KEY PROJECT PERSONNEL
SWMU 9 QAPP ADDENDUM NO. 4
NAMES, PHONE NUMBERS, AND ADDRESSES
NSWC CRANE
CRANE, INDIANA

PERSON / TITLE / ORGANIZATION	ADDRESS	TELEPHONE
Peter Ramanauskas U.S. EPA Region 5 Oversight	EPA Region 5 77 West Jackson Blvd. Chicago, Illinois 60604	Phone: (312) 886-7890 FAX: (312) 353-4788
Howard Hickey Remedial Project Manager U.S. Navy NAVFAC SE	Department of the Navy Building 1A, Code 45313 201 Decatur Avenue Great Lakes, IL 60080	Phone: (847) 688-5999 FAX: (847) 688-2319
Tom Brent Environmental Restoration Site Manager NSWC Crane	NSWC Crane Code 0592-TB B-3260 300 Highway 361 Crane, Indiana 47522-5009	Phone: (812) 854-6160 FAX: (812) 854-4177
Debbie Dills Officer in Charge of Construction NSWC Crane	NAVFAC MW PWD Crane Naval Support Activity Building 2516 Code PRCR22 300 Highway 361 Crane, Indiana 47522-5009	Phone (812) 854-3234 FAX: (812) 854-3800
John Trepanowski Program Manager Tetra Tech	Tetra Tech 234 Mall Boulevard, Suite 260 King of Prussia, Pennsylvania 19406	Phone: (610) 491-9688 FAX: (610) 491-9645
Kelly Carper Quality Assurance Advisor Tetra Tech	Tetra Tech 661 Andersen Drive Pittsburgh, Pennsylvania 15220-2745	Phone: (412) 921-7273 FAX: (412) 921-4040
Matthew Soltis Health and Safety Manager Tetra Tech	Tetra Tech 661 Andersen Drive Pittsburgh, Pennsylvania 15220-2745	Phone: (412) 921-8912 FAX: (412) 921-4040
Steven H. Ruffing Project Manager Tetra Tech	Tetra Tech 661 Andersen Drive Pittsburgh, Pennsylvania 15220-2745	Phone: (412) 921-8989 FAX: (412) 921-4040
Jim Goerdt Field Operations Leader Tetra Tech	Tetra Tech 661 Andersen Drive Pittsburgh, Pennsylvania 15220-2745	Phone: (412) 921-8425 FAX: (412)921-4040
Joseph Samchuck Data Validation Manager Tetra Tech	Tetra Tech 661 Andersen Drive Pittsburgh, Pennsylvania 15220-2745	Phone: (412) 921-8510 FAX: (412) 921-4040
Edward Sedlmyer Project Chemist Tetra Tech	Tetra Tech 661 Andersen Drive Pittsburgh, Pennsylvania 15220-2745	Phone: (412) 921-8704 FAX: (412) 921-4040

TABLE 2-1

KEY PROJECT PERSONNEL
SWMU 9 QAPP ADDENDUM NO. 4
NAMES, PHONE NUMBERS, AND ADDRESSES
NSWC CRANE
CRANE, INDIANA
PAGE 2 OF 3

PERSON / TITLE / ORGANIZATION	ADDRESS	TELEPHONE
Tom Johnston Quality Assurance Manager Tetra Tech	Tetra Tech 661 Andersen Drive Pittsburgh, Pennsylvania 15220-2745	Phone: (412) 921-8615 FAX: (412) 921-4040
Elaine Walker Project Manager Laucks Testing Laboratories, Inc.	Laucks Testing Laboratories, Inc. 940 South Harney Street Seattle, WA 98108	Phone: (206) 957-2433 FAX: (206) 767-5063
Harry Romberg Lab QA Manager Laucks Testing Laboratories, Inc.	Laucks Testing Laboratories, Inc. 940 South Harney Street Seattle, WA 98108	Phone: (206) 767-5060 FAX: (206) 767-5063
Todd Carmichael NWRS Project Manager	NWRS c/o Weston Solutions, Inc. 20 N. Wacker Drive Suite 1210 Chicago, Illinois 60606	Phone: (312) 424-3304 FAX: (312) 424-3330
Tim Walls NWRS Field Operations Leader	NWRS c/o Weston Solutions, Inc. 750 East Bunker Court Suite 500 Vernon Hills, Illinois 60061	Phone: (847) 918-4130 FAX: (847) 918-4055
Lance Moen Alternate Field Operations Leader	NWRS c/o Weston Solutions, Inc. 20 N. Wacker Dr. Suite 1210 Chicago, IL 60606	Phone: (312) 424-3334 FAX: (312) 424-3330
Jerry Richardson Alternate Field Operations Leader	NWRS c/o Weston Solutions, Inc. 750 East Bunker Court Suite 500 Vernon Hills, Illinois 60061	Phone: (812) 325-7198 FAX: (847) 918-4055
Stephen A. Berry NWRS Health and Safety Manager	The Entrepreneurs Center, 714 East Monument Avenue, Dayton, Ohio 45402	Phone: (937) 384-4220 Cell: (937) 602-3085 FAX: (937) 384-4201
Tonya Balla NWRS Quality Assurance Manager	NWRS c/o Weston Solutions, Inc. 750 East Bunker Court Suite 500 Vernon Hills, Illinois 60061	Phone: (847) 918-4094 FAX: (847) 918-4055

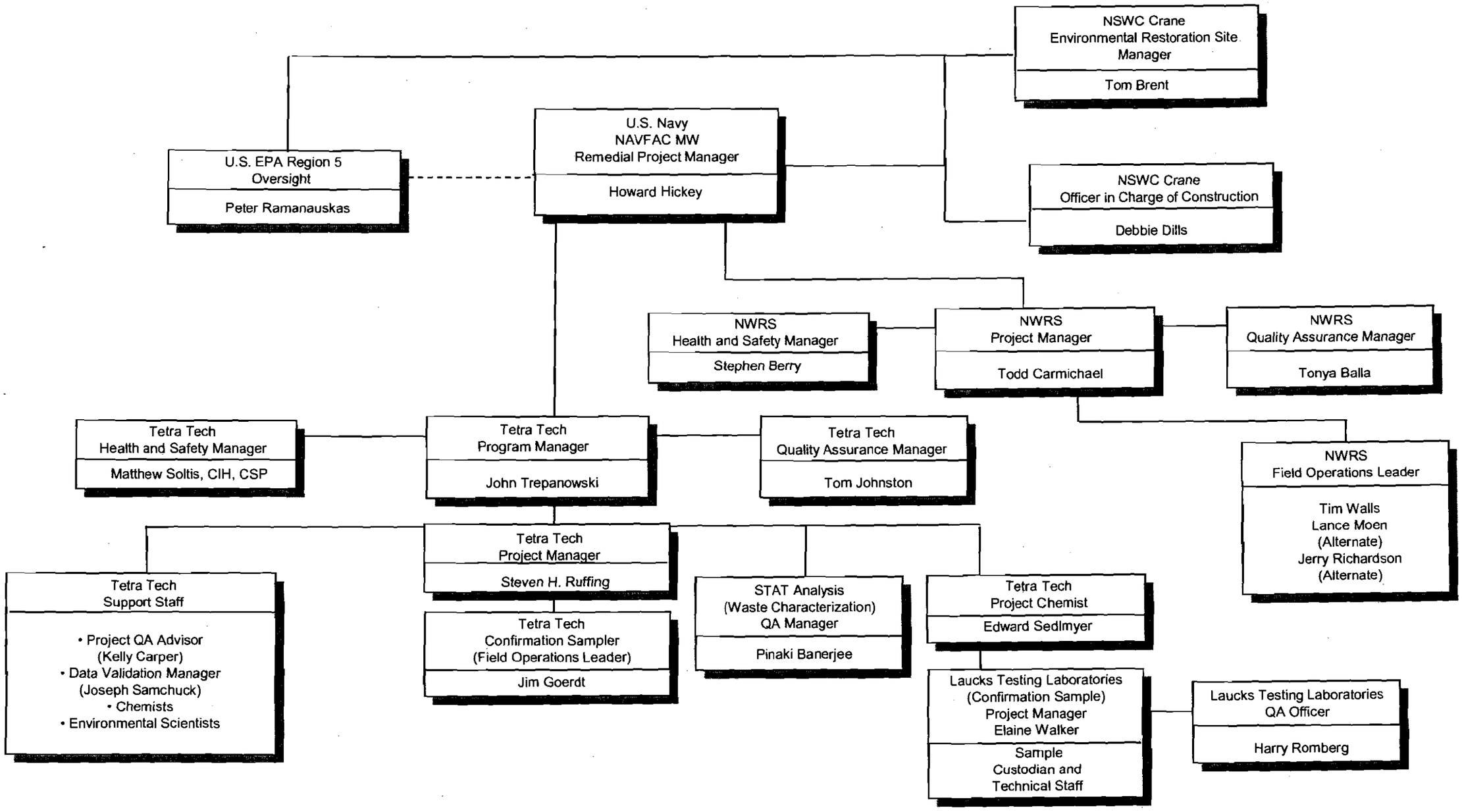
TABLE 2-1

KEY PROJECT PERSONNEL
SWMU 9 QAPP ADDENDUM NO. 4
NAMES, PHONE NUMBERS, AND ADDRESSES
NSWC CRANE
CRANE, INDIANA

PERSON / TITLE / ORGANIZATION	ADDRESS	TELEPHONE
Pinaki Banerjee Lab QA Manager STAT Analysis Corporation	STAT Analysis Corporation 2242 W. Harrison Suite 200 Chicago, Illinois 60612	Phone: (312) 563-0371 FAX: (312) 733-2386

FIGURE 2-1

PROJECT ORGANIZATION CHART
SWMU 9 QAPP ADDENDUM NO. 4
NSWC CRANE
CRANE, INDIANA



NWSR – North Wind Remediation Services, Inc.

3.0 FIELD OPERATIONS - SAMPLING AND ANALYSIS

3.1 GENERAL APPROACH

This section describes sampling locations, methods, and rationales for the sampling activities to be conducted in support of the IM at SWMU 9. Because this QAPP Addendum No. 4 is based on the existing SWMU 8 and 15 QAPP (Tetra Tech, 2004), the requirements regarding field operations as presented in Tetra Tech (2004) will be met during the remediation at SWMU 9, in the event information contained in this QAPP Addendum No. 4 conflicts with the original QAPP, this QAPP Addendum No. 4 shall take precedence.

The equipment and procedures to be used for collecting, handling, preserving, recording, logging, and shipping samples to an analytical laboratory are presented in this QAPP Addendum No. 4. Corresponding Standard Operating Procedures (SOPs) can be found in Appendices A and B. Soil sampling will generally be performed using trowels and buckets.

Prior to any field activities, the Tetra Tech PM and the NWRS PM will ensure that all field personnel read and understand this QAPP Addendum No. 4 and associated HASPs. Tetra Tech and NWRS will each have organization-specific HASPs. Each worker or visitor to the site must sign an acknowledgment that he or she has read and understands the HASPs, as applicable.

The FOLs will ensure that all required field equipment for non-health-and-safety-related operations is available and operational, and the SSOs will ensure that all health-and-safety-related equipment is available and operational.

3.2 SAMPLE IDENTIFICATION SYSTEM

Confirmation Sampling

All samples collected for fixed-base laboratory analyses will be properly labeled with an adhesive-backed sample label affixed to each sample container in accordance with SOP CTO467-01 (Appendix A). The sample labels will include the following information: project name, project location, sample tracking number, sampling date, sampling time, type of analysis required, matrix type, preservative, initials of sampler, and name of the analytical laboratory to which the sample will be submitted.

Surface and subsurface soil composite confirmation samples will be composited from multiple aliquots (grab samples) collected to represent a specific area of an excavation floor or sidewall for the PCB, pesticide, and herbicide analyses. Individual grab samples will be collected for DRO analysis. Composite samples will be formed by blending the aliquots together (blending is described in Section 3.5 and the composite samples will be labeled in accordance with SOP CTO467-02 (Appendix A).

Individual aliquots will be labeled as "A," "B," "C," or "D" to indicate sequential aliquots collected for compositing. The locations where the aliquots are acquired will be noted in the field log using a simple, hand-draw diagram. Aqueous wastewater samples collected to determine disposal requirements will be individual grab samples.

The sampling time recorded on the chain-of-custody form, labels, and tags for duplicate samples will be 0000 so that the samples are "blind" to the laboratory. Notes detailing the sample number, time, date, and type will be recorded on the sample log sheets and will document the location of the duplicate sample (sample log sheets are not provided to the laboratory). Samples to be used as matrix spike (MS) and matrix spike duplicate (MSD) samples must be identified on the field documentation and chain-of-custody forms (see SOP CTO467-03 in Appendix A).

Waste Characterization Sampling

The same sample numbering system developed for confirmation sampling will also be used for the waste characterization sampling.

3.3 SAMPLE CUSTODY PROCEDURES

Confirmation Sampling

Sample custody will be in accordance with CTO467-03 (Appendix A).

Waste Characterization Sampling

Sample custody will be in accordance with CTO467-03 (Appendix A).

3.4 FIELD INSTRUMENT CALIBRATION PROCEDURES AND FREQUENCIES

Confirmation Sampling

Field instrument calibration requirements are specific to the instruments and chemical test kits. These requirements are governed by SOPs in Appendix A or, in the case of PCB test kits, the calibration or standardization instructions that accompany each test kit. It is important that the instructions in each PCB test kit be followed accurately to ensure that the QC requirements specific to each kit are satisfied.

Waste Characterization Sampling

Due to the nature of waste characterization sampling, field instruments are not expected to be used. However, in the case that they are used, the instruments will be calibrated daily in accordance with factory guidelines to ensure proper operation and maintenance. Calibration records will be maintained in a logbook. Malfunctioning instruments will be replaced, as necessary. Spare parts for equipment will be kept on site whenever possible.

3.5 SAMPLING LOCATIONS, ANALYSES, AND RATIONALES

Confirmation Sampling

This section presents sampling rationales, locations, QA/QC samples to be collected, and analyses to be performed for the confirmation sampling and analytical program. 24-hour turnaround times will be requested for all fixed-base laboratory analyses so as to minimize excavation equipment and field personnel down time while samples are analyzed. Field instruments and test kits will be used to guide the field activities, but fixed-base laboratory analyses will be considered the definitive data for determining whether IMs have been completed satisfactorily.

The overall rationale for confirmatory sampling is to ensure that remedial measures have been extensive enough that surface and subsurface soil that are contaminated at concentrations above the media cleanup standard (MCS) have been removed from SWMU 9. Confirmatory samples collected from excavations will be collected as surface soils at the exposed surface, but they will not represent surface soil depths when compared to the original ground elevations at the same locations. Limited depth information will be preserved in the sample numbers to convey to data users the depths bgs represented by the samples. However, continued excavation in a particular area may expose a yet deeper soil surface. The continued excavation at a particular location will be encoded in sample numbers (see SOP CTO467-02 in Appendix A), but it may be necessary to consult the field notes to estimate the depth below

original ground elevation represented by any particular sample. This is not anticipated to be a problem because the goal of this project is to excavate until clean material is encountered, in which case the unacceptably contaminated material is assumed to have been removed.

If QC sampling and analysis is required by the off-site disposal facility, the facility's requirements for QC sample collection will be followed.

Table 3-1 (solid samples) present summaries of the sample analyses, container types and volumes, preservation requirements, and holding times for the confirmation samples to be collected under this QAPP Addendum No. 4. Table 3-2 presents a list of the compounds that will be reported for each analytical method. The total number of samples to be collected is unknown; however, the samples to be collected are described below and in the IMWPs (Tetra Tech, 2007).

Waste Characterization Sampling

This section presents sampling rationale, locations, and analyses to be performed for the waste characterization sampling and analytical program. The following types of sampling will be conducted: excavated soil waste characterization, wastewater disposal characterization, and clean fill (backfill) characterization. The overall rationale for characterization sampling is to ensure that solid and liquid wastes generated during the IM are properly disposed and that the soil used to backfill the excavations is not contaminated.

Tables 3-3 (soil waste), 3-4 (wastewater), and 3-5 (clean fill) present summaries of the sample analyses, container types and volumes, preservation requirements, and holding times for the waste and clean fill characterization samples to be collected under this QAPP Addendum No. 4.

Additional details are provided in Section 3.5.3.

3.5.1 General Sampling Requirements and Considerations

Confirmation Sampling

This section describes requirements and considerations that apply to confirmation sampling during IMs to be conducted at SWMU 9.

Sample collectors have the option to use disposable equipment or reusable equipment for sampling. Disposable sampling equipment will not require decontamination. Reusable sampling equipment must be

decontaminated between samples in accordance with SOP CTO467-04 (Appendix A). Decontamination source water blanks, however, will not be collected because contaminant concentrations in the source water are not anticipated to be present at levels that will influence excavation decisions. Furthermore, results from analysis of field blanks are not expected to influence the course of excavation. All sample collection must be recorded in accordance with the sampling procedures (SOP CTO467-05 for soil in Appendix A and Section 3.5.3 of this QAPP Addendum No. 4).

Sample packaging and shipping for off-site laboratory analyses shall be conducted under chain of custody (see SOP CTO467-03 in Appendix A) in accordance with SOP CTO467-06 (Appendix A). One-day quick turnaround analyses shall be requested from the analytical laboratory. The request for quick turnaround analyses must be noted on each chain of custody.

Uniform random numbers were generated on the interval of 0 to 1 with Microsoft Excel® 2003 (11.6560.6568) SP2 and converted to percentages for Table 3-6. This table indicates relative positions from where confirmation grab samples and composite samples will be collected in excavations. The use of Table 3-6 is described in Section 3.5.3 for each excavation at SWMU 9. Example sample numbers are presented in the text of Section 3.5.3 to demonstrate how samples are to be numbered for the first samples to be collected for each environmental medium at SWMU 9.

Waste Characterization Sampling

General field sampling guidelines are provided in NWRS SOP 2001 (Appendix B). Sample collectors have the option to use disposable equipment or reusable equipment for sampling. Disposable sampling equipment will not require decontamination. Reusable sampling equipment must be decontaminated between samples in accordance with NWRS SOP 2006 (Appendix B). Waste characterization samples may be collected from drums (NWRS SOP 2009, Appendix B), tanks (NWRS SOP 2010, Appendix B), in-situ soil (NWRS SOP 2012, Appendix B), surface water (NWRS SOP 2013, Appendix B), or waste piles (NWRS SOP 2017, Appendix B). All sample collection must be recorded in accordance with the NWRS SOPs (Appendix B). Appendix B also includes additional information on sample containers, decontamination procedures, sample packaging and shipment, and waste transportation and off-site disposal.

3.5.2 Field Instrument Calibration

Confirmation Sampling

Calibration checks of the PCB test kits shall be conducted in accordance with the test kit instructions.

Waste Characterization Sampling

Field instruments are not expected to be used for waste characterization. In the case that they are used, the instruments will be calibrated daily in accordance with factory guidelines.

3.5.3 SWMU 9 Sampling and Analysis

3.5.3.1 Soil Confirmation Sampling and Analysis

Table 3-6, Sets #1 and #2, present random coordinates for composite soil sample aliquots in terms of the percentage of distance from one end of a rectangular excavation to the other end for both X- and Y-directions. The coordinates in Table 3-6 will be used as follows to identify the locations from which to obtain individual aliquots that will then be combined to form a composite sample:

1. If collecting aliquots from an excavation floor, select Set #1.
2. If collecting aliquots from an excavation wall, select Set #2.
3. Select the next sequential composite sample number in the list of composite samples in Table 3-6 (the first sample selected for work conducted at the SWMU 9 will be Sample 1).

Note 1: The sample numbers in Table 3-6 do not represent the sample numbers to be assigned to the composite samples. The Table 3-6 sample numbers should be viewed as index numbers used to distinguish one set of random coordinates from another.

4. Collect a soil aliquot from each of the four pairs (floors and support facilities) or two pairs (side walls) of indicated X- and Y- coordinates for the selected composite sample.

Note 2: If the end of Table 3-6 is reached for a given set of coordinates (e.g., Sample 20 in Set #1 for excavation floors), return to the beginning of that set in the table and continue again to the end of the set in sequential order for each additional composite sample.

Figure 3-1 shows a schematic diagram of how to measure the coordinates for each of the four (or two) sample aliquots that are to be composited from excavation floors (or side walls).

Excavated areas are not likely to be exactly rectangular. The sample collector will use professional judgment to measure the aliquot coordinates in the actual excavation while keeping as close as possible to the prescribed sampling scheme. After coordinates have been selected, collect the soil aliquots in accordance with SOP CTO467-05 (Appendix A) and composite them as follows:

1. Mix soil aliquots of approximately equal volume (determined by visual observation) in a stainless steel bowl until the mixture is homogeneous in texture and color.

2. Remove stones the size of a small pea or larger, sticks, root fragments, leaves, twigs, or other naturally occurring debris to ensure that the sample represents primarily soil.

3.5.3.2 Soil Confirmation PCB Samples

Analyze the composite samples in accordance with the instructions included in the PCB test kit identified in Table 3-1 and the instructions in SOP CTO467-07 (Appendix A). Perform at least one calibration/standardization check daily. Record the total PCB concentration in the field log. QC checks for field analyses shall be conducted at the frequencies indicated in the test kit instructions. The information to be recorded includes but is not limited to the following:

- Analyst's name
- Date/time of analysis
- Test kit identifier, including serial number, if provided
- Reference to corresponding calibration/standardization check
- Sample number
- Measured concentration, including the measurement units

Report the total PCB concentration to NWRS and the Navy RPM so a decision can be made concerning the need for continued excavation.

As long as samples are being produced with field PCB concentrations greater than 1 milligrams per kilogram (mg/kg) in surface samples or 25 mg/kg in subsurface samples, 1 of 10 composite samples will be sent for laboratory verification of PCB concentrations (as Aroclors). In this case, surface soil samples are samples collected within 2 feet of original grade as estimated through visual observation and simple field measurement with a tape measure or other suitable measuring device. If any sample at the limit of excavation has a total PCB concentration less than 1 mg/kg (surface soil) or 25 mg/kg (subsurface soil), that sample will be sent for laboratory verification of PCBs as Aroclors. This will ensure that a minimum of 10 percent or more of field analyses and all final results supporting the conclusion to terminate excavation are verified with laboratory results. For any sample that is analyzed in the field and the fixed-base laboratory, both the field and the laboratory analyzed portions will have the same sample number (see CTO467-02 in Appendix A).

3.5.3.3 Soil Waste Characterization

Prior to the excavation and removal of identified contaminated soils, waste characterization sampling will be conducted as necessary to obtain disposal approval at the selected disposal facilities. Required waste characterization samples will be collected and analyzed prior to the commencement of excavation activities.

A minimum of one waste characterization composite sample will be collected prior to transportation and disposal of soils from the south and west of former Building 55 to comply with the disposal facility requirements and federal, state, and local regulations. NWRS will collect a five-point composite sample using a hand-auger, with effort made to sample from multiple areas and depths to adequately verify the soil. Samples will be collected in accordance with NWRS SOPs 2001, 2012, and/or 2017, as applicable (Appendix B).

The existing RFI Report data, presented in Appendix A of the SWMU 9 IMWP (Tetra Tech, 2007) has been evaluated for SWMU 9 fire training area, Building 150 area, and Building 55 area. The disposal facility determined that the RFI Report data for the fire training area and the Building 150 soils was sufficient for waste characterization profiling and stated that no further characterization sampling was required.

3.5.3.4 Wastewater Characterization

Wastewater is characterized as water from excavation dewatering (stormwater and groundwater) and decontamination water. All wastewater collected at SWMU 9 will be containerized and characterized prior to transport and disposal. Wastewater disposal characterization is necessary in order to properly classify the materials being disposed off site and to ensure that all disposals will be conducted in accordance with federal, state, and local regulations.

All wastewater will be collected in 55-gallon drums or larger vessels depending on the volumes collected. It is not expected that a large amount of wastewater will be generated; therefore, one disposal characterization sample will be collected from the wastewater container(s) prior to transport and disposal. A drum thief will be used to collect the characterization sample. Sample(s) will be collected in accordance with NWRS SOPs 2001, 2009, 2010, and/or 2013, as applicable (Appendix B).

3.5.3.5 Clean Fill Characterization

Excavation areas will be backfilled to preconstruction grades. The types of backfill material required are common fill and topsoil. Clean fill characterization will be completed prior to receiving any backfill at the site. The backfill material must satisfy the following requirements:

- TPH, diesel range organics (DRO) - Less than 1 ppm
- TPH, gasoline range organics (GRO) - Less than 1 ppm
- Sum of benzene, toluene, ethylbenzene, and xylenes - Less than 1 ppm
- Characteristic waste determination - shall not fail the test for characteristic waste
- Total PCBs - Less than 1 ppm
- 4,4'-DDD - Less than 3.2 ppb
- 4,4'-DDE - Less than 3.2 ppb
- 4,4'-DDT - Less than 3.2 ppb
- Dieldrin - Less than 3.2 ppb
- Heptachlor - Less than 1.5 ppb
- Alpha-chlordane - Less than 1.5 ppb
- Gamma-chlordane - Less than 1.5 ppb

All clean fill characterization samples will be collected as composite samples with a hand-auger and disposable scoops. Composite samples will be collected as five-point composite samples, with effort made to sample from multiple areas and depths to adequately characterize the fill source. For example, if clean fill is in stockpiles, samples will be collected from multiple locations on the piles and from multiple depths within the piles. The exact location of the samples will be based on the sampler's discretion and ability to access depth with hand-digging methods. Volatile samples will be collected as a discrete sample. Sample(s) will be collected in accordance with NWRS SOPs 2001, 2012, and/or 2017, as applicable (Appendix B).

There will be a minimum of one sample per type of clean fill, and each source area will be characterized in a one-time sampling event. No in-place sampling will be conducted after the fill has been installed at the site. A site history will be obtained from each clean fill source site.

3.6 QUALITY CONTROL REQUIREMENTS

Refer to Tetra Tech (2004) for generic QC requirements. Project-specific requirements are provided in this section.

In addition to instrument- or test kit-specific calibration requirements (see Section 3.4), the following field QA/QC samples will be collected at the indicated frequencies to support confirmation sampling and analyses.

- In general, duplicate confirmation samples will be collected at a rate of one for every 20 regular samples and analyzed for the same analytes as the corresponding regular samples.

- When fixed-base laboratory analyses are used, enough additional sample volume will be collected to support MS/MSD sample analyses (organic chemical analyses only). The rate of MS/MSD analysis will be one for every 20 regular samples.

- A temperature blank will be added to each cooler that contain samples which must be kept cooled as a preservation requirement.

Definitions of each of these QC sample types are presented in Tetra Tech (2004). Collection of QC samples will not be required for waste characterization sampling and analyses unless required by the off-site disposal facility.

Equipment rinsate blanks (rinsate blanks) will be collected to ensure that cross-contamination of confirmation samples and waste disposal samples does not occur. Source water blanks will not be collected because cross-contamination from source water is not a concern.

3.7 DATA REDUCTION, VALIDATION, ASSESSMENT, AND REPORTING

Generic data reduction, validation, assessment, and reporting requirements are provided in Section 8.0 of Tetra Tech (2004). Project-specific instructions are provided below for this project.

3.7.1 Confirmation Analysis Data

Data from field analyses and other field measurements must be recorded at the time of generation in the field log book or, when provided in the governing SOP, on the SOP-specific data forms. Confirmation sampling results will be entered into the Tetra Tech electronic database soon enough after the data collection to prevent loss of data and to support the generation of reports to the Navy. The data entry process will make use of a dual entry system whereby two independent data entry clerks enter the data and compare the results. Discrepancies, if detected, will be investigated to determine the correct values,

and the correct values will be entered into the database. Non-discrepant results will be considered accurate unless subsequent data review or use indicates otherwise.

The data will be transferred to the Navy in accordance with requirements to be found at the following web site:

https://www.sdirport.com/customer/ttnus/irgateway.nsf/MAINLOADER?OpenFrameSet

The password required to access this site may be obtained through the Navy RPM. The information at this link provides detailed instructions for reporting environmental data. The intent is to standardize reporting formats to improve how environmental data are acquired, managed, and transmitted. The following items are available at this link and the Electronic Data Exchange (EDE) Examples button located at the link:

- SOP
- Electronic Data Deliverable (EDD) spreadsheets and databases
- Electronic data processor
- Example electronic data submittal

3.7.2 Waste Characterization Data

Waste characterization analyses will be provided to the waste disposal facility and NAVFAC MW in the form of hard copies of laboratory data packages as well as data summaries. The data summaries shall identify each sample analyzed, the laboratory conducting the analysis, the results of analysis, and any qualifying notes indicating limitations on data use. At the Navy's discretion, data may also be provided in electronic format in accordance with the specifications identified in Section 3.7.1.

3.8 MANAGEMENT OF INVESTIGATION-DERIVED WASTE

It is anticipated that this investigation could generate the following types of potentially contaminated residues or investigation-derived waste (IDW):

- Personal protective equipment (PPE)
- Equipment decontamination fluids

IDW will be handled as described in CTO467-08 (Appendix A).

3.9 SAFETY

The health and safety activities described in the following sections will ensure that field activities are performed at a high level of safety.

3.9.1 Health and Safety Plan

Separate HASPs will be prepared by Tetra Tech and NWRS. These HASPs describe specific health and safety requirements, concerns, and information related to the site activities. These documents will be read and understood by each person working at the site. Each worker or visitor to the site must sign an acknowledgment that he or she has read and understands the HASP.

3.9.2 Health and Safety Training

All workers involved with the site investigations shall have successfully completed the OSHA-mandated 40-hour health and safety training and the current annual 8-hour refresher courses when appropriate.

3.9.3 Medical Approval and Personal Protective Clothing and Equipment

Tetra Tech workers at the site must be part of a medical monitoring program and must be medically approved to perform their duties without physical limitations. Protective clothing and equipment, as specified in the HASP, will be worn while performing site activities.

3.9.4 Safety Meetings

Safety meetings will be held among on-site workers whenever the SSO for each contractor feels it is appropriate. The SSO will discuss safety issues related to activities being performed and will make site workers aware of any new conditions that could potentially affect health or safety.

3.10 PERFORMANCE AND SYSTEM AUDITS

Section 9.1 of the SWMU 8 and 15 QAPP (Tetra Tech, 2004) presents generic requirements for field operations performance and system audits. No special requirements are anticipated for this project.

3.11 INSPECTION AND MAINTENANCE

Sections 10.1 and 10.3 of Tetra Tech (2004) present generic inspection and maintenance requirements to ensure that field consumables and equipment are in proper working order and available when needed. In addition, project-specific requirements are provided below.

Chemical Test Kits - PCBs

The receipt date and the expiration date of receipts (i.e., purchase date plus 1 year) shall be written on the test kit (receipt date) and the reagents (expiration date) on each reagent bottle and the kit if the expiration date is not already indicated. Follow manufacturer instructions for storage and handling of the kits. Do not use kits or kit components past their expiration dates.

3.12 FIELD CORRECTIVE ACTIONS

Field non-conformances or conditions adverse to quality must be identified and corrected as quickly as possible so that work integrity or product quality is not compromised. The need for corrective action may arise based on deviations from project plans and procedures, adverse field conditions, or other unforeseen circumstances. Corrective action needs may become apparent during the performance of daily work tasks or as a consequence of internal or external field audits.

Corrective action may include resampling, re-excavation or other rework and may involve amending previously approved field procedures. Minor modifications to field activities, such as the collection of additional samples, will be initiated at the discretion of the FOL, subject to on-site approval by NSWC Crane personnel. Major modifications or situations that affect compliance with or achievement of Data Quality Objectives (DQOs) must be approved and documented via a Field Task Modification Request (FTMR). Approval of the corrective action will be obtained by the United States Navy (in conjunction with IDEM). The Tetra Tech or NWRS FOL is responsible for initiating FTMRs. An FTMR will be prepared for all deviations from the project plan documents, as applicable. Copies of all FTMRs will be maintained with the on-site project planning documents and will be placed in the final evidence file.

3.13 QUALITY ASSURANCE REPORTS TO MANAGEMENT

The Tetra Tech FOL will provide the PM with daily verbal field progress reports during the course of the IM. The NWRS FOL will provide daily verbal reports to the NWRS PM during the course of IM. These reports will explain accomplishments, deviations from the QAPP, and upcoming activities, and will provide a QA summary. The Tetra Tech PM and NWRS PM will provide written monthly progress reports to the

Navy that address the project budget, schedule, accomplishments, planned activities, and QA/QC issues and intended corrective actions.

TABLE 3-1

SUMMARY OF SAMPLE ANALYSES, CONTAINER TYPES AND VOLUMES, PRESERVATION REQUIREMENTS, AND HOLDING TIMES FOR FIELD ANALYSIS AND LABORATORY CONFIRMATION ANALYSIS OF SOILS SWMU 9 QAPP ADDENDUM NO. 4 NSWC CRANE CRANE, INDIANA

Parameter	Analyte/Methodology/ SOP	Sample Container	Container Volume	Preservation	Maximum Holding Time[1]
Field Analyses					
PCBs	RaPID Assay Test Kit (0.5 to 10 ppm) with SDI Sample Extraction Kit	Wide-mouth jar, Teflon-lined plastic cap	8-ounce	NA	Analysis within 14 days
PCBs	SW-846 8082A LTL-3303 / LTL-8084	Wide-mouth jar, Teflon-lined plastic cap	8-ounce	Cool to 4 °C	Extraction within 14 days; analysis within 40 days of extraction.
DRO	SW-846 Modified 8015B LTL-3112 / LTL-8013	Wide-mouth jar, Teflon-lined plastic cap	8-ounce	Cool to 4 °C	Extraction within 14 days; analysis within 40 days of extraction.
Pesticides	SW-846 8081A LTL-3303 / LTL-8084	Wide-mouth jar, Teflon-lined plastic cap	8-ounce	Cool to 4 °C	Extraction within 14 days; analysis within 40 days of extraction.

1 All holding times for analysis are from date of collection. Minimum turnaround times will be requested from the laboratory. Miminum turnaround will be based upon the analytical method; however, one-day turnaround from laboratory receipt of samples is preferred.

°C - Degrees Celsius.
LTL - Laucks Testing Laboratories, Inc.
PCBs - Polychlorinated biphenyls.
ppm - Parts per million.
SOP - Standard operating procedure.
SW-846 - U.S. EPA, 1986. Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods. SW-846, Third Edition and subsequent updates.
DRO – Diesel range organics.

TABLE 3-1

SUMMARY OF SAMPLE ANALYSES, CONTAINER TYPES AND VOLUMES, PRESERVATION REQUIREMENTS, AND HOLDING TIMES FOR FIELD ANALYSIS AND LABORATORY CONFIRMATION ANALYSIS OF SOILS SWMU 9 QAPP ADDENDUM NO. 4 NSWC CRANE CRANE, INDIANA

Parameter	Analyte/Methodology/ SOP	Sample Container	Container Volume	Preservation	Maximum Holding Time[1]
Field Analyses					
PCBs	RaPID Assay Test Kit (0.5 to 10 ppm) with SDI Sample Extraction Kit	Wide-mouth jar, Teflon-lined plastic cap	8-ounce	NA	Analysis within 14 days
PCBs	SW-846 8082A LTL-3303 / LTL-8084	Wide-mouth jar, Teflon-lined plastic cap	8-ounce	Cool to 4 °C	Extraction within 14 days; analysis within 40 days of extraction.
DRO	SW-846 Modified 8015B LTL-3112 / LTL-8013	Wide-mouth jar, Teflon-lined plastic cap	8-ounce	Cool to 4 °C	Extraction within 14 days; analysis within 40 days of extraction.
Pesticides	SW-846 8081A LTL-3303 / LTL-8084	Wide-mouth jar, Teflon-lined plastic cap	8-ounce	Cool to 4 °C	Extraction within 14 days; analysis within 40 days of extraction.

1 All holding times for analysis are from date of collection. Minimum turnaround times will be requested from the laboratory. Miminum turnaround will be based upon the analytical method; however, one-day turnaround from laboratory receipt of samples is preferred.

°C - Degrees Celsius.
LTL - Laucks Testing Laboratories, Inc.
PCBs - Polychlorinated biphenyls.
ppm - Parts per million.
SOP - Standard operating procedure.
SW-846 - U.S. EPA, 1986. Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods. SW-846, Third Edition and subsequent updates.
DRO – Diesel range organics.

TABLE 3-2

COMPOUND LIST
SWMU 9 QAPP ADDENDUM NO. 4
NSWC CRANE
CRANE, INDIANA

PARAMETER	CASRN
ORGANOCHLORINE PESTICIDES (SW-846 METHOD 8081A)	
alpha-chlordane	5103-71-9
4,4'-DDD	72-54-8
4,4'-DDE	72-55-9
4,4'-DDT	50-29-3
Dieldrin	60-57-1
gamma-chlordane	12789-03-6
Heptachlor	76-44-8
POLYCHLORINATED BIPHENYLS (SW-846 METHOD 8082)	
Aroclor-1016	12674-11-2
Aroclor-1221	11104-28-2
Aroclor-1232	11141-16-5
Aroclor-1242	53469-21-9
Aroclor-1248	12672-29-6
Aroclor-1254	11097-69-1
Aroclor-1260	11096-82-5
DIESEL RANGE ORGANICS (SW-846 METHOD 8015)	
Diesel range organics	NA

CASRN - Chemical Abstract Registry Number.
NA - Not applicable
QAPP - Quality Assurance Project Plan.

TABLE 3-3

SUMMARY OF SAMPLE ANALYSES, CONTAINER TYPES AND VOLUMES, PRESERVATION REQUIREMENTS, AND HOLDING TIMES FOR SOIL WASTE CHARACTERIZATION
SWMU 9 QAPP ADDENDUM NO. 4
NSWC CRANE
CRANE, INDIANA

Parameter	Analytical Method/SOP	Sample Container	Preservation	Maximum Holding Time[1]
TCLP Metals	SW-846 1311/6020/7471A STAT 2125/4510/4530	8- or 32-ounce glass	Cool to 4 °C; HCl to pH<2 (after extraction)	Extraction within 14 days; analysis within 40 days of extraction.
TCLP Volatiles	SW-846 1311/8260B STAT 2125/4000	8- or 32-ounce glass	Cool to 4 °C; HNO_3 to pH<2 (after extraction)	Analysis within 14 days.
TCLP Semivolatiles	SW-846 1311/8270C STAT 2125/4020	8- or 32-ounce glass	Cool to 4 °C	Extraction within 14 days; analysis within 40 days of extraction.
TCLP Pesticides and Herbicides	SW-846 1311/8081A/8321A STAT 2125/4050/4080	8- or 32-ounce glass	Cool to 4 °C	Extraction within 14 days; analysis within 40 days of extraction.
Characteristic Waste Determination – Ignitability, Corrosivity, Reactivity	STAT 4210	8- or 32-ounce glass	Cool to 4 °C	As soon as possible.

1 All holding times are from date of collection.

°C – Degrees Celsius.
HCl – Hydrochloric acid.
HNO_3 – Nitric acid.
SOP – Standard Operating Procedure.
STAT – STAT Analysis Corporation.
SW-846 – U.S. EPA, 1986. Test Methods for Evaluating Solid Wastes, Physical Chemical Methods. Third edition and subsequent updates.

TABLE 3-4

SUMMARY OF SAMPLE ANALYSES, CONTAINER TYPES AND VOLUMES, PRESERVATION REQUIREMENTS, AND HOLDING TIMES FOR WASTEWATER CHARACTERIZATION
SWMU 9 QAPP ADDENDUM NO. 4
NSWC CRANE
CRANE, INDIANA

Parameter	Analytical Method/SOP	Sample Container	Preservation	Maximum Holding Time[1]
Total Volatiles	SW-846 8260B STAT 4000	40-ml VOA vial	Cool to 4 °C; HCl to pH<2	Analysis within 14 days.
Total PCBs	SW-846 8082 STAT 4050	1-L amber glass	Cool to 4 °C	Extraction within 14 days; analysis within 40 days of extraction.
Total Semivolatiles	SW-846 8270C STAT 4020	1-L amber glass	Cool to 4 °C	Extraction within 14 days; analysis within 40 days of extraction.
Total RCRA 8 Heavy Metals	SW-846 6020/7470A STAT4510/4530	500-mL plastic	Cool to 4 °C; HNO_3 to pH<2	Extraction within 14 days; analysis within 40 days of extraction.
Total Pesticides	SW-846 8081A STAT 4050	1-L amber glass	Cool to 4 °C	Extraction within 14 days; analysis within 40 days of extraction.
Total Herbicides	SW-846 8321A STAT 4080	1-L amber glass	Cool to 4 °C	Extraction within 14 days; analysis within 40 days of extraction.
Characteristic Waste Determination – Ignitability, Corrosivity, Reactivity	STAT 4210	1-L amber glass	Cool to 4 °C	As soon as possible.

1 All holding times are from date of collection.

°C – Degrees Celsius.
HCl – Hydrochloric acid.
HNO_3 – Nitric acid.
L – Liter.
mL – Milliliter.
PCBs – Polychlorinated biphenyls.
SOP – Standard Operating Procedure.
STAT – STAT Analysis Corporation.
SW-846 – U.S. EPA, 1986. Test Methods for Evaluating Solid Wastes, Physical Chemical Methods. Third edition and subsequent updates.
VOA – Volatile organic analysis.

TABLE 3-5

SUMMARY OF SAMPLE ANALYSES, CONTAINER TYPES AND VOLUMES, PRESERVATION REQUIREMENTS, AND HOLDING TIMES FOR CLEAN FILL CHARACTERIZATION
SWMU 9 QAPP ADDENDUM NO. 4
NSWC CRANE
CRANE, INDIANA

Parameter	Analytical Method/SOP	Sample Container	Preservation	Maximum Holding Time[1]
TPH – DRO, GRO	SW-846 8015M STAT 4090	8- or 32-ounce glass	Cool to 4 °C	Extraction within 7 days; analysis within 40 days of extraction.
Total benzene, toluene, ethylbenzene, and xylenes	SW-846 5035 STAT 4000	40-mL VOA vials	Cool to 4 °C; two 40-mL vials with sodium bisulfate and one 40-mL vials with methanol.	Analysis within 14 days.
Total PCBs	SW-846 8082 STAT 4050	8- or 32-ounce glass	Cool to 4 °C	Extraction within 14 days; analysis within 40 days of extraction.
Pesticides – 4,4'-DDD, 4,4'-DDE, 4,4'-DDT, dieldrin, heptachlor, alpha- and gamma-chlordane	SW-846 – 8081A STAT 4050	8- or 32-ounce glass	Cool to 4 °C	Extraction within 14 days; analysis within 40 days of extraction.
TCLP Metals	SW-846 1311/6020/7471A STAT 2125/4510/4530	8- or 32-ounce glass	Cool to 4 °C; HCl to pH<2 (after extraction)	Extraction within 14 days; analysis within 40 days of extraction.
TCLP Volatiles	SW-846 1311/8260B STAT 2125/4000	8- or 32-ounce glass	Cool to 4 °C; HNO_3 to pH<2 (after extraction)	Analysis within 14 days.
TCLP Semivolatiles	SW-846 1311/8270C STAT 2125/4020	8- or 32-ounce glass	Cool to 4 °C	Extraction within 14 days; analysis within 40 days of extraction.
TCLP Pesticides and Herbicides	SW-846 1311/8081A/8321A STAT 2125/4050/4080	8- or 32-ounce glass	Cool to 4 °C	Extraction within 14 days; analysis within 40 days of extraction.
Characteristic Waste Determination – Ignitability, Corrosivity, Reactivity	STAT 4210	8- or 32-ounce glass	Cool to 4 °C	As soon as possible.

TABLE 3-5

SUMMARY OF SAMPLE ANALYSES, CONTAINER TYPES AND VOLUMES, PRESERVATION REQUIREMENTS, AND HOLDING TIMES FOR CLEAN FILL CHARACTERIZATION
SWMU 9 QAPP ADDENDUM NO. 4
NSWC CRANE
CRANE, INDIANA

1 All holding times are from date of collection.

°C – Degrees Celsius.
DRO – Diesel range organics.
GRO – Gasoline range organics.
HCl – Hydrochloric acid.
HNO_3 – Nitric acid.
mL – Milliliter.
SOP – Standard Operating Procedure.
STAT – STAT Analysis Corporation.
SW-846 – U.S. EPA, 1986. Test Methods for Evaluating Solid Wastes, Physical Chemical Methods. Third edition and subsequent updates.
TPH – Total petroleum hydrocarbons.
VOA – Volatile organic analysis.

TABLE 3-6

EXCAVATION FLOOR AND SIDE WALL SAMPLES
SWMU 9 QAPP ADDENDUM NO. 4
NSWC CRANE
CRANE, INDIANA

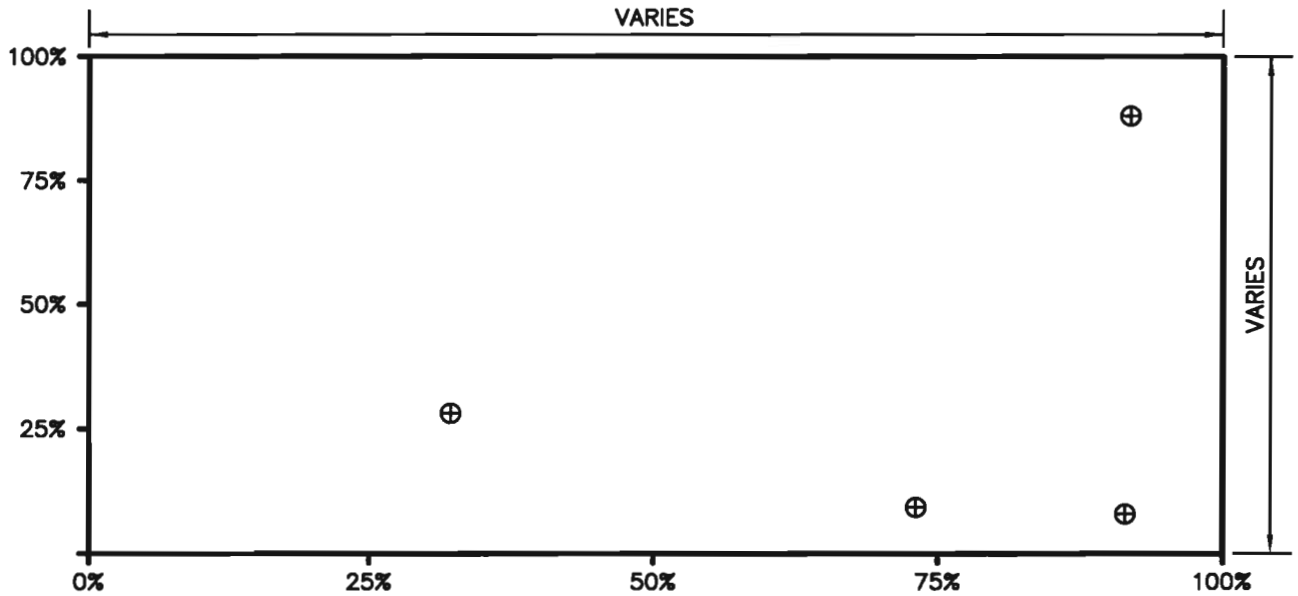
Set #1 - Excavation Floor and Interim Measures Support Facility Composite Samples for SWMU 9

Sample Rotation	Grid Location		Sample Rotation	Grid Location		Sample Rotation	Grid Location		Sample Rotation	Grid Location	
	X %	Y %		X %	Y %		X %	Y %		X %	Y %
Sample Series 1	93	85	Sample Series 6	21	79	Sample Series 11	48	66	Sample Series 16	33	24
	74	6		21	21		23	67		20	75
	94	5		75	24		80	72		59	69
	35	30		58	50		67	36		88	2
Sample Series 2	89	38	Sample Series 7	65	46	Sample Series 12	57	62	Sample Series 17	57	72
	22	87		48	31		91	80		67	30
	98	52		60	3		37	22		17	81
	15	47		74	96		11	41		25	39
Sample Series 3	15	48	Sample Series 8	55	1	Sample Series 13	87	89	Sample Series 18	30	84
	92	63		31	27		87	87		89	93
	49	1		22	56		65	3		59	83
	52	88		42	83		85	35		43	99
Sample Series 4	97	13	Sample Series 9	5	85	Sample Series 14	39	71	Sample Series 19	22	39
	31	32		84	38		100	46		9	78
	28	2		93	20		87	31		91	15
	3	70		51	22		56	36		36	11
Sample Series 5	53	9	Sample Series 10	10	48	Sample Series 15	14	36	Sample Series 20	83	100
	53	82		94	91		73	51		13	74
	77	11		81	89		30	29		13	1
	95	3		39	72		89	83		40	58

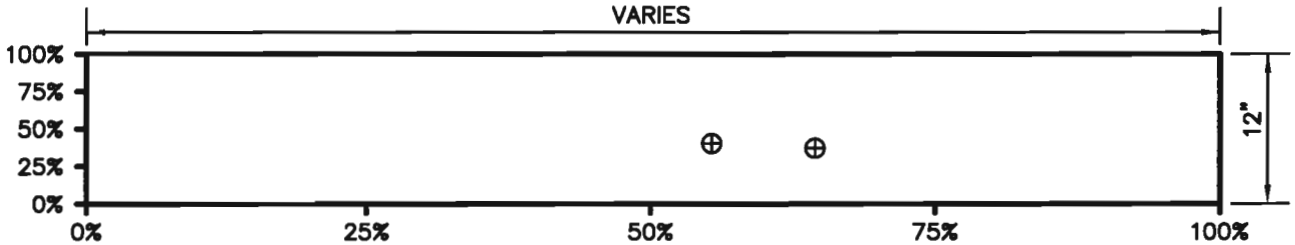
Set #2 - Excavation Wall / Bank Composite Samples for SWMU 9

Sample Rotation	Grid Location		Sample Rotation	Grid Location		Sample Rotation	Grid Location		Sample Rotation	Grid Location	
	X %	Y %		X %	Y %		X %	Y %		X %	Y %
Sample Series 1	5	85	Sample Series 6	49	20	Sample Series 11	99	1	Sample Series 16	40	11
	69	36		58	29		43	98		30	64
Sample Series 2	62	45	Sample Series 7	19	44	Sample Series 12	62	49	Sample Series 17	98	78
	56	46		27	53		44	30		78	4
Sample Series 3	34	60	Sample Series 8	53	7	Sample Series 13	50	38	Sample Series 18	25	71
	70	5		93	29		59	29		70	19
Sample Series 4	21	93	Sample Series 9	23	45	Sample Series 14	45	24	Sample Series 19	4	49
	95	6		52	95		92	2		37	11
Sample Series 5	100	29	Sample Series 10	32	49	Sample Series 15	66	86	Sample Series 20	76	32
	91	21		48	66		71	34		29	70

ACAD: 0352CP09.dwg 11/16/07 MF PIT



TYPICAL SWMU 9 EXCAVATION FLOOR
LOCATION REPRESENTS SAMPLE SERIES 1, SET 1, ON TABLE 3-6



TYPICAL SWMU 9 EXCAVATION SIDEWALL
LOCATION REPRESENTS SAMPLE SERIES 2, SET 2, ON TABLE 3-6

LEGEND:

⊕ ALIQUOT SAMPLE LOCATION

0% PERCENT DISTANCE ALONG EXPOSED SURFACE

DRAWN BY MF	DATE 11/16/07	SWMU 9 EXCAVATION SAMPLE LOCATIONS EXAMPLE INTERIM MEASURES QAPP ADDENDUM NO. 4 NSWC CRANE CRANE, INDIANA	CONTRACT NO. 0467
CHECKED BY	DATE		OWNER NO.
REVISED BY	DATE		APPROVED BY / DATE
SCALE NONE			DRAWING NO. FIGURE 3-1 / REV. 0

NAVFAC

FORM CADD NO. SDIV-AH.DWG – REV 1 – 9/10/98

4.0 LABORATORY OPERATIONS AND DATA REDUCTION, REVIEW, AND MANAGEMENT

4.1 SAMPLE CUSTODY PROCEDURES

Samples will be labeled and shipped to the analytical laboratory in accordance with Section 3.0 of this document. Laboratory-specific custody procedures are governed by Section 4.0 of the SWMUs 8 and 15 QAPP (Tetra Tech, 2004).

4.2 LABORATORY INSTRUMENT CALIBRATION PROCEDURES AND FREQUENCIES

Refer to Section 5.2 of the SWMUs 8 and 15 QAPP (Tetra Tech, 2004) for laboratory calibration requirements. Only requirements for PCB (as Aroclors), pesticides, herbicides, and DRO analyses will be applicable.

4.3 LABORATORY ANALYTICAL AND MEASUREMENT PROCEDURES

4.3.1 Confirmation Sample Analyses

The laboratory analyses of confirmation samples will be performed by Laucks Testing Laboratories. Laucks Testing Laboratories has successfully completed the laboratory evaluation process required as part of the Naval Facilities Engineering Services Command (NFESC) QA Program and described in the Navy Installation Restoration Laboratory Quality Assurance Guide (NFESC, 1996). Table 3-1 provides a summary of the laboratory analytical methods and associated laboratory SOPs to be used during this investigation. Laboratory SOPs are included in Appendix C.

4.3.2 Waste Characterization Analyses

The laboratory analysis of waste characterization samples will be performed by STAT Analysis Corporation. Tables 3-3 through 3-5 provide a summary of the laboratory analytical methods and associated laboratory SOPs to be used for waste soil characterization, wastewater characterization, and clean fill characterization, respectively. Laboratory SOPs are included in Appendix D.

4.3.3 List of Project Target Compounds and Detection Limits

A list of the laboratory target analytes and laboratory-specific target values (TVs) for organic compounds and reporting limits (RLs) for all applicable analytes, except DRO is provided in Table 1-5 of the SWMUs

8 and 15 QAPP (Tetra Tech, 2004). Table 3-1 of this QAPP Addendum No. 4 identifies the analyses to be conducted. The analytical fractions (i.e., pesticides, herbicides, and PCBs) correspond to the same entries in Table 1-5 of Tetra Tech (2004). The DRO fraction laboratory-specific TV and RL are 2.5 mg/kg and 5.0 mg/kg respectively for soils.

4.4 LABORATORY QUALITY CONTROL CHECKS

Descriptions of various data quality indicators and the types of laboratory QC samples used to measure or verify data quality indicators (DQIs) are presented in Sections 7.0 through 7.5 of SWMUs 8 and 15 QAPP (Tetra Tech, 2004). Requirements for laboratory QC checks are presented in Section 7.8 of Tetra Tech (2004).

4.5 DATA REDUCTION, VALIDATION, ASSESSMENT, AND REPORTING

Refer to Section 8.0 of the SWMUs 8 and 15 QAPP (Tetra Tech, 2004) for laboratory-specific requirements. Section 8.0 of Tetra Tech (2004) also identifies requirements for reconciling data against DQOs.

4.6 LABORATORY PERFORMANCE AND SYSTEM AUDITS

4.6.1 Confirmation Analyses

Laboratory performance and system audit requirements are presented in Section 9.2 of the SMWUs 8 and 15 QAPP (Tetra Tech, 2004) for confirmation analyses.

4.6.2 Waste Characterization

4.6.2.1 Laboratory Performance and Systems Audits

This section presents the responsibilities, frequencies, and procedures associated with internal and external laboratory performance and system audits.

4.6.2.1.1 Internal Laboratory Audits

Internal Laboratory Audit Responsibilities

The Quality Assurance Director or appropriate designee of the laboratory performs routine internal audits of the laboratory. NWRS has no responsibility for such audits. Performance and system audits of laboratories are coordinated through STAT's Quality Assurance Director.

Internal Laboratory Audit Frequency

Internal audits are performed approximately annually at the laboratory. In addition, each laboratory department analyzes blind performance evaluation (PE) samples as described in their applicable SOPs and QA plans.

Internal Laboratory Audit Procedures

Internal systems audits are conducted to detect any problems in sample flow, analytical procedures, or documentation and to ensure adherence to laboratory SOPs. The internal audit procedures for STAT Laboratories are presented in applicable laboratory SOPs or the QA Plan.

4.6.2.1.2 External Laboratory Audits

External Laboratory Audit Responsibilities

IDEM and U.S. EPA Region 5 may perform external audits at their discretion.

The laboratory is also involved in various other external audits and performance evaluation studies throughout the year, as required, to maintain certifications and approvals by other regulatory agencies or programs.

External Laboratory Audit Frequency

IDEM or U.S. EPA Region 5 may conduct an external laboratory audit prior to or during sampling and analysis activities.

Overview of the External Laboratory Audit Process

External audit procedures are at the discretion of IDEM and U.S. EPA Region 5. External laboratory audits may include (but are not limited to) review of laboratory analytical procedures, laboratory on-site audits, and submission of PE samples to the laboratory for analysis.

4.7 LABORATORY INSTRUMENT PREVENTIVE MAINTENANCE

Proper maintenance of laboratory instruments and equipment is essential. Depending on manufacturers' recommendations, maintenance intervals are established for each instrument. All instruments will be labeled with a model number and serial number, and a maintenance logbook will be maintained for each instrument. Personnel will be alert to the maintenance status of the equipment they are using at all times.

4.7.1 Confirmation Analysis

Refer to Section 10.2 of Tetra Tech (2004) for specific preventive maintenance requirements related to confirmation sampling.

4.7.2 Waste Characterization

Proper maintenance of laboratory instruments and equipment is essential. Depending on manufacturers' recommendations, maintenance intervals are established for each instrument. All instruments are labeled with a model number and serial number, and a maintenance logbook is maintained for each instrument. Personnel will be alert to the maintenance status of the equipment they are using at all times.

The use of manufacture-recommended grades or better of supporting supplies and reagents is also a form of preventive maintenance. For example, gases used in the inductively coupled plasma (ICP) instruments will be of sufficient quality to minimize fouling of the instrument. The routine use of other supporting supplies from reputable manufacturers will help prevent unnecessary periods of instrument downtime.

4.8 LABORATORY CORRECTIVE ACTION

In general, laboratory corrective actions are warranted whenever an out-of-control event or potential out-of-control event is noted. The specific corrective action taken depends on the specific analysis and the nature of the event. Generally, the following occurrences alert laboratory personnel that corrective action may be necessary:

- QC data are outside established warning or control limits
- Method blank analyses yield concentrations of target analytes greater than acceptable levels
- Undesirable trends are detected in spike percent recoveries (%Rs) or in duplicate Relative Percent Differences (RPDs)
- There is an unexplained change in compound detection capability
- Inquiries concerning data quality are received
- Deficiencies are detected by laboratory QA staff during audits or from performance evaluation (PE) sample test results

4.8.1 Corrective Action Documentation

Specific procedures for laboratory corrective actions are specified in the associated laboratory SOPs. Any corrective action taken above the analyst level that cannot be performed immediately at the instrument will be documented.

Laboratory corrective actions must be documented and included as part of the final evidence file. The Tetra Tech PM will be informed of all major corrective actions that do not bring DQO-related nonconformances into conformance with project DQOs. The Tetra Tech PM will advise all levels of project management in accordance with Section 12.0 of the SWMU 8s and 15 QAPP (Tetra Tech, 2004).

4.8.2 Corrective Action During Data Validation and Data Assessment

The need for corrective action may become apparent during data validation, interpretation, or presentation activities. Rework (i.e., resampling or reanalysis), a change in work procedures, or additional or refresher training are possible corrective actions relevant to data evaluation activities. The Tetra Tech PM will be responsible for approving the implementation of a corrective action and ensuring that it is documented appropriately for all deficiencies except those that are internal to NWRS. The NWRS PM will be responsible for the latter corrective actions. Analytical data may be qualified during data validation to alert data users of the potential that particular analytical results are potentially deficient relative to expected performance standards. Such validation practices are described in Section 8.0 of the

SWMUs 8 and 15 QAPP (Tetra Tech, 2004). When conducting data assessment for project decision making, a number of situation-dependent qualifications of data or decisions are possible. The number of possible situations or conditions precludes enumeration of all possible corrective actions; however, the approach used to identify and impose such qualifications is described in Section 8.0 of Tetra Tech (2004).

4.9 QUALITY ASSURANCE REPORTS TO MANAGEMENT

QA reports to management will be provided in four primary formats during the course of this investigation: data validation reports, reports summarizing accomplishments and QA/QC issues during the field investigation, project-wide progress reports, and laboratory QA reports. The report frequencies, content, preparers, and recipients are summarized in Table 12-1 of the SWMUs 8 and 15 QAPP (Tetra Tech, 2004). In that table, actions associated with the FOL will also apply to the NRS PM, except for data validation, which will not be done on waste characterization samples.

Data validation reports for confirmation samples will address all major and minor laboratory non-compliances, as well as noted sample matrix effects. In the event that major problems occur with the analytical laboratory (e.g., repeated or extreme holding time exceedances or calibration non-compliances, etc.), the data validation manager will notify the PM, QAM, technical coordinator, and laboratory services coordinator. Such notifications (if necessary) are typically provided via internal memoranda and are placed in the project file. These reports contain a summary of the noncompliance, a synopsis of the impact on individual projects, and recommendations regarding corrective action and compensation adjustments. Corrective actions for major non-compliances are initiated at the program level.

The Tetra Tech FOL will provide the Tetra Tech PM and the NRS FOL will provide the NRS PM with daily verbal field progress reports during the course of the sampling events. These reports will explain accomplishments, deviations from the QAPP, and upcoming activities, and will provide a QA summary. The Tetra Tech PM and NRS PM will provide a monthly progress report to the Navy that addresses the project budget, schedule, accomplishments, planned activities, and QA/QC issues and intended corrective actions.

The analytical laboratory for confirmation analyses will provide QA reports to Tetra Tech if QC limits are updated or if other significant plan deviations result from unanticipated circumstances. Because method detection limits (MDLs) will be included in the analytical data packages for confirmation and waste characterization samples, it is not necessary for the laboratories to include updated MDLs in their QA reports unless the updates result in MDLs that exceed cleanup levels or waste acceptance criteria applicable to this project. Cleanup levels are provided in the IMWP (Tetra Tech 2007) and Sections 1.2.1

and 1.2.2 of this QAPP Addendum No. 4; waste acceptance criteria will be provided by the waste disposal facility.

4.10 FINAL EVIDENCE FILES

Refer to Section 4.3 of the SWMUs 8 and 15 QAPP (Tetra Tech, 2004) for requirements governing the management of project records up to and including final disposition.

5.0 REFERENCES

NFESC (Naval Facilities Engineering Services Center), 1996. Navy Installation Restoration Laboratory Quality Assurance Guide.

Tetra Tech (Tetra Tech NUS, Inc.), 2004. Quality Assurance Project Plan for RCRA Facility Investigation at Building 106 Pond (SWMU 8) Roads and Grounds Area (SWMU 15) and Environmental Indicator Investigation for SWMU 18 (Load and Fill Area Buildings), SWMU 19 (Pyrotechnic Test Area), SWMU 20 (Crane Army Ammunition Activity Quality Assurance/Quality Control Test Area), and the Old Gun Tub Storage Lot. September.

Tetra Tech, 2007. Interim Measures Work Plan for SWMU 9 - Pesticide Control Area Naval Surface Warfare Center Crane Crane, Indiana. October.

APPENDIX A

FIELD STANDARD OPERATING PROCEDURES

APPENDIX A

FIELD SOP TABLE OF CONTENTS

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CTO467-02	Sample Identification Nomenclature
CTO467-03	Sample Custody and Documentation of Field Activities
CTO467-04	Decontamination of Field Sampling Equipment
CTO467-05	Soil and Sediment Sampling
CTO467-06	Sample Preservation, Packaging, and Shipping
CTO467-07	Field Analysis of PCB by Test Kit
CTO467-08	Management of Investigation-Derived Waste

STANDARD OPERATING PROCEDURE
NUMBER CTO467-01

SAMPLE LABELING

1.0 PURPOSE

This Standard Operating Procedure (SOP) describes the procedures to be used for labeling sample containers. Sample labels are used to document the sample ID, date, time, analysis to be performed, preservative, matrix, sampler, and the analytical laboratory. A sample label will be attached to each sample container. The label for each container will contain identical information.

2.0 REQUIRED FIELD FORMS AND EQUIPMENT

Writing utensil

Disposable medical-grade gloves (e.g. latex, nitrile)

Sample logsheets

Required sample containers: All sample containers for analysis by fix-based laboratories will be supplied and deemed certified clean by the laboratory.

Preprinted sample labels

Chain-of-custody records

Sealable polyethylene bags

Heavy-duty cooler

Ice

3.0 PROCEDURES

3.1 The following information will be electronically printed on each sample label during field activities.

- Project number (CTO 0042)
- Project location (NSWC Crane)
- Sample ID
- Preservative
- Analysis to be performed

- Matrix type
- Laboratory name

3.2 Fill in appropriate information on the electronic Sample Collection Log Form which will automatically update the Chain-of-Custody Form upon submitting the information.

3.3 Select the containers that are appropriate for a given sample. Print the associated sample label and affix to the sample container.

3.4 Fill the appropriate containers with sample material. Securely close the container lids without overtightening.

3.5 Check to determine if the information printed on the label is correct.

3.6 Place the sample container in a ziplock plastic bag and place in a cooler containing ice.

Example of a sample label is attached at the end of this SOP.

4.0 ATTACHMENTS

1. Sample Label

ATTACHMENT 1
SAMPLE LABEL

Tetra Tech NUS, Inc. 661 Andersen Drive Pittsburgh, 15220 (412)921-7090	Project: Location: CTO:	
Sample No:		Matrix:
Date:	Time:	Preserve:
Analysis:		
Sampled by:	Laboratory	

STANDARD OPERATING PROCEDURE
NUMBER CTO467-02

SAMPLE IDENTIFICATION NOMENCLATURE

1.0 PURPOSE

The purpose of this Standard Operating Procedure (SOP) is to establish a consistent sample nomenclature system that will facilitate subsequent data management at the Naval Surface Warfare Center (NSWC). The sample nomenclature system has been devised such that the following objectives can be attained.

- Sorting of data by site, location, or matrix
- Maintenance of consistency (field, laboratory, and database sample numbers)
- Accommodation of all project-specific requirements
- Accommodation of laboratory sample number length constraints
- Ease of sample identification

The NSWC Crane Environmental Protection Department must approve any deviations from this procedure.

2.0 REQUIRED FIELD FORMS AND EQUIPMENT

Pen with indelible ink
Sample container labels

3.0 SAMPLE IDENTIFICATION NOMENCLATURE

3.1 Confirmation Samples

All confirmation samples will be properly labeled with a sample label affixed to the sample container. Each sample will be assigned a unique sample tracking number.

3.1.1 Confirmation Sample numbering Scheme

The sample tracking number will consist of a four- or five-segment alpha-numeric code that identifies the sample's associated solid waste management unit (SWMU), sample type, location, and for aqueous samples, where applicable, whether a sample is filtered, and/or the sample round number. For soil and sediment samples, the final four tracking numbers will identify the depth in units of feet below ground surface at which the sample was collected.

The alphanumeric coding to be used is explained in the following diagram and subsequent definitions:

NN	AA	NNNA	NNNN (Soils and Sediment only)
SWMU Number	Matrix	Sample Location Number and Grab or Composite	Sequential depth interval from freshly exposed surface

Character Type:

A = Alpha

N = Numeric

SWMU Number (AN):

09 = SWMU 09

Matrix Code (AA):

SS = Surface Soil Sample

Individual aliquots used to form composite samples will be designated "A", "B", "C", "D", "etc.". Each of the aliquots for a given sample will be recorded in the field log. The number of aliquots combined to form a composite and the locations of the aliquots within the sampled area must be recorded in the "OBSERVATONS/NOTES" section of the Soil and Sediment Sample Log Sheet.

Location Number (NNNA):

Sequential number beginning with "001" for each matrix, followed by a letter indicating grab (G) or composite (C) sample.

Depth Interval:

This code section will be used for soil and sediment samples only.

The depth code is used to note the depth below ground surface (bgs) at which a soil or sediment sample is collected. The first two numbers of the four-number code specify the top interval, and the third and fourth specify the bottom interval in feet bgs of the sample. The depths will be noted in whole numbers only; further detail, if needed, will be recorded on the sample log sheet, boring log, logbook, etc. In certain cases, where a sample may be composite sample, "location" refers to a particular sampling grid represented by a composite sample. Each composite sample will be comprised of aliquots identified as "A", "B", "C", etc. used to identify individual aliquots associated with a particular sample.

3.1.2 Examples of Confirmation Sample Nomenclature

The first composite surface soil sample collected from SWMU 09, sampling location 001, at a depth of 2 feet would be labeled as "09SS001C0002". The individual aliquots making up the composite sample should be described as Aliquots "A", "B", "C", etc. for that particular sample and noted on the sample log sheet.

3.3 Field Quality Assurance/Quality Control (QA/QC) Sample Nomenclature

Field QA/QC samples are described in the IMWP (TtNUS, 2006a through 2006d) and this QAPP Addendum No. 4. They will be designated using a different coding system than the one used for regular field samples.

3.3.1 QC Sample Numbering

The QC code will consist of a three- to four-segment alpha-numeric code that identifies the sample QC type, the date the sample was collected, and the number of this type of QC sample collected on that date.

AA	NNNNNN	NN
QC Type	Date	Sequence Number (per day)

The QC types are identified as:

TB = Trip Blank
FD = Field Duplicate

The sampling time recorded on the Chain-of-Custody Form and labels for duplicate samples will be 0000 so that the samples are "blind" to the laboratory. Notes detailing the sample number, time, date, and type will be recorded on the sample log sheets and will document the location of the duplicate sample (sample log sheets are not provided to the laboratory).

3.3.2 Examples of Field QA/QC Sample Nomenclature

The first duplicate of the day at SWMU 09 for a surface soil sample collected on October 24, 2007 would be designated as 09FD10240701.

The third duplicate of the day taken at SWMU 09 of a surface soil sample collected on October 27, 2007 would be designated as 09FD10270703.

The first trip blank associated with samples collected on October 12, 2007 would be designated as TB10120701.

STANDARD OPERATING PROCEDURE
NUMBER CTO467-03

SAMPLE CUSTODY AND DOCUMENTATION OF FIELD ACTIVITIES

1.0 PURPOSE

This Standard Operating Procedure (SOP) establishes the procedures for sample custody and documentation of field sampling and field analyses activities.

2.0 REQUIRED FIELD FORMS AND EQUIPMENT

The following logbooks, forms, and labels are required.

Site logbook
Field logbook
Sample label
Chain-of-Custody Form
Custody seals
Equipment calibration log
Monitoring Well Inspection Form
Water-Level Measurement Form
Low-Flow Purge Data Sheet
Soil and Sediment Sample Log Sheet
Ground Water Sample Log Sheet
Surface Water Sample Log Sheet

3.0 PROCEDURES

This section describes custody and documentation procedures. All entries made into the logbooks, custody documents, logs, and log sheets described in this SOP must be made in indelible ink (black is preferred). No erasures are permitted. If an incorrect entry is made, the entry will be crossed out with a single strike mark, initialed, and dated. Note: In lieu of the above logs, electronic documentation may be used to store data.

3.1 Site Logbook

The site logbook is a hard-bound, paginated, controlled-distribution record book in which all major on-site activities are documented. At a minimum, the following activities and events will be recorded (daily) in the site logbook:

- All field personnel present
- Arrival/departure of site visitors
- Arrival/departure of equipment
- Start or completion of sampling activities
- Daily on-site activities performed each day
- Sample pickup information
- Health and safety issues
- Weather conditions

The site logbook is initiated at the start of the first on-site activity (e.g., site visit or initial reconnaissance survey). Entries are to be made for every day that on-site activities take place.

The following information must be recorded on the cover of each site logbook:

- Project name
- Project number
- Book number
- Start date
- End date

Information recorded daily in the site logbook need not be duplicated in other field notebooks but must summarize the contents of these other notebooks and refer to specific page locations in these notebooks for detailed information (where applicable). At the completion of each day's entries, the site logbook must be signed and dated by the field operations leader (FOL).

3.2 Field Logbooks

The field logbook is a separate dedicated notebook used by field personnel to document his or her activities in the field. This notebook is hardbound and paginated.

3.3 Sample Labels

Adhesive sample container labels must be completed and applied to every sample container. Information on the label includes the project name, location, sample number, date, time, preservative, analysis, matrix, sampler's initials, and the name of the laboratory performing the analysis.

3.4 Chain-of-Custody Form

The Chain-of-Custody Form (COC) is a multi-part form that is initiated as samples are acquired and accompanies a sample (or group of samples) as it is transferred from person to person. Each COC is numbered. This form must accompany any samples collected for laboratory chemical analysis. A copy of a blank COC form is attached at the end of this SOP.

The FOL or must include the name of the laboratory in the "Remarks" section to ensure that the samples are forwarded to the correct location. If more than one COC is necessary for any cooler, the FOL will indicate "Page __ of __" on each COC. The original (top) signed copy of the COC will be placed inside a large Ziploc-type bag and taped inside the lid of the shipping cooler. Once the samples are received at the laboratory, the sample custodian checks the contents of the cooler(s) against the enclosed COC(s). Any problems are noted on the enclosed COC Form (bottle breakage, discrepancies between the sample labels, COC form, etc.) and will be resolved through communication between the laboratory point-of-contact and the Project Manager (PM). The COC form is signed and retained by the laboratory and becomes part of the sample's corresponding analytical data package.

3.5 Custody Seal

The custody seal is an adhesive-backed label with a number on each seal. It is part of the chain-of-custody process and is used to prevent tampering with samples after they have been collected in the field and sealed in coolers for transit to the laboratory. The custody seals are signed and dated by the samplers and affixed across the opening edges of each cooler (two seals per cooler) containing environmental samples. The laboratory sample custodian will examine the custody seal for evidence of tampering and will notify the TtNUS PM if evidence of tampering is observed.

3.6 Equipment Calibration Log

The Equipment Calibration Log is used to document calibration of measuring equipment used in the field. The Equipment Calibration Log documents that the manufacturer's instructions were followed for calibration of the equipment, including frequency and type of standard or calibration device. An Equipment Calibration Log must be maintained for each electronic measuring device requiring calibration. Entries must be made for each day the equipment is used.

3.7 Soil and Sediment Sample Log Sheet

The Soil and Sediment Sample Log Sheets are used to document the sampling of soils and sediments (see SOP CTO0042-05).

4.0 ATTACHMENTS

1. Chain-of-Custody Record

ATTACHMENT 1
CHAIN-OF-CUSTODY RECORD

CHAIN OF CUSTODY | NUMBER | PAGE ____ OF _____

PROJECT NO:	SITE NAME:	PROJECT MANAGER AND PHONE NUMBER	LABORATORY NAME AND CONTACT:
SAMPLERS (SIGNATURE)		FIELD OPERATIONS LEADER AND PHONE NUMBER	ADDRESS
		CARRIER/WAYBILL NUMBER	CITY, STATE

STANDARD TAT ☐
RUSH TAT ☐
☐ 24 hr. ☐ 48 hr. ☐ 72 hr. ☐ 7 day ☐ 14 day

DATE YEAR ____	TIME	SAMPLE ID	MATRIX	GRAB (G) COMP (C)	No. OF CONTAINERS	CONTAINER TYPE PLASTIC (P) or GLASS (G) / PRESERVATIVE USED / TYPE OF ANALYSIS								COMMENTS

1. RELINQUISHED BY	DATE	TIME	1. RECEIVED BY	DATE	TIME
2. RELINQUISHED BY	DATE	TIME	2. RECEIVED BY	DATE	TIME
3. RELINQUISHED BY	DATE	TIME	3. RECEIVED BY	DATE	TIME

COMMENTS

DISTRIBUTION: WHITE (ACCOMPANIES SAMPLE) YELLOW (FIELD COPY) PINK (FILE COPY)

3/99
FORM NO. TINUS-001

STANDARD OPERATING PROCEDURE
NUMBER CTO467-04

DECONTAMINATION OF FIELD SAMPLING EQUIPMENT

1.0 PURPOSE

This Standard Operating Procedure (SOP) establishes the procedures to be followed when decontaminating non-dedicated field sampling equipment during the field investigations at the NSWC Crane facility.

2.0 REQUIRED FIELD FORMS AND EQUIPMENT

Waterproof pens
Non-latex rubber or plastic gloves
Cotton gloves
Field logbook
Potable water
Deionized water
LiquiNox detergent
Brushes, spray bottles, paper towels, etc.
55-gallon drum or other container to collect and transport decontamination fluids

3.0 DECONTAMINATION PROCEDURES

3.1 Don non-latex and/or cotton gloves and decontaminate sampling equipment (in accordance with the following steps) prior to field sampling and between samples.

3.2 Rinse the equipment with potable water. Rinsing may be conducted by spraying with water from a spray bottle or by dipping. Collect the potable water rinsate into a container.

3.3 Wash the equipment with a solution of LiquiNox detergent. Prepare the LiquiNox wash solution in accordance with the instructions on the LiquiNox container. Collect the LiquiNox wash solution into a container. Use brushes or sprays as appropriate for the equipment. If oily residue has

accumulated on the sampling equipment, remove the residue with an isopropanol wash and repeat the Liquinox wash.

3.4 Rinse the equipment with potable water. Rinsing may be conducted by spraying with water from a spray bottle or by dipping. Collect the potable water rinsate into a container.

3.5 Rinse the equipment with deionized water. Rinsing may be conducted by spraying with water from a spray bottle or by dipping. Collect the deionized water rinsate into a container.

3.6 Remove excess water by air drying, shaking, or by wiping with paper towels as necessary.

3.7 Document decontamination by recording it in the field logbook.

3.8 Containerized decontamination solutions will be managed in accordance with the procedures described in SOP CTO0042-09 and the QAPP Addendum No. 2.

STANDARD OPERATING PROCEDURE
NUMBER CTO467-05

SOIL AND SEDIMENT SAMPLING

1.0 PURPOSE

This Standard Operating Procedure (SOP) establishes the procedure for collecting surface soil samples using the hand auger technique to support confirmation sampling at SWMU 09 in accordance with the requirements of this QAPP Addendum No. 4.

2.0 REQUIRED FIELD FORMS AND EQUIPMENT

The following field forms and equipment are required for sediment sampling.

Disposable medical-grade gloves (e.g., latex, nitrile)

Indelible marker

Plastic storage bags

Shipping containers (containing ice)

Disposable plastic trowels or Stainless steel trowels

Stainless steel mixing bowls

Sample containers: Sample containers are certified clean by the laboratory supplying the containers.

Electronic notebook containing:

- **Soil Sample Log Forms.**
- **Daily Activity Logs.**
- **Chain-of-Custody Form.**
- **Soil Boring Log.**

Electronic label maker

3.0 SAMPLING PROCEDURES

Disposable plastic trowels or stainless steel trowels will be employed to collect soil cores. The sampler will wear clean, disposable, medical-grade gloves.

3.1 Clear the area to be sampled of any surface debris (herbaceous vegetation, twigs, rocks, litter, etc.).

3.2 Use the trowel to dig up and homogenize the soil or sediment in a 10-inch-diameter circular area that is 6 inches deep at each aliquot location. Stir the soil or sediment within the circular area; do not move the soil or sediment outside the circle. Also, do not dig or stir soil or sediment that is deeper than 6 inches below the ground surface.

3.3 For a grab sample, place the soil core in a stainless-steel mixing bowl and homogenize. For a composite sample, place equal amounts of the soil cores in a stainless-steel mixing bowl and homogenize. Place soil sample into laboratory supplied sampling container, print, and affix electronically printed label.

3.4 For samples that are to be submitted for laboratory analysis place the labeled sample container into a plastic storage bag and then place the plastic storage bag holding the sample container into a cooler containing ice.

3.5 Complete required information on the electronic Soil Sample Log Sheet (copy attached at the end of this SOP). Note the location of each aliquot in the "OBSERVATIONS/NOTES" section of the Soil and Sediment Sample Log Sheet. The information will be automatically updated to the Chain-of-Custody (COC) Form.

4.0 ATTACHMENTS

1. Soil and Sediment Sample Log Sheet

ATTACHMENT 1

SOIL AND SEDIMENT SAMPLE LOG SHEET

SOIL & SEDIMENT SAMPLE LOG SHEET

Page___ of ___

Project Site Name: _____
Project No.: _____

[] Surface Soil
[] Subsurface Soil
[] Sediment
[] Other: _____
[] QA Sample Type: _____

Sample ID No.: _____
Sample Location: _____
Sampled By: _____
C.O.C. No.: _____

Type of Sample:
[] Low Concentration
[] High Concentration

GRAB SAMPLE DATA:

Date:	Depth Interval	Color	Description (Sand, Silt, Clay, Moisture, etc.)
Time:			
Method:			
Monitor Reading (ppm):			

COMPOSITE SAMPLE DATA:

Date:	Time	Depth Interval	Color	Description (Sand, Silt, Clay, Moisture, etc.)
Method:				
Monitor Readings (Range in ppm):				

SAMPLE COLLECTION INFORMATION:

Analysis	Container Requirements	Collected	Other

OBSERVATIONS / NOTES:

MAP:

Circle if Applicable:

MS/MSD	Duplicate ID No.:

Signature(s):

STANDARD OPERATING PROCEDURE
NUMBER CTO467-06

SAMPLE PRESERVATION, PACKAGING, AND SHIPPING

1.0 PURPOSE

This Standard Operating Procedure (SOP) describes the procedures for sample preservation, packaging, and shipping to be used in handling aqueous samples, soils, and sediments collected at the NSWC Crane.

2.0 REQUIRED FIELD FORMS AND EQUIPMENT

Shipping labels

Custody seals

Chain-of-custody (COC) form(s)

Sample containers with preservatives: All sample containers for analysis by fixed-base laboratories will be supplied, with preservatives added (if required) and deemed certified clean by the laboratory.

Sample shipping containers (coolers): All sample shipping containers are supplied by the laboratory.

Packaging material: Bubble wrap, ZipLoc® bags, strapping tape, etc.

3.0 PROCEDURES FOR SAMPLE PRESERVATION, PACKAGING, AND SHIPPING

3.1 The laboratory provides sample containers with preservative already included (as required) for the analytical parameter for which the sample is to be analyzed. All samples will be held, stored, and shipped at 4°C. This will be accomplished through refrigeration (used to hold samples prior to shipment) and/or ice.

3.2 The sampler shall maintain custody of the samples until the samples are relinquished to another custodian or to the common carrier.

3.3 Check that each sample container is properly labeled, the container lid is securely fastened, and the container is sealed in a ZipLoc® bag.

3.4 If the container is glass, place the sample container into a bubble-out shipping bag and seal the bag using the self-sealing, pressure sensitive tape supplied with the bag.

3.5 Inspect the insulated shipping cooler. Check for any cracks, holes, broken handles, etc. If the cooler has a drain plug, make certain it is sealed shut, both inside and outside of the cooler. If the cooler is questionable for shipping, the cooler must be discarded.

3.6 Put ice into ZipLoc® bags and place a layer of the sealed bags on the bottom of the cooler. Place the sample containers into the shipping cooler on top of the ice in an upright position (containers will be upright, with the exception of the 40-ml vials). Place ZipLoc® bags of ice flat against the sides of the cooler. Continue filling the cooler with samples until the cooler is nearly full and the movement of the sample containers is limited.

3.7 Add a final layer of ice sealed in ZipLoc® bags to the top of the samples just before the cooler is closed and sealed.

3.8 Place the original (top) signed copy of the COC form inside a large ZipLoc® bag. Tape the bag to the inside of the lid of the shipping cooler that contains the samples for VOC analysis.

3.9 Close the cooler and seal the cooler with approximately four wraps of strapping tape at each end of the cooler. Prior to wrapping the last wrap of strapping tape, apply a signed, numbered, and dated custody seal to each side of the cooler (one per side). Cover the custody seal with the last wrap of tape. This will provide a tamper evident custody seal system for the sample shipment.

3.10 Affix a shipping label to the top of the cooler containing samples for VOC analysis, ensuring all of the shipping information is filled in properly. Overnight (e.g., FedEx Priority Overnight) courier services will be used for all sample shipments.

3.11 All samples will be shipped to the laboratory no more than 72 hours after collection. Under no circumstances will sample hold times be exceeded.

STANDARD OPERATING PROCEDURE
NUMBER CTO467-07

FIELD ANALYSIS FOR PCB BY TEST KIT

STRATEGIC DIAGNOSTICS INC.

RaPID Assay® PCB Test Kit
A00133/A00134

Intended Use

The RaPID Assay® PCB Test Kit can be used as a quantitative, semi-quantitative or qualitative enzyme immunoassay (EIA) for the analysis of PCB (polychlorinated biphenyl) in water (groundwater, surface water, well water). For applications in other matrices please contact our Technical Service department or refer to the soil application procedure provided. The RaPID Assay® PCB Test Kit allows reliable and rapid screening for PCB (measured and reported as Aroclor 1254), with quantitation between 0.5 and 10 ppb (as Aroclor 1254), in water. The minimum detection level of the kit is 0.2 ppb (as Aroclor 1254.)

Test Principles

The PCB RaPID Assay® kit applies the principles of enzyme linked immunosorbent assay (ELISA) to the determination of PCB and related compounds. The sample to be tested is added, along with an enzyme conjugate, to a disposable test tube, followed by paramagnetic particles with antibodies specific to PCB attached. Both PCB (which may be in the sample) and the enzyme labeled PCB (the enzyme conjugate) compete for antibody binding sites on the magnetic particles. At the end of an incubation period, a magnetic field is applied to hold the paramagnetic particles (with PCB and labeled PCB analog bound to the antibodies on the particles, in proportion to their original concentration) in the tube and allow the unbound reagents to be decanted. After decanting, the particles are washed with Washing Solution.

The presence of PCB is detected by adding the enzyme substrate (hydrogen peroxide) and the chromogen (3,3',5,5' – tetramethylbenzidine). The enzyme labeled PCB analog bound to the PCB antibody catalyzes the conversion of the substrate/chromogen mixture to a colored product. After an incubation period, the reaction is stopped and stabilized by the addition of acid. Since the labeled PCB (conjugate) was in competition with the unlabeled PCB (sample) for the antibody sites, the color developed is inversely proportional to the concentration of PCB in the sample.

NOTE: Color development is inversely proportional to the PCB concentration.

Darker color = lower concentration
Lighter color = higher concentration

The determination of the PCB level in an unknown sample is interpreted relative to the standard curve generated from kit standards after reading with a spectrophotometer.

Performance Characteristics

The PCB RaPID Assay® will detect different PCB Aroclors to different degrees. Refer to the table below for data on several of these. The PCB RaPID Assay® kit provides screening results. As with any analytical technique (GC, HPLC, etc.) positive results requiring some action should be confirmed by an alternative method.

The PCB RaPID Assay® immunoassay test does not differentiate between PCB and other related compounds. The table below shows compounds at the method detection limit (MDL) which is the lowest concentration of the compound, in water, that can be picked up in the assay. The limit of quantitation (LOQ) is an approximate concentration, in water, required to yield a positive result at the lowest standard. **This is the lowest concentration of the compound that can be quantified in the assay.** The IC50 is the concentration required to, inhibit one half of the color produced by the negative control. It is also used to calculate cross-reactivity values to similar compounds.

Compound	MDL (ppb)	LOQ (ppb)	IC50 (ppb)
Aroclor 1254	0.20	0.50	3.6
Aroclor 1260	0.20	0.32	2.3
Aroclor 1248	0.22	0.59	4.22
Aroclor 1242	0.34	1.22	8.8
Aroclor 1262	0.36	0.66	4.74
Aroclor 1232	0.84	2.61	18.76

Aroclor 1268	0.92	3.03	21.80
Aroclor 1016	0.94	3.56	25.60
Aroclor 1221	13.54	22.58	162.60

*The following compounds demonstrated no reactivity in the PCB RaPID Assay® test kit at concentrations up to 10,000 ppb: Biphenyl, 2,5-Dichlorophenol, 2,3,5-Trichlorophenol, Di-n-octyl-phthalate.

The presence of the following substances up to 250 ppm were found to have no significant effect on PCB RaPID Assay® results: copper, nickel, zinc, mercury, manganese, phosphate, sulfate, sulfite, magnesium, calcium, nitrate and thiosulfate. Humic acid up to 25 ppm and iron to 100 ppm were found to have no significant effect. In addition, sodium chloride concentrations up to 1.0 M showed no effect on results.

Precautions

- Training is strongly recommended prior to using the RaPID Assay® test system. Contact Strategic Diagnostics for additional information.
- Treat PCB, solutions that contain PCB, and potentially contaminated samples as hazardous materials.
- Use gloves, proper protective clothing, and methods to contain and handle hazardous material where appropriate.
- Reagents must be added in a consistent manner to the entire rack. A consistent technique is the key to optimal performance. Be sure to treat each tube in an identical manner.
- Water samples should be at a neutral pH prior to analysis. Samples containing gross particulate should be filtered (e.g. 0.2 um Anotop™ 25 Plus, Whatman, Inc.) to remove particles.
- Store all test kit components at 2°C to 8°C (36°F to 46°F). Storage at ambient temperature (18°C to 27°C or 64°F to 81°F) on the day of use is acceptable. *Test tubes require no special storage and may be stored separately to conserve refrigerator space.*
- Allow all reagents to reach ambient temperature (18°C to 27°C or 64°F to 81°F) before beginning the test. This typically requires at least 1 hour to warm from recommended storage conditions.
- Do not freeze test kit components or expose them to temperatures above 100°F (39°C).
- Do not use test kit components after the expiration date.
- Do not use reagents or test tubes from one test kit with reagents or test tubes from a different test kit.
- Do not mix reagents from kits of different lot numbers.
- Use approved methodologies to confirm any positive results.
- Do not under any circumstances attempt to disassemble the base of the magnetic rack. Magnets will be violently attracted to each other.
- Adequate sample number and distribution are the responsibility of the analyst.
- The photometer provided in the accessory kit requires electricity and comes with a 110V adapter. Adapters for 220V are available. Do not attempt to operate with a car adaptor.
- Do not expose color solution to direct sunlight.
- Do not dilute or adulterate test reagents or use samples not called for in the test procedure; this may give inaccurate results.
- Tightly recap the standard vials when not in use to prevent evaporative loss.

Materials Provided

- Antibody Coupled Paramagnetic Particles in buffered saline containing preservative and stabilizers.

  30 test kit: one 20 mL vial
  100 test kit: one 65 mL vial

- Enzyme Conjugate.

  30 test kit: one 10 mL vial
  100 test kit: one 35 mL vial

- Standards

  Three concentrations (0.25, 1.0 and 5.0 ppb) of PCB standards (as Aroclor 1254) in buffered saline

containing preservative and stabilizers are supplied. Each vial contains 4 mL.

- Control

  A concentration (approximately 3 ppb) of PCB (as Aroclor 1254) in buffered saline containing preservative and stabilizers. A 4 mL volume is supplied in one vial.

- Diluent/Zero Standard

  Buffered saline containing preservative and stabilizers without any detectable PCB.

  30 test kit: one 10 mL vial
  100 test kit: one 35 mL vial

- Color Solution containing hydrogen peroxide and 3,3',5,5'-tetramethylbenzidine in an organic base.

  30 test kit: one 20 mL vial
  100 test kit: one 65 mL vial

- Stop Solution containing a solution of 2M sulfuric acid.

  30 test kit: one 20 mL vial
  100 test kit: one 60 mL vial

- Washing Solution containing preserved deionized water.

  30 test kit: one 70 mL vial
  100 test kit: one 250 mL vial

- Polystyrene test tubes

  30 test kit: one 36 tube box
  100 test kit: three 36 tube boxes

- User's Guide

Materials Required and Ordered Separately

See "Ordering Information" for the appropriate catalogue numbers.

Rapid Assay® Accessory Kit

Accessory equipment may be rented or purchased from Strategic Diagnostics. See "Ordering Information" for the appropriate catalogue numbers.

The accessory kit contains the following items:

- Adjustable Volume Pipet
- Eppendorf™ Repeater® Pipettor
- Electronic timer
- Portable balance capable of weighing 10 g (for soil samples)
- Vortex mixer
- Magnetic separation rack
- RPA-I RaPID Analyzer (or equivalent spectrophotometer capable of reading 450 nm in a 1 mL sample size).

Other Items

- 12.5 mL Combitips® for the Repeater pipettor - for 0.25 mL to 1.25 mL dispensing volumes (5)
- Pipet tips for adjustable volume pipet (100-1000 uL)

NOTE: Order replacement Combitips® and pipet tips separately. See the "Ordering Information" section.

Materials Required but Not Provided

- Methanol (HPLC grade or equivalent) – for water analysis
- Protective clothing (e.g., latex gloves)
- Absorbent paper for blotting test tubes
- Liquid and solid waste containers
- Marking pen
- Instructional video (optional)

Suggestions for Pipettor Use

- Practice using both pipettes (adjustable volume and Repeater pipettor) with water and extra tips before you analyze your samples.
- Use a new tip each time you use the Repeater pipettor to pipette a different reagent to avoid reagent cross-contamination. Tips can be rinsed thoroughly, dried completely and reused. By using the same tip to dispense the same reagent each time you can avoid cross contamination.

NOTE: Repeator tips should be changed periodically (after ~10 uses) since precision deteriorates with use.

- Draw the desired reagent volume into the Repeater pipettor and dispense one portion of the reagent back into the container to properly engage the ratchet mechanism. If you do not do this, the first volume delivered may be inaccurate.
- To add reagents using the Repeater pipettor, pipette down the side of the test tube just below the rim.
- When adding samples and standard using the positive displacement pipettor, always pipette into the bottom of the tube without touching the sides or bottom of the tube.
- Use a new adjustable volume pipet tip each time you pipette a new unknown.

Assay Procedure

Prior to performing your first Rapid Assay®, please take time to read the package inserts in their entirety and review the videotape if available. **On site training is strongly recommended for new users of this test system.** Please contact your account manager for further information. This procedure is designed for quantitative analysis. For running the kit semi-quantitatively or qualitatively, please contact Technical Support.

Collect/Store the Sample

The following steps explain how to properly collect and store your samples.

1. Water samples should be collected in glass vessels with teflon cap liners). **Immediately upon collection, water samples should be diluted with an equal volume (1:1) of methanol (HPLC grade) to prevent adsorptive losses to the glass containers.** This is a 2x dilution, which must be accounted for when interpreting results. See "Results Interpretation", Section 3a for further details. Use this diluted sample as "sample" in "Perform the Test".

NOTE: This 2x dilution is <u>not</u> required for soil samples.

2. Samples should be collected in appropriately sized and labeled containers.
3. If testing soil samples, follow the SDI Sample Extraction Kit User's Guide or the appropriate technical bulletin to properly collect and store your sample.
4. Samples should be tested as soon as possible after collection. If this is not possible, storage at 4°C (39°F) is recommended to minimize evaporative losses.

Set Up

1. Remove kits from refrigerator. All reagents must be allowed to come to room temperature prior to analysis. Remove reagents from packaging and place at room temperature <u>at least</u> 1 hour prior to testing.
2. Turn on the RPA-1 or other spectrophotometer. The RPA-1 should be warmed up for at least 30 minutes prior to the run.
3. Label five 12.5 mL Combitips "Conjugate", "Particles", "Wash", "Color" and "Stop". In addition, add the name of the compound you are testing for to each Combitip.
4. Remove nine clean blank test tubes for standards and control and one test tube for each sample (if testing in singlicate). Label the test tubes according to contents as follows.

Tube #	Contents
1	Negative control (replicate 1)
2	Negative control (replicate 2)
3	Standard 1 (replicate 1)
4	Standard 1 (replicate 2)
5	Standard 2 (replicate 1)
6	Standard 2 (replicate 2)
7	Standard 3 (replicate 1)
8	Standard 3 (replicate 2)
9	Control
10	Sample 1
11	Etc.

***Label at top of tubes to avoid interference with reading of tubes in photometer**

Sample Extraction, Filtration and Dilution

Filtration may be necessary to remove gross particulate from the water sample. If testing samples at levels higher than standard kit level is desired, contact SDI for special instructions. Water samples should be diluted 1:1 in methanol as described in "Collect/Store the Sample". Please follow the instructions from the SDI Sample Extraction Kit to prepare and dilute the soil extract prior to running the assay.

Perform the Test

1. Separate the upper rack from the magnetic base. Place labeled test tubes into the rack.

2. Add **200 uL** of standards, control or samples to the appropriate tubes using the adjustable volume pipet with the dial set on **0200**. The negative control, standards and control must be run with each batch of samples.

NOTE: Sample should be added to the bottom of the tube by inserting the pipet tip into the tube without touching the sides or the bottom of the tube. Take care not to contact sample with pipette tip once dispensed into bottom of the tube.

3. Using the Repeater Pipettor with the "Conjugate" tip attached and the dial set on **"1"**, add **250 uL** of Enzyme conjugate down the **inside wall** of each tube. (Aim the pipet tip ¼" to ½" below the tube rim or tube wall; deliver liquid gently to avoid splashback.)

4. Thoroughly mix the magnetic particles by swirling (avoid vigorous shaking) and attach the "Particles" tip to the Repeater Pipettor. With the dial set on **"2"** add **500 uL** of magnetic particles to each tube, aiming down the side of the tube as described above. Vortex, mixing each tube 1 to 2 seconds at low speed to minimize foaming. Pipetting of magnetic particles should be kept to 2 minutes or less.

5. Incubate 15 minutes at room temperature.

6. After the incubation, combine the upper rack with the magnetic base and press all tubes into the base; allow 2 minutes for the particles to separate.

7. With the upper rack and magnetic base combined, use a smooth motion to invert the combined rack assembly over a sink and pour out the tube contents.

NOTE: If the rack assembly inadvertently comes apart when lifting to pour out tube contents, re-combine and wait an additional 2 minutes to allow particles to separate.

8. **Keep the rack inverted** and gently blot the test tube rims on several layers of paper towels. It is important to remove as much liquid as possible but **do not bang** the rack or you may dislodge the magnetic particles and affect the results.

9. Set the Repeater Pipettor dial to **"4"** and put on the tip labeled "Wash". Add **1 mL** of Washing Solution down the inside wall of each tube by using the technique described earlier. Vortex tubes for 1-2 seconds. **Wait 2 minutes** and pour out the tube contents as described previously. **Repeat this step one more time.**

NOTE: The number of washes and wash volume are important in ensuring accurate results.

10. Remove the upper rack (with its tubes) from the magnetic base. With the "Color" tip attached to the Repeater Pipet and the dial set to **"2"** add **500 uL** of Color Reagent down the inside wall of each tube as described previously. Vortex 1 to 2 seconds (at low speed).

11. Incubate 20 minutes at room temperature. During this period, add approximately 1 mL of Washing solution to a clean tube for use as an instrument blank for "Results Interpretation".

12. After the incubation, position the Repeater pipettor at Setting **"2"** and use the "Stop" tip to add **500 uL** of Stop solution to all test tubes.

13. Proceed with results interpretation.

WARNING: Stop solution contains 2M sulfuric acid. Handle carefully.

Results Interpretation

1. After addition of Stop Solution to the test tubes, results should be read within 15 minutes.

2. Wipe the outside of all antibody coated tubes prior to photometric analysis to remove fingerprints and smudges.

Photometric Interpretation Using the RPA-I

1. The RPA-I photometer (provided in the Rapid Assay® Accessory kit) can be used to calculate and store calibration curves. It is preprogrammed with various RaPID Assay® protocols. For the PCB RaPID Assay® test kit, parameter settings are as follows:

   Data Reduct: Lin. Regression

Xformation :	Ln/LogitB
Read Mode :	Absorbance
Wavelength :	450 nm
Units :	PPB
# Rgt Blk :	0

Calibrators:

# of Cals :	4
# of Reps :	2

Concentrations:

#1 :	0.00 ppb
#2 :	0.25 ppb
#3 :	1.00 ppb
#4 :	5.00 ppb
Range :	0.10 – 5.00
Correlation :	0.990
Rep. %CV :	10%

NOTE: Prior to analysis the RPA-I User's Manual should be thoroughly reviewed for more detailed operation instructions.

2. Follow the instrument prompts to read the absorbance of all tubes:

Instrument Display	Operator Response
SELECT COMMAND	Press RUN
RUN PROTOCOL	Scroll using the YES [] or NO [] keys until the desired protocol appears. Then press ENTER
SPL. REPLICATES (1-5)	Press 1 (for analysis of samples in singlicate.) Press ENTER
BLANK TUBE, INSERT TUBE, EVALUATING TUBE,	Insert blank tube containing 1mL wash solution.
REMOVE TUBE (Beep)	Remove tube
CAL #1, REP. #1, INSERT TUBE,	Insert Tube #1
EVALUATING TUBE, REMOVE TUBE (Beep)	Remove tube

Follow prompts to read tubes.

NOTE: Tube order is important. The RPA-I expects to see the standards in ascending order, in duplicate, starting with the negative control.

Following evaluation of all standards, the instrument will display:

PRINTING DATA,	Data will print
PRINTING CURVE	Curve will print only if programmed to print (See RPA1 User's Manual).
CTRL #1 REP #1, INSERT TUBE, EVALUATING TUBE,	Insert Control Tube
REMOVE TUBE (Beep)	Remove Tube
EDIT CALIBRATORS YES/NO	Press NO (if editing is necessary press YES and refer to the RPA1 User's Manual).
SPL #1 REP#1 INSERT TUBE EVALUATING TUBE	Insert first sample tube
REMOVE TUBE (Beep)	Remove tube

Continue to follow prompts. After all samples have been read, press STOP.

Expected Results:

- **%CV (coefficient of variation) between standard duplicates of 10% or less.**
- **Absorbance reading for the 0 ppb standard should be between 0.8 and 2.0 for all assays.**
- **Correlation (r) of 0.990 or greater for all assays.**
- **Kit control within range specified on vial.**
- **Absorbance of negative control and standards should be as follows:**

  Negative Control>Std. 1>Std. 2>Std. 3.

3. Concentrations will be indicated for all samples on the RPA-I printout.

   a) The concentration, as indicated on the printout, is multiplied by the appropriate dilution factor (if applicable) introduced in the procedure. The quantitation range of the kit is also multiplied by this factor.

EXAMPLE: Water samples were diluted 2-fold with methanol upon collection (see "Collect/Store the Sample" in this User's Guide). As a result, the concentrations listed on the printout should be multiplied by 2 to determine the sample concentration. The standard concentrations are also multiplied by 2 to give a quantitation range in water for this test kit of 0.5 to 10 ppb.

   b) Samples with an "nd" and no concentration listed have an absorbance greater than the negative control; therefore, no concentration can be computed for these samples. Results must be reported as < 0.5 ppb (or Standard 1 multiplied by the dilution factor.)

   c) Samples with an "nd" next to a listed concentration have an estimated concentration below the minimum detection level of the test kit. Results must be reported as <0.5 ppb (or Standard 1 multiplied by the dilution factor.)

NOTE: Any samples with concentrations determined to be lower than Standard 1 (the limit of quantitation) must be reported as < 0.5 (or Standard 1 multiplied by the dilution factor.) Quantitation is not possible below this standard as this is outside the linear range of the assay.

   d) Similarly, samples with a "hi" next to a listed concentration have an estimated concentration higher than Standard 3 and must be reported as >10 ppb (or Standard 3 multiplied by the dilution factor.)

NOTE: In order to determine the concentration of samples with concentrations greater than Standard 3, they must be subjected to repeat testing using a diluted sample. A ten-fold or greater dilution of the sample is recommended with an appropriate amount of PCB diluent. This additional dilution must then be taken into account when calculating the concentration. Please contact technical support for assistance in performing dilutions.

Photometric Interpretation Using Other Photometers

Other photometers may also be used to interpret results obtained from the RPA-I photometer. It is important that the photometer be able to read absorbance at 450nm and that the instrument can read at a 1 mL fill volume. Absorbances obtained from other spectrophotometers (reading at 450 nm) may be used to manually calculate sample concentrations as outlined below.

1. Calculate the mean absorbance for each of the three standards and the negative control.

2. Determine the standard deviation and %CV (coefficient of variation) of each standard and ensure %CV is less than 10% for each.

3. Calculate the %B/Bo for each standard by dividing the mean absorbance value for the standard by the mean absorbance value for the negative control and multiplying the results by 100.

4. Construct a standard curve by plotting the %B/Bo for each standard on the vertical logit (y) axis versus the corresponding analyte concentration on the horizontal logarithmic (x) axis on the graph paper provided in the test kit. **Graph papers are specific for each method. Use only the graph paper supplied with each kit.**

5. Draw the best straight line through all points. Using the %B/Bo of the sample, the concentration can be interpolated from the standard curve.

6. Multiply results by the appropriate dilution factor (if applicable) introduced in the procedure. For example, if the sample was diluted 10-fold to increase the detection levels of the kit then the results must be multiplied by 10. This dilution also changes the range of the assay (standards) by the same factor.

NOTE: Do not forget to account for the 2x dilution introduced in the "Collect/Store the Sample" procedure for water samples.

Limitations of the Procedure

The Rapid Assay® PCB Test Kit is a screening test **only**. Sampling error may significantly affect testing reliability. Adequate sample number and distribution are the responsibility of the analyst.

Ordering Information

Description	Catalogue Number
Rapid Assay® PCB Kit	A00133/A00134
Rapid Assay® Accessory Kit**	6050100
Adjustable Volume Pipet Tips (100-1000 uL)	A00013
12.5 mL Combitip for Repeating Pipette (1 each)	A00009
PCB Diluent	A00136
PCB Soil Proficiency Sample	A00175
Rapid Assay® Accessory Kit Rental	6997010
**** To obtain part numbers and pricing for individual items in the Accessory Kit contact SDI at the number below.**	

Ordering/Technical Assistance

Should you have any questions regarding this procedure prior to analysis contact Technical Service to avoid costly mistakes.

To Place an Order or Receive Technical Assistance, please call Strategic Diagnostics Inc. at:

Call toll-free **800-544-8881**`

Or 302-456-6789 Phone
302-456-6782 Fax
Web site: www.sdix.com
E-mail: techservice@sdix.com

General Limited Warranty

SDI's products are manufactured under strict quality control guidelines and are warranted to be free from defects in materials and workmanship. New instruments and related non-expendable items are warranted for one year from date of shipment against defective materials or workmanship under normal use and service.
Warranty obligation is limited to repair or replacement of the defective product or to refund of the purchase price, at the discretion of SDI. Other warranties, express or implied, are disclaimed. SDI's liability under any warranty claim shall not exceed the refund of the purchase price paid by the customer. Under no circumstances shall SDI be liable for special, indirect or consequential damages.

Safety

To receive an MSDS for this product, visit our web site at www.sdix.com.

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Z00245.1, Rev 4/4/00

Operation of the Repeater Pipet

To Set or Adjust Volume

To determine the pipetting volume, the dial setting (1-5) is multiplied by the minimum pipetting volume of the tip (indicated on the side of the Combitip, e.g. 1~100 uL.)

To Assemble Pipet Tip

Slide filling lever down until it stops. Then raise the locking clamp and insert the tip until it clicks into position. Be sure the tip plunger is fully inserted into the barrel before lowering the locking clamp to affix the tip in place.

To Fill Tip

With tip mounted in position on pipet, immerse end of tip into solution. Slide filling lever upward slowly. Combitip will fill with liquid.

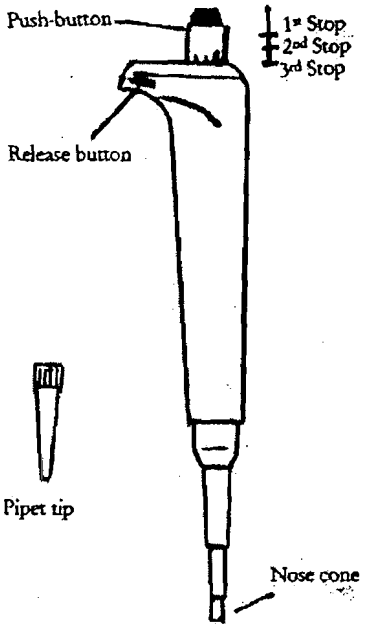
To Dispense Sample

Check the volume selection dial to ensure pipetting volume. Place tip inside test tube so that tip touches the inner wall of tube. Completely depress the pipetting lever to deliver sample. NOTE: Dispense one portion of reagent back into the container to engage the ratchet mechanism and ensure accuracy.

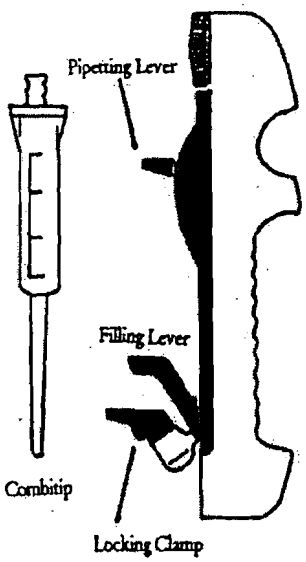
To Eject Tip

Empty tip of any remaining solution into appropriate container by pushing filling lever down. Raise locking clamp upward, and remove the Combitip.

Adjustable Volume Pipet



Repeater Pipet



Operation of the Adjustable Volume Pipet

To Set or Adjust Volume

Press release button on side of pipette and turn the push-button to adjust volume up or down. Volume setting is displayed on top of pipet. See kit instructions for appropriate setting. Pipet will accurately dispense volumes between 100 and 1000 uL.

To Assemble Pipet Tip

Gently push nose cone of pipet firmly into a pipet tip contained in the pipet tip rack.

To Withdraw Sample

Keep pipet almost vertical. With tip mounted in position on pipet, press push-button to 1st stop and hold it. Place tip at bottom of liquid sample and slowly release push-button to withdraw measured sample. Ensure that no air bubbles exist in the pipette tip. If bubbles exist, dispense sample and re-withdraw. Slide tip out along the inside of the vessel.

To Dispense Sample

Wipe any liquid from outside of tip taking care not to touch orifice. Place tip into tube, almost to the bottom, and slowly press push-button to 2nd stop. Hold push-button at 2nd stop when removing tip from tube.

To Eject Tip

Press push-button to 3rd stop. Tip is ejected.

STRATEGIC DIAGNOSTICS INC.

RaPID Assay® PCB In Soil Application

Intended Use

For detection of Polychlorinated Biphenyls (PCB's) (as Aroclor 1254) in soil. For testing in other matrices, please contact our technical support department at 1-800-544-8881.

Materials Required but Not Provided

SDI Sample Extraction Kit
(Part Number: A00137EA/A00137EB)

Procedural Notes and Precautions

- Prepare soil samples for analysis according to the procedure in the SDI Sample Extraction Kit Users Guide.
- After extraction and dilution of samples, follow the immunoassay procedure as described in the Rapid Assay ® PCB Test Kit User's Guide.
- The initial 2x dilution described for water samples in Step 1 of "Collect/Store the Sample" does not need to be performed for soil samples.

Quality Control

A control solution at approximately 3 ppb (as Aroclor 1254) is provided with the PCB RaPID Assay® Kit. It is recommended that it be included in every run and treated in the same manner as unknown samples. If running standard soil procedures an acceptable result should be 2000 times the value stated on the control vial (i.e. 6.0 + or – 1.2 ppm) when the control results are corrected for the dilution factors (see Results section below).

Results Interpretation

Interpret soil sample results as described in the RaPID Assay® PCB Test Kit procedure, accounting for the total dilution factor indicated in the table of the SDI Sample Extraction Kit Users Guide. Alternatively, program the RPA-1 Analyzer as listed below to automatically correct for this dilution factor.

1. The RPA-I photometer (provided in the Rapid Assay® Accessory kit) can be used to calculate and store calibration curves. To obtain soil results from the PCB Rapid Assay® test kit on the RPA-I the following parameter settings are recommended:

Data Reduct:	Lin. Regression
Xformation :	Ln/LogitB
Read Mode :	Absorbance
Wavelength :	450 nm
Units :	PPM
# Rgt Blk :	0

Calibrators:

# of Cals :	4
# of Reps :	2

Concentrations:

#1 :	0.00 PPM
#2 :	0.50 PPM
#3 :	2.00 PPM
#4 :	10.00 PPM
Range :	0.5 – 10.00
Correlation :	0.990
Rep. %CV :	10%

Performance Data

The PCB RaPID Assay® does not differentiate between PCB and other related compounds. The table below shows compounds at the method detection limit (MDL) which is the lowest concentration of the compound in soil that can be picked up in the assay. The limit of

quantitation (LOQ) is an approximate concentration required to yield a positive result at the lowest standard, this is the lowest concentration of the compound in soil that can be quantified in the assay. The IC50 is the concentration in soil required to inhibit one half of the color produced by the negative control. It is also used to calculate cross-reactivity values to similar compounds.

Compound	MDL (ppm)	LOQ (ppm)	IC50 (ppm)
Aroclor 1254	0.20	0.5	3.60
Aroclor 1260	0.20	0.3	2.30
Aroclor 1248	0.22	0.6	4.22
Aroclor 1242	0.34	1.2	8.80
Aroclor 1262	0.36	0.7	4.74
Aroclor 1232	0.84	2.6	18.76
Aroclor 1268	0.92	3.0	21.80
Aroclor 1016	0.94	3.6	25.60
Aroclor 1221	13.54	22.6	162.6

Soil Contaminants

Some contaminants found in soils that also contain PCB's can interfere with the analysis and cause false positives, false negatives or both when the compound is present at elevated concentrations. Interferences were assessed by adding increasing concentrations of some relevant contaminants to blank and PCB spiked soils prior to the extraction procedure. The concentration of the compound shown below produced no evidence of interference in a positive or negative direction in the 500 ppb to 10 ppm detection range of the procedure described above.

soil contaminant	concentration in soil producing no interference
trichloroethylene	100,000 ppm or 10%
gasoline	25,000 ppm or 2.5%
transformer oil	5,000 ppm or 0.5%
1-chloronapthalene	2,000 ppm or 0.2%
1,2,4 trichlorobenzene	1,000 ppm or 0.1%
diesel fuel	1,000 ppm or 0.1%

If additional dilutions of the soil extract are made to detect soil PCB concentrations greater than 10 ppm, these interferences are diminished in direct proportions to the dilution made.

Range of Detection

The PCB RaPID Assay® has a range of detection in soil of 500 ppb to 10 ppm (as Aroclor 1254) when used in conjunction with the SDI Sample Extraction Kit.

Recovery

PCB recoveries will vary depending on soil type, retention mechanism, solvent and extraction apparatus used, length of extraction period and levels of potentially interfering substances in the soil.

STRATEGIC DIAGNOSTICS INC.

Sample Extraction Kit User's Guide

Intended Use

This extraction kit is for use with the appropriate immunoassay test kit. Each Sample Extraction kit contains the materials necessary to process twelve (12) soil or wipe samples.

Test Principles

The reagents contained in the Sample Extraction kit have been optimized for fast, efficient removal of compounds from soil or surfaces and convenient preparation of the sample for immunoassay testing at levels of interest to the investigator. The system allows for reliable, convenient and cost effective determinations at the field testing or remediation site.

Performance Characteristics

Precautions

- Treat potentially contaminated samples as hazardous materials.
- Use gloves, proper protective clothing, and methods to contain and handle hazardous material where appropriate.
- Store all kit components at ambient temperature (18°C to 27°C or 64°F to 81°F).
- Do not mix reagents from kits of different lot numbers.
- When testing soil samples, samples obtained from areas adjacent to standing water, surface soils collected during or immediately after rain or snow, or any soils with relatively high amounts of water ($\geq$ 30% by weight) should be dried prior to extraction. Contact technical service for recommended methods.
- Adequate sample number and distribution are the responsibility of the analyst.
- Do not dilute or adulterate test reagents; this may give inaccurate results.
- Cloudy or dark sample extracts may indicate the presence of an interference in your sample. Please contact Technical Support if this occurs.

Materials Provided

- Filter unit bottoms: 12 per kit
- Filter unit tops: 12 per kit
- Wooden spatulas: 12 per kit
- Plastic Weigh Boats: 12 per kit
- Bulb Pipettes: 12 per kit
- Ampule crackers: 12 per kit
- Extraction jars: 12 per kit
  (jars for **soil** extraction contain 3 ball bearings)
- 10 cm x 10 cm Plastic Wipe Templates: 12 per kit
  (PCB Wipe Kit only)
- Gauze Wipes: 12 per kit
  (PCB Wipe Kit only)
- Protective gloves: 24 per kit
  (PCB Wipe Kit only)
- User's Guide
- Kit Specific Extraction Solution: 12 per kit as described below:

  20 mL of 100% Methanol for use with:

  Ensys PCB Soil/Wipe (Part #7020301/7021301) *
  Ensys Petro Soil (Part #7042301)
  Ensys PAH Soil (Part #7061301) *
  Ensys Penta Soil (Part #7000301) *
  RaPID Assay PCB (Part # A00133/A00134) *
  RaPID Assay PAH (Part # A00156/A00157) *
  RaPID Assay CaPAH (Part # A00200/A00201) *
  RaPID Assay TNT (Part # A00186) *

  10 mL of 100% Methanol for use with:

  Envirogard PAH in Soil (Part #7060600) *
  Envirogard BTEX in Soil (Part #7004000)

Envirogard TPH in Soil (Part # 7042000)
Envirogard DDT in Soil (Part #7310000) *
Envirogard PCB Soil/Wipe *
(Part #7020800/7021600 or #7021500/7021600)

20 mL of 90% Methanol for use in:

Envirogard Chlordane in Soil (Part #7311000)
Envirogard Toxaphene in Soil (Part #7420000)
Envirogard Lindane in Soil (Part #7630000)

10 mL of 75% Methanol for use in:

Rapid Assay BTEX (Part #A00161/A00162)

20 mL of 75% Methanol with Sodium Hydroxide for use in:

Rapid Assay PCP (Part #A00110/A00111)

10 mL of 100% Methanol with Surfactant for use in:

Rapid Assay Cyclodienes (Part #A00216)

*** Indicates extraction solution is also available in bulk (i.e. two 125 mL bottles per kit)**

- Kit specific dilution material (for Ensys and RaPID Assay test kits)
  - For Ensys test kits dilution ampules will be provided based on customer specified detection levels.
  - For Rapid Assay test kits, 12 dilution vials with the appropriate volume of assay diluent (see "Dilute the Sample" section of this User's Guide) will be provided. The kit may also contain fixed volume disposable pipets and tips as appropriate.

Materials Required and Ordered Separately

- 50 mL Combitips® for the Repeater pipettor - for 1.0 mL to 5.0 mL dispensing volumes (if using bulk extraction solution)
- Eppendorf Repeater pipettor (if using bulk extraction solution)
- Portable balance capable of weighing 10 g (for soil samples)
- Electronic timer

NOTE: Order replacement Combitips® separately. See the "Ordering Information" section.

Materials Required but Not Provided

- Protective clothing (e.g., latex gloves)
- Liquid and solid waste containers
- Marking pen

Soil Procedure

Collect/Store the Sample

The following steps explain how to properly collect and store your samples.

1. Collect soil in appropriately sized and labeled containers.
2. Take care to remove excess twigs, organic matter, and rocks or pebbles from the soil sample to be tested.
3. Soils obtained from areas adjacent to standing water, surface soils collected during or immediately after rain or snow, or any soils with relatively high amounts of water ($\geq$ 30% by weight) should be dried before testing. Contact Technical Services for recommended methods.
4. When comparing data from fields and laboratory methods it is important that split samples are obtained from thoroughly homogenized samples.
5. Store soil samples at 4°C (39°F), staying within the EPA recommended holding times for your analyte of interest.

Weigh the Sample

1. Verify digital balance is calibrated correctly by pressing the ON/MEMORY button on the instrument and placing the 100 g weight (in the pocket of the instrument cover) onto the balance. If the instrument does not read 100$\pm$0.1 g, you must recalibrate the instrument as per the manufacturer's instructions provided with your accessory kit.
2. Place an unused plastic weigh boat on the digital balance (provided in the Field Accessory Kit).
3. Press the ON/MEMORY button on the digital balance. The balance will beep and display 0.0.
4. Weigh out 10 $\pm$ 0.1 grams of sample into the weigh boat on the balance using a wooden spatula.

NOTE: If the balance turns off prior to completing the weighing of the sample, use an empty weigh boat to retare the instrument and then continue.

5. Repeat Steps 1-3 for each sample to be tested, using a new weigh boat and wooden spatula for each sample.

Extract the Soil

1. Uncap an extraction jar (containing ball bearings) and place it on a flat surface. Label the extraction jar with the sample identification. Transfer 10 grams of sample from the weigh boat into the appropriately labelled extraction jar, using the same wooden spatula used to weigh the sample. Be careful to get all of your sample into the extraction jar.
2. Open the solvent ampule using the ampule cracker provided in your extraction kit by placing the ampule cracker over the scored neck of the ampule. The ampule cracker is designed to protect your hands from broken glass.
3. Pour the entire contents of one solvent ampule into the extraction jar and immediately recap the extraction jar. Do not leave the jar open or the solvent will evaporate and affect results.
4. Shake the jar vigorously for one full minute.
5. Allow the sample to settle for one minute or until a liquid solvent layer is observed above the sample.

NOTE: If the solvent layer is not observed within 15 minutes, contact Technical Support for assistance. Clay samples are often difficult to extract because they absorb the solvent. In this case, Technical Support may recommend decreasing the soil to solvent ratio. This will affect detection levels and should be discussed in advance

6. Repeat Steps 1-5 for each sample to be tested.

Filter the Extract

1. Insert the bulb pipet into the top (liquid) layer in the extraction jar (being careful not to disturb the lower, solid layer) and draw up some of the sample. Transfer at least ½ bulb capacity into the bottom portion of the filtration unit. **Do not use more than one full bulb.**
2. Press the top portion of the filtration unit (which is the piece with the cap and filter) into the bottom portion (containing the sample) until it snaps together or until the majority of the liquid has passed upward through the filter. Place on a flat surface.
3. Repeat Steps 1-2 for each sample to be tested.

NOTE: Do not store sample in the filtration unit for extended periods of time. The seal on the unit will not sufficiently prevent evaporative losses of the solvent. Evaporation of the solvent will affect results.

Dilute the Sample

I. Envirogard and Ensys test kits – Use the filtered extract as "SAMPLE" in the test kit User's Guide procedure. The Ensys User's Guide describes a sample dilution method based on your individual testing needs.

II. Rapid Assay – Dilute the filtered extract into the appropriate sample diluent as described in the following table:

Kit	Extract Vol. (uL)	Diluent (mL)	*Total Dil. Factor	Test Range (ppm)
PCB	25	25	2000	0.5 to 10 (Aroclor 1254)
PAH	250	12.25	100	0.2 to 5 (phenanthrene)
CaPAH	200	9.8	100	0.01 to 0.5 (Benzo(a)pyrene)
BTEX/ TPH	500	4.5	10	0.9 to 30 (total BTEX)
PCP	50	25	1000	0.1 to 10 (PCP)
TNT	50	25	1000	0.25 to 5 (TNT)
Cyclo-dienes	250	12.25	50	0.1 to 2 (Dieldrin)

***Note: "Total dilution factor" takes the extraction dilution into account as well as the kit dilution (i.e. 10 g soil to 20 mL solvent is a 2x dilution).**

a. Remove a premeasured diluent vial from your extraction kit for each sample to be tested. Label vials with the appropriate sample identification. Vials contain the volume of diluent specified in the preceding table corresponding to your test kit.

b. Using the adjustable volume pipet (for volumes between 100 and 1000 uL) or the tan fixed volume pipet provided in the extraction kit (for 25 or 50 uL volumes) pipet the volume of filtered extract specified

in the table above directly *into* the liquid in the corresponding diluent vial.

c. Screw the cap tightly onto the diluent vial and mix by inverting several times. Repeat steps 1 and 2 for each sample being tested using a new, clean pipet tip for each one.

d. The diluted extract should be used as "Sample" in the test kit User's guide procedure.

Wipe Procedure

Collect/Store the Sample

The following steps explain how to properly collect and store your samples.

1. Collect sample in appropriately sized and labeled containers.
2. Wearing a clean pair of protective gloves provided in the extraction kit, uncap an extraction jar.
3. Open the solvent ampule using the ampule cracker provided in your extraction kit by placing the ampule cracker over the scored neck of the ampule. The ampule cracker is designed to protect your hands from broken glass.
4. Pour the entire contents of one solvent ampule into the extraction jar and immediately recap the extraction jar. Do not leave the jar open or the solvent will evaporate and affect results.
5. Soak a gauze pad in the extraction jar containing solvent. Remove the gauze wipe from the extraction jar carefully squeezing the excess solvent from the pad back into the extraction jar.
6. Hold a clean 10 x 10 plastic template on the surface to be wiped. Wipe the entire exposed area according to proper wipe sampling techniques. The wipe should be damp when finished.
7. Place the wipe back into the same extraction jar used in Step 4 and cap tightly.
8. Remove and discard the gloves.
9. Repeat Steps 1-7 for each sample to be tested.
10. Store samples at 4°C (39°F), staying within the EPA recommended holding times for your analyte of interest.

Extract the Sample

1. Shake the jar vigorously for one full minute.
2. Repeat for each sample to be tested.

Filter the Extract

1. Insert the bulb pipet into the top (liquid) layer in the extraction jar and draw up some of the sample. Transfer at least ½ bulb capacity into the bottom portion of the filtration unit. **Do not use more than one full bulb.**
2. Press the top portion of the filtration unit (which is the piece with the cap and filter) into the bottom portion (containing the sample) until it snaps together. Place on a flat surface.
3. Repeat Steps 1-2 for each sample to be tested.

NOTE: Do not store sample in the filtration unit for extended periods of time. The seal on the unit will not sufficiently prevent evaporative losses of the solvent. Evaporation of the solvent will affect results.

Dilute the Sample

I. Envirogard and Ensys test kits – Use the filtered extract as "SAMPLE" in the test kit User's Guide procedure. The Ensys User's Guide describes a sample dilution method based on your individual testing needs.

II. Rapid Assay – Dilute the filtered extract into the appropriate sample diluent as described below.

Kit	Extract Vol. (uL)	Diluent (mL)	Total Dil. Factor *	Test Range (ppm)
PCB	25	25	2000	5 to 100 ug/100 cm2 (Aroclor 1254)

***Note: "Total dilution factor" takes the extraction dilution into account as well as the kit dilution (i.e. 10 g soil to 20 mL solvent is a 2x dilution).**

a. Remove a premeasured diluent vial from your extraction kit for each sample to be tested. Label vials with the appropriate sample identification. Vials contain the volume of diluent specified in the table above corresponding to your test kit.

b. Using the adjustable volume pipet (for volumes between 100 and 1000 uL) or the tan fixed volume pipet provided in the extraction kit (for 25 or 50 uL

volumes) pipet the volume of filtered extract specified in the table above directly *into* the liquid in the corresponding diluent vial.

c. Screw the cap tightly onto the diluent vial and mix by inverting several times. Repeat steps 1 and 2 for each sample being tested using a new, clean pipet tip for each.

d. The diluted extract should be used as "Sample" in the test kit User's guide procedure.

Limitations of the Procedure.

Sampling error may significantly affect testing reliability. The distribution of contaminants in soils can be extremely heterogeneous. Adequate sample number and distribution are the responsibility of the analyst.

Ordering Information

Description	Catalogue Number
SDI Sample Extraction Kit (with methanol in ampules or bulk)	Contact Customer Support
50 mL Combitip for Repeating Pipette (1 each)	6005600
Portable balance**	A00131
Eppendorf Repeater Pipettor**	A00008
Electronic Timer**	A00015
**** These items are also included in our field accessory kits which are available for rent or purchase.**	

Ordering/Technical Assistance

Should you have any questions regarding this procedure prior to analysis contact Technical Service to avoid costly mistakes.

To Place an Order or Receive Technical Assistance, please call Strategic Diagnostics Inc. at:

Call toll-free **800-544-8881**

Or 302-456-6789 Phone
302-456-6782 Fax
web site: www.sdix.com
e-mail: techservice@sdix.com

General Limited Warranty

SDI's products are manufactured under strict quality control guidelines and are warranted to be free from defects in materials and workmanship. New instruments and related non-expendable items are warranted for one year from date of shipment against defective materials or workmanship under normal use and service.
Warranty obligation is limited to repair or replacement of the defective product or to refund of the purchase price, at the discretion of SDI. Other warranties, express or implied, are disclaimed. SDI's liability under any warranty claim shall not exceed the refund of the purchase price paid by the customer. Under no circumstances shall SDI be liable for special, indirect or consequential damages.

Safety

To receive an MSDS for this product, visit our web site at www.sdix.com.

Rev 10/19/99

Material Safety Data Sheet

PCB Soil 12 Test Kit

MATERIAL IDENTIFICATION

Manufacturer/Distributor:	Strategic Diagnostics Inc. 111 Pencader Drive Newark, DE 19702
Phone Number:	1-(302) 456-6789
Trade Names and Synonyms:	PCB Soil 12 Test Kit (7020301)
NFPA Ratings	Health: 3 Flammability: 3 Reactivity: 1

OSHA HAZARD DETERMINATION

Hazardous Ingredients	CAS Number	Weight Percent
Methanol Methyl alcohol, Wood alcohol	67-56-1	≤ 100
N,N-Dimethylformamide	68-12-2	≤ 26
Sulfuric Acid Oil of Vitriol; Hydrogen Sulfate; Sulphuric acid	7664-93-9	≤ 6

PHYSICAL DATA

Plastic kit containing small amounts of various liquids and powders.

HAZARDOUS REACTIVITY

Instability Stable - Reactivity not expected with the product.

FIRE AND EXPLOSION DATA

Fire and Explosion Hazards Methanol is a fire and explosion hazard. Methanol has a flash point of 50° F. Fire hazard when exposed to heat, flame, or oxidizers. Vapors are explosive. N,N'-Dimethylformamide has a flash point of 58°C.

Extinguishing Media Use alcohol foam, Carbon Dioxide or dry chemical to extinguish fire.

Special Fire Fighting Instructions Firefighters should wear self – contained breathing apparatus and protective clothing.

HEALTH HAZARD INFORMATION

Primary Route(s) of Exposure/Entry: Skin, Eyes and Mouth. Flush skin and eyes with large amounts of water for at least 15 minutes. If inhaled or ingested, seek prompt medical attention.

Signs and Symptoms of Exposure/Medical Conditions Aggravated by Exposure:
Methanol may be harmful, if inhaled or ingested. May be fatal, if sufficient quantity is ingested. If ingested,

induce vomiting immediately. Methanol can also cause headache, nausea, blindness and gastrointestinal disturbance.
N,N – Dimethylformamide may cause irritation to skin, eyes, and mucous membranes. Flush skin and eyes with large amounts of water. The other adverse effects that may occur with this chemical are : headache and nausea.

Eye exposure to concentrated sulfuric acid solution may cause severe damage, often leading blindness. Dilute solutions produce a more transient effect from which recovery may be complete. Exposure to mist may cause eye irritation and lacrimation. Skin contact with sulfuric acid may cause severe irritation and pain, burns and vesiculation.
The toxicological properties of the kit components have not been fully defined. Contact may cause irritation to eyes, skin, and mucous membranes. May cause irritation if inhaled or ingested. Limit exposure to material.

Sulfuric acid is corrosive and may cause severe burning pain in the mouth, throat, and abdomen followed by vomiting and diarrhea. Asphyxia may occur from the swelling of the throat. Perforation of the esophagus and stomach may occur.

Carcinogenicity: None of the components in this material is listed by IARC, NTP, OSHA, or ACGIH as a carcinogen.

Applicable Exposure Limits

Methanol
OSHA/PEL 262 mg/m3
ACGIH /TLV 262 mg/ m3
TXDS: orl-rat LD_{50} 5628 mg/kg
ihl-rat LC_{50} 64000 ppm/4H
orl-mice LD_{50} 7300 mg/kg
skn-rbt LD_{50} 15800 mg/kg

N.N – Dimethylformamide
OSHA/PEL 30 mg/m3 (10 ppm)
ACGIH / TLV 30 mg/m3 (10 ppm)

Sulfuric acid
OSHA/ PEL 1 mg/m^3
ACGTH/TLV 1 mg/m^3

FIRST AID

Inhalation No specific intervention is indicated as the compound is not likely to be hazardous by inhalation. Consult a physician if necessary.

Skin Contact The compound is not likely to be hazardous by skin contact, but may cause irritation. If irritation occurs flush skin with large amounts of water. If irritation persists, contact a physician.

Eye Contact In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Call a physician.

Ingestion The compound is toxic by ingestion. Call a physician.

PROTECTION INFORMATION

General Control Measures and Precautions: Ventilation - Natural ventilation.

Personal Protective Equipment: Respiratory Protection: None required.

Protective Gloves: Are highly recommended.

Eye Protection: Safety glasses are required.

Other Protective Equipment: A lab coat or other long – sleeved garment is required to limit skin exposure. Access to a safety shower and eyewash is required.

SPILL, LEAK AND DISPOSAL INFORMATION

Spill, Leak, or Release Review FIRE AND EXPLOSION HAZARDS and SAFETY PRECAUTIONS before proceeding with clean up.

Use appropriate PERSONAL PROTECTIVE EQUIPMENT during clean up. Contain spill and collect in suitable container. Eliminate any ignition sources in the area. Use adequate ventilation.

No special clean up practices are required.

Waste Disposal Dispose of as solid waste in accordance with any applicable federal, state, and local requirements.

SHIPPING INFORMATION

DOT	Proper Shipping Name	Not DOT regulated.
IATA/IMO	Proper Shipping Name	Not restricted.

TITLE III HAZARD CLASSIFICATION

Acute	No
Chronic	No
Fire	No
Reactivity	No
Pressure	No

REGULATORY INFORMATION

OSHA HAZARD DETERMINATION: This material is not known to be hazardous as defined by OSHA's Hazard Communication Standard, 29 CFR 1910.1200

EPA DETERMINATIONS:
COMPREHENSIVE ENVIRONMENTAL RESPONSE, COMPENSATION, & LIABILITY ACT (CERCLA/SUPERFUND), 40 CFR 302 - This material is not known to contain hazardous substances in sufficient quantity to make it subject to CERCLA regulations.

TOXIC SUBSTANCES CONTROL ACT (TSCA), 40 CFR 710
The material is a mixture as defined by TSCA. The chemical ingredients in this material are in the Section 8(b) Chemical Substance Inventory and/or are otherwise in compliance with TSCA. In the case of ingredients obtained from other manufacturers, Strategic Diagnostics, Inc. relies on the assurance of responsible third parties in providing this statement.

RESOURCE CONSERVATION AND RECOVERY ACT (RCRA), 40 CFR 261, SUBPARTS C AND D
The material, when discarded or disposed of, is not specifically listed as a hazardous waste in Federal regulations; however, it could be considered hazardous if it meets criteria for being toxic, corrosive, ignitable or reactive according to U.S. EPA definitions (40 CFR 261). This material could also become a hazardous waste if it is mixed with or comes in contact with a listed hazardous waste. If it is a hazardous waste, regulations 40 CFR 262-266 and 268 may apply.

HAZARDOUS MATERIALS TRANSPORTATION REGULATIONS, 49 CFR 171-178 - This material is not known to contain hazardous substances in sufficient quantity to make it subject to the Regulations.

FOREIGN REGULATIONS: CANADIAN HAZARDOUS PRODUCTS ACT (WHMIS)
The material is not a WHMIS Controlled Product.

STATE REGULATIONS:
CALIFORNIA SAFE DRINKING WATER AND TOXIC ENFORCEMENT ACT OF 1986 ("PROPOSITION 65")
The material is not known to contain any ingredients (s) subject to the Act.

PENNSYLVANIA WORKER AND COMMUNITY RIGHT TO KNOW ACT
This material is not known to contain any ingredient(s) subject to the Act. Non-hazardous ingredient(s) information is withheld as trade secret in accordance with Section 11 of the Pennsylvania Worker and Community Right to Know Act.

The above data are based on tests, experience, and other information which Strategic Diagnostics Inc. believes reliable and are supplied for informational purposes only. However, some ingredients may have been purchased or obtained from third-party manufacturers. In these instances, Strategic Diagnostics, Inc., in good faith, relies on information provided by those third parties. Since conditions of use are outside our control, STRATEGIC DIAGNOSTICS INC. DISCLAIMS ANY LIABLITITY FOR DAMAGE OR INJURY WHICH RESULTS FROM USE OF THE ABOVE DATA. NOTHING CONTAINED HEREIN SHALL CONSTITUTE A GUARANTEE, WARRANTY (INCLUDING WARRANTY OF MERCHANTABILITY) OR REPRESENTATION (INCLUDING FREEDOM FROM PATENT LIABILITY) BY STRATEGIC DIAGNOSTICS, INC. WITH RESPECT TO THE DATA, THE MATERIAL DESCRIBED, OR ITS USE FOR ANY SPECIFIC PURPOSE, EVEN IF THAT PURPOSE IS KNOWN TO STRATEGIC DIAGNOSTICS INC.

Responsibility for MSDS:

Strategic Diagnostics Inc.
111 Pencader Drive
Newark, DE 19702
(302) 456-6789

* End of MSDS *

STANDARD OPERATING PROCEDURE
NUMBER CTO467-08

MANAGEMENT OF INVESTIGATION-DERIVED WASTE

1.0 PURPOSE

This Standard Operating Procedure (SOP) describes how investigation-derived waste (IDW) will be collected, segregated, classified, and managed during the field investigations at the NSWC Crane facility. The following types of IDW will be generated during this investigation:

- Decontamination solutions
- Personal protective equipment and clothing (PPE)
- Miscellaneous trash and incidental items

2.0 REQUIRED FIELD FORMS AND EQUIPMENT

Health and safety equipment (with PPE)
Decontamination equipment
Field logbook and indelible ink pen
Plastic sheeting and/or tarps
55-gallon drums with sealable lids
IDW labels for drums
Wastewater container tanks
Plastic garbage bags

3.0 PROCEDURES

Management of IDW includes the collection, segregation, temporary storage, classification, final disposal, and documentation of the waste-handling activities if necessary.

3.1 Liquid Wastes

Liquid wastes that will be generated during the site activities include decontamination solutions from sampling equipment. These wastes will be collected and transported to a central location at NSWC

Crane (adjacent to a Crane-designated sanitary sewer manhole). The water will be discharged to the sewer by gravity draining.

3.2 PPE and Incidental Trash

All PPE wastes and incidental trash materials (e.g., wrapping or packing materials from supply cartons, waste paper) will be decontaminated (if contaminated), double bagged, securely tied shut, and placed in a designated waste receptacle at NSWC Crane.

APPENDIX B

NWRS STANDARD OPERATING PROCEDURES

APPENDIX B

NWRS SOP TABLE OF CONTENTS

2001 General Field Sampling Guidelines

2006 Sample Equipment Decontamination

2009 Drum Sampling

2010 Tank Sampling

2012 Soil Sampling

2013 Surface Water Sampling

2017 Waste Pile Sampling

Sample Containers

Decontamination Procedures

Sample Packaging and Shipment

Transportation and Off-Site Disposal

1.0 SCOPE AND APPLICATION

The purpose of this Standard Operating Procedure (SOP) is to provide general field sampling guidelines that will assist NWRS personnel in choosing sampling strategies, location, and frequency for proper assessment of site characteristics. This SOP is applicable to all field activities that involve sampling.

These are standard (i.e., typically applicable) operating procedures which may be varied or changed as required, dependent on site conditions, equipment limitations or limitations imposed by the procedure. In all instances, the ultimate procedures employed should be documented and associated with the final report.

Mention of trade names or commercial products does not constitute U.S. EPA endorsement or recommendation for use.

2.0 METHOD SUMMARY

Sampling is the selection of a representative portion of a larger population, universe, or body. Through examination of a sample, the characteristics of the larger body from which the sample was drawn can be inferred. In this manner, sampling can be a valuable tool for determining the presence, type, and extent of contamination by hazardous substances in the environment.

The primary objective of all sampling activities is to characterize a hazardous waste site accurately so that its impact on human health and the environment can be properly evaluated. It is only through sampling and analysis that site hazards can be measured and the job of cleanup and restoration can be accomplished effectively with minimal risk. The sampling itself must be conducted so that every sample collected retains its original physical form and chemical composition. In this way, sample integrity is insured, quality assurance standards are maintained, and the sample can accurately represent the larger body of material under investigation.

The extent to which valid inferences can be drawn from a sample depends on the degree to which the sampling effort conforms to the project's objectives. For example, as few as one sample may produce adequate, technically valid data to address the project's objectives. Meeting the project's objectives requires thorough planning of sampling activities, and implementation of the most appropriate sampling and analytical procedures. These issues will be discussed in this procedure.

3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

The amount of sample to be collected, and the proper sample container type (i.e., glass, plastic), chemical preservation, and storage requirements are dependent on the matrix being sampled and the parameter(s) of interest. Sample preservation, containers, handling, and storage for air and waste samples are discussed in the specific SOPs for air and waste sampling techniques.

4.0 INTERFERENCES AND POTENTIAL PROBLEMS

The nature of the object or materials being sampled may be a potential problem to the sampler. If a material is homogeneous, it will generally have a uniform composition throughout. In this case, any sample increment can be considered representative of the material. On the other hand, heterogeneous samples present problems to the sampler because of changes in the material over distance, both laterally and vertically.

Samples of hazardous materials may pose a safety threat to both field and laboratory personnel. Proper health and safety precautions should be implemented when handling this type of sample.

Environmental conditions, weather conditions, or non-target chemicals may cause problems and/or interferences when performing sampling activities or when sampling for a specific parameter. Refer to the specific SOPs for sampling techniques.

5.0 EQUIPMENT/APPARATUS

The equipment/apparatus required to collect samples must be determined on a site specific basis. Due to the wide variety of sampling equipment available, refer to the specific SOPs for sampling techniques which include lists of the equipment/apparatus required for sampling.

6.0 REAGENTS

Reagents may be utilized for preservation of samples and for decontamination of sampling equipment. The preservatives required are specified by the analysis to be performed. Decontamination solutions are specified in NWRS SOP #2006, Sampling Equipment Decontamination.

7.0 PROCEDURE

7.1 Types of Samples

In relation to the media to be sampled, two basic types of samples can be considered: the environmental sample and the hazardous sample.

Environmental samples are those collected from streams, ponds, lakes, wells, and are off-site samples that are not expected to be contaminated with hazardous materials. They usually do not require the special handling procedures typically used for concentrated wastes. However, in certain instances, environmental samples can contain elevated concentrations of pollutants and in such cases would have to be handled as hazardous samples.

Hazardous or concentrated samples are those collected from drums, tanks, lagoons, pits, waste piles, fresh spills, or areas previously identified as contaminated, and require special handling procedures because of their potential toxicity or hazard. These samples can be further subdivided based on their degree of hazard; however, care should be taken when handling and shipping any wastes believed to be concentrated regardless of the degree.

The importance of making the distinction between environmental and hazardous samples is two-fold:

(1) Personnel safety requirements: Any sample thought to contain enough hazardous materials to pose a safety threat should be designated as hazardous and handled in a manner which ensures the safety of both field and laboratory personnel.

(2) Transportation requirements: Hazardous samples must be packaged, labeled, and shipped according to the International Air Transport Association (IATA) Dangerous Goods Regulations or Department of Transportation (DOT) regulations and U.S. EPA guidelines.

7.2 Sample Collection Techniques

In general, two basic types of sample collection techniques are recognized, both of which can be used for either environmental or hazardous samples.

Grab Samples

A grab sample is defined as a discrete aliquot representative of a specific location at a given point in time. The sample is collected all at once at one particular point in the sample medium. The representativeness of such samples is defined by the nature of the materials being sampled. In general, as sources vary over time and distance, the representativeness of grab samples will decrease.

Composite Samples

Composites are nondiscrete samples composed of more than one specific aliquot collected at various sampling locations and/or different points in time. Analysis of this type of sample produces an average value and can in certain instances be used as an alternative to analyzing a number of individual grab samples and calculating an average value. It should be noted, however, that compositing can mask problems by diluting isolated concentrations of some hazardous compounds below detection limits.

Compositing is often used for environmental samples and may be used for hazardous samples under certain conditions. For example, compositing of hazardous waste is often performed after compatibility tests have

been completed to determine an average value over a number of different locations (group of drums). This procedure generates data that can be useful by providing an average concentration within a number of units, can serve to keep analytical costs down, and can provide information useful to transporters and waste disposal operations.

For sampling situations involving hazardous wastes, grab sampling techniques are generally preferred because grab sampling minimizes the amount of time sampling personnel must be in contact with the wastes, reduces risks associated with compositing unknowns, and eliminates chemical changes that might occur due to compositing.

7.3 Types of Sampling Strategies

The number of samples that should be collected and analyzed depends on the objective of the investigation. There are three basic sampling strategies: random, systematic, and judgmental sampling.

Random sampling involves collection of samples in a nonsystematic fashion from the entire site or a specific portion of a site. Systematic sampling involves collection of samples based on a grid or a pattern which has been previously established. When judgmental sampling is performed, samples are collected only from the portion(s) of the site most likely to be contaminated. Often, a combination of these strategies is the best approach depending on the type of the suspected/known contamination, the uniformity and size of the site, the level/type of information desired, etc.

7.4 QA Work Plans (QAWP)

A QAWP is required when it becomes evident that a field investigation is necessary. It should be initiated in conjunction with, or immediately following, notification of the field investigation. This plan should be clear and concise and should detail the following basic components, with regard to sampling activities:

- Objective and purpose of the investigation.
- Basis upon which data will be evaluated.
- Information known about the site including location, type and size of the facility, and length of operations/abandonment.
- Type and volume of contaminated material, contaminants of concern (including concentration), and basis of the information/data.
- Technical approach including media/matrix to be sampled, sampling equipment to be used, sample equipment decontamination (if necessary), sampling design and rationale, and SOPs or description of the procedure to be implemented.
- Project management and reporting, schedule, project organization and responsibilities, manpower and cost projections, and required deliverables.
- QA objectives and protocols including tables summarizing field sampling and QA/QC analysis and objectives.

Note that this list of QAWP components is not all-inclusive and that additional elements may be added or altered depending on the specific requirements of the field investigation. It should also be recognized that although a detailed QAWP is quite important, it may be impractical in some instances. Emergency responses and accidental spills are prime examples of such instances where time might prohibit the development of site-specific QAWPs prior to field activities. In such cases, investigators would have to rely on general guidelines and personal judgment, and the sampling or response plans might simply be a strategy based on preliminary information and finalized on site. In any event, a plan of action should be developed, no matter how concise or informal, to aid investigators in maintaining a logical and consistent order to the implementation of their task.

7.5 Legal Implications

The data derived from sampling activities are often introduced as critical evidence during litigation of a hazardous waste site cleanup. Legal issues in which sampling data are important may include cleanup cost recovery, identification of pollution sources and responsible parties, and technical validation of remedial design methodologies. Because of the potential for involvement in legal actions, strict adherence to technical and administrative SOPs is essential during both the development and implementation of sampling activities.

Technically valid sampling begins with thorough planning and continues through the sample collection and analytical procedures. Administrative requirements involve thorough, accurate

documentation of all sampling activities. Documentation requirements include maintenance of a chain of custody, as well as accurate records of field activities and analytical instructions. Failure to observe these procedures fully and consistently may result in data that are questionable, invalid and non-defensible in court, and the consequent loss of enforcement proceedings.

8.0 CALCULATIONS

Refer to the specific SOPs for any calculations which are associated with sampling techniques.

9.0 QUALITY ASSURANCE/ QUALITY CONTROL

Refer to the specific SOPs for the type and frequency of QA/QC samples to be analyzed, the acceptance criteria for the QA/QC samples, and any other QA/QC activities which are associated with sampling techniques.

10.0 DATA VALIDATION

Refer to the specific SOPs for data validation activities that are associated with sampling techniques.

11.0 HEALTH AND SAFETY

When working with potentially hazardous materials, follow U.S. EPA, OSHA, and corporate health and safety procedures.

1.0 SCOPE AND APPLICATION

The purpose of this Standard Operating Procedure (SOP) is to provide a description of the methods used for preventing, minimizing, or limiting cross-contamination of samples due to inappropriate or inadequate equipment decontamination and to provide general guidelines for developing decontamination procedures for sampling equipment to be used during hazardous waste operations as per 29 Code of Federal Regulations (CFR) 1910.120. This SOP does not address personnel decontamination.

These are standard (i.e. typically applicable) operating procedures which may be varied or changed as required, dependent upon site conditions, equipment limitation, or limitations imposed by the procedure. In all instances, the ultimate procedures employed should be documented and associated with the final report.

Mention of trade names or commercial products does not constitute U.S. Environmental Protection Agency (U.S. EPA) endorsement or recommendation for use.

2.0 METHOD SUMMARY

Removing or neutralizing contaminants from equipment minimizes the likelihood of sample cross contamination, reduces or eliminates transfer of contaminants to clean areas, and prevents the mixing of incompatible substances.

Gross contamination can be removed by physical decontamination procedures. These abrasive and non-abrasive methods include the use of brushes, air and wet blasting, and high and low pressure water cleaning.

The first step, a soap and water wash, removes all visible particulate matter and residual oils and grease. This may be preceded by a steam or high pressure water wash to facilitate residuals removal. The second step involves a tap water rinse and a distilled/deionized water rinse to remove the detergent. An acid rinse provides a low pH media for trace metals removal and is included in the decontamination process if metal samples are to be collected. It is followed by another distilled/deionized water rinse. If sample analysis does not include metals, the acid rinse step can be omitted. Next, a high purity solvent rinse is performed for trace organics removal if organics are a concern at the site. Typical solvents used for removal of organic contaminants include acetone, hexane, or water. Acetone is typically chosen because it is an excellent solvent, miscible in water, and not a target analyte on the Priority Pollutant List. If acetone is known to be a contaminant of concern at a given site or if Target Compound List analysis (which includes acetone) is to be performed, another solvent may be substituted. The solvent must be allowed to evaporate completely and then a final distilled/deionized water rinse is performed. This rinse removes any residual traces of the solvent.

The decontamination procedure described above may be summarized as follows:

1. Physical removal
2. Non-phosphate detergent wash
3. Tap water rinse
4. Distilled/deionized water rinse
5. 10% nitric acid rinse
6. Distilled/deionized water rinse
7. Solvent rinse (pesticide grade)
8. Air dry
9. Distilled/deionized water rinse

If a particular contaminant fraction is not present at the site, the nine (9) step decontamination procedure specified above may be modified for site specificity. For example, the nitric acid rinse may be eliminated if metals are not of concern at a site. Similarly, the solvent rinse may be eliminated if organics are not of

concern at a site. Modifications to the standard procedure should be documented in the site specific work plan or subsequent report.

3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

The amount of sample to be collected and the proper sample container type (i.e., glass, plastic), chemical preservation, and storage requirements are dependent on the matrix being sampled and the parameter(s) of interest.

More specifically, sample collection and analysis of decontamination waste may be required before beginning proper disposal of decontamination liquids and solids generated at a site. This should be determined prior to initiation of site activities.

4.0 INTERFERENCES AND POTENTIAL PROBLEMS

- The use of distilled/deionized water commonly available from commercial vendors may be acceptable for decontamination of sampling equipment provided that it has been verified by laboratory analysis to be analyte free (specifically for the contaminants of concern).

- The use of an untreated potable water supply is not an acceptable substitute for tap water. Tap water may be used from any municipal or industrial water treatment system.

- If acids or solvents are utilized in decontamination they raise health and safety, and waste disposal concerns.

- Damage can be incurred by acid and solvent washing of complex and sophisticated sampling equipment.

5.0 EQUIPMENT/APPARATUS

Decontamination equipment, materials, and supplies are generally selected based on availability. Other considerations include the ease of decontaminating or disposing of the equipment. Most equipment and supplies can be easily procured. For example, soft-bristle scrub brushes or long-handled bottle brushes can be used to remove contaminants. Large galvanized wash tubs, stock tanks, or buckets can hold wash and rinse solutions. Children's wading pools can also be used. Large plastic garbage cans or other similar containers lined with plastic bags can help segregate contaminated equipment. Contaminated liquid can be stored temporarily in metal or plastic cans or drums.

The following standard materials and equipment are recommended for decontamination activities:

5.1 Decontamination Solutions

- Non-phosphate detergent
- Selected solvents (acetone, hexane, nitric acid, etc.)
- Tap water
- Distilled or deionized water

5.2 Decontamination Tools/Supplies

- Long and short handled brushes
- Bottle brushes
- Drop cloth/plastic sheeting
- Paper towels
- Plastic or galvanized tubs or buckets
- Pressurized sprayers (H_2O)
- Solvent sprayers
- Aluminum foil

5.3 Health and Safety Equipment

Appropriate personal protective equipment (i.e., safety glasses or splash shield, appropriate gloves, aprons or coveralls, respirator, emergency eye wash)

5.4 Waste Disposal

- Trash bags
- Trash containers
- 55-gallon drums
- Metal/plastic buckets/containers for storage and disposal of decontamination solutions

6.0 REAGENTS

There are no reagents used in this procedure aside from the actual decontamination solutions. Table 1 (Appendix A) lists solvent rinses which may be required for elimination of particular chemicals. In

general, the following solvents are typically utilized for decontamination purposes:

- 10% nitric acid is typically used for inorganic compounds such as metals. An acid rinse may not be required if inorganics are not a contaminant of concern.
- Acetone (pesticide grade)[1]
- Hexane (pesticide grade)[1]
- Methanol[1]

[1] - Only if sample is to be analyzed for organics.

7.0 PROCEDURES

As part of the health and safety plan, a decontamination plan should be developed and reviewed. The decontamination line should be set up before any personnel or equipment enter the areas of potential exposure. The equipment decontamination plan should include:

- The number, location, and layout of decontamination stations.
- Decontamination equipment needed.
- Appropriate decontamination methods.
- Methods for disposal of contaminated clothing, equipment, and solutions.
- Procedures can be established to minimize the potential for contamination. This may include: (1) work practices that minimize contact with potential contaminants; (2) using remote sampling techniques; (3) covering monitoring and sampling equipment with plastic, aluminum foil, or other protective material; (4) watering down dusty areas; (5) avoiding laying down equipment in areas of obvious contamination; and (6) use of disposable sampling equipment.

7.1 Decontamination Methods

All samples and equipment leaving the contaminated area of a site must be decontaminated to remove any contamination that may have adhered to equipment. Various decontamination methods will remove contaminants by: (1) flushing or other physical action, or (2) chemical complexing to inactivate contaminants by neutralization, chemical reaction, disinfection, or sterilization.

Physical decontamination techniques can be grouped into two categories: abrasive methods and non-abrasive methods, as follows:

7.1.1 Abrasive Cleaning Methods

Abrasive cleaning methods work by rubbing and wearing away the top layer of the surface containing the contaminant. The mechanical abrasive cleaning methods are most commonly used at hazardous waste sites. The following abrasive methods are available:

Mechanical

Mechanical methods of decontamination include using metal or nylon brushes. The amount and type of contaminants removed will vary with the hardness of bristles, length of time brushed, degree of brush contact, degree of contamination, nature of the surface being cleaned, and degree of contaminant adherence to the surface.

Air Blasting

Air blasting equipment uses compressed air to force abrasive material through a nozzle at high velocities. The distance between nozzle and surface cleaned, air pressure, time of application, and angle at which the abrasive strikes the surface will dictate cleaning efficiency. Disadvantages of this method are the inability to control the amount of material removed and the large amount of waste generated.

Wet Blasting

Wet blast cleaning involves use of a suspended fine abrasive. The abrasive/water mixture is delivered by compressed air to the contaminated area. By using a very fine abrasive, the amount of materials removed can be carefully controlled.

7.1.2 Non-Abrasive Cleaning Methods

Non-abrasive cleaning methods work by forcing the contaminant off a surface with pressure. In general, the equipment surface is not removed using non-abrasive methods.

Low-Pressure Water

This method consists of a container which is filled with water. The user pumps air out of the container to create a vacuum. A slender nozzle and hose allow the user to spray in hard-to-reach places.

High-Pressure Water

This method consists of a high-pressure pump, an operator controlled directional nozzle, and a high-pressure hose. Operating pressure usually ranges from 340 to 680 atmospheres (atm) and flow rates usually range from 20 to 140 liters per minute.

Ultra-High-Pressure Water

This system produces a water jet that is pressured from 1,000 to 4,000 atmospheres. This ultra-high-pressure spray can remove tightly-adhered surface films. The water velocity ranges from 500 meters/second (m/s) (1,000 atm) to 900 m/s (4,000 atm). Additives can be used to enhance the cleaning action.

Rinsing

Contaminants are removed by rinsing through dilution, physical attraction, and solubilization.

Damp Cloth Removal

In some instances, due to sensitive, non-waterproof equipment or due to the unlikelihood of equipment being contaminated, it is not necessary to conduct an extensive decontamination procedure. For example, air sampling pumps hooked on a fence, placed on a drum, or wrapped in plastic bags are not likely to become heavily contaminated. A damp cloth should be used to wipe off contaminants which may have adhered to equipment through airborne contaminants or from surfaces upon which the equipment was set.

Disinfection/Sterilization

Disinfectants are a practical means of inactivating infectious agents. Unfortunately, standard sterilization methods are impractical for large equipment. This method of decontamination is typically performed off-site.

7.2 Field Sampling Equipment Decontamination Procedures

The decontamination line is setup so that the first station is used to clean the most contaminated item. It progresses to the last station where the least contaminated item is cleaned. The spread of contaminants is further reduced by separating each decontamination station by a minimum of three (3) feet. Ideally, the contamination should decrease as the equipment progresses from one station to another farther along in the line.

A site is typically divided up into the following boundaries: Hot Zone or Exclusion Zone (EZ), the Contamination Reduction Zone (CRZ), and the Support or Safe Zone (SZ). The decontamination line should be setup in the Contamination Reduction Corridor (CRC) which is in the CRZ. Figure 1 (Appendix B) shows a typical contaminant reduction zone layout. The CRC controls access into and out of the exclusion zone and confines decontamination activities to a limited area. The CRC boundaries should be conspicuously marked. The far end is the hotline, the boundary between the exclusion zone and the contamination reduction zone. The size of the decontamination corridor depends on the number of stations in the decontamination process, overall dimensions of the work zones, and amount of space available at the site. Whenever possible, it should be a straight line.

Anyone in the CRC should be wearing the level of protection designated for the decontamination crew. Another corridor may be required for the entry and exit of heavy equipment. Sampling and monitoring equipment and sampling supplies are all maintained outside of the CRC. Personnel don their equipment away from the CRC and enter the exclusion zone through a separate access control point at the hotline. One person (or more) dedicated to decontaminating equipment is recommended.

7.2.1 Decontamination Setup

Starting with the most contaminated station, the decontamination setup should be as follows:

Station 1: Segregate Equipment Drop

Place plastic sheeting on the ground (Figure 2, Appendix B). Size will depend on amount of

equipment to be decontaminated. Provide containers lined with plastic if equipment is to be segregated. Segregation may be required if sensitive equipment or mildly contaminated equipment is used at the same time as equipment which is likely to be heavily contaminated.

Station 2: Physical Removal With A High-Pressure Washer (Optional)

As indicated in 7.1.2, a high-pressure wash may be required for compounds which are difficult to remove by washing with brushes. The elevated temperature of the water from the high-pressure washers is excellent at removing greasy/oily compounds. High pressure washers require water and electricity.

A decontamination pad may be required for the high-pressure wash area. An example of a wash pad may consist of an approximately 1 1/2 foot-deep basin lined with plastic sheeting and sloped to a sump at one corner. A layer of sand can be placed over the plastic and the basin is filled with gravel or shell. The sump is also lined with visqueen and a barrel is placed in the hole to prevent collapse. A sump pump is used to remove the water from the sump for transfer into a drum.

Typically heavy machinery is decontaminated at the end of the day unless site sampling requires that the machinery be decontaminated frequently. A separate decontamination pad may be required for heavy equipment.

Station 3: Physical Removal With Brushes And A Wash Basin

Prior to setting up Station 3, place plastic sheeting on the ground to cover areas under Station 3 through Station 10.
Fill a wash basin, a large bucket, or child's swimming pool with non-phosphate detergent and tap water. Several bottle and bristle brushes to physically remove contamination should be dedicated to this station . Approximately 10 - 50 gallons of water may be required initially depending upon the amount of equipment to decontaminate and the amount of gross contamination.

Station 4: Water Basin

Fill a wash basin, a large bucket, or child's swimming pool with tap water. Several bottle and bristle brushes should be dedicated to this station. Approximately 10-50 gallons of water may be required initially depending upon the amount of equipment to decontaminate and the amount of gross contamination.

Station 5: Low-Pressure Sprayers

Fill a low-pressure sprayer with distilled/deionized water. Provide a 5-gallon bucket or basin to contain the water during the rinsing process. Approximately 10-20 gallons of water may be required initially depending upon the amount of equipment to decontaminate and the amount of gross contamination.

Station 6: Nitric Acid Sprayers

Fill a spray bottle with 10% nitric acid. An acid rinse may not be required if inorganics are not a contaminant of concern. The amount of acid will depend on the amount of equipment to be decontaminated. Provide a 5-gallon bucket or basin to collect acid during the rinsing process.

Station 7: Low-Pressure Sprayers

Fill a low-pressure sprayer with distilled/deionized water. Provide a 5-gallon bucket or basin to collect water during the rinsate process.

Station 8: Organic Solvent Sprayers

Fill a spray bottle with an organic solvent. After each solvent rinse, the equipment should be rinsed with distilled/deionized water and air dried. Amount of solvent will depend on the amount of equipment to decontaminate. Provide a 5-gallon bucket or basin to collect the solvent during the rinsing process.

Solvent rinses may not be required unless organics are a contaminant of concern, and may be eliminated from the station sequence.

Station 9: Low-Pressure Sprayers

Fill a low-pressure sprayer with distilled/deionized water. Provide a 5-gallon bucket or basin to collect water during the rinsate process.

Station 10: Clean Equipment Drop

Lay a clean piece of plastic sheeting over the bottom

plastic layer. This will allow easy removal of the plastic in the event that it becomes dirty. Provide aluminum foil, plastic, or other protective material to wrap clean equipment.

7.2.2 Decontamination Procedures

Station 1: Segregate Equipment Drop

Deposit equipment used on-site (i.e., tools, sampling devices and containers, monitoring instruments radios, clipboards, etc.) on the plastic drop cloth/sheet or in different containers with plastic liners. Each will be contaminated to a different degree. Segregation at the drop reduces the probability of cross contamination. Loose leaf sampling data sheets or maps can be placed in plastic zip lock bags if contamination is evident.

Station 2: Physical Removal With A High-Pressure Washer (Optional)

Use high pressure wash on grossly contaminated equipment. Do not use high- pressure wash on sensitive or non-waterproof equipment.

Station 3: Physical Removal With Brushes And A Wash Basin

Scrub equipment with soap and water using bottle and bristle brushes. Only sensitive equipment (i.e., radios, air monitoring and sampling equipment) which is waterproof should be washed. Equipment which is not waterproof should have plastic bags removed and wiped down with a damp cloth. Acids and organic rinses may also ruin sensitive equipment. Consult the manufacturers for recommended decontamination solutions.

Station 4: Equipment Rinse

Wash soap off of equipment with water by immersing the equipment in the water while brushing. Repeat as many times as necessary.

Station 5: Low-Pressure Rinse

Rinse sampling equipment with distilled/deionized water with a low-pressure sprayer.

Station 6: Nitric Acid Sprayers (required only if metals are a contaminant of concern)

Using a spray bottle rinse sampling equipment with nitric acid. Begin spraying (inside and outside) at one end of the equipment allowing the acid to drip to the other end into a 5-gallon bucket. A rinsate blank may be required at this station. Refer to Section 9.

Station 7: Low-Pressure Sprayers

Rinse sampling equipment with distilled/deionized water with a low-pressure sprayer.

Station 8: Organic Solvent Sprayers

Rinse sampling equipment with a solvent. Begin spraying (inside and outside) at one end of the equipment allowing the solvent to drip to the other end into a 5-gallon bucket. Allow the solvent to evaporate from the equipment before going to the next station. A QC rinsate sample may be required at this station.

Station 9: Low-Pressure Sprayers

Rinse sampling equipment with distilled/deionized water with a low-pressure washer.

Station 10 : Clean Equipment Drop

Lay clean equipment on plastic sheeting. Once air dried, wrap sampling equipment with aluminum foil, plastic, or other protective material.

7.2.3 Post Decontamination Procedures

1. Collect high-pressure pad and heavy equipment decontamination area liquid and waste and store in appropriate drum or container. A sump pump can aid in the collection process. Refer to the Department of Transportation (DOT) requirements for appropriate containers based on the contaminant of concern.

2. Collect high-pressure pad and heavy equipment decontamination area solid waste and store in appropriate drum or container. Refer to the DOT requirements for appropriate containers based on the contaminant of concern.

3. Empty soap and water liquid wastes from basins and buckets and store in appropriate

drum or container. Refer to the DOT requirements for appropriate containers based on the contaminant of concern.

4. Empty acid rinse waste and place in appropriate container or neutralize with a base and place in appropriate drum. pH paper or an equivalent pH test is required for neutralization. Consult DOT requirements for appropriate drum for acid rinse waste.

5. Empty solvent rinse sprayer and solvent waste into an appropriate container. Consult DOT requirements for appropriate drum for solvent rinse waste.

6. Using low-pressure sprayers, rinse basins, and brushes. Place liquid generated from this process into the wash water rinse container.

7. Empty low-pressure sprayer water onto the ground.

8. Place all solid waste materials generated from the decontamination area (i.e., gloves and plastic sheeting, etc.) in an approved DOT drum. Refer to the DOT requirements for appropriate containers based on the contaminant of concern.

9. Write appropriate labels for waste and make arrangements for disposal. Consult DOT regulations for the appropriate label for each drum generated from the decontamination process.

8.0 CALCULATIONS

This section is not applicable to this SOP.

9.0 QUALITYASSURANCE/ QUALITY CONTROL

A rinsate blank is one specific type of quality control sample associated with the field decontamination process. This sample will provide information on the effectiveness of the decontamination process employed in the field.

Rinsate blanks are samples obtained by running analyte free water over decontaminated sampling equipment to test for residual contamination. The blank water is collected in sample containers for handling, shipment, and analysis. These samples are treated identical to samples collected that day. A rinsate blank is used to assess cross contamination brought about by improper decontamination procedures. Where dedicated sampling equipment is not utilized, collect one rinsate blank per day per type of sampling device samples to meet QA2 and QA3 objectives.

If sampling equipment requires the use of plastic tubing it should be disposed of as contaminated and replaced with clean tubing before additional sampling occurs.

10.0 DATA VALIDATION

Results of quality control samples will be evaluated for contamination. This information will be utilized to qualify the environmental sample results in accordance with the project's data quality objectives.

11.0 HEALTH AND SAFETY

When working with potentially hazardous materials, follow OSHA, U.S. EPA, corporate, and other applicable health and safety procedures.

Decontamination can pose hazards under certain circumstances. Hazardous substances may be incompatible with decontamination materials. For example, the decontamination solution may react with contaminants to produce heat, explosion, or toxic products. Also, vapors from decontamination solutions may pose a direct health hazard to workers by inhalation, contact, fire, or explosion.

The decontamination solutions must be determined to be acceptable before use. Decontamination materials may degrade protective clothing or equipment; some solvents can permeate protective clothing. If decontamination materials do pose a health hazard, measures should be taken to protect personnel or substitutions should be made to eliminate the hazard. The choice of respiratory protection based on contaminants of concern from the site may not be appropriate for solvents used in the decontamination process.

Safety considerations should be addressed when using abrasive and non-abrasive decontamination

equipment. Maximum air pressure produced by abrasive equipment could cause physical injury. Displaced material requires control mechanisms.

Material generated from decontamination activities requires proper handling, storage, and disposal. Personal Protective Equipment may be required for these activities.

Material safety data sheets are required for all decontamination solvents or solutions as required by the Hazard Communication Standard (i.e., acetone, alcohol, and trisodiumphosphate).

In some jurisdictions, phosphate containing detergents (i.e., TSP) are banned.

12.0 REFERENCES

Field Sampling Procedures Manual, New Jersey Department of Environmental Protection, February, 1988.

A Compendium of Superfund Field Operations Methods, EPA 540/p-87/001.

Engineering Support Branch Standard Operating Procedures and Quality Assurance Manual, USEPA Region IV, April 1, 1986.

Guidelines for the Selection of Chemical Protective Clothing, Volume 1, Third Edition, American Conference of Governmental Industrial Hygienists, Inc., February, 1987.

Occupational Safety and Health Guidance Manual for Hazardous Waste Site Activities, NIOSH/OSHA/USCG/EPA, October, 1985.

APPENDIX A

Table

Table 1. Soluble Contaminants and Recommended Solvent Rinse

TABLE 1 Soluble Contaminants and Recommended Solvent Rinse		
SOLVENT[1]	EXAMPLES OF SOLVENTS	SOLUBLE CONTAMINANTS
Water	Deionized water Tap water	Low-chain hydrocarbons Inorganic compounds Salts Some organic acids and other polar compounds
Dilute Acids	Nitric acid Acetic acid Boric acid	Basic (caustic) compounds (e.g., amines and hydrazines)
Dilute Bases	Sodium bicarbonate (e.g., soap detergent)	Acidic compounds Phenol Thiols Some nitro and sulfonic compounds
Organic Solvents [2]	Alcohols Ethers Ketones Aromatics Straight chain alkalines (e.g., hexane) Common petroleum products (e.g., fuel, oil, kerosene)	Nonpolar compounds (e.g., some organic compounds)
Organic Solvent[2]	Hexane	PCBs

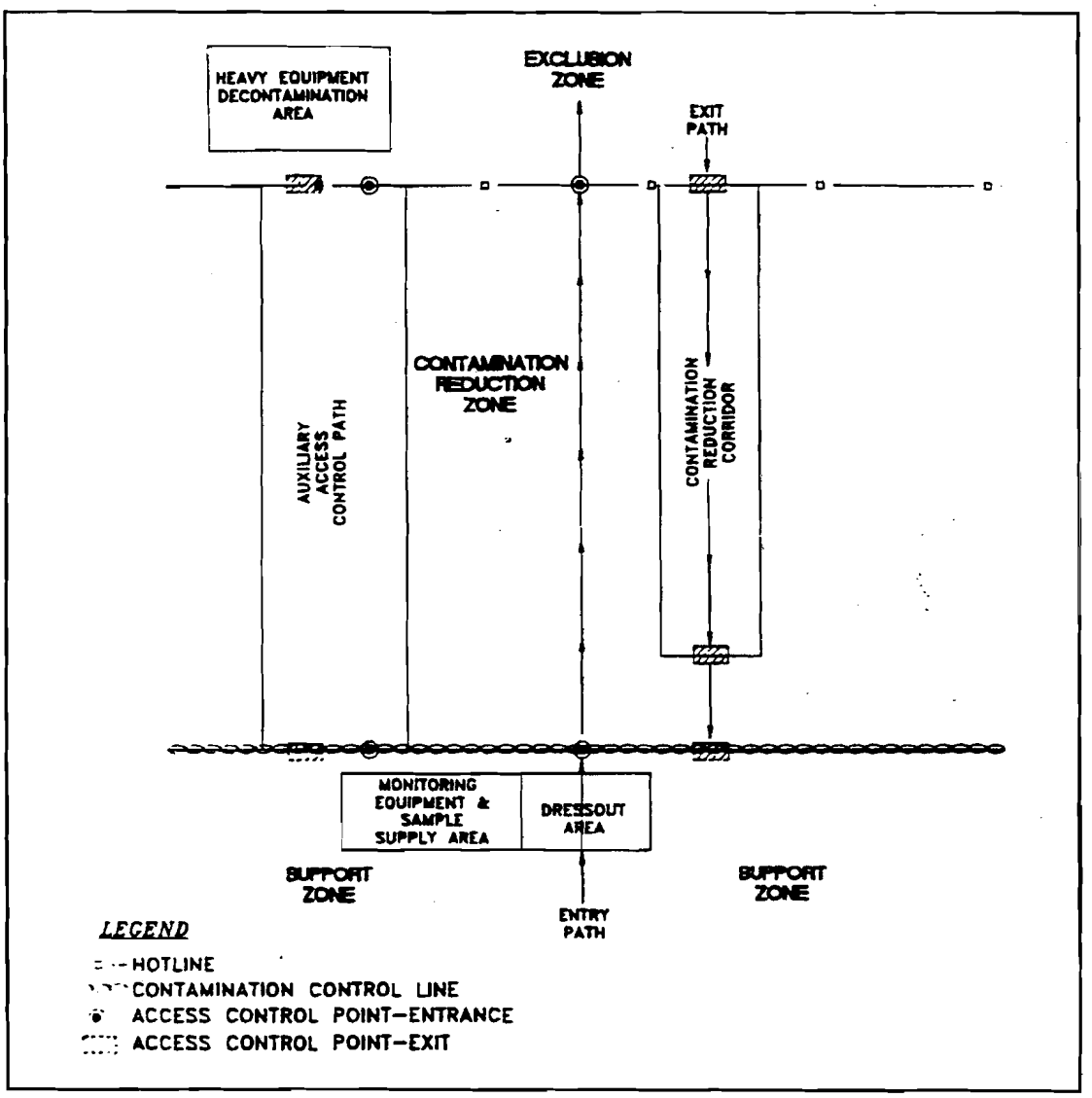
[1] - Material safety data sheets are required for all decontamination solvents or solutions as required by the Hazard Communication Standard

[2] - WARNING: Some organic solvents can permeate and/or degrade the protective clothing

APPENDIX B

Figures

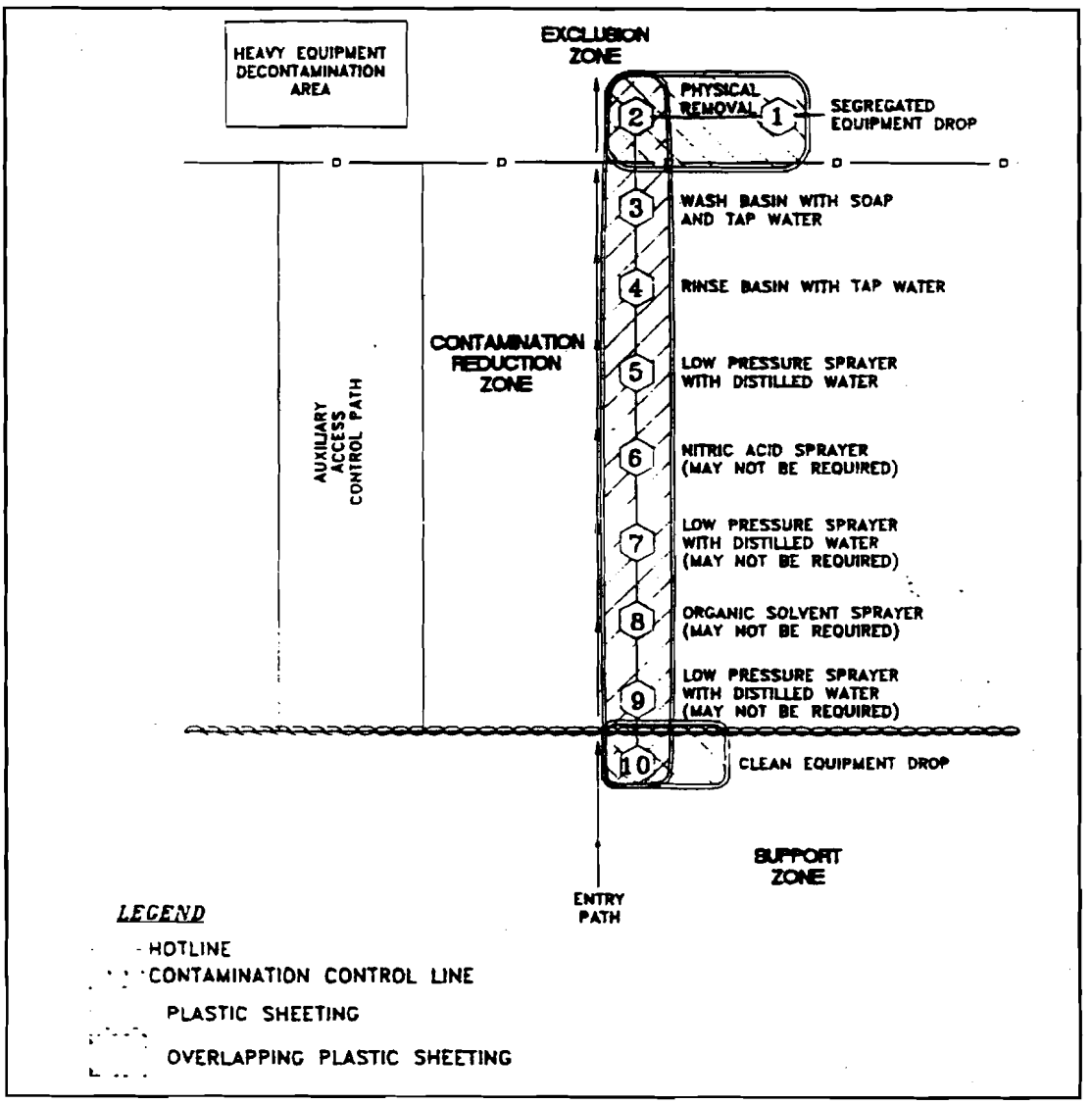
Figure 1. Contamination Reduction Zone Layout



APPENDIX B (Cont'd.)

Figures

Figure 2. Decontamination Layout



1.0 SCOPE AND APPLICATION

The purpose of this standard operating procedure (SOP) is to provide technical guidance on implementing safe and cost-effective response actions at hazardous waste sites containing drums with unknown contents. Container contents are sampled and characterized for disposal, bulking, recycling, segregation, and classification purposes.

These are standard (i.e., typically applicable) operating procedures which may be varied or changed as required, dependent on site conditions, equipment limitations or limitations imposed by the procedure. In all instances, the ultimate procedures employed should be documented and associated with the final report.

Mention of trade names or commercial products does not constitute U.S. Environmental Protection Agency (U.S. EPA) endorsement or recommendation for use.

2.0 METHOD SUMMARY

Prior to sampling, drums must be excavated, (if necessary), inspected, staged, and opened. Drum excavation must be performed by qualified personnel. Inspection involves the observation and recording of visual qualities of each drum and any characteristics pertinent to the classification of the drum's contents. Staging involves the physical grouping of drums according to classifications established during the physical inspection. Opening of closed drums can be performed manually or remotely. Remote drum opening is recommended for worker safety. The most widely used method of sampling a drum involves the use of a glass thief. This method is quick, simple, relatively inexpensive, and requires no decontamination. The contents of a drum can be further characterized by performing various field tests.

3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

Samples collected from drums are considered waste samples and as such, adding preservatives is not required due to the potential reaction of the sample with the preservative. Samples should, however, be cooled to 4°C and protected from sunlight in order to minimize any potential reaction due to the light sensitivity of the sample.

Sample bottles for collection of waste liquids, sludges, or solids are typically wide mouth amber jars with Teflon-lined screw caps. Actual volume required for analysis should be determined in conjunction with the laboratory performing the analysis.

Waste sample handling procedures should be as follows:

1. Label the sample container with the appropriate sample label and complete the appropriate field data sheet(s). Place sample container into two resealable plastic bags.

2. Place each bagged sample container into a shipping container which has been lined with plastic. Pack the container with enough non-combustible, absorbent, cushioning material to minimize the possibility of containers breaking, and to absorb any material which may leak.

   Note: Depending on the nature and quantity of the material to be shipped, different packaging may be required. The transportation company or a shipping/receiving expert should be consulted prior to packing the samples.

3. Complete a chain of custody record for each shipping container, place into a resealable

plastic bag, and affix to the inside lid of the shipping container.

4. Secure and custody seal the lid of the shipping container. Label the shipping container appropriately and arrange for the appropriate transportation mode consistent with the type of hazardous waste involved.

4.0 INTERFERENCES AND POTENTIAL PROBLEMS

If buried drums are suspected, geophysical investigation techniques such as magnetometry or ground penetrating radar may be employed in an attempt to determine the location and depth of drums. During excavation, the soil must be removed with great caution to minimize the potential for drum rupture.

Until the contents are characterized, sampling personnel should assume that unlabelled drums contain hazardous materials. Labelled drums are frequently mislabelled, especially drums that are reused. Because a drum's label may not accurately describe its contents, extreme caution must be exercised when working with or around drums.

If a drum which contains a liquid cannot be moved without rupture, its contents may be immediately transferred to a sound drum using an appropriate method of transfer based on the type of waste. In any case, preparations should be made to contain the spill (i.e., spill pads, dike, etc.) should one occur.

If a drum is leaking, open, or deteriorated, then it must be placed immediately in overpack containers.

The practice of tapping drums to determine their contents is neither safe nor effective and should not be used if the drums are visually overpressurized or if shock-sensitive materials are suspected. A laser thermometer may be effective in order to determine the level of the drum contents via surface temperature differences.

Drums that have been overpressurized to the extent that the head is swollen several inches above the level of the chime should not be moved. A number of devices have been developed for venting critically swollen drums. One method that has proven to be effective is a tube and spear device. A light aluminum tube (3 meters long) is positioned at the vapor space of the drum. A rigid, hooking device attached to the tube, goes over the chime and holds the tube securely in place. The spear is inserted in the tube and positioned against the drum wall. A sharp blow on the end of the spear drives the sharpened tip through the drum and the gas vents along the grooves. Venting should be done from behind a wall or barricade. Once the pressure has been relieved, the bung can be removed and the drum sampled.

Because there is potential for accidents to occur during handling, particularly initial handling, drums should only be handled if necessary. All personnel should be warned of the hazards prior to handling drums. Overpack drums and an adequate volume of absorbent material should be kept near areas where minor spills may occur. Where major spills may occur, a containment berm adequate to contain the entire volume of liquid in the drums should be constructed before any handling takes place. If drum contents spill, personnel trained in spill response should be used to isolate and contain the spill.

5.0 EQUIPMENT/APPARATUS

The following are standard materials and equipment required for sampling:

- Personal protection equipment
- Wide-mouth amber glass jars with Teflon cap liner, approximately 500 mL volume
- Other appropriate sample jars
- Uniquely numbered sample identification labels with corresponding data sheets
- Drum/Tank Sampling Data Sheets and Field Test Data Sheets for Drum/Tank Sampling
- Chain of Custody records
- Decontamination materials
- Glass thieving tubes or COLIWASA
- Coring device
- Stainless steel spatula or spoons
- Laser thermometer
- Drum overpacks
- Absorbent material for spills
- Drum opening devices

Bung Wrench

A common method for opening drums manually is using a universal bung wrench. These wrenches have fittings made to

remove nearly all commonly encountered bungs. They are usually constructed of a non-sparking metal alloy (i.e., brass, bronze/manganese, aluminum, etc.) formulated to reduce the likelihood of sparks. The use of a "NON-SPARKING" wrench does not completely eliminate the possibility of a spark being produced.

Drum Deheader

One means by which a drum can be opened manually when a bung is not removable with a bung wrench is by using a drum deheader. This tool is constructed of forged steel with an alloy steel blade and is designed to cut the lid of a drum off or part way off by means of a scissors-like cutting action. A limitation of this device is that it can be attached only to closed head drums. Drums with removable heads must be opened by other means.

Hand Pick, Pickaxe, and Hand Spike

These tools are usually constructed of brass or a non-sparking alloy with a sharpened point that can penetrate the drum lid or head when the tool is swung. The hand picks or pickaxes that are most commonly used are commercially available; whereas, the spikes are generally uniquely fabricated four foot long poles with a pointed end.

Backhoe Spike

Another means used to open drums remotely for sampling is a metal spike attached or welded to a backhoe bucket. This method is very efficient and is often used in large-scale operations.

Hydraulic Drum Opener

Recently, remotely operated hydraulic devices have been fabricated to open drums. This device uses hydraulic pressure to force a non-sparking spike through the wall of a drum. It consists of a manually operated pump which pressurizes fluid through a length of hydraulic line.

Pneumatic Devices

A pneumatic bung remover consists of a compressed air supply that is controlled by a two-stage regulator. A high pressure air line of desired length delivers compressed air to a pneumatic drill, which is adapted to turn bung fitting selected to fit the bung to be removed. An adjustable bracketing system has been designed to position and align the pneumatic drill over the bung. This bracketing system must be attached to the drum before the drill can be operated. Once the bung has been loosened, the bracketing system must be removed before the drum can be sampled. This remote bung opener does not permit the slow venting of the container, and therefore appropriate precautions must be taken. It also requires the container to be upright and relatively level. Bungs that are rusted shut cannot be removed with this device.

6.0 REAGENTS

Reagents are not typically required for preserving drum samples. However, reagents will be utilized for decontamination of sampling equipment.

7.0 PROCEDURES

7.1 Preparation

1. Determine the extent of the sampling effort, the sampling methods to be employed, and the types and amounts of equipment and supplies needed.

2. Obtain necessary sampling and monitoring equipment.

3. Decontaminate or preclean equipment, and ensure that it is in working order.

4. Prepare scheduling and coordinate with staff, clients, and regulatory agency, if appropriate.

5. Perform a general site survey prior to site entry in accordance with the site specific Health and Safety Plan.

6. Use stakes, flagging, or buoys to identify and mark all sampling locations. If required the proposed locations may be adjusted based on site access, property boundaries, and surface obstructions.

7.2 Drum Excavation

If it is presumed that buried drums are on-site and prior to beginning excavation activities, geophysical investigation techniques should be utilized to approximate the location and depth of the drums. In addition, it is important to ensure that all locations where excavation will occur are clear of utility lines, pipes and poles (subsurface as well as above surface).

Excavating, removing, and handling drums are generally accomplished with conventional heavy construction equipment. These activities should be performed by an equipment operator who has experience in drum excavation. During excavation activities, drums must be approached in a manner that will avoid digging directly into them.

The soil around the drum should be excavated with non-sparking hand tools or other appropriate means and as the drums are exposed, a visual inspection should be made to determine the condition of the drums. Ambient air monitoring should be done to determine the presence of unsafe levels of volatile organics, explosives, or radioactive materials. Based on this preliminary visual inspection, the appropriate mode of drum excavation and handling may be determined.

Drum identification and inventory should begin before excavation. Information such as location, date of removal, drum identification number, overpack status, and any other identification marks should be recorded on the Drum/Tank Sampling Data Sheet (Attachment 1, Appendix A).

7.3 Drum Inspection

Appropriate procedures for handling drums depend on the contents. Thus, prior to any handling, drums should be visually inspected to gain as much information as possible about their contents. The drums should be inspected for the following:

1. Drum condition, corrosion, rust, punctures, bungs, and leaking contents.

2. Symbols, words, or other markings on the drum indicating hazards (i.e., explosive, radioactive, toxic, flammable), or further identifying the drums.

3. Signs that the drum is under pressure.

4. Shock sensitivity.

Monitoring should be conducted around the drums using instruments such as radiation meters, organic vapor analyzers (OVA) and combustible gas indicators (CGI).

Survey results can be used to classify the drums into categories, for instance:

- Radioactive
- Leaking/deteriorating
- Bulging
- Lab packs
- Explosive/shock sensitive
- Empty

All personnel should assume that unmarked drums contain hazardous materials until their contents have been categorized. Once a drum has been visually inspected and any immediate hazard has been eliminated by overpacking or transferring the drum's contents, the drum is affixed with a numbered tag and transferred to a staging area. Color-coded tags, labels or bands should be used to identify the drum's category based on visual inspection. A description of each drum, its condition, any unusual markings, the location where it was buried or stored, and field monitoring information are recorded on a Drum/Tank Sampling Data Sheet (Attachment 1, Appendix A). This data sheet becomes the principal record keeping tool for tracking the drum on-site.

7.4 Drum Staging

Prior to sampling, the drums should be staged to allow easy access. Ideally, the staging area should be located just far enough from the drum opening area to prevent a chain reaction if one drum should explode or catch fire when opened.

During staging, the drums should be physically separated into the following categories: those containing liquids, those containing solids, those containing lab packs, and those which are empty.

This is done because the strategy for sampling and handling drums/containers in each of these categories will be different. This may be achieved by visual inspection of the drum and its labels, codes, etc. Solids and sludges are typically disposed of in open top drums. Closed head drums with a bung opening generally contain liquid.

Where there is good reason to suspect that drums contain radioactive, explosive, or shock-sensitive materials, these drums should be staged in a separate, isolated area. Placement of explosives and shock-sensitive materials in diked and fenced areas will minimize the hazard and the adverse effects of any premature detonation of explosives.

Where space allows, the drum opening area should be physically separated from the drum removal and drum staging operations. Drums are moved from the staging area to the drum opening area one at a time using forklift trucks equipped with drum grabbers or a barrel grappler. In a large-scale drum handling operation, drums may be conveyed to the drum opening area using a roller conveyor. Drums may be restaged as necessary after opening and sampling.

7.5 Drum Opening

There are three basic techniques available for opening drums at hazardous waste sites:

- Manual opening with non-sparking bung wrenches
- Drum deheading
- Remote drum puncturing or bung removal

The choice of drum opening techniques and accessories depends on the number of drums to be opened, their waste contents, and physical condition. Remote drum opening equipment should always be considered in order to protect worker safety. Under OSHA 1910.120, manual drum opening with bung wrenches or deheaders should be performed ONLY with structurally sound drums and waste contents that are known to be non-shock sensitive, non-reactive, non-explosive, and non-flammable.

7.5.1 Manual Drum Opening with a Bung Wrench

Manual drum opening with bung wrenches (Figure 1, Appendix B) should not be performed unless the drums are structurally sound (no evidence of bulging or deformation) and their contents are known to be non-shock sensitive, non-reactive, non-explosive or non-flammable. If opening the drum with bung wrenches is deemed safe, then certain procedures should be implemented to minimize the hazard:

- Field personnel should be fully outfitted with protective gear.
- Drums should be positioned upright with the bung up, or, for drums with bungs on the side, laid on their sides with the bung plugs up.
- The wrenching motion should be a slow, steady pull across the drum. If the length of the bung wrench handle provides inadequate leverage for unscrewing the plug, a "cheater bar" can be attached to the handle to improve leverage.

7.5.2 Manual Drum Opening with a Drum Deheader

Drums are opened with a drum deheader (Figure 2, Appendix B) by first positioning the cutting edge just inside the top chime and then tightening the adjustment screw so that the deheader is held against the side of the drum. Moving the handle of the deheader up and down while sliding the deheader along the chime will enable the entire top to be rapidly cut off if so desired. If the top chime of a drum has been damaged or badly dented it may not be possible to cut the entire top off. Since there is always the possibility that a drum may be under pressure, the initial cut should be made very slowly to allow for the gradual release of any built-up pressure. A safer technique would be to employ a remote method prior to using the deheader.

Self-propelled drum openers which are either electrically or pneumatically driven are available and can be used for quicker and more efficient deheading.

The drum deheader should be decontaminated, as necessary, after each drum is opened to avoid cross contamination and/or adverse chemical reactions from incompatible materials.

7.5.3 Manual Drum Opening with a Hand Pick, Pickaxe, or Spike

When a drum must be opened and neither a bung

wrench nor a drum deheader is suitable, then it can be opened for sampling by using a hand pick, pickaxe, or spike (Figure 3, Appendix B). Often the drum lid or head must be hit with a great deal of force in order to penetrate it. Because of this, the potential for splash or spraying is greater than with other opening methods and therefore, this method of drum opening is not recommended, particularly when opening drums containing liquids. Some spikes used have been modified by the addition of a circular splash plate near the penetrating end. This plate acts as a shield and reduces the amount of splash in the direction of the person using the spike. Even with this shield, good splash gear is essential.

Since drums, some of which may be under pressure, cannot be opened slowly with these tools, spray from drums is common and appropriate safety measures must be taken. The pick or spike should be decontaminated after each drum is opened to avoid cross contamination and/or adverse chemical reaction from incompatible materials.

7.5.4 Remote Drum Opening with a Backhoe Spike

Remotely operated drum opening tools are the safest available means of drum opening. Remote drum opening is slow, but provides a high degree of safety compared to manual methods of opening.

In the opening area, drums should be placed in rows with adequate aisle space to allow ease in backhoe maneuvering. Once staged, the drums can be quickly opened by punching a hole in the drum head or lid with the spike.

The spike (Figure 4, Appendix B) should be decontaminated after each drum is opened to prevent cross contamination and/or adverse reaction from incompatible material. Even though some splash or spray may occur when this method is used, the operator of the backhoe can be protected by mounting a large shatter-resistant shield in front of the operator's cage. This combined with the normal personal protection gear should be sufficient to protect the operator. Additional respiratory protection can be afforded by providing the operator with an on-board airline system.

7.5.5 Remote Drum Opening with Hydraulic Devices

A piercing device with a non-sparking, metal point is attached to the end of a hydraulic line and is pushed into the drum by the hydraulic pressure (Figure 5, Appendix B). The piercing device can be attached so that a hole for sampling can be made in either the side or the head of the drum. Some of the metal piercers are hollow or tube-like so that they can be left in place if desired and serve as a permanent tap or sampling port. The piercer is designed to establish a tight seal after penetrating the container.

7.5.6 Remote Drum Opening with Pneumatic Devices

Pneumatically-operated devices utilizing compressed air have been designed to remove drum bungs remotely (Figure 6, Appendix B). Prior to opening the drum, a bung fitting must be selected to fit the bung to be removed. The adjustable bracketing system is then attached to the drum and the pneumatic drill is aligned over the bung. This must be done before the drill can be operated. The operator then moves away from the drum to operate the equipment. Once the bung has been loosened, the bracketing system must be removed before the drum can be sampled. This remote bung opener does not permit the slow venting of the container, and therefore appropriate precautions must be taken. It also requires the container to be upright and relatively level. Bungs that are rusted shut cannot be removed with this device.

7.6 Drum Sampling

After the drum has been opened, preliminary monitoring of headspace gases should be performed first with an explosimeter/oxygen meter. Afterwards, an OVA or other instruments should be used. If possible, these instruments should be intrinsically safe. In most cases it is impossible to observe the contents of these sealed or partially sealed drums. Since some layering or stratification is likely in any solution left undisturbed, a sample that represents the entire depth of the drum must be taken.

When sampling a previously sealed drum, a check should be made for the presence of a bottom sludge. This is easily accomplished by measuring the depth to apparent bottom then comparing it to the known interior depth.

7.6.1 Glass Thief Sampler

The most widely used implement for sampling drum liquids is a glass tube commonly referred to as a glass thief (Figure 7, Appendix B). This tool is cost effective, quick, and disposable. Glass thieves are typically 6mm to 16mm I.D. and 48 inches long.

Procedures for Use:

1. Remove the cover from the sample container.

2. Insert glass tubing almost to the bottom of the drum or until a solid layer is encountered. About one foot of tubing should extend above the drum.

3. Allow the waste in the drum to reach its natural level in the tube.

4. Cap the top of the sampling tube with a tapered stopper or thumb, ensuring liquid does not come into contact with stopper.

5. Carefully remove the capped tube from the drum and insert the uncapped end into the appropriate sample container.

6. Release stopper and allow the glass thief to drain until the container is approximately two-thirds full.

7. Remove tube from the sample container, break it into pieces and place the pieces in the drum.

8. Cap the sample container tightly and label it. Place the sample container into a carrier.

9. Replace the bung or place plastic over the drum.

10. Log all samples in the site logbook and on Drum/Tank Sampling Data Sheets.

11. Perform hazard categorization analyses if included in the project scope.

12. Transport the sample to the decontamination zone and package it for transport to the analytical laboratory, as necessary. Complete chain of custody records.

In many instances a drum containing waste material will have a sludge layer on the bottom. Slow insertion of the sample tube into this layer; then a gradual withdrawal will allow the sludge to act as a bottom plug to maintain the fluid in the tube. The plug can be gently removed and placed into the sample container by the use of a stainless steel lab spoon.

It should be noted that in some instances disposal of the tube by breaking it into the drum may interfere with eventual plans for the removal of its contents. The use of this technique should be cleared with the project officer or other glass thief disposal techniques should be evaluated.

7.6.2 COLIWASA Sampler

The Composite Liquid Waste Sampler (COLIWASA) and modifications thereof are equipment that collect a sample from the full depth of a drum and maintain it in the transfer tube until delivery to the sample bottle. The COLIWASA (Figure 8, Appendix B) is a much cited sampler designed to permit representative sampling of multiphase wastes from drums and other containerized wastes. One configuration consists of a 152 cm by 4 cm I.D. section of tubing with a neoprene stopper at one end attached by a rod running the length of the tube to a locking mechanism at the other end.

Manipulation of the locking mechanism opens and closes the sampler by raising and lowering the neoprene stopper. One model of the COLIWASA is shown in Appendix B; however, the design can be modified and/or adapted somewhat to meet the needs of the sampler.

The major drawbacks associated with using a COLIWASA concern decontamination and costs. The sampler is difficult to decontaminate in the field and its high cost in relation to alternative procedures (glass tubes) make it an impractical throwaway item. It still has applications, however, especially in instances where a true representation of a multiphase waste is absolutely necessary.

Procedures for Use

1. Put the sampler in the open position by placing the stopper rod handle in the T-position and pushing the rod down until the handle sits against the sampler's locking block.

2. Slowly lower the sampler into the liquid waste. Lower the sampler at a rate that permits the levels of the liquid inside and outside the sampler tube to be about the same. If the level of the liquid in the sample tube is lower than that outside the sampler, the sampling rate is too fast and will result in a non-representative sample.

3. When the sampler stopper hits the bottom of the waste container, push the sampler tube downward against the stopper to close the sampler. Lock the sampler in the closed position by turning the T-handle until it is upright and one end rests tightly on the locking block.

4. Slowly withdraw the sample from the waste container with one hand while wiping the sampler tube with a disposable cloth or rag with the other hand.

5. Carefully discharge the sample into the appropriate sample container by slowly pulling the lower end of the T-handle away from the locking block while the lower end of the sampler is positioned in a sample container.

6. Cap the sample container tightly and label it. Place the sample container in a carrier.

7. Replace the bung or place plastic over the drum.

8. Log all samples in the site logbook and on Drum/Tank Sampling Data Sheets.

9. Perform hazard categorization analyses if included in the project scope.

10. Transport the sample to the decontamination zone and package for transport to the analytical laboratory, as necessary. Complete the Chain of Custody records.

7.6.3 Coring Device

A coring device may be used to sample drum solids. Samples should be taken from different areas within the drum. This sampler consists of a series of extensions, a T- handle, and the coring device.

Procedures for use:

1. Assemble the sampling equipment.

2. Remove the cover from the sample container.

3. Insert the sampling device to the bottom of the drum. The extensions and the "T" handle should extend above the drum.

4. Rotate the sampling device to cut a core of material.

5. Slowly withdraw the sampling device so that as much sample material as possible is retained within it.

6. Transfer the sample to the appropriate sample container, and label it. A stainless steel spoon or scoop may be used as necessary.

7. Cap the sample container tightly and place it in a carrier.

8. Replace the bung or place plastic over the drum.

9. Log all samples in the site log book and on Drum/Tank Sampling Data Sheets.

10. Perform hazard categorization analyses if included in the project scope.

11. Transport the sample to the decontamination zone and package it for transport to the analytical laboratory, as necessary. Complete chain of custody records.

7.7 Hazard Categorization

The goal of characterizing or categorizing the contents of drums is to obtain a quick, preliminary assessment of the types and levels of pollutants contained in the drums. These activities generally involve rapid, non-rigorous methods of analysis. The data obtained from these methods can be used to make decisions regarding drum staging or restaging, bulking or compositing of the drum contents.

As a first step in obtaining these data, standard tests should be used to classify the drum contents into general categories such as auto-reactives, water reactives, inorganic acids, organic acids, heavy metals, pesticides, cyanides, inorganic oxidizers, and organic oxidizers. In some cases, further analyses should be conducted to more precisely identify the drum contents.

There are several methods available to perform these tests:

- the HazCat[R] chemical identification system
- the Chlor-N-Oil Test Kit
- Spill-fyter Chemical Classifier Strips
- Setaflash (for ignitability)

These methods must be performed according to the manufacturers' instructions and the results must be documented on the Field Test Data Sheet for Drum/Tank Sampling (Attachment 2, Appendix A).

Other tests which may be performed include:

- Water Reactivity
- Specific Gravity Test (compared to water)
- Water Solubility Test
- pH of Aqueous Solution

The tests must be performed in accordance with the instructions on the Field Test Data Sheet for Drum/Tank Sampling and results of the tests must be documented on these data sheets.

The specific methods that will be used for hazard categorization must be documented in the Quality Assurance Work Plan.

8.0 CALCULATIONS

This section is not applicable to this SOP.

9.0 QUALITY ASSURANCE/ QUALITY CONTROL

The following general quality assurance procedures apply:

1. All data must be documented on Chain of Custody records, Drum/Tank Sampling Data Sheets, Field Test Data Sheet for Drum/Tank Sampling, or within site logbooks.

2. All instrumentation must be operated in accordance with operating instructions as supplied by the manufacturer, unless otherwise specified in the work plan. Equipment checkout and calibration activities must occur prior to sampling/operation, and they must be documented.

10.0 DATA VALIDATION

This section is not applicable to this SOP.

11.0 HEALTH AND SAFETY

When working with potentially hazardous materials, follow U.S. EPA, OSHA, and corporate health and safety procedures.

More specifically, the opening of closed containers is one of the most hazardous site activities. Maximum efforts should be made to ensure the safety of the sampling team. Proper protective equipment and a general awareness of the possible dangers will minimize the risk inherent to sampling operations. Employing proper drum opening techniques and equipment will also safeguard personnel. The use of remote sampling equipment whenever feasible is highly recommended.

12.0 REFERENCES

Guidance Document for Cleanup of Surface Tank and Drum Sites, OSWER Directive 9380.0-3.

Drum Handling Practices at Hazardous Waste Sites, EPA-600/2-86-013.

APPENDIX A

Attachments

ATTACHMENT 1. Drum/Tank Sampling Data Sheet

Samplers: _____ Date: _____

Site Name: _____ Work Order Number: _____

Container Number/Sample Number: _____ Task Leader: _____

SITE INFORMATION:

1. Terrain, drainage description: _____

2. Weather conditions (from observation): _____

MET station on site: No Yes

CONTAINER INFORMATION:

1. Container type: Drum Tank Other: _____

2. Container dimensions: Shape: _____

Approximate size: _____

3. Label present: No
Yes: _____

Other Markings: _____

4. Spill or leak present: No Yes Dimensions: _____

5. Container location: (Circle one) N/A See Map Other: _____

APPENDIX A (Cont'd)

Attachments

ATTACHMENT 1. Drum/Tank Sampling Data Sheet (cont'd)

SAMPLE INFORMATION:

1. Description: _____ liquid _____ solid (_____ powder or _____ crystals) _____ sludge

2. Color: _____ Vapors:_____
   Other:_____

3. Local effects present: (damage - environmental, material)_____

FIELD MONITORING:

1. PID: _____ Background (clean zone)

   _____ Probe used/Model used

   _____ Reading from container opening

2. FID: _____ Background (clean zone)

   _____ Reading from container opening

3. Radiation Meter:

   _____ Model used

   _____ Background (clean zone)

   _____ Reading from container opening

4. Explosimeter/Oxygen Meter:

   _____ Oxygen level from container opening

   _____ LEL level from container opening

APPENDIX A (Cont'd)

Attachments

ATTACHMENT 2. Field Test Data Sheet for Drum/Tank Sampling

Samplers: _____ Date: _____

Site Name: _____ Work Order Number: -_____

Container Number/Sample Number: _____ Task Leader: _____

SAMPLE MONITORING INFORMATION:

1. PID: _____ Background (clean zone)

_____ Probe used/Model used

_____ Reading from sample

2. FID: _____ Background (clean zone)

_____ Reading from sample

3. Radiation Meter: _____ Model used

_____ Background (clean zone)

_____ Reading from sample

4. Explosimeter/Oxygen Meter: _____ Oxygen level (sample)

_____ LEL level (sample)

SAMPLE DESCRIPTION:

_____ Liquid _____ Solid _____ Sludge _____ Color _____ Vapors

WATER REACTIVITY:

1. Add small amount of sample to water: _____ bubbles _____ color change to _____

_____ vapor formation _____ heat _____ No Change

SPECIFIC GRAVITY TEST (compared to water):

1. Add small amount of sample to water: _____ sinks _____ floats

2. If liquid sample sinks, screen for chlorinated compounds. If liquid sample floats and appears to be oily, screen for PCBs (Chlor-N-Oil kit).

APPENDIX A (Cont'd)

Attachments

ATTACHMENT 2. Field Test Data Sheet for Drum/Tank Sampling (cont'd)

CHLOR N OIL TEST KIT INFORMATION:

1. Test kit used for this sample: Yes No

2. Results: _____ PCB not present _____ PCB present, less than 50 ppm

_____ PCB present, greater than 50 ppm _____ 100% PCB present

WATER SOLUBILITY TEST:

1. Add approximately one part sample to five parts water. You may need to stir and heat gently. **[DO NOT HEAT IF WATER REACTIVE!]** Results: _____ total _____ partial _____ no solubility

pH OF AQUEOUS SOLUTION:

1. Using 0-14 pH paper, check pH of water/sample solution: _____.

SPILL-FYTER CHEMICAL CLASSIFIER STRIPS:

1. Acid/Base Risk: (Circle one)	Color Change
Strong acid (0)	RED
Moderately acidic (1-3)	ORANGE
Weak acid (5)	YELLOW
Neutral (7)	GREEN
Moderately basic (9-11)	Dark GREEN
Strong Base (13-14)	Dark BLUE
2. Oxidizer Risk: (Circle one)	
Not Present	WHITE
Present	BLUE, RED, OR ANY DIVERGENCE FROM WHITE
3. Fluoride Risk: (Circle one)	
Not Present	PINK
Present	YELLOW

APPENDIX A (Cont'd)

Attachments

ATTACHMENT 2. Field Test Data Sheet for Drum/Tank Sampling (cont'd)

4. Petroleum Product, Organic Solvent Risk: (Circle one)

Not Present	LIGHT BLUE
Present	DARK BLUE

5. Iodine, Bromine, Chlorine Risk: (Circle one)

Not Present	PEACH
Present	WHITE OR YELLOW

SETAFLASH IGNITABILITY TEST:

140°F	Ignitable: _____	Non-Ignitable _____
160°F	Ignitable: _____	Non-Ignitable _____
_____	Ignitable: _____	Non-Ignitable _____
_____	Ignitable: _____	Non-Ignitable _____
_____	Ignitable: _____	Non-Ignitable _____
_____	Ignitable: _____	Non-Ignitable _____

Comments:

_____

_____

_____

_____

_____

_____

HAZCAT KIT TESTS:

1. Test: _____ Outcome: _____

Comments: _____

_____

2. Test: _____ Outcome: _____

Comments: _____

_____

APPENDIX A (Cont'd)

Attachments

ATTACHMENT 2. Field Test Data Sheet for Drum/Tank Sampling (cont'd)

3. Test: _____ Outcome: _____

Comments: _____

_____

4. Test: _____ Outcome: _____

Comments: _____

_____

5. Test: _____ Outcome: _____

Comments: _____

_____

HAZCAT PESTICIDES KIT:

Present: _____ Not Present: _____

Comments: _____

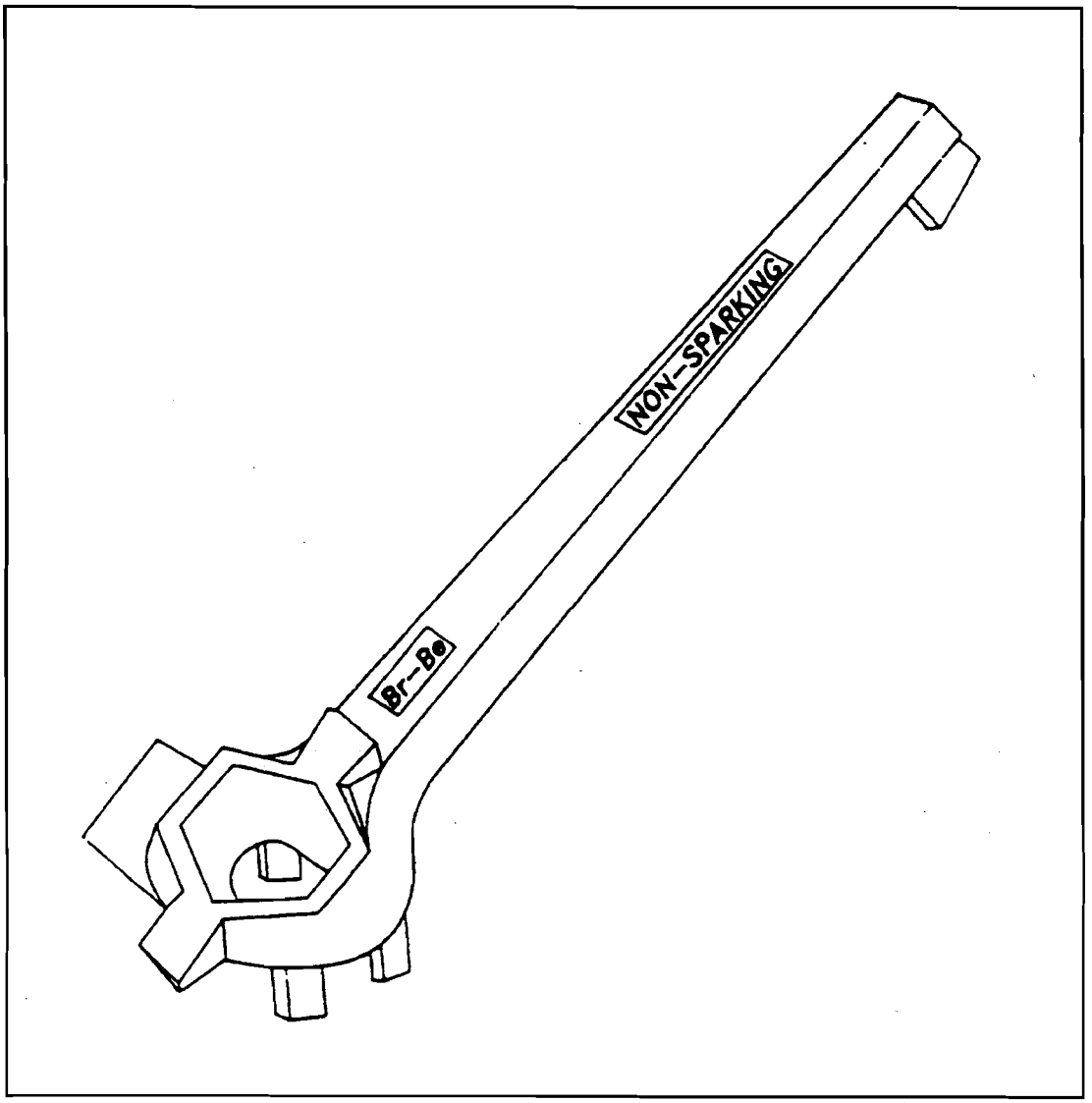
_____

_____

APPENDIX B

Figures

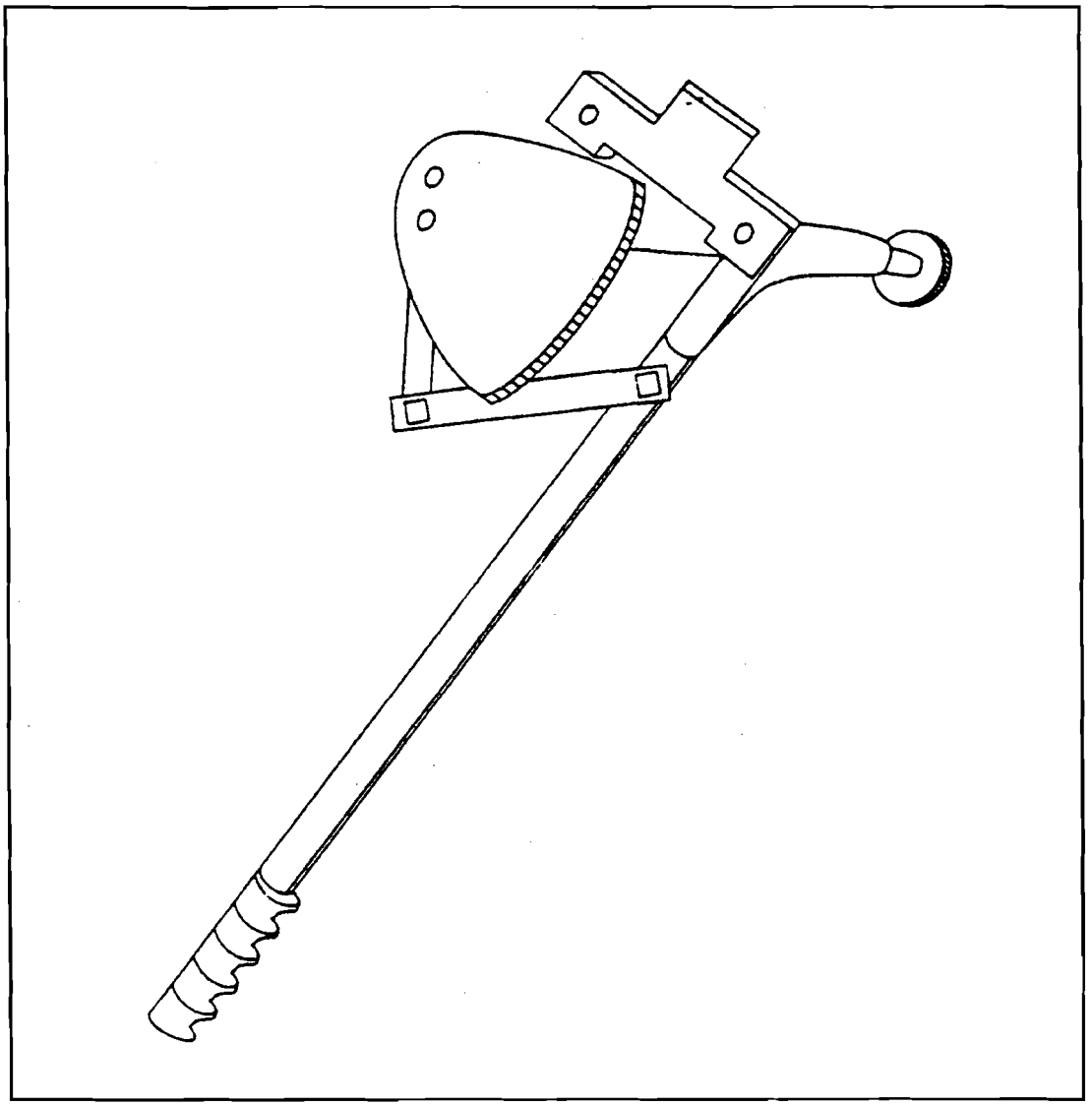
Figure 1. Universal Bung Wrench



APPENDIX B (Cont'd)

Figures

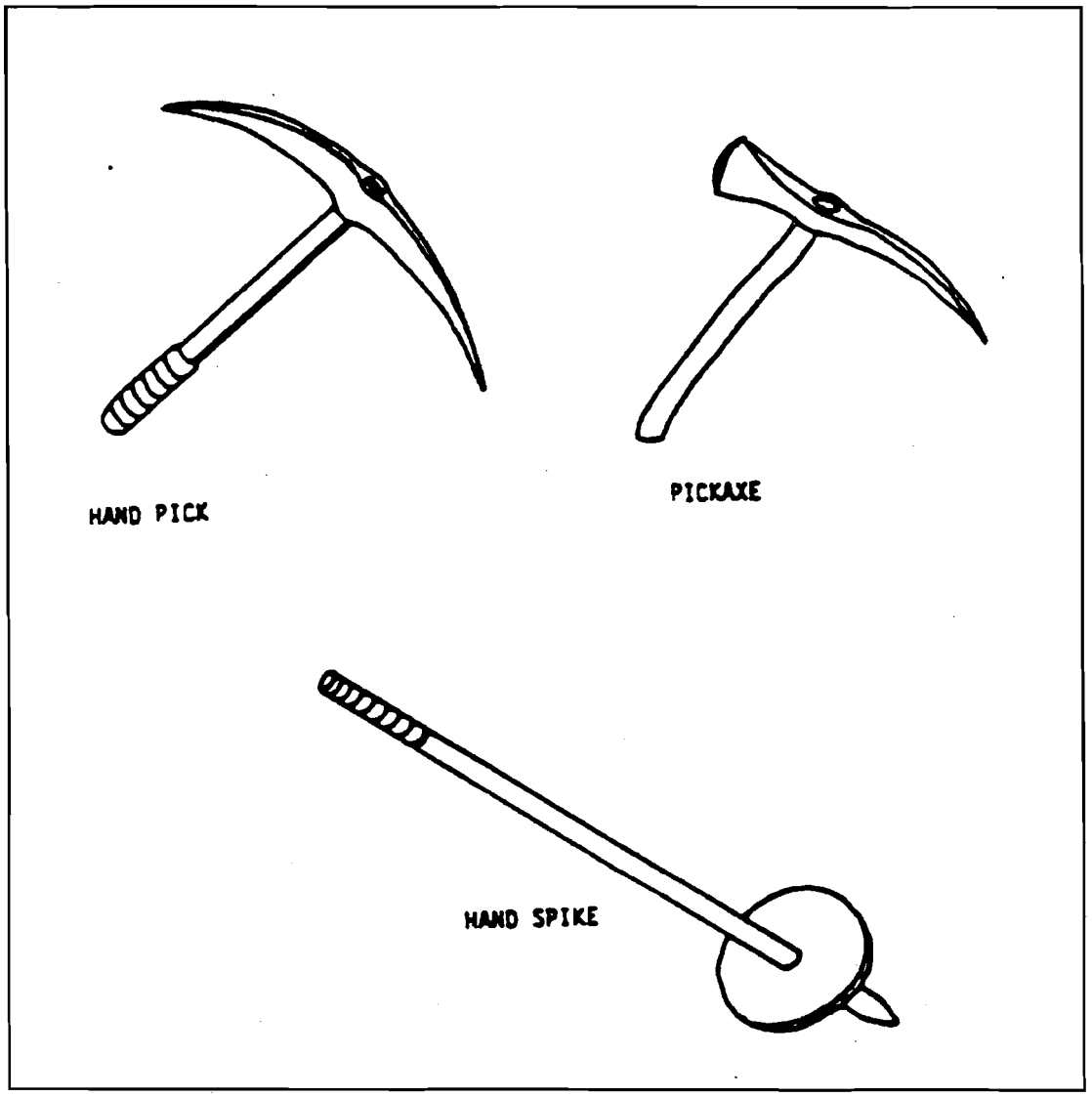
Figure 2. Drum Deheader



APPENDIX B (Cont'd)

Figures

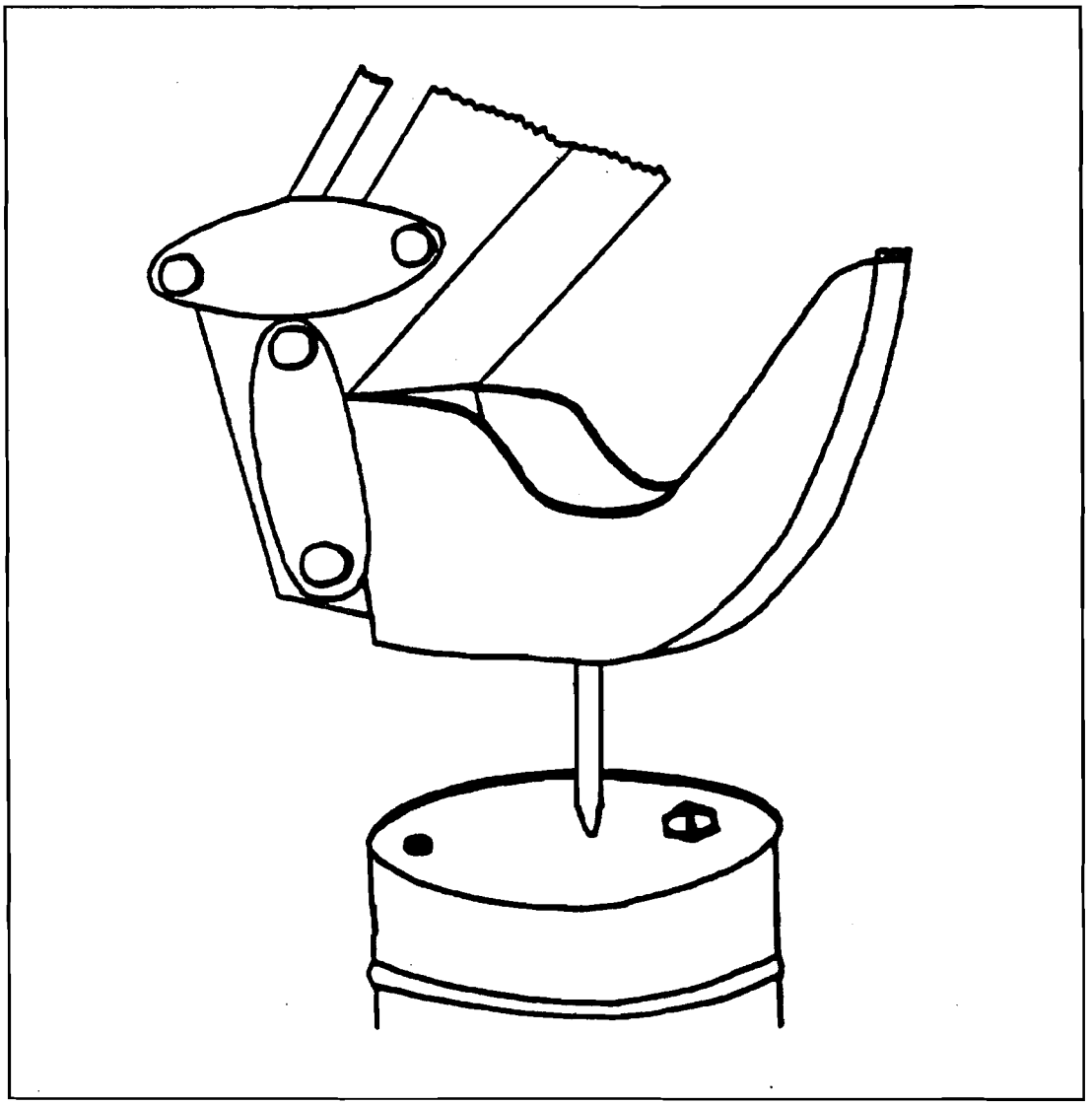
Figure 3. Hand Pick, Pickaxe, and Hand Spike



APPENDIX B (Cont'd)

Figures

Figure 4. Backhoe Spike



APPENDIX B (Cont'd)

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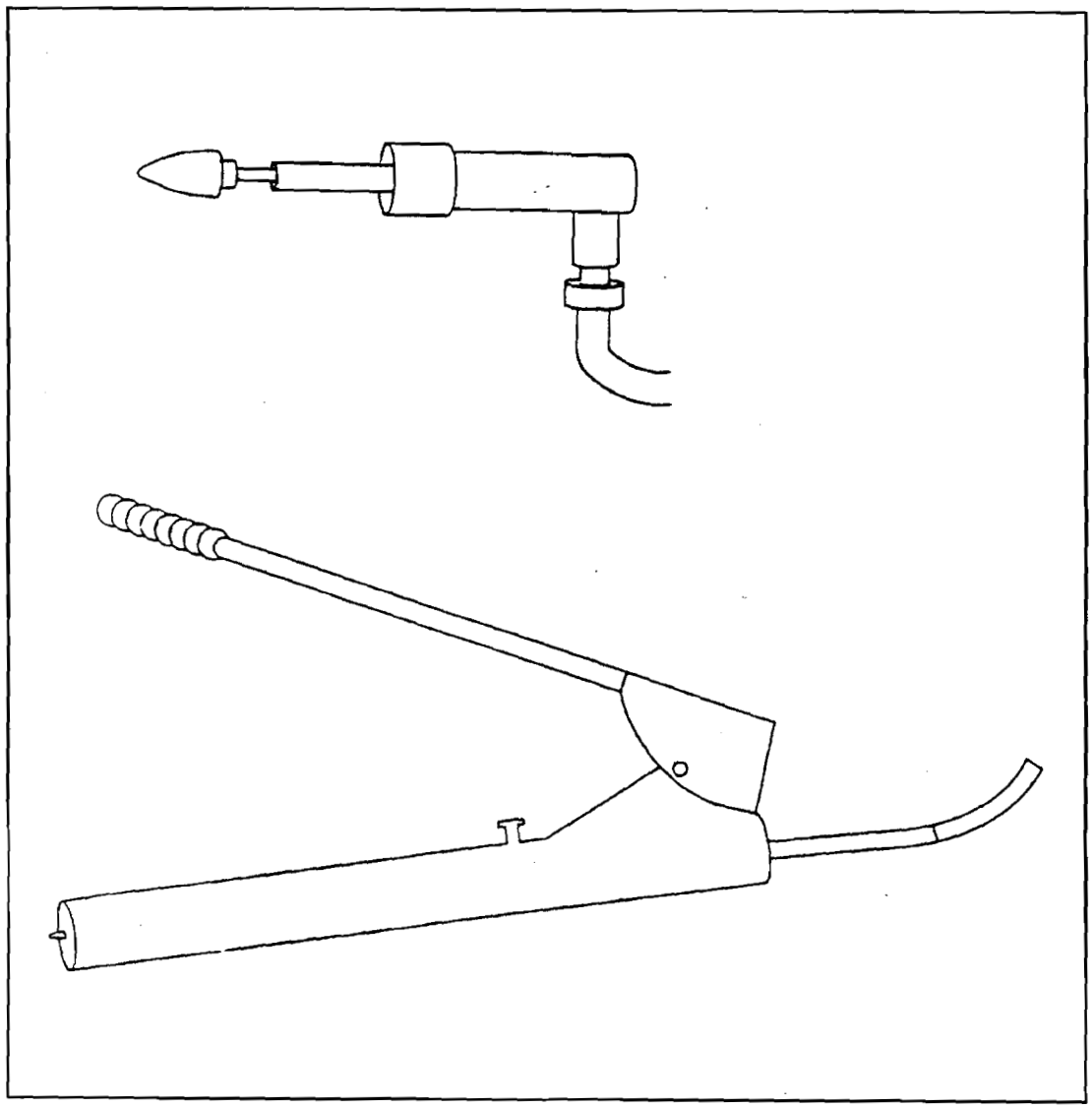
Figure 5. Hydraulic Drum Opener



APPENDIX B (Cont'd)

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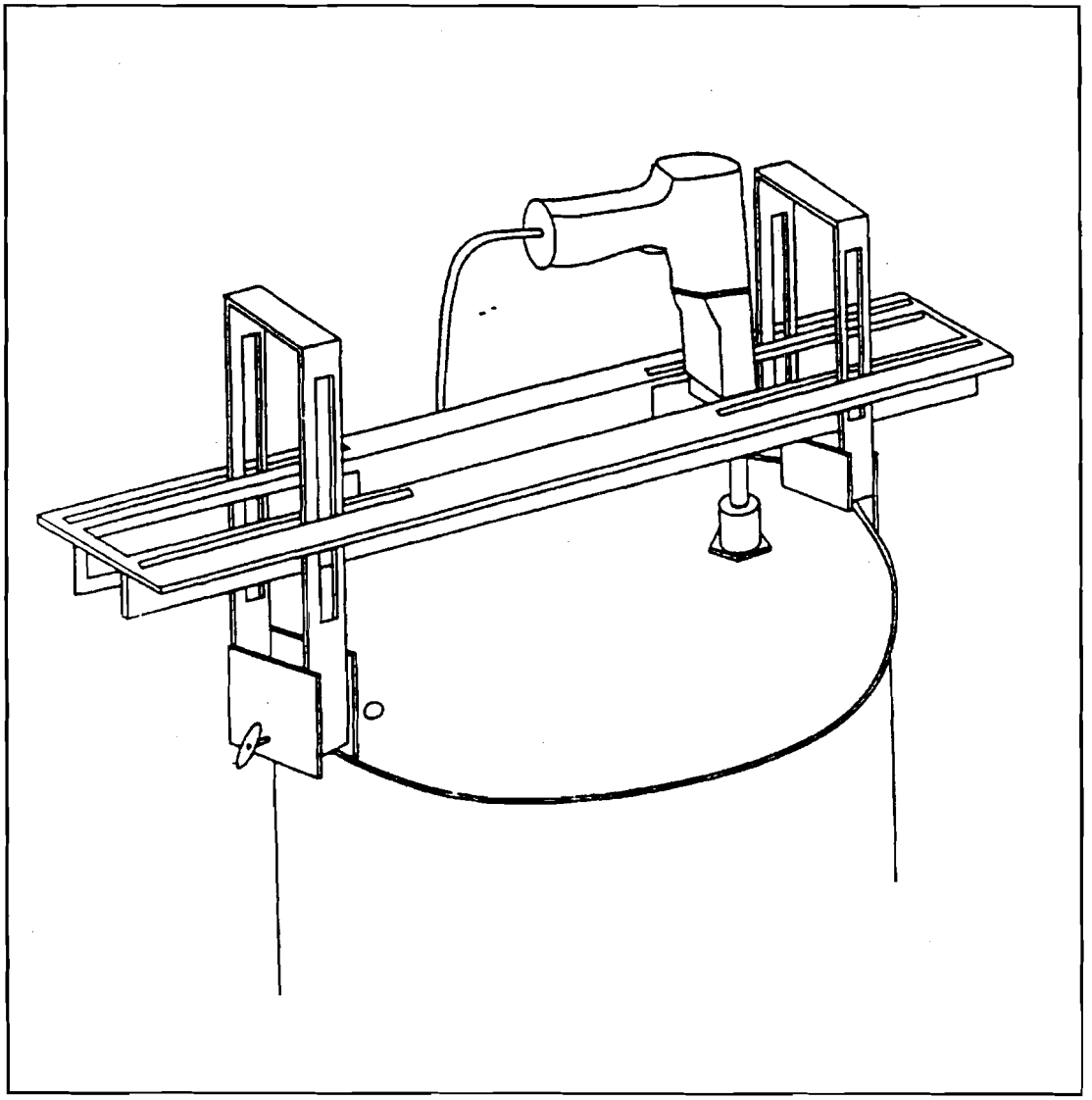
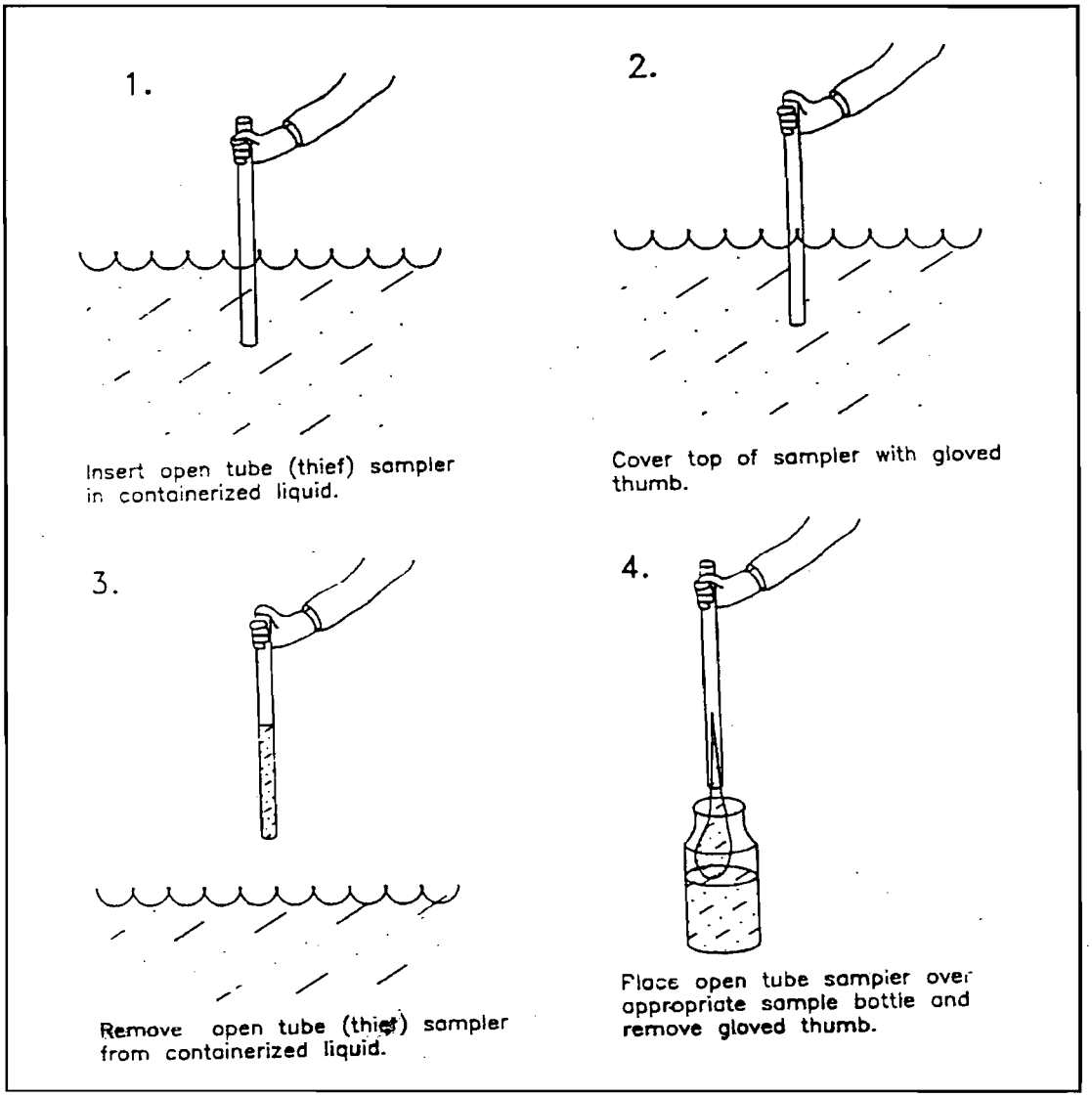
Figure 6. Pneumatic Bung Remover



APPENDIX B (Cont'd)

Figures

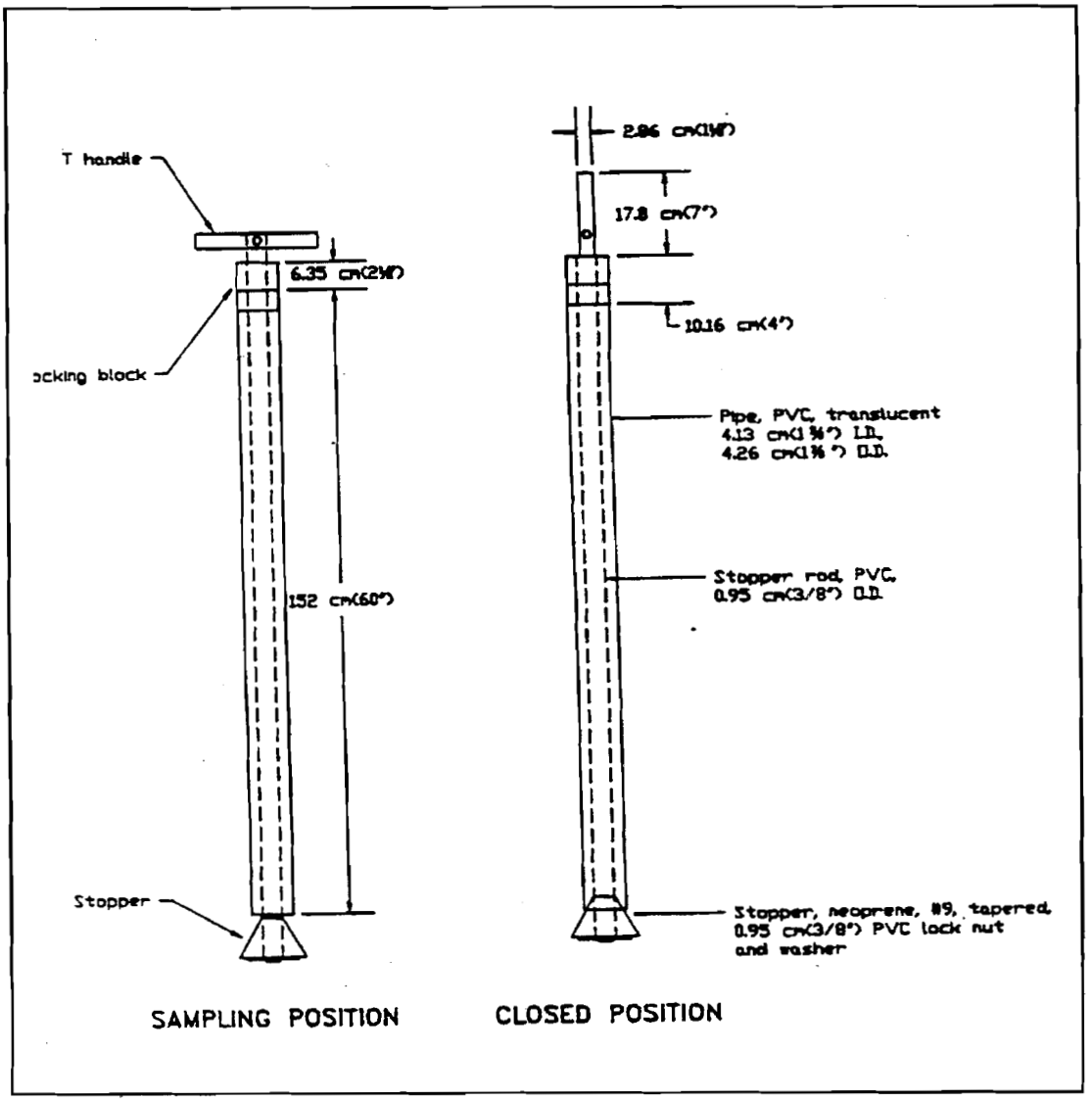
Figure 7. Glass Thief



APPENDIX B (Cont'd)

Figures

Figure 8. COLIWASA



1.0 SCOPE AND APPLICATION

The purpose of this standard operating procedure (SOP) is to provide technical guidance for the implementation of sampling protocols for tanks and other confined spaces from outside the vessel.

These are standard (i.e., typically applicable) operating procedures which may be varied or changed as required, dependent on site conditions, equipment limitations or limitations imposed by the procedure or other procedure limitations. In all instances, the ultimate procedures employed should be documented and associated with the final report.

Mention of trade names or commercial products does not constitute U.S. EPA endorsement or recommendation for use.

2.0 METHOD SUMMARY

The safe collection of a representative sample should be the criteria for selecting sample locations. A representative sample can be collected using techniques or equipment that are designed for obtaining liquids or sludges from various depths. The structure and characteristics of storage tanks present problems with collection of samples from more than one location; therefore, the selection of sampling devices is an important consideration.

Depending on the type of vessel and characteristics of the material to be sampled, one can choose a bacon bomb sampler, sludge judge, subsurface grab sampler, glass thief, bailer or Composite Liquid Waste Sampler (COLIWASA) to collect the sample. A sludge judge, bacon bomb or COLIWASA can be used to determine if the tank contents are stratified. Various other custom-made samplers may be used depending on the specific application.

All sample locations should be surveyed for air quality prior to sampling. At no time should sampling continue with an LEL reading greater than 25%.

3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

Samples collected from tanks are considered waste samples and as such, addition of preservatives is not required due to the potential reaction of the sample with the preservative. Samples should however, be cooled to 4°C with ice and protected from sunlight in order to minimize any potential reaction due to the light sensitivity of the sample.

Sample bottles for collection of waste liquids, sludges, or solids are typically wide mouth amber jars with Teflon-lined screw caps. Actual volume required for analysis should be determined in conjunction with the laboratory performing the analysis.

Waste sample handling procedures should be as follows:

1. Place sample container in two ziplock plastic bags.
2. Place each bagged container in a 1-gallon covered can containing absorbent packing material. Place the lid on the can.
3. Mark the sample identification number on the outside of the can.
4. Place the marked cans in a cooler, and fill remaining space with absorbent packing material.
5. Fill out chain of custody record for each cooler, place in plastic, and affix to inside lid of cooler.
6. Secure and custody seal the lid of cooler.

7. Arrange for the appropriate transportation mode consistent with the type of hazardous waste involved.

4.0 INTERFERENCES AND POTENTIAL PROBLEMS

Sampling a storage tank requires a great deal of manual dexterity, often requiring climbing to the top of the tank upon a narrow vertical or spiral stairway or ladder while wearing protective clothing and carrying sampling equipment.

Before climbing onto the vessel, a structural survey should be performed. This will ensure appropriate consideration of safety and accessibility prior to initiation of any field activities.

As in all opening of containers, extreme caution should be taken to avoid ignition or combustion of volatile contents. All tools used must be constructed of a non-sparking material and electronic instruments must be intrinsically safe.

All sample locations should be surveyed for air quality prior to sampling. At no time should sampling continue with a lower explosive limit (LEL) reading greater than 25%.

5.0 EQUIPMENT/APPARATUS

Storage tank materials include liquids, sludges, still bottoms, and solids of various types. The type of sampler chosen should be compatible with the waste. Samplers commonly used for tanks include: a bacon bomb sampler, sludge judge, glass thief, bailer, COLIWASA, and subsurface grab sampler.

Tank Sampling Equipment Checklist:

- Sampling plan
- Safety equipment
- Tape measure
- Weighted tape line, measuring stick or equivalent
- Camera/film
- Stainless steel bucket or bowl
- Sample containers
- Ziplock plastic bags
- Logbook
- Labels
- Field data sheets
- Chain of Custody records
- Flashlight (explosion proof)
- Coolers
- Ice
- Decontamination supplies
- Bacon bomb sampler
- Sludge judge
- Glass thieves
- Bailers
- COLIWASA
- Subsurface grab sampler
- Water/oil level indicator
- OVA (organic vapor analyzer or equivalent)
- Explosimeter/oxygen meter
- High volume blower

6.0 REAGENTS

Reagents are not typically required for the preservation of waste samples. However, reagents will be utilized for decontamination of equipment. Decontamination solutions required are specified in the Sampling Equipment Decontamination SOP.

7.0 PROCEDURE

7.1 Preparation

1. Determine the extent of the sampling effort, the sampling methods to be employed, and the types and amounts of equipment and supplies needed.

2. Obtain necessary sampling and monitoring equipment.

3. Decontaminate or preclean equipment, and ensure that it is in working order.

4. Prepare scheduling and coordinate with staff, clients, and regulatory agency, if appropriate.

5. Perform a general site survey prior to site entry in accordance with the site specific Health and Safety Plan.

6. Identify and mark all sampling locations.

7.2 Preliminary Inspection

1. Inspect the external structural characteristics of each tank and record in the site logbook.

Potential sampling points should be evaluated for safety, accessibility and sample quality.

2. Prior to opening a tank for internal inspection, the tank sampling team shall:

   - Review safety procedures and emergency contingency plans with the Health and Safety Officer.
   - Ensure that the tank is properly grounded.
   - Remove all sources of ignition from the immediate area.

3. Each tank should be mounted using appropriate means. Remove manway covers using non-sparking tools.

4. Collect air quality measurements for each potential sample location using an explosimeter/oxygen meter for a lower explosive limit (LEL/O_2) reading and an OVA/HNU for an organic vapor concentration. Both readings should be taken from the tank headspace, above the sampling port, and in the breathing zone.

5. Prior to commencing sampling, the tank headspace should be cleared of any toxic or explosive vapor concentration using a high volume explosion proof blower. No work shall start if LEL readings exceed 25%. At 10% LEL, work can continue but with extreme caution.

7.3 Sampling Procedure

1. Determine the depth of any and all liquid, solid, and liquid/solid interface, and depth of sludge using a weighted tape measure, probe line, sludge judge, or equivalent.

2. Collect liquid samples from one (1) foot below the surface, from mid-depth of liquid, and from one (1) foot above the bottom sludge layer. This can be accomplished with a subsurface grab sampler or bacon bomb. For liquids less than five (5) feet in depth, use a glass thief or COLIWASA to collect the sample.

   If sampling storage tanks, vacuum trucks, or process vessels, collect at least one sample from each compartment in the tank. Samples should always be collected through an opened hatch at the top of the tank. Valves near the bottom should not be used, because of their questionable or unknown integrity. If such a valve cannot be closed once opened, the entire tank contents may be lost to the ground surface. Also, individual strata cannot be sampled separately through a valve near the bottom.

3. Compare the three samples for visual phase differences. If phase differences appear, systematic iterative sampling should be performed. By halving the distance between two discrete sampling points, one can determine the depth of the phase change.

4. If another sampling port is available, sample as above to verify the phase information.

5. Measure the inside diameter of the tank and determine the volume of wastes using the depth measurements (Appendix A). Measuring the external diameter may be misleading as some tanks are insulated or have external supports that are covered.

6. Sludges can be collected using a bacon bomb sampler, glass thief, or sludge judge.

7. Record all information on the sample data sheet or site logbook. Label the container with the appropriate sample tag.

8. Decontaminate sampling equipment as per the steps listed in the Sampling Equipment Decontamination SOP.

7.4 Sampling Devices

7.4.1 Bacon Bomb Sampler

The bacon bomb sampler (Figure 1, Appendix B) is designed for the collection of material from various levels within a storage tank. It consists of a cylindrical body, usually made of chrome-plated brass and bronze with an internal tapered plunger that acts as a valve to admit the sample. A line attached to the top of the plunger opens and closes the valve. A line

is attached to the removable top cover which has a locking mechanism to keep the plunger closed after sampling.

Procedures for Use:

1. Attach the sample line and the plunger line to the sampler.

2. Measure and then mark the sampling line at the desired depth.

3. Gradually lower the sampler by the sample line until the desire level is reached.

4. When the desired level is reached, pull up on the plunger line and allow the sampler to fill before releasing the plunger line to seal off the sampler.

5. Retrieve the sampler by the sample line being careful not to pull up on the plunger line and thereby prevent accidental opening of the bottom valve.

6. Rinse or wipe off the exterior of the sampler body.

7. Position the sampler over the sample container and release its contents by pulling up on the plunger line.

8. Cap the sample container tightly and place prelabeled sample container in a carrier.

9. Replace the flange or manway or place plastic over the tank.

10. Log all samples in the site logbook and on field data sheets and label all samples.

11. Package samples and complete necessary paperwork.

12. Transport sample to decontamination zone for preparation for transport to analytical laboratory.

7.4.2 Sludge Judge

A sludge judge (Figure 2, Appendix B) is used for obtaining an accurate reading of settleable solids in any liquid. The sampling depth is dependent upon the length of the sludge judge. The sampler consists of 3/4" plastic pipe in 5-ft. sections, marked at 1-ft. increments, with screw-type fittings.

Procedures for Use:

1. Lower the sludge judge to the bottom of the tank.

2. When the bottom has been reached, the pipe is allowed to fill to the surface level. This will seat the check valve, trapping the column of material.

3. When the unit has been raised clear of the tank liquid, the amount of sludge in the sample can be read using the one foot increments marked on the pipe sections.

4. By touching the pin extending from the bottom section against a hard surface, the material is released from the unit.

5. Cap the sample container tightly and place prelabeled sample container in a carrier.

6. Replace the flange or manway or place plastic over the tank.

7. Log all samples in the site logbook and on field data sheets and label all samples.

8. Package samples and complete necessary paperwork.

9. Transport sample to decontamination zone for preparation for transport to analytical laboratory.

7.4.3 Subsurface Grab Sampler

Subsurface grab samplers (Figure 3, Appendix B) are designed to collect samples of liquids at various depths. The sampler is usually constructed of aluminum or stainless steel tubing with a polypropylene or teflon head that attaches to a 1-liter sample container.

Procedures for Use:

1. Screw the sample bottle onto the sampling head.

2. Lower the sampler to the desired depth.

3. Pull the ring at the top which opens the spring-loaded plunger in the head assembly.

4. When the bottle is full, release the ring, lift sampler, and remove sample bottle.

5. Cap the sample container tightly and place prelabeled sample container in a carrier.

6. Replace the flange or manway or place plastic over the tank.

7. Log all samples in the site logbook and on field data sheets and label all samples.

8. Package samples and complete necessary paperwork.

9. Transport sample to decontamination zone for preparation for transport to analytical laboratory.

7.4.4 Glass Thief

The most widely used implement for sampling is a glass tube commonly referred to as a glass thief (Figure 4, Appendix B). This tool is simple, cost effective, quick, and collects a sample without having to decontaminate. Glass thieves are typically 6mm to 16mm I.D. and 48 inches long.

Procedures for Use:

1. Remove cover from sample container.

2. Insert glass tubing almost to the bottom of the tank or until a solid layer is encountered. About one foot of tubing should extend above the drum.

3. Allow the waste in the tank to reach its natural level in the tube.

4. Cap the top of the sampling tube with a tapered stopper or thumb, ensuring liquid does not come into contact with stopper.

5. Carefully remove the capped tube from the tank and insert the uncapped end in the sample container. Do not spill liquid on the outside of the sample container.

6. Release stopper and allow the glass thief to drain until the container is approximately 2/3 full.

7. Remove tube from the sample container, break it into pieces and place the pieces in the tank.

8. Cap the sample container tightly and place prelabeled sample container in a carrier.

9. Replace the bung or place plastic over the tank.

10. Log all samples in the site logbook and on field data sheets and label all samples.

11. Package samples and complete necessary paperwork.

12. Transport sample to decontamination zone for preparation for transport to analytical laboratory.

In many instances a tank containing waste material will have a sludge layer on the bottom. Slow insertion of the sample tube down into this layer and then a gradual withdrawal will allow the sludge to act as a bottom plug to maintain the fluid in the tube. The plug can be gently removed and placed into the sample container by the use of a stainless steel lab spoon.

7.4.5 Bailer

The positive-displacement volatile sampling bailer (Figure 5, Appendix B) (by GPI) is perhaps the most appropriate for collection of water samples for volatile analysis. Other bailer types (messenger, bottom fill, etc.) are less desirable, but may be mandated by cost and site conditions. Generally, bailers can provide an acceptable sample, providing that the sampling personnel use extra care in the collection process.

Operation

1. Make sure clean plastic sheeting surrounds the tank.

2. Attach a line to the bailer.

3. Lower the bailer slowly and gently into the tank so as not to splash the bailer into the tank contents.

4. Allow the bailer to fill completely and retrieve the bailer from the tank.

5. Begin slowly pouring from the bailer.

6. Cap the sample container tightly and place prelabeled sample container in a carrier.

7. Replace the flange or manway or place plastic over the tank.

8. Log all samples in the site logbook and on field data sheets and label all samples.

9. Package samples and complete necessary paperwork.

10. Transport sample to decontamination zone for preparation for transport to analytical laboratory.

7.4.6 COLIWASA

Sampling devices are available that allow collection of a sample from the full depth of a tank and maintain its integrity in the transfer tube until delivery to the sample bottle. The sampling device is known as a Composite Liquid Waste Sampler (COLIWASA) (Figure 6, Appendix B). The COLIWASA is a much cited sampler designed to permit representative sampling of multiphase wastes from tanks and other containerized wastes.

One configuration consists of a 152 cm by 4 cm I.D. section of tubing with a neoprene stopper at one end attached by a rod running the length of the tube to a locking mechanism at the other end. Manipulation of the locking mechanism opens and closes the sampler by raising and lowering the neoprene stopper.

The major drawbacks associated with using a COLIWASA concern decontamination and costs. The sampler is difficult to decontaminate in the field, and its high cost in relation to alternative procedures (glass tubes) makes it an impractical throwaway item. Disposable COLIWASA's are a viable alternative. However, the COLIWASA is still the sampling device of choice for specific applications, especially in instances where a true representation of a multiphase waste is absolutely necessary.

Procedures for Use:

1. Put the sampler in the open position by placing the stopper rod handle in the T-position and pushing the rod down until the handle sits against the sampler's locking block.

2. Slowly lower the sampler into the liquid waste. Lower the sampler at a rate that permits the levels of the liquid inside and outside the sampler tube to be about the same. If the level of the liquid in the sample tube is lower than that outside the sampler, the sampling rate is too fast and will result in a non-representative sample.

3. When the sampler stopper hits the bottom of the waste container, push the sampler tube downward against the stopper to close the sampler. Lock the sampler in the closed position by turning the T-handle until it is upright and one end rests tightly on the locking block.

4. Slowly withdraw the sample from the waste container with one hand while wiping the sampler tube with a disposable cloth or rag with the other hand.

5. Carefully discharge the sample into a suitable sample container by slowly pulling the lower end of the T-handle away from the locking block while the lower end of the sampler is positioned in a sample container.

6. Cap the sample container tightly and place prelabeled sample container in a carrier.

7. Replace the bung or place plastic over the tank.

8. Log all samples in the site logbook and on field data sheets and label all samples.

9. Package samples and complete necessary paperwork.

10. Transport sample to decontamination zone for preparation for transport to analytical laboratory.

8.0 CALCULATIONS

There are no specific calculations for these procedures. Refer to Appendix A regarding calculations utilized in determining tank volumes.

9.0 QUALITY ASSURANCE/ QUALITY CONTROL

There are no specific quality assurance activities which apply to the implementation of these procedures. However, the following general QA procedures apply:

1. All data must be documented on field data sheets or within site logbooks.

2. All instrumentation must be operated in accordance with operating instructions as supplied by the manufacturer, unless otherwise specified in the work plan. Equipment checkout and calibration activities must occur prior to sampling/operation and they must be documented.

10.0 DATA VALIDATION

This section is not applicable to this SOP.

11.0 HEALTH AND SAFETY

When working with potentially hazardous materials, follow U.S. EPA, OSHA, and corporate health and safety procedures. More specifically, the hazards associated with tank sampling may cause bodily injury, illness, or death to the worker. Failure to recognize potential hazards of waste containers is the cause of most accidents. It should be assumed that the most unfavorable conditions exist, and that the danger of explosion and poisoning will be present. Hazards specific to tank sampling are:

1. Hazardous atmospheres which are either flammable, toxic, asphyxiating, or corrosive.

2. If activation of electrical or mechanical equipment would cause injury, each piece of equipment should be manually isolated to prevent inadvertent activation while workers are occupied.

3. Communication is of utmost importance between the sampling worker and the standby person to prevent distress or injury going unnoticed.

4. Proper procedures to evacuate a tank with forced air and grounding of equipment and tanks should be reviewed.

12.0 REFERENCES

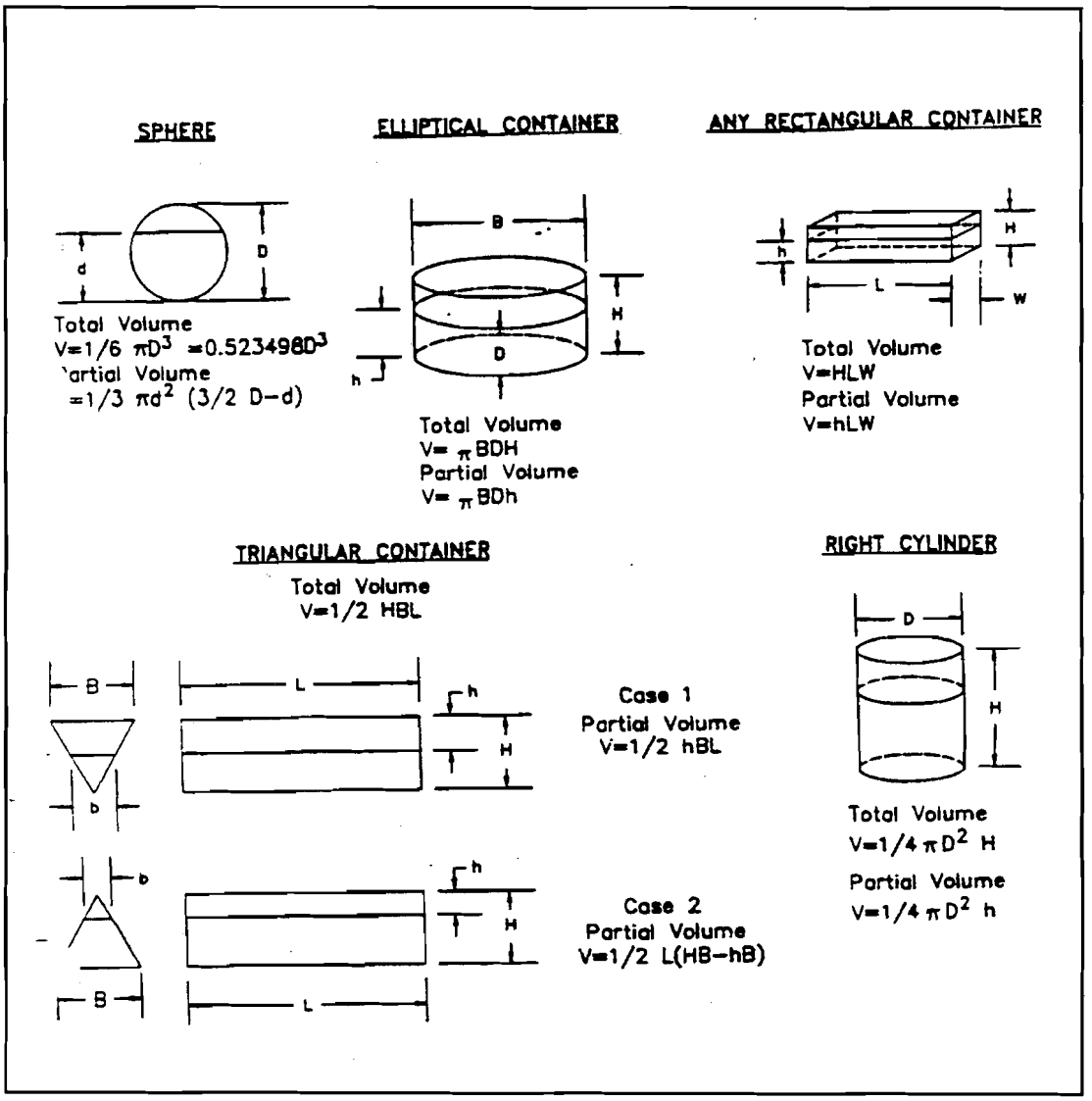
Guidance Document for Cleanup of Surface Tank and Drum Sites, OSWER Directive 9380.0-3.

Drum Handling Practices at Hazardous Waste Sites, EPA-600/2-86-013.

APPENDIX A

Calculations

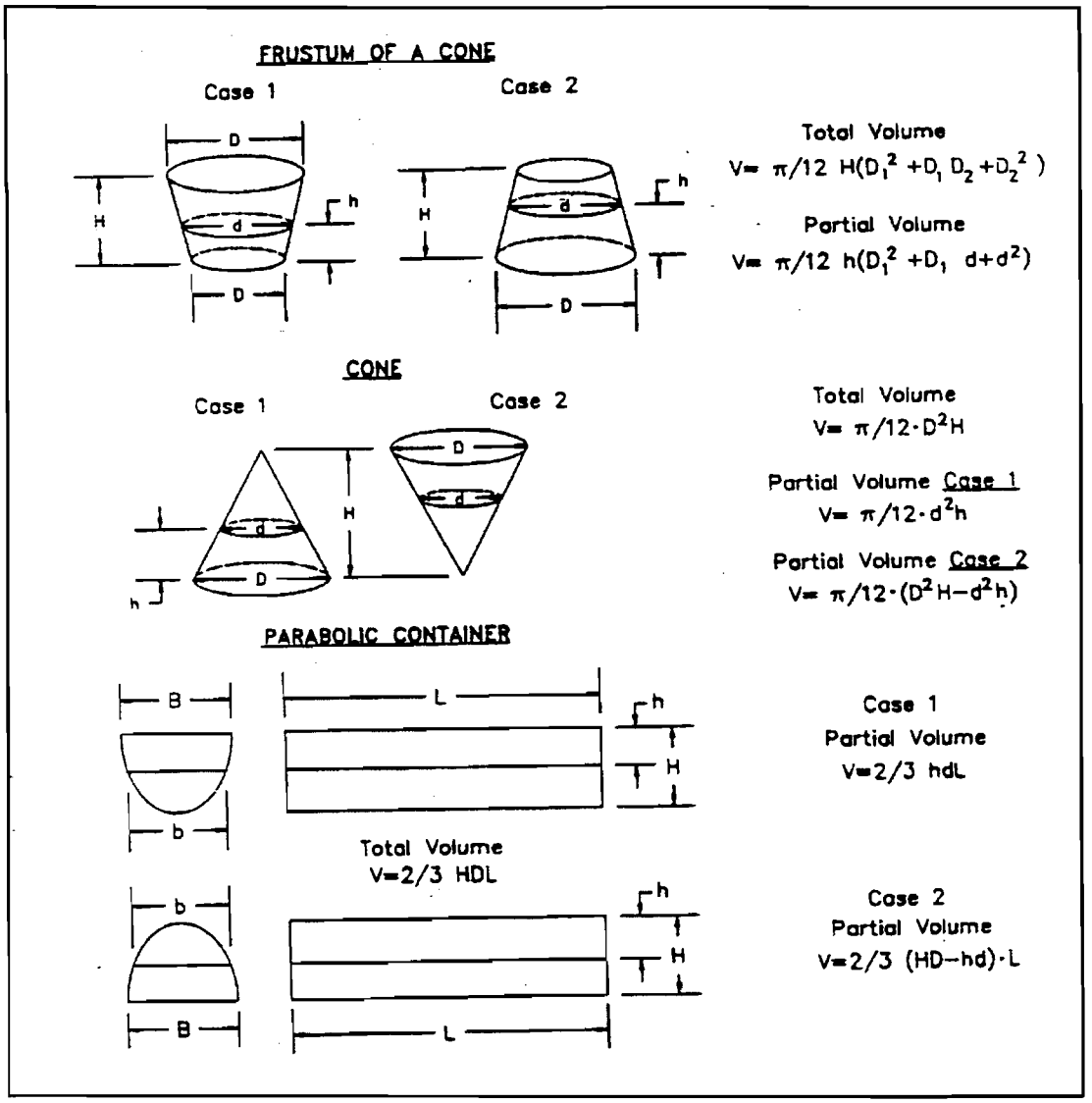
Various Volume Calculations



APPENDIX A (Cont'd)

Calculations

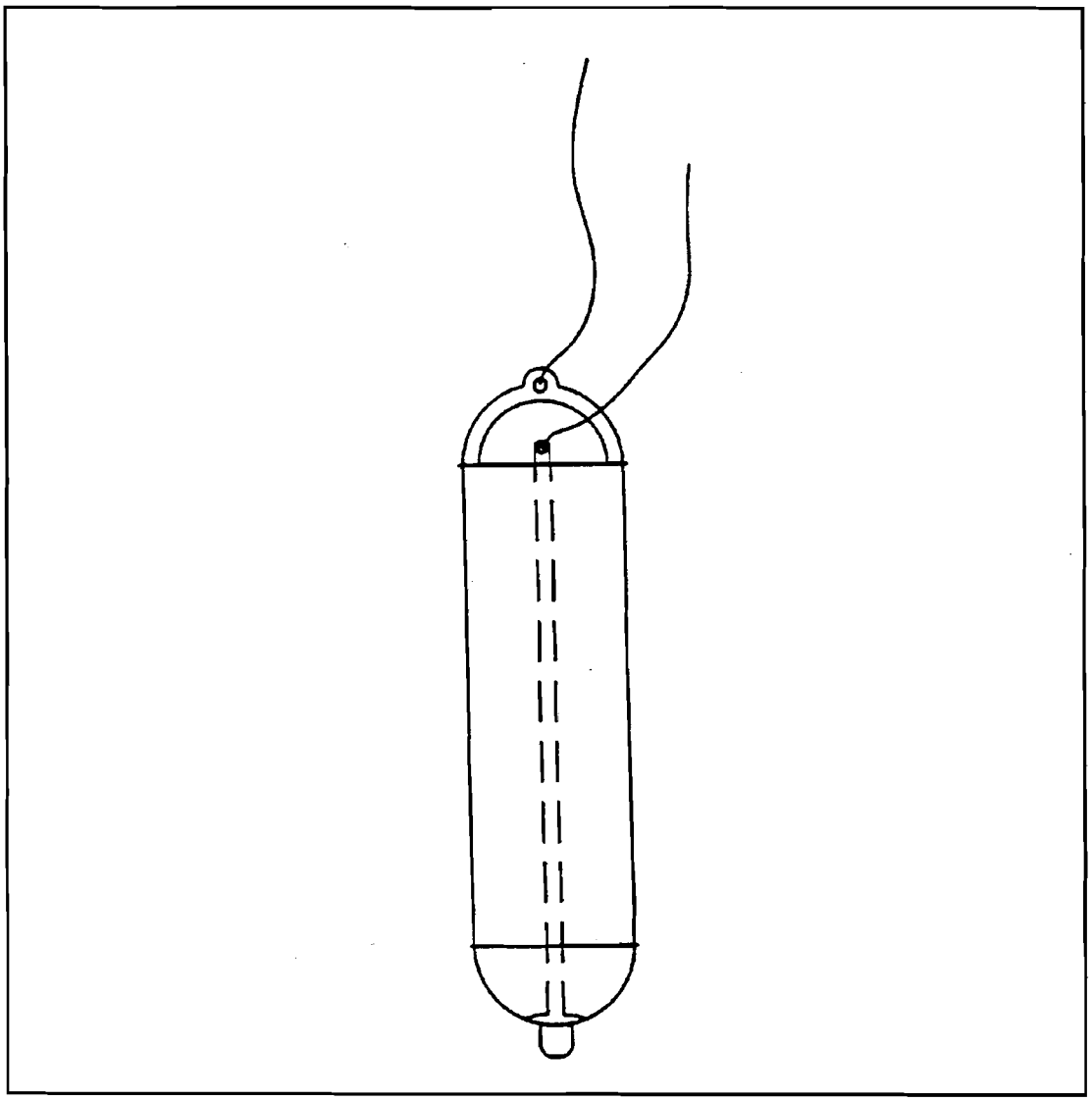
Various Volume Calculations (Cont'd)



APPENDIX B

Figures

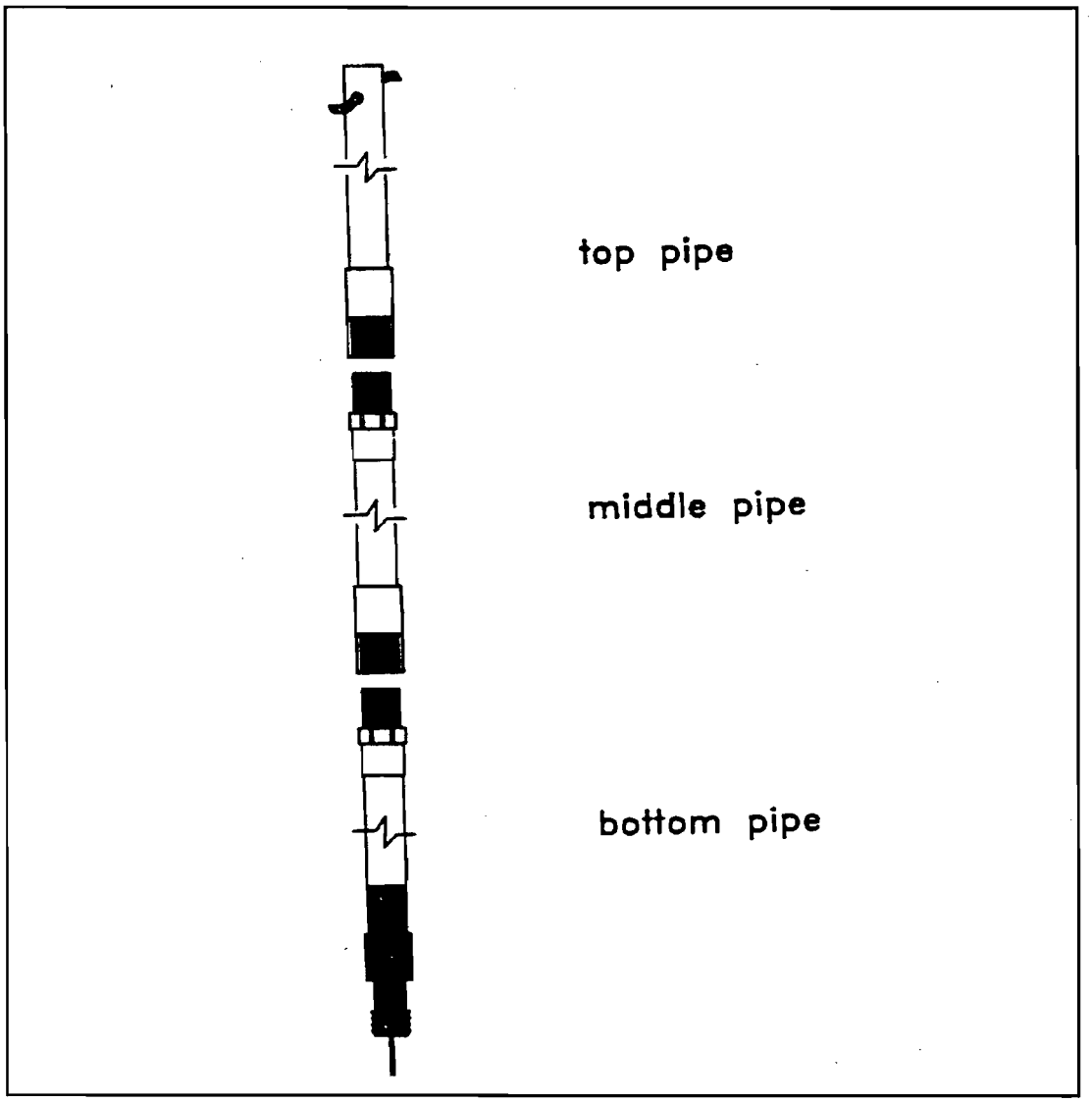
FIGURE 1. Bacon Bomb Sampler



APPENDIX B (Cont'd)

Figures

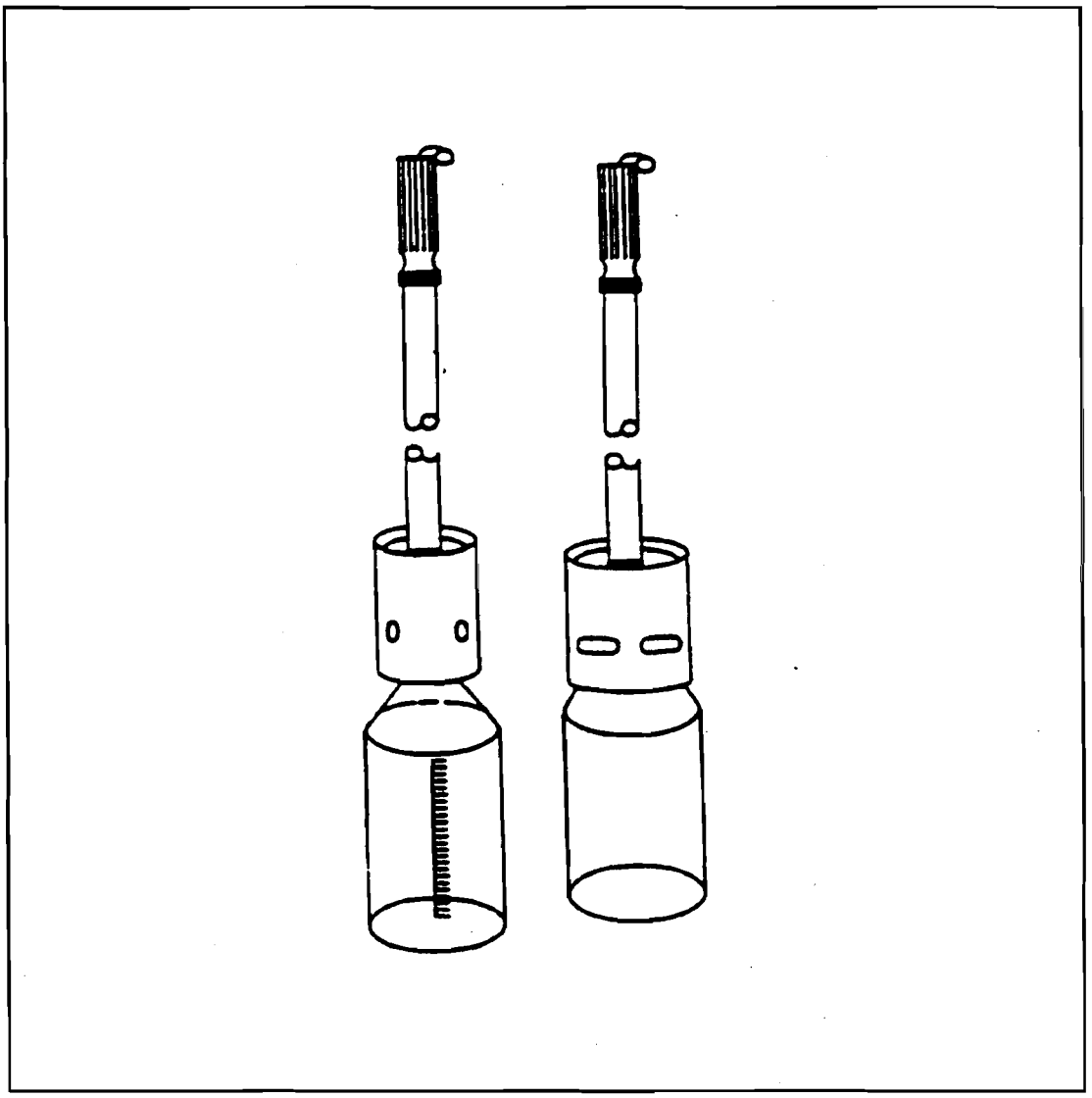
FIGURE 2. Sludge Judge



APPENDIX B (Cont'd)

Figures

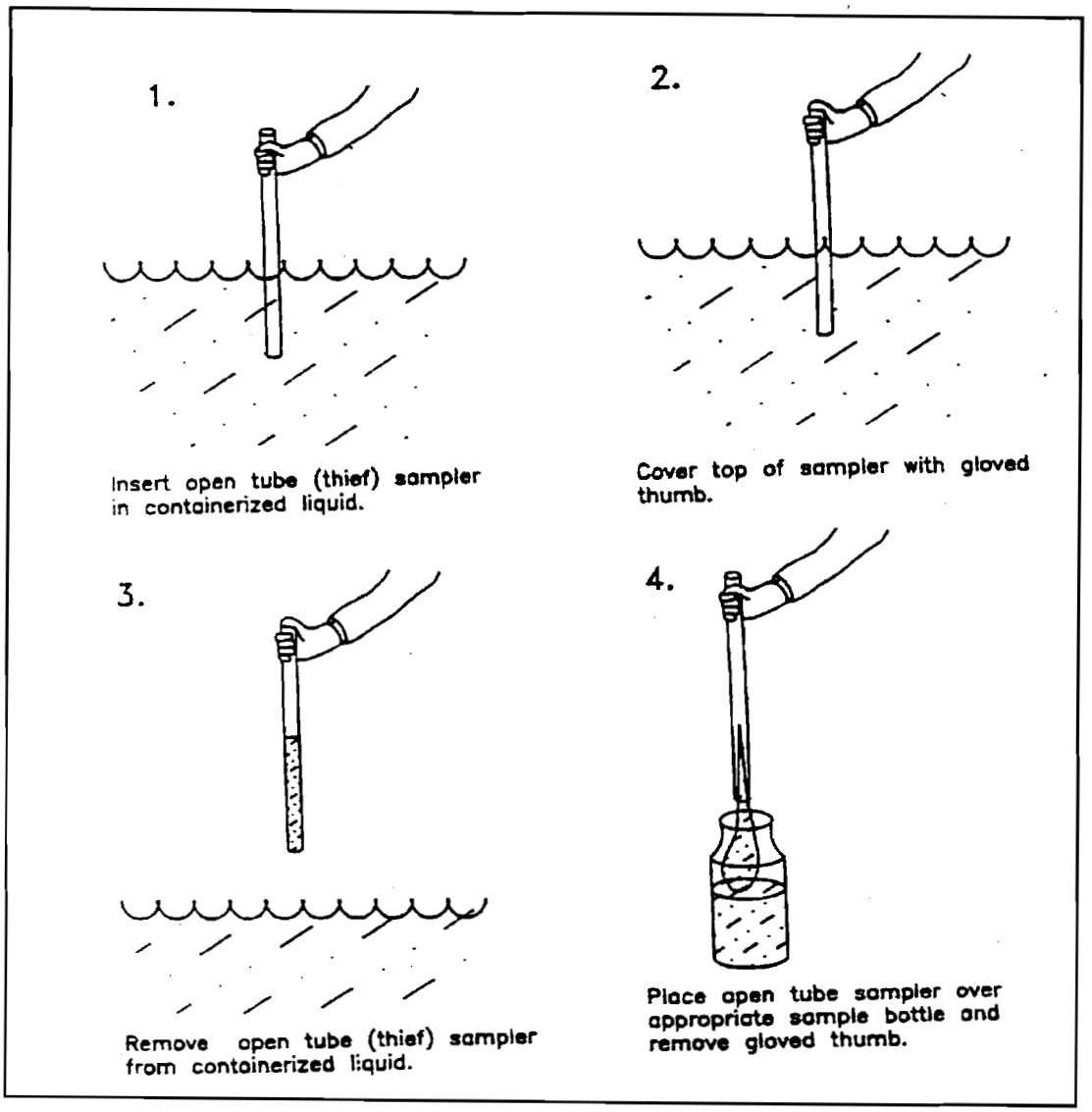
FIGURE 3. Subsurface Grab Sampler



APPENDIX B (Cont'd)

Figures

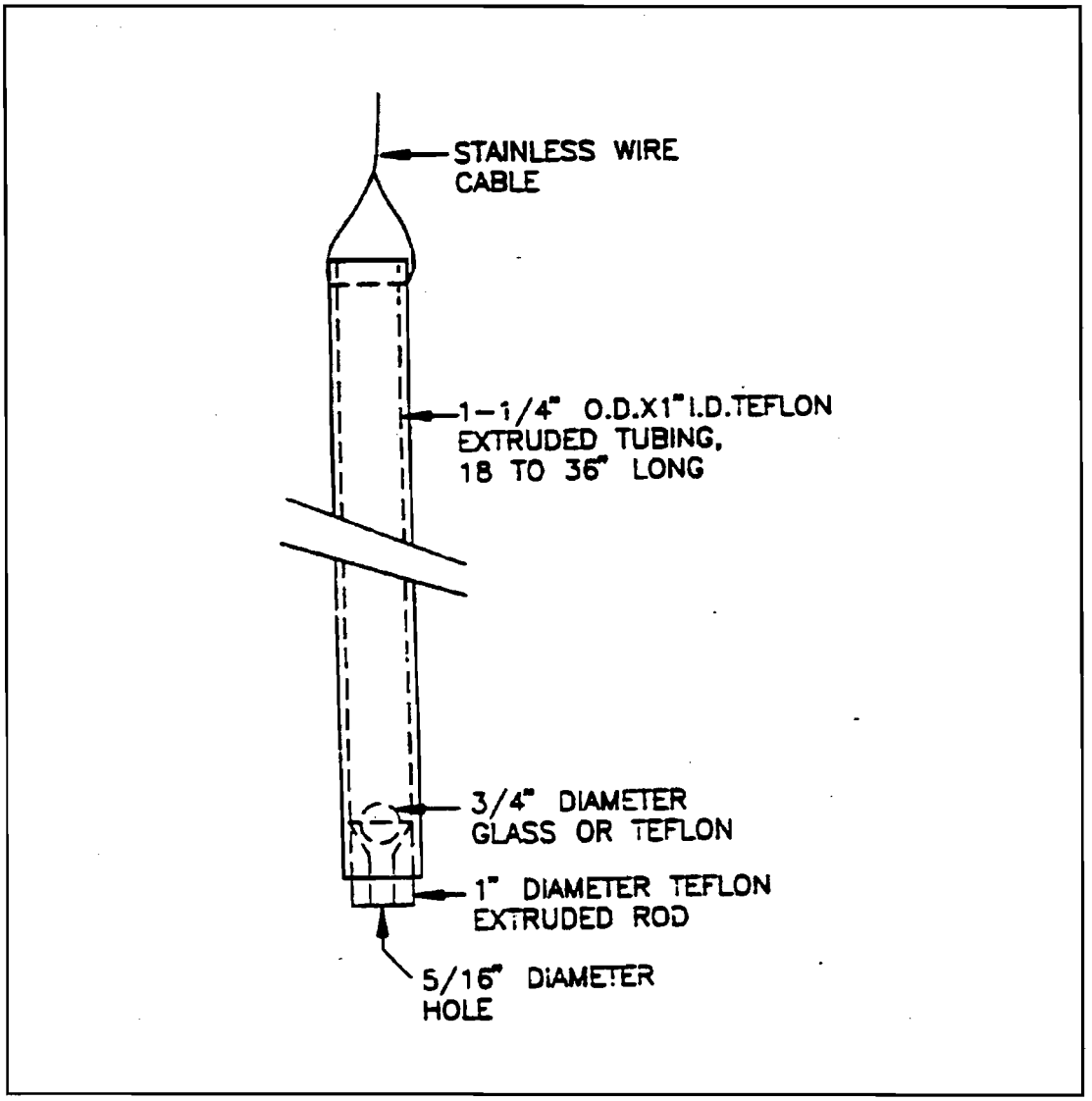
FIGURE 4. Glass Thief



APPENDIX B (Cont'd)

Figures

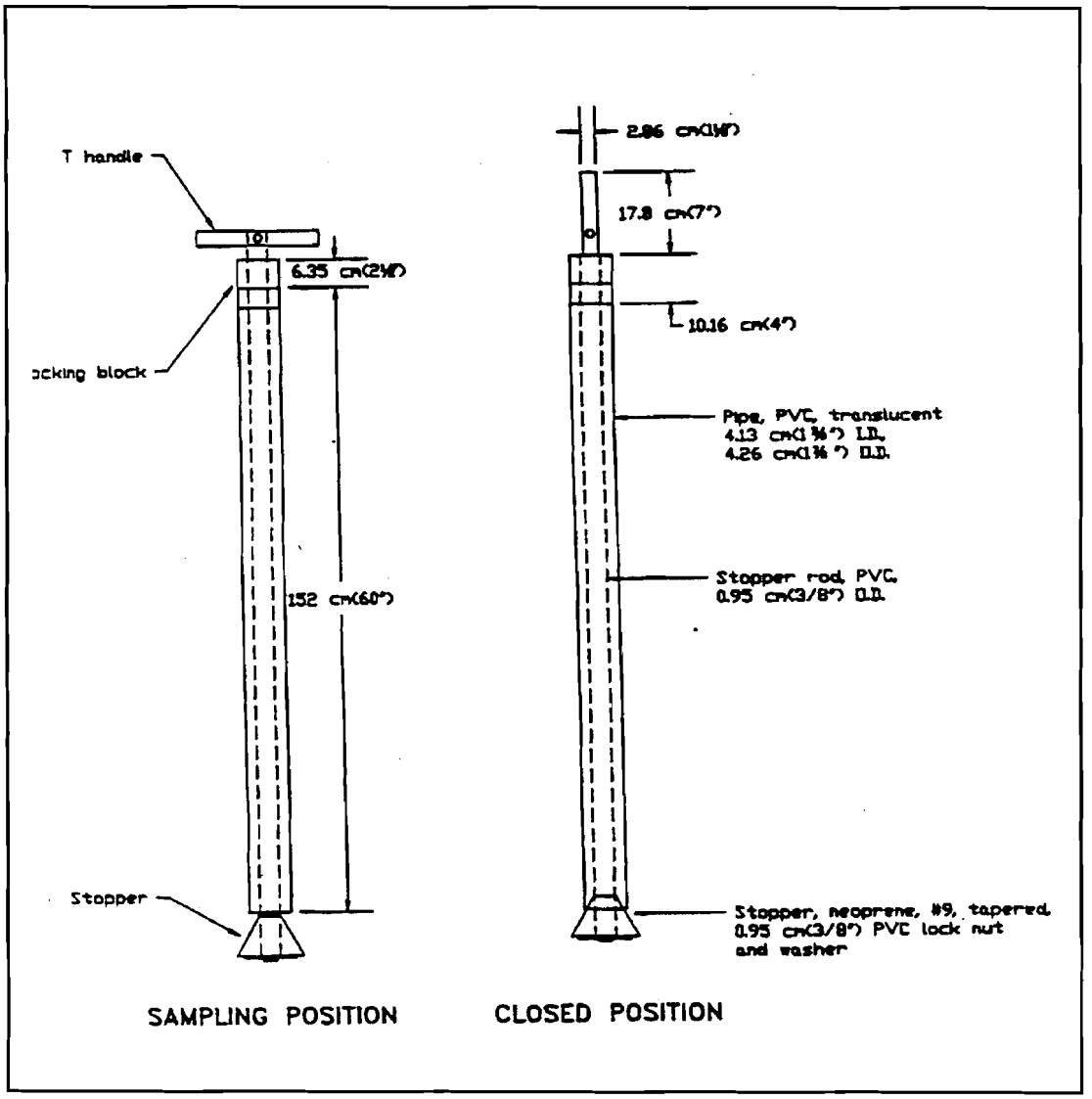
FIGURE 5. Bailer



APPENDIX B (Cont'd)

Figures

FIGURE 6. COLIWASA



1.0 SCOPE AND APPLICATION

The purpose of this standard operating procedure (SOP) is to describe the procedures for the collection of representative soil samples. Analysis of soil samples may determine whether concentrations of specific pollutants exceed established action levels, or if the concentrations of pollutants present a risk to public health, welfare, or the environment.

These are standard (i.e., typically applicable) operating procedures which may be varied or changed as required, dependent upon site conditions, equipment limitations or limitations imposed by the procedure. In all instances, the ultimate procedures employed should be documented and associated with the final report.

Mention of trade names or commercial products does not constitute U.S. Environmental Protection Agency (EPA) endorsement or recommendation for use.

2.0 METHOD SUMMARY

Soil samples may be collected using a variety of methods and equipment. The methods and equipment used are dependent on the depth of the desired sample, the type of sample required (disturbed vs. undisturbed), and the soil type. Near-surface soils may be easily sampled using a spade, trowel, and scoop. Sampling at greater depths may be performed using a hand auger, continuous flight auger, a trier, a split-spoon, or, if required, a backhoe.

3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

Chemical preservation of solids is not generally recommended. Samples should, however, be cooled and protected from sunlight to minimize any potential reaction.

4.0 INTERFERENCES AND POTENTIAL PROBLEMS

There are two primary interferences or potential problems associated with soil sampling. These include cross contamination of samples and improper sample collection. Cross contamination problems can be eliminated or minimized through the use of dedicated sampling equipment. If this is not possible or practical, then decontamination of sampling equipment is necessary. Improper sample collection can involve using contaminated equipment, disturbance of the matrix resulting in compaction of the sample or inadequate homogenization of the samples where required, resulting in variable, non-representative results.

5.0 EQUIPMENT/APPARATUS

Soil sampling equipment includes the following:

- Sampling plan
- Maps/plot plan
- Safety equipment, as specified in the Health and Safety Plan
- Survey equipment
- Tape measure
- Survey stakes or flags
- Camera and film
- Stainless steel, plastic, or other appropriate homogenization bucket, bowl or pan
- Appropriate size sample containers
- Ziplock plastic bags
- Logbook
- Labels
- Chain of Custody records and seals
- Field data sheets
- Cooler(s)
- Ice
- Vermiculite
- Decontamination supplies/equipment
- Canvas or plastic sheet
- Spade or shovel

- C Spatula
- C Scoop
- C Plastic or stainless steel spoons
- C Trowel
- C Continuous flight (screw) auger
- C Bucket auger
- C Post hole auger
- C Extension rods
- C T-handle
- C Sampling trier
- C Thin wall tube sampler
- C Split spoons
- C Vehimeyer soil sampler outfit
  - Tubes
  - Points
  - Drive head
  - Drop hammer
  - Puller jack and grip
- C Backhoe

6.0 REAGENTS

Reagents are not used for the preservation of soil samples. Decontamination solutions are specified in the Sampling Equipment Decontamination SOP and the site specific work plan.

7.0 PROCEDURES

7.1 Preparation

1. Determine the extent of the sampling effort, the sampling methods to be employed, and the types and amounts of equipment and supplies required.

2. Obtain necessary sampling and monitoring equipment.

3. Decontaminate or pre-clean equipment, and ensure that it is in working order.

4. Prepare schedules, and coordinate with staff, client, and regulatory agencies, if appropriate.

5. Perform a general site survey prior to site entry in accordance with the site specific Health and Safety Plan.

6. Use stakes, flagging, or buoys to identify and mark all sampling locations. Specific site factors, including extent and nature of contaminant should be considered when selecting sample location. If required, the proposed locations may be adjusted based on site access, property boundaries, and surface obstructions. All staked locations will be utility-cleared by the property owner prior to soil sampling.

7.2 Sample Collection

7.2.1 Surface Soil Samples

Collection of samples from near-surface soil can be accomplished with tools such as spades, shovels, trowels, and scoops. Surface material can be removed to the required depth with this equipment, then a stainless steel or plastic scoop can be used to collect the sample.

This method can be used in most soil types but is limited to sampling near surface areas. Accurate, representative samples can be collected with this procedure depending on the care and precision demonstrated by the sample team member. A stainless steel scoop, lab spoon, or plastic spoon will suffice in most other applications. The use of a flat, pointed mason trowel to cut a block of the desired soil can be helpful when undisturbed profiles are required. Care should be exercised to avoid use of devices plated with chrome or other materials. Plating is particularly common with garden implements such as potting trowels.

The following procedure is used to collect surface soil samples:

1. Carefully remove the top layer of soil or debris to the desired sample depth with a pre-cleaned spade.

2. Using a pre-cleaned, stainless steel scoop, plastic spoon, or trowel, remove and discard a thin layer of soil from the area which came in contact with the spade.

3. If volatile organic analysis is to be performed, transfer the sample directly into an appropriate, labeled sample container with a stainless steel lab spoon, or equivalent and secure the cap tightly. Place the remainder of the sample into a stainless steel, plastic, or

other appropriate homogenization container, and mix thoroughly to obtain a homogenous sample representative of the entire sampling interval. Then, either place the sample into appropriate, labeled containers and secure the caps tightly; or, if composite samples are to be collected, place a sample from another sampling interval or location into the homogenization container and mix thoroughly. When compositing is complete, place the sample into appropriate, labeled containers and secure the caps tightly.

7.2.2 Sampling at Depth with Augers and Thin Wall Tube Samplers

This system consists of an auger, or a thin-wall tube sampler, a series of extensions, and a "T" handle (Figure 1, Appendix A). The auger is used to bore a hole to a desired sampling depth, and is then withdrawn. The sample may be collected directly from the auger. If a core sample is to be collected, the auger tip is then replaced with a thin wall tube sampler. The system is then lowered down the borehole, and driven into the soil to the completion depth. The system is withdrawn and the core is collected from the thin wall tube sampler.

Several types of augers are available; these include: bucket type, continuous flight (screw), and post-hole augers. Bucket type augers are better for direct sample recovery since they provide a large volume of sample in a short time. When continuous flight augers are used, the sample can be collected directly from the flights. The continuous flight augers are satisfactory for use when a composite of the complete soil column is desired. Post-hole augers have limited utility for sample collection as they are designed to cut through fibrous, rooted, swampy soil and cannot be used below a depth of three feet.

The following procedure will be used for collecting soil samples with the auger:

1. Attach the auger bit to a drill rod extension, and attach the "T" handle to the drill rod.

2. Clear the area to be sampled of any surface debris (e.g., twigs, rocks, litter). It may be advisable to remove the first three to six inches of surface soil for an area approximately six inches in radius around the drilling location.

3. Begin augering, periodically removing and depositing accumulated soils onto a plastic sheet spread near the hole. This prevents accidental brushing of loose material back down the borehole when removing the auger or adding drill rods. It also facilitates refilling the hole, and avoids possible contamination of the surrounding area.

4. After reaching the desired depth, slowly and carefully remove the auger from boring. When sampling directly from the auger, collect the sample after the auger is removed from the boring and proceed to Step 10.

5. Remove auger tip from drill rods and replace with a pre-cleaned thin wall tube sampler. Install the proper cutting tip.

6. Carefully lower the tube sampler down the borehole. Gradually force the tube samplerinto soil. Care should be taken to avoid scraping the borehole sides. Avoid hammering the drill rods to facilitate coring as the vibrations may cause the boring walls to collapse.

7. Remove the tube sampler, and unscrew the drill rods.

8. Remove the cutting tip and the core from the device.

9. Discard the top of the core (approximately 1 inch), as this possibly represents material collected before penetration of the layer of concern. Place the remaining core into the appropriate labeled sample container. Sample homogenization is not required.

10. If volatile organic analysis is to be performed, transfer the sample into an appropriate, labeled sample container with a stainless steel lab spoon, or equivalent and secure the cap tightly. Place the remainder of the sample into a stainless steel, plastic, or other appropriate homogenization container, and mix thoroughly to obtain a homogenous sample representative of the entire sampling interval. Then, either place the sample into appropriate, labeled containers and secure the

caps tightly; or, if composite samples are to be collected, place a sample from another sampling interval into the homogenization container and mix thoroughly.

When compositing is complete, place the sample into appropriate, labeled containers and secure the caps tightly.

11. If another sample is to be collected in the same hole, but at a greater depth, reattach the auger bit to the drill and assembly, and follow steps 3 through 11, making sure to decontaminate the auger and tube sampler between samples.

12. Abandon the hole according to applicable State regulations. Generally, shallow holes can simply be backfilled with the removed soil material.

7.2.3 Sampling at Depth with a Trier

The system consists of a trier, and a "T" handle. The auger is driven into the soil to be sampled and used to extract a core sample from the appropriate depth.

The following procedure will be used to collect soil samples with a sampling trier:

1. Insert the trier (Figure 2, Appendix A) into the material to be sampled at a 0° to 45° angle from horizontal. This orientation minimizes the spillage of sample.

2. Rotate the trier once or twice to cut a core of material.

3. Slowly withdraw the trier, making sure that the slot is facing upward.

4. If volatile organic analysis is to be performed, transfer the sample into an appropriate, labeled sample container with a stainless steel lab spoon, or equivalent and secure the cap tightly. Place the remainder of the sample into a stainless steel, plastic, or other appropriate homogenization container, and mix thoroughly to obtain a homogenous sample representative of the entire sampling interval. Then, either place the sample into appropriate, labeled containers and secure the caps tightly; or, if composite samples are to be collected, place a sample from another sampling interval into the homogenization container and mix thoroughly. When compositing is complete, place the sample into appropriate, labeled containers and secure the caps tightly.

7.2.4 Sampling at Depth with a Split Spoon (Barrel) Sampler

The procedure for split spoon sampling describes the collection and extraction of undisturbed soil cores of 18 or 24 inches in length. A series of consecutive cores may be extracted with a split spoon sampler to give a complete soil column profile, or an auger may be used to drill down to the desired depth for sampling. The split spoon is then driven to its sampling depth through the bottom of the augured hole and the core extracted.

When split spoon sampling is performed to gain geologic information, all work should be performed in accordance with ASTM D 1586-67 (reapproved 1974).

The following procedures will be used for collecting soil samples with a split spoon:

1. Assemble the sampler by aligning both sides of barrel and then screwing the drive shoe on the bottom and the head piece on top.

2. Place the sampler in a perpendicular position on the sample material.

3. Using a well ring, drive the tube. Do not drive past the bottom of the head piece or compression of the sample will result.

4. Record in the site logbook or on field data sheets the length of the tube used to penetrate the material being sampled, and the number of blows required to obtain this depth.

5. Withdraw the sampler, and open by unscrewing the bit and head and splitting the barrel. The amount of recovery and soil type should be recorded on the boring log. If a split sample is desired, a cleaned, stainless steel knife should be used to divide the tube contents in half, longitudinally. This sampler

is typically available in 2 and 3 1/2 inch diameters. However, in order to obtain the required sample volume, use of a larger barrel may be required.

6. Without disturbing the core, transfer it to appropriate labeled sample container(s) and seal tightly.

7.2.5 Test Pit/Trench Excavation

These relatively large excavations are used to remove sections of soil, when detailed examination of soil characteristics (horizontal, structure, color, etc.) are required. It is the least cost effective sampling method due to the relatively high cost of backhoe operation.

The following procedures will be used for collecting soil samples from test pit/trench excavations:

1. Prior to any excavation with a backhoe, it is important to ensure that all sampling locations are clear of utility lines, subsurface pipes and poles (subsurface as well as above surface).

2. Using the backhoe, a trench is dug to approximately three feet in width and approximately one foot below the cleared sampling location. Place excavated soils on plastic sheets. Trenches greater than five feet deep must be sloped or protected by a shoring system, as required by OSHA regulations.

3. A shovel is used to remove a one to two inch layer of soil from the vertical face of the pit where sampling is to be done.

4. Samples are taken using a trowel, scoop, or coring device at the desired intervals. Be sure to scrape the vertical face at the point of sampling to remove any soil that may have fallen from above, and to expose fresh soil for sampling. In many instances, samples can be collected directly from the backhoe bucket.

5. If volatile organic analysis is to be performed, transfer the sample into an appropriate, labeled sample container with a stainless steel lab spoon, or equivalent and secure the cap tightly. Place the remainder of the sample into a stainless steel, plastic, or other appropriate homogenization container, and mix thoroughly to obtain a homogenous sample representative of the entire sampling interval. Then, either place the sample into appropriate, labeled containers and secure the caps tightly; or, if composite samples are to be collected, place a sample from another sampling interval into the homogenization container and mix thoroughly. When compositing is complete, place the sample into appropriate, labeled containers and secure the caps tightly.

6. Abandon the pit or excavation according to applicable state regulations. Generally, shallow excavations can simply be backfilled with the removed soil material.

8.0 CALCULATIONS

This section is not applicable to this SOP.

9.0 QUALITY ASSURANCE/ QUALITY CONTROL

There are no specific quality assurance (QA) activities which apply to the implementation of these procedures. However, the following QA procedures apply:

1. All data must be documented on field data sheets or within site logbooks.

2. All instrumentation must be operated in accordance with operating instructions as supplied by the manufacturer, unless otherwise specified in the work plan. Equipment checkout and calibration activities must occur prior to sampling/operation, and they must be documented.

10.0 DATA VALIDATION

This section is not applicable to this SOP.

11.0 HEALTH AND SAFETY

When working with potentially hazardous materials, follow U.S. EPA, OHSA and corporate health and safety procedures.

12.0 REFERENCES

Mason, B.J., Preparation of Soil Sampling Protocol: Technique and Strategies. 1983 EPA-600/4-83-020.

Barth, D.S. and B.J. Mason, Soil Sampling Quality Assurance User's Guide. 1984 EPA-600/4-84-043.

U.S. EPA. Characterization of Hazardous Waste Sites - A Methods Manual: Volume II. Available Sampling Methods, Second Edition. 1984 EPA-600/4-84-076.

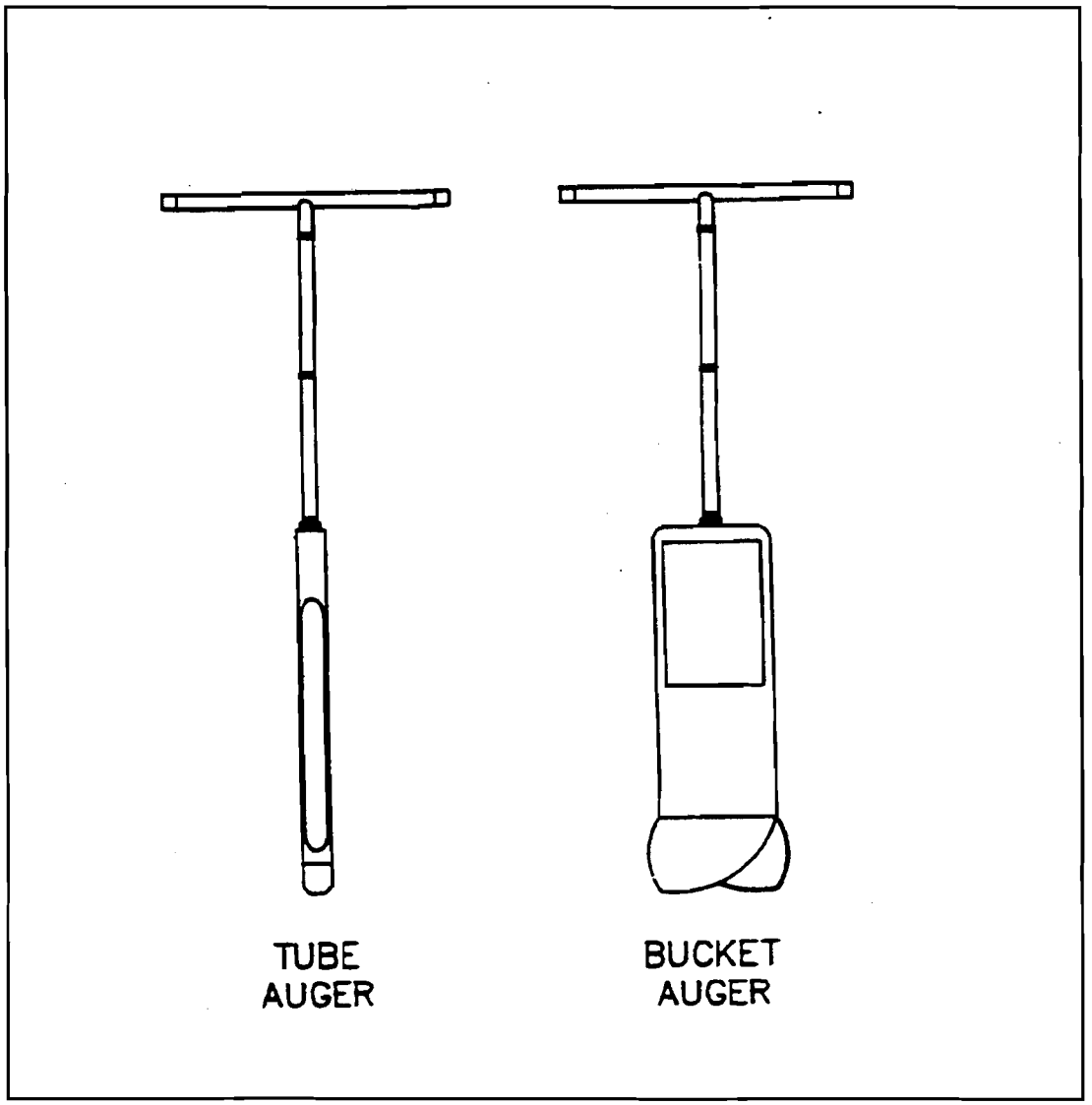
de Vera, E.R., B.P. Simmons, R.D. Stephen, and D.L. Storm. Samplers and Sampling Procedures for Hazardous Waste Streams. 1980 EPA-600/2-80-018.

ASTM D 1586-67 (reapproved 1974), ASTM Committee on Standards, Philadelphia, PA.

APPENDIX A

Figures

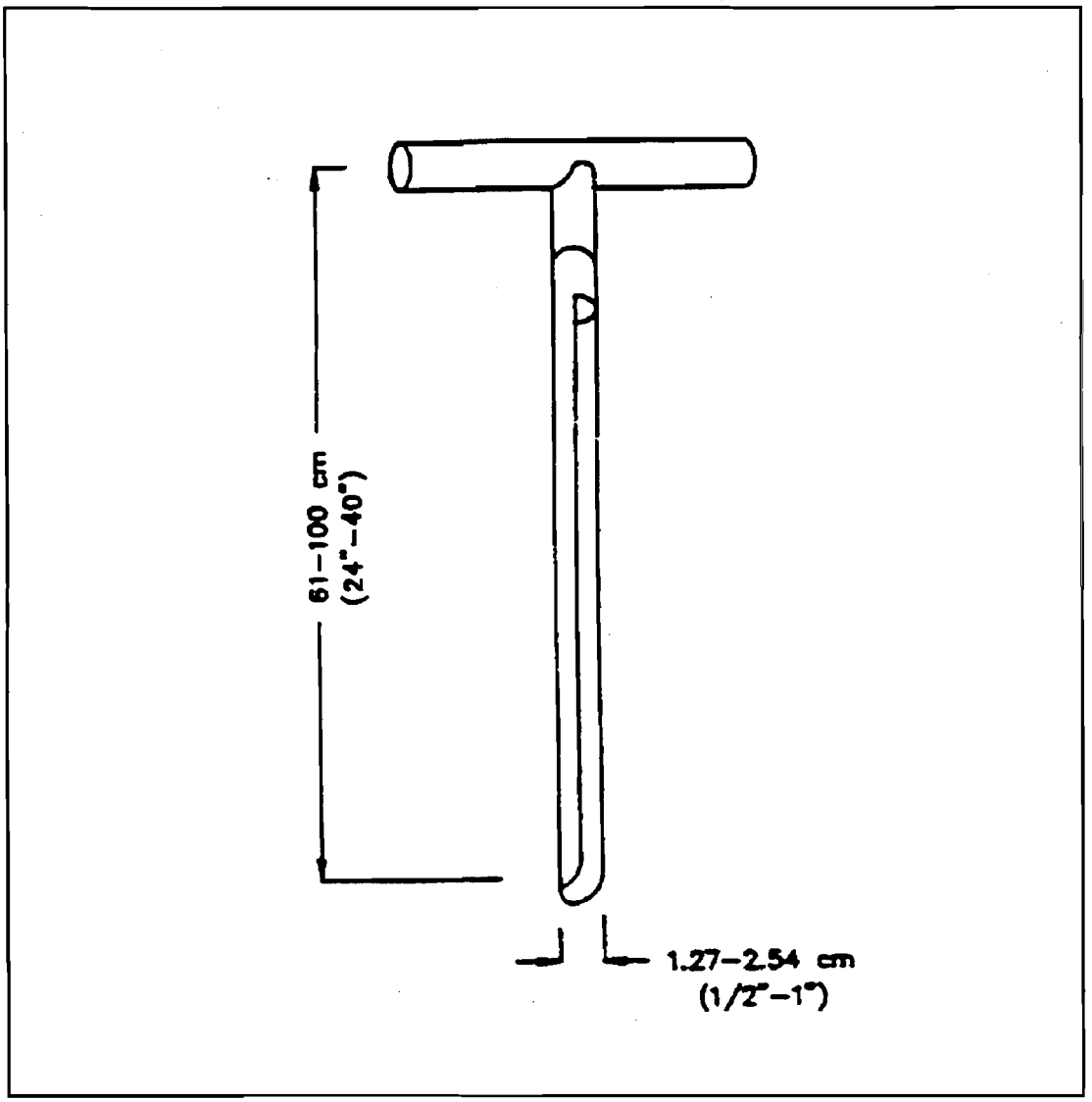
FIGURE 1. Sampling Augers



APPENDIX A (Cont'd)

Figures

FIGURE 2. Sampling Trier



1.0 SCOPE AND APPLICATION

This standard operating procedure (SOP) is applicable to the collection of representative liquid samples, both aqueous and non-aqueous from streams, rivers, lakes, ponds, lagoons, and surface impoundments. It includes samples collected from depth, as well as samples collected from the surface.

These are standard (i.e., typically applicable) operating procedures which may be varied or changed as required, dependent upon site conditions, equipment limitations or limitations imposed by the procedure or other procedure limitations. In all instances, the ultimate procedures employed should be documented and associated with the final report.

Mention of trade names or commercial products does not constitute U.S. Environmental Protection Agency (EPA) endorsement or recommendation for use.

2.0 METHOD SUMMARY

Sampling situations vary widely, therefore, no universal sampling procedure can be recommended. However, sampling of both aqueous and non-aqueous liquids from the above mentioned sources is generally accomplished through the use of one of the following samplers or techniques:

- Kemmerer bottle
- Bacon bomb sampler
- Dip sampler
- Direct method

These sampling techniques will allow for the collection of representative samples from the majority of surface waters and impoundments encountered.

3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

Once samples have been collected, the following procedure should be followed:

1. Transfer the sample(s) into suitable, labeled sample containers.
2. Preserve the sample if appropriate, or use pre-preserved sample bottles. Do not overfill bottles if they are pre-preserved.
3. Cap the container, place in a ziploc plastic bag and cool to 4°C.
4. Record all pertinent data in the site logbook and on field data sheets.
5. Complete the Chain of Custody record.
6. Attach custody seals to cooler prior to shipment.
7. Decontaminate all sampling equipment prior to the collection of additional samples with that sampling device.

4.0 INTERFERENCES AND POTENTIAL PROBLEMS

There are two primary interferences or potential problems with surface water sampling. These include cross contamination of samples and improper sample collection.

1. Cross contamination problems can be eliminated or minimized through the use of dedicated sampling equipment. If this is not possible or practical, then decontamination of sampling equipment is necessary. Refer to the Sampling Equipment Decontamination SOP.

2. Improper sample collection can involve using contaminated equipment, disturbance of the stream or impoundment substrate, and sampling in an obviously disturbed area.

Following proper decontamination procedures and minimizing disturbance of the sample site will eliminate these problems.

5.0 EQUIPMENT/APPARATUS

Equipment needed for collection of surface water samples may include (depending on technique chosen):

- Kemmerer bottles
- Bacon bomb sampler
- Dip sampler
- Line and messengers
- Sample bottles/preservatives
- Ziploc bags
- Ice
- Coolers
- Chain of Custody records, custody seals
- Field data sheets
- Decontamination equipment
- Maps/plot plan
- Safety equipment
- Compass
- Tape measure
- Survey stakes, flags, or buoys and anchors
- Camera and film
- Logbook/waterproof pen
- Sample bottle labels

6.0 REAGENTS

Reagents will be utilized for preservation of samples and for decontamination of sampling equipment. The preservatives required are specified by the analysis to be performed.

7.0 PROCEDURES

7.1 Preparation

1. Determine the extent of the sampling effort, the sampling methods to be employed, and the types and amounts of equipment and supplies needed.

2. Obtain the necessary sampling and monitoring equipment.

3. Decontaminate or pre-clean equipment, and ensure that it is in working order.

4. Prepare scheduling and coordinate with staff, clients, and regulatory agency, if appropriate.

5. Perform a general site survey prior to site entry, in accordance with the site specific Health and Safety Plan.

6. Use stakes, flagging, or buoys to identify and mark all sampling locations. If required the proposed locations may be adjusted based on site access, property boundaries, and surface obstructions. If collecting sediment samples, this procedure may disturb the bottom.

7.2 Representative Sampling Considerations

In order to collect a representative sample, the hydrology and morphometrics of a stream or impoundment should be determined prior to sampling. This will aid in determining the presence of phases or layers in lagoons, or impoundments, flow patterns in streams, and appropriate sample locations and depths.

Water quality data should be collected in impoundments, and to determine if stratification is present. Measurements of dissolved oxygen, pH, and temperature can indicate if strata exist which would effect analytical results. Measurements should be collected at one-meter intervals from the substrate to the surface using the appropriate instrument (i.e., a Hydrolab or equivalent).

Water quality measurements such as dissolved oxygen, pH, temperature, conductivity, and oxidation-reduction potential can assist in the interpretation of analytical data and the selection of sampling sites and depths when surface water samples are collected.

Generally, the deciding factors in the selection of a sampling device for sampling liquids in streams, rivers, lakes, ponds, lagoons, and surface impoundments are:

1. Will the sample be collected from shore or from a boat?

2. What is the desired depth at which you wish to collect the sample?

3. What is the overall depth and flow direction of river or stream?

4. What type of sample will be collected (i.e., water or lagoon liquids)?

7.2.1 Sampler Composition

The appropriate sampling device must be of a proper composition. Selection of samplers constructed of glass, stainless steel, PVC or PFTE (Teflon) should be based upon the analyses to be performed.

7.3 Sample Collection

7.3.1 Kemmerer Bottle

A Kemmerer bottle (Figure 1, Appendix A) may be used in most situations where site access is from a boat or structure such as a bridge or pier, and where samples at depth are required. Sampling procedures are as follows:

1. Use a properly decontaminated Kemmerer bottle. Set the sampling device so that the sampling end pieces (upper and lower stoppers) are pulled away from the sampling tube (body), allowing the substance to be sampled to pass through this tube.

2. Lower the pre-set sampling device to the predetermined depth. Avoid bottom disturbance.

3. When the Kemmerer bottle is at the required depth, send down the messenger, closing the sampling device.

4. Retrieve the sampler and discharge from the bottom drain the first 10-20 mL to clear any potential contamination of the valve. Transfer the sample to the appropriate sample container.

7.3.2 Bacon Bomb Sampler

A bacon bomb sampler (Figure 2, Appendix A) may be used in situations similar to those outlined for the Kemmerer bottle. Sampling procedures are as follows:

1. Lower the bacon bomb sampler carefully to the desired depth, allowing the line for the trigger to remain slack at all times. When the desired depth is reached, pull the trigger line until taut. This will allow the sampler to fill.

2. Release the trigger line and retrieve the sampler.

3. Transfer the sample to the appropriate sample container by pulling up on the trigger.

7.3.3 Dip Sampler

A dip sampler (Figure 3, Appendix A) is useful in situations where a sample is to be recovered from an outfall pipe or along a lagoon bank where direct access is limited. The long handle on such a device allows access from a discrete location. Sampling procedures are as follows:

1. Assemble the device in accordance with the manufacturer's instructions.

2. Extend the device to the sample location and collect the sample by dipping the sampler into the substance.

3. Retrieve the sampler and transfer the sample to the appropriate sample container.

7.3.4 Direct Method

For streams, rivers, lakes, and other surface waters, the direct method may be utilized to collect water samples from the surface directly into the sample bottle. This method is not to be used for sampling lagoons or other impoundments where contact with contaminants is a concern.

Using adequate protective clothing, access the sampling station by appropriate means. For shallow stream stations, collect the sample under the water surface while pointing the sample container upstream; the container must be upstream of the collector. Avoid disturbing the substrate. For lakes and other impoundments, collect the sample under the water surface avoiding surface debris and the boat wake.

When using the direct method, do not use pre-preserved sample bottles as the collection method may dilute the concentration of preservative necessary for proper sample preservation.

8.0 CALCULATIONS

This section is not applicable to this SOP.

9.0 QUALITY ASSURANCE/ QUALITY CONTROL

There are no specific quality assurance (QA) activities which apply to the implementation of these procedures. However, the following general QA procedures apply:

1. All data must be documented on field data sheets or within site logbooks.

2. All instrumentation must be operated in accordance with operating instructions as supplied by the manufacturer, unless otherwise specified in the work plan. Equipment checkout and calibration activities must occur prior to sampling/operation and they must be documented.

10.0 DATA VALIDATION

This section is not applicable to this SOP.

11.0 HEALTH AND SAFETY

When working with potentially hazardous materials, follow U.S. EPA, OSHA and corporate health and safety procedures.

More specifically, when sampling lagoons or surface impoundments containing known or suspected hazardous substances, adequate precautions must be taken to ensure the safety of sampling personnel. The sampling team member collecting the sample should not get too close to the edge of the impoundment, where bank failure may cause him/her to lose his/her balance. The person performing the sampling should be on a lifeline and be wearing adequate protective equipment. When conducting sampling from a boat in an impoundment or flowing waters, appropriate boating safety procedures should be followed.

12.0 REFERENCES

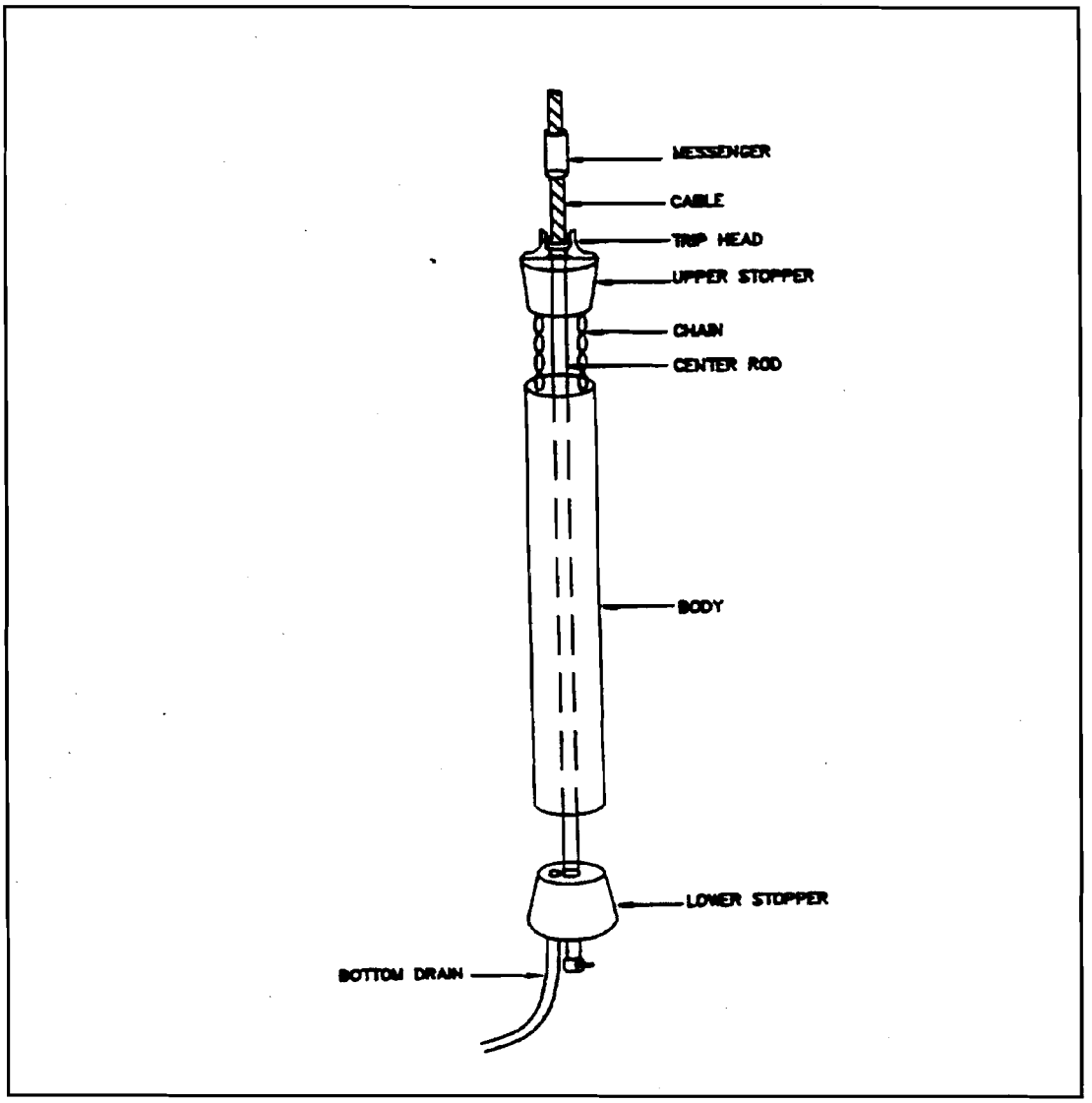
U.S. Geological Survey. 1977. National Handbook or Recommended Methods for Water Data Acquisition. Office of Water Data Coordination Reston, Virginia. (Chapter Updates available).

U.S. Environmental Protection Agency. 1984. Characterization of Hazardous Waste Sites - A Methods Manual: Volume II. Available Sampling Methods, Second Edition. EPA/600/4-84-076.

APPENDIX A

Figures

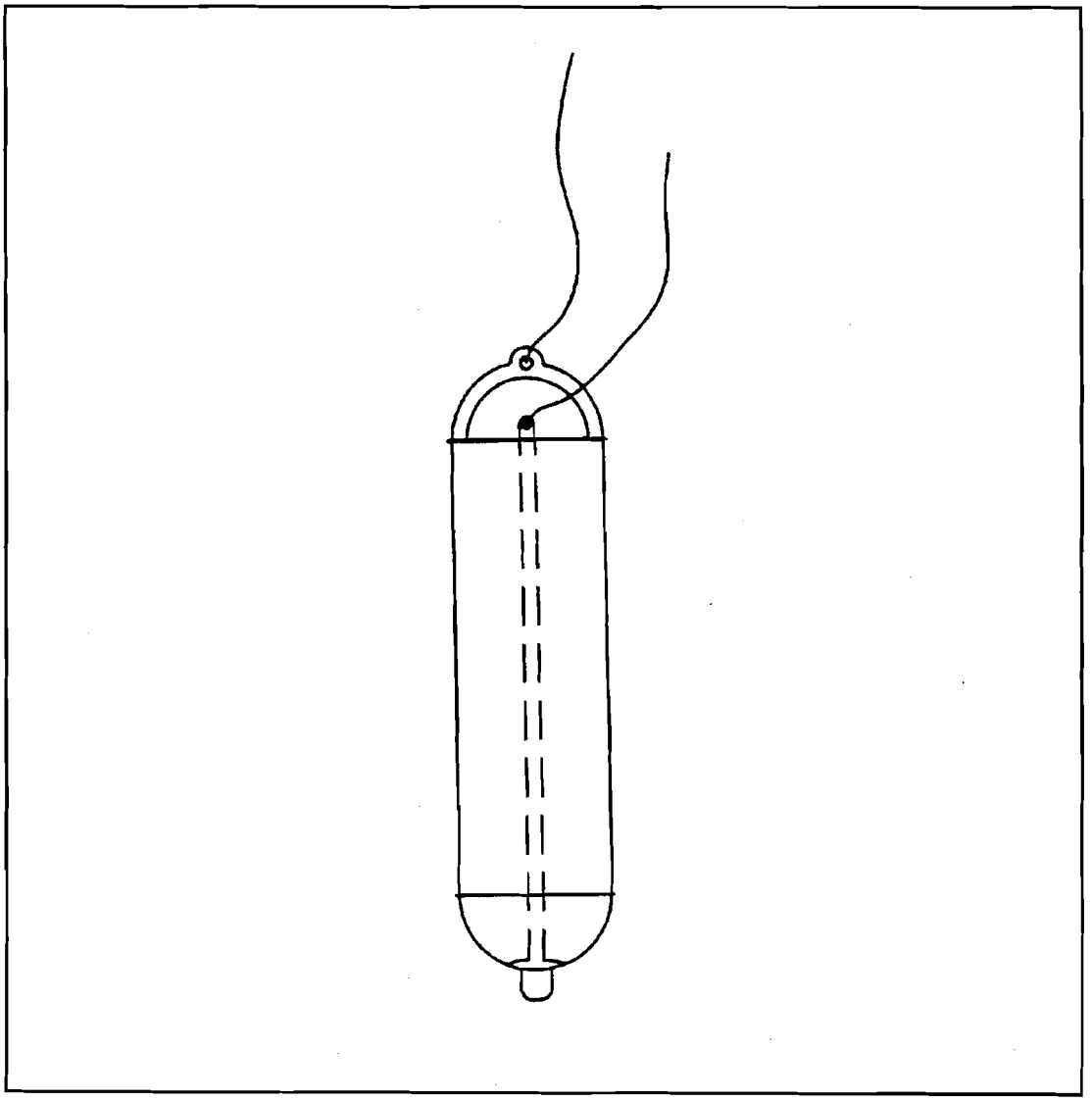
FIGURE 1. Kemmerer Bottle



APPENDIX A (Cont'd)

Figures

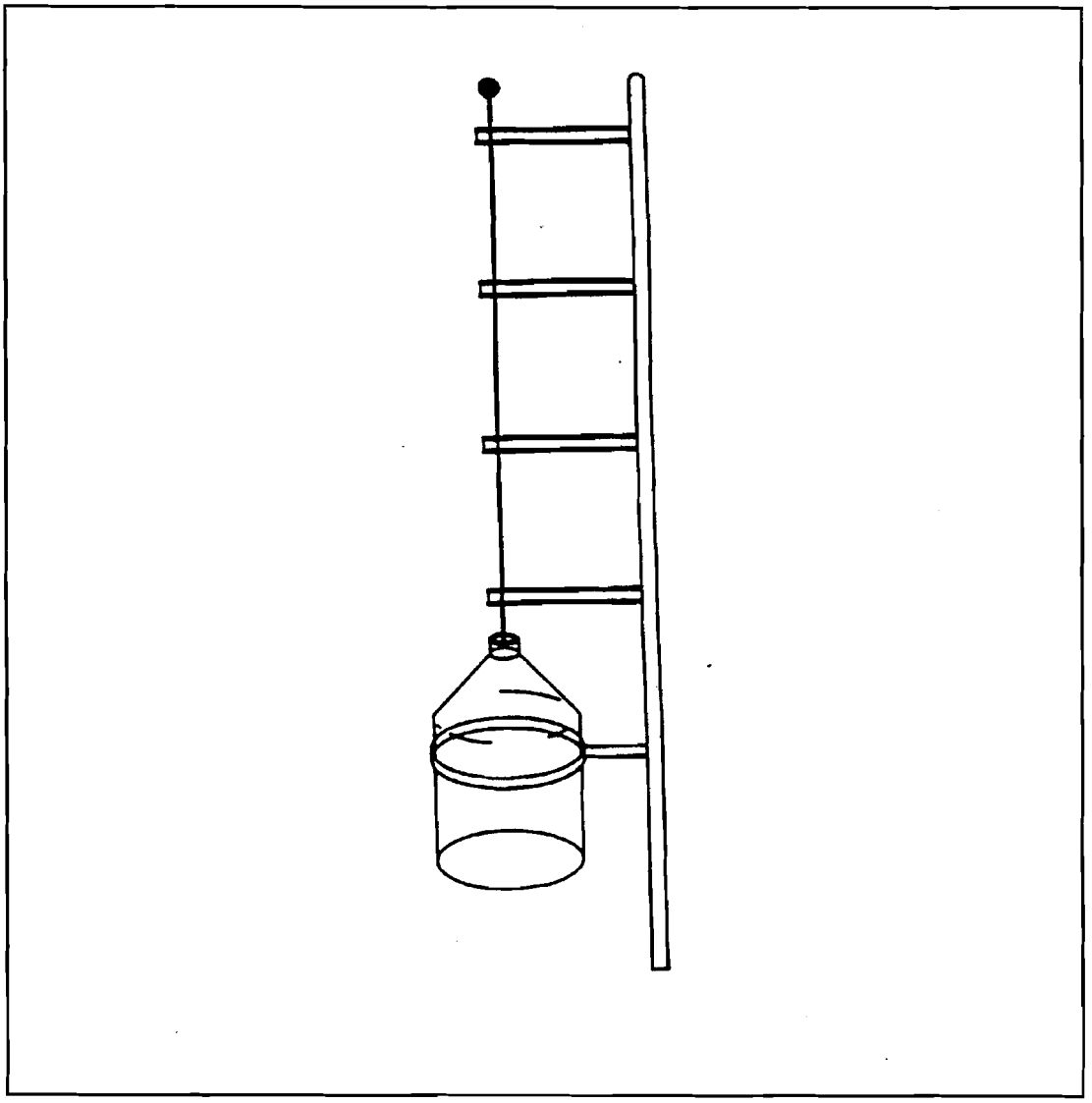
FIGURE 2. Bacon Bomb Sampler



APPENDIX A (Cont'd)

Figures

FIGURE 3. Dip Sampler



1.0 SCOPE AND APPLICATION

The objective of this standard operating procedure (SOP) is to outline the equipment and methods used in collecting representative samples from waste piles, sludges or other solid or liquid waste mixed with soil.

These are standard (i.e., typically applicable) operating procedures which may be varied or changed as required, dependent on site conditions, equipment limitations or other procedure limitations. In all instances, the ultimate procedures employed should be documented and associated with the final report.

Mention of trade names or commercial products does not constitute U.S. EPA endorsement or recommendation for use.

2.0 METHOD SUMMARY

Stainless steel shovels, trowels, or scoops should be used to clear away surface material before samples are collected. For depth samples, a decontaminated auger may be required to advance the hole, then another decontaminated auger used for sample collection. For a sample core, thin-wall tube samplers or grain samplers may be used. Near surfaces, samples can be collected with a clean stainless steel spoon or trowel.

All samples collected, except those for volatile organic analysis, should be placed into a Teflon lined or stainless steel pail and mixed thoroughly before transfer to appropriate sample container.

3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

Chemical preservation of solids is generally not recommended. Refrigeration to 4°C is usually the best approach, supplemented by a minimal holding time, depending on contaminants of concern.

Wide mouth glass containers with Teflon lined caps are typically used for waste pile samples. Sample volume required is a function of the analytical requirements and should be specified in the work plan.

4.0 INTERFERENCES AND POTENTIAL PROBLEMS

There are several variables involved in waste sampling, including shape and size of piles, compactness, and structure of the waste material. Shape and size of waste material or waste piles vary greatly in areal extent and height. Since state and federal regulations often require a specified number of samples per volume of waste, the size and shape must be used to calculate volume and to plan for the correct number of samples. Shape must also be accounted for when planning physical access to the sampling point and the equipment necessary to successfully collect the sample at that location.

Material to be sampled may be homogeneous or heterogeneous. Homogeneous material resulting from known situations may not require an extensive sampling protocol. Heterogeneous and unknown wastes require more extensive sampling and analysis to ensure the different components (i.e. layers, strata) are being represented.

The term "representative sample" is commonly used to denote a sample that has the properties and composition of the population from which it was collected and in the same proportions as found in the population. This can be misleading unless one is dealing with a homogenous waste from which one sample can represent the whole population.

The usual options for obtaining the most "representative sample" from waste piles are simple random sampling or stratified random sampling. Simple random sampling is the method of choice unless: (1) there are known distinct strata; (2) one wants to prove or disprove that there are distinct

strata; or (3) one is limited in the number of samples and desires to statistically minimize the size of a "hot spot" that could go unsampled. If any of these conditions exist, stratified random sampling would be the better strategy.

Stratified random sampling can be employed only if all points within the pile can be accessed. In such cases, the pile should be divided into a three-dimensional grid system with, the grid cubes should be numbered, and the grid cubes to be sampled should be chosen by random number tables or generators. The only exceptions to this are situations in which representative samples cannot be collected safely or where the investigative team is trying to determine worst case conditions.

If sampling is limited to certain portions of the pile, a statistically based sample will be representative only of that portion, unless the waste is homogenous.

5.0 EQUIPMENT/APPARATUS

Waste pile solids include powdered, granular, or block materials of various sizes, shapes, structure, and compactness. The type of sampler chosen should be compatible with the waste. Samplers commonly used for waste piles include: stainless steel scoops, shovels, trowels, spoons, and stainless steel hand augers, sampling triers, and grain samplers.

Waste pile sampling equipment check list:

- Sampling plan
- Maps/plot plan
- Safety equipment, as specified in the Health and Safety Plan
- Compass
- Tape measure
- Survey stakes or flags
- Camera and film
- Stainless steel, plastic, or other appropriate homogenization bucket or bowl
- Appropriate size sample jars
- Ziplock plastic bags
- Logbook
- Labels
- Chain of Custody records and seals
- Field data sheets
- Cooler(s)
- Ice
- Decontamination supplies/equipment
- Canvas or plastic sheet
- Spade or shovel
- Spatula
- Scoop
- Plastic or stainless steel spoons
- Trowel
- Continuous flight (screw) augers
- Bucket auger
- Post hole auger
- Extension rods
- T-Handle
- Thin-wall tube sampler with cutting tips
- Sampling trier
- Grain sampler

6.0 REAGENTS

No chemical reagents are used for the preservation of waste pile samples; however, decontamination solutions may be required. If decontamination of equipment is required, refer to the Sampling Equipment Decontamination SOP, and the site specific work plan.

7.0 PROCEDURES

7.1 Preparation

1. Review all information available on the waste pile and expected or unknown contaminants.

2. Determine the extent of the sampling effort, the sampling methods to be employed, and the types and amounts of equipment and supplies required.

3. Obtain necessary sampling and monitoring equipment.

4. Decontaminate or pre-clean equipment, and ensure that it is in working order.

5. Prepare schedules, and coordinate with staff, client, and regulatory agencies, if appropriate.

6. Perform a general site survey prior to site entry in accordance with the site specific Health and Safety Plan.

7. Use stakes or flagging to identify and mark

all sampling locations. Specific site factors, including extent and nature of contaminant should be considered when selecting sample locations. If required, the proposed locations may be adjusted based on site access, property boundaries, and surface obstructions.

7.2 Sample Collection

7.2.1 Sampling with Shovels and Scoops

Collection of samples from surface portions of the pile can be accomplished with tools such as spades, shovels, and scoops. Surface material can be removed to the required depth with this equipment, then a stainless steel or plastic scoop, or equivalent can be used to collect the sample.

Accurate, representative samples can be collected with this procedure depending on the care and precision demonstrated by sample team members. Use of a flat, pointed mason trowel to cut a block of the desired material can be helpful when undisturbed profiles are required. A stainless steel scoop, lab spoon, plastic spoon, or equivalent will suffice in most other applications. Care should be exercised to avoid the use of devices plated with chrome or other materials. Plating is particularly common with implements such as garden trowels.

The following procedure is used to collect the surface samples:

1. Carefully remove the top layer of material to the desired sample depth with a pre-cleaned spade.

2. Using a pre-cleaned stainless steel scoop, plastic spoon, trowel, or equivalent remove and discard a thin layer of material from the area which came in contact with the spade.

3. If volatile organic analysis is to be performed, transfer the sample into an appropriate, labeled sample container with a stainless steel lab spoon, or equivalent, and secure the cap tightly. Place the remainder of the sample into a stainless steel, plastic, or other appropriate homogenization container, and mix thoroughly to obtain a homogenous sample representative of the entire sampling interval. Then, either place the sample into appropriate, labeled containers and secure the caps tightly; or, if composite samples are to be collected, place a sample from another sampling interval into the homogenization container and mix thoroughly. When compositing is complete, place the sample into appropriate, labeled containers and secure the caps tightly.

7.2.2 Sampling with Bucket Augers and Thin-Wall Tube Samplers

These samplers consist of a series of extensions, a "T" handle, and a bucket auger or thin-wall tube sampler (Appendix A, Figure 1). The auger is used to bore a hole to a desired sampling depth, and is then withdrawn. The sample may be collected directly from the bucket auger. If a core sample is to be collected, the auger tip is then replaced with a thin-wall tube sampler. The sampler is then lowered down the borehole, and driven into the pile to the completion depth. The sampler is withdrawn and the core collected from the thin-wall tube sampler.

Several augers are available.. These include: bucket, continuous flight (screw), and post hole augers. Bucket augers are better for direct sample recovery since they provide a large volume of sample in a short time. When continuous flight augers are used, the sample can be collected directly from the flights, which are usually at five (5) foot intervals. The continuous flight augers are satisfactory for use when a composite of the complete waste pile column is desired. Post hole augers have limited utility for sample collection as they are designed to cut through fibrous, rooted, swampy areas.

The following procedure will be used for collecting waste pile samples with the bucket augers and thin-wall tube samplers:

1. Attach the auger bit to a drill rod extension, and attach the "T" handle to the drill rod.

2. Clear the area to be sampled of any surface debris. It may be advisable to remove the first three to six inches of surface material for an area approximately six inches in radius around the drilling location.

3. Begin augering, periodically removing and depositing accumulated materials onto a plastic sheet spread near the hole. This prevents accidental brushing of loose

material back down the borehole when removing the auger or adding drill rod extensions. It also facilitates refilling the hole, and avoids possible contamination of the surrounding area.

4. After reaching the desired depth, slowly and carefully remove the auger from the borehole. When sampling directly from the auger, collect the sample after the auger is removed from the borehole and proceed to Step 10.

5. Remove auger tip from drill rods and replace with a pre-cleaned thin-wall tube sampler. Install proper cutting tip.

6. Carefully lower the tube sampler down the borehole. Gradually force the tube sampler into the pile. Care should be taken to avoid scraping the borehole sides. Avoid hammering the drill rod extensions to facilitate coring as the vibrations may cause the borehole walls to collapse.

7. Remove the tube sampler, and unscrew the drill rod extensions.

8. Remove the cutting tip and the thin-wall tube sampler.

9. Discard the top of the core (approximately one-inch), as this represents material collected before penetration of the layer of concern. Place the remaining core into the appropriate labeled sample container. Sample homogenization is not required.

10. If volatile organic analysis is to be performed, transfer the sample into an appropriate, labeled sample container with a stainless steel lab spoon, or equivalent and secure the cap tightly. Place the remainder of the sample into a stainless steel, plastic, or other appropriate homogenization container, and mix thoroughly to obtain a homogenous sample representative of the entire sampling interval. Then, either place the sample into appropriate, labeled containers and secure the caps tightly; or, if composite samples are to be collected, place a sample from another sampling interval into the homogenization container and mix thoroughly. When compositing is complete, place the sample into appropriate, labeled containers and secure the caps tightly.

11. If another sample is to be collected in the same hole, but at a greater depth, reattach the bucket auger to the drill and assembly, and follow steps 3 through 11, making sure to decontaminate the bucket auger and thin-wall tube sampler between samples.

7.2.3 Sampling with a Trier

This sampling device consists of a trier, and a "T" handle. The trier is driven into the waste pile and used to extract a core sample from the appropriate depth.

The following procedure will be used to collect waste pile samples with a sampling trier:

1. Insert the trier (Appendix A, Figure 2) into the material to be sampled at a 0E to 45E angle from horizontal. This orientation minimizes spillage of the sample. Extraction of the samples might require tilting of the sample containers.

2. Rotate the trier once or twice to cut a core of material.

3. Slowly withdraw the trier, making sure that the slot is facing upward.

4. If volatile organic analysis is to be performed, transfer the sample into an appropriate, labeled sample container with a stainless steel lab spoon, plastic lab spoon, or equivalent and secure the cap tightly. Place the remainder of the sample into a stainless steel, plastic, or other appropriate homogenization container, and mix thoroughly to obtain a homogenous sample representative of the entire sampling interval. Then, either place the sample into appropriate, labeled containers and secure the caps tightly; or, if composite samples are being collected, place samples from the other sampling intervals into the homogenization container and mix thoroughly. When compositing is complete, place the sample

into appropriate, labeled containers and secure the caps tightly.

7.2.4 Sampling with a Grain Sampler

The grain sampler (Appendix A, Figure 3) is used for sampling powdered or granular wastes or materials in bags, fiber drums, sacks, similar containers or piles. This sampler is most useful when the solids are no greater than 0.6 cm (1/4") in diameter.

This sampler consists of two slotted telescoping brass or stainless steel tubes. The outer tube has a conical, pointed tip at one end that permits the sampler to penetrate the material being sampled. The sampler is opened and closed by rotating the inner tube. Grain samplers are generally 61 to 100 cm (24 to 40 in.) long by 1.27 to 2.54 cm (1/2 to 1 in.) in diameter and are commercially available at laboratory supply houses.

The following procedures will be used to collect waste pile samples with a grain sampler:

1. With the sampler in the closed position, insert it into the granular or powdered material or waste being sampled from a point near a top edge or corner, through the center, and to a point diagonally opposite the point of entry.

2. Rotate the sampler inner tube into the open position.

3. Wiggle the sampler a few times to allow material to enter the open slots.

4. Place the sampler in the closed position and withdraw from the material being sampled.

5. Place the sampler in a horizontal position with the slots facing upward.

6. Rotate the outer tube and slide it away from the inner tube.

7. If volatile organic analysis is to be performed, transfer the sample into an appropriate, labeled sample container with a stainless steel lab spoon, plastic lab spoon, or equivalent and secure the cap tightly. Place the remainder of the sample into a stainless steel, plastic, or other appropriate homogenization container, and mix thoroughly to obtain a homogenous sample representative of the entire sampling interval. Then, either place the sample into appropriate, labeled containers and secure the caps tightly; or, if composite samples are to be collected, place a sample from another sampling interval into the homogenization container and mix thoroughly. When compositing is complete, place the sample into appropriate, labeled containers and secure the caps tightly.

8.0 CALCULATIONS

This section is not applicable to this SOP.

9.0 QUALITY ASSURANCE/ QUALITY CONTROL

There are no specific quality assurance activities which apply to the implementation of these procedures. However, the following QA procedures apply:

1. All data must be documented on field data sheets or within site logbooks.

2. All instrumentation must be operated in accordance with operating instructions as supplied by the manufacturer, unless otherwise specified in the work plan. Equipment checkout and calibration activities must occur prior to sampling/operation, and they must be documented.

10.0 DATA VALIDATION

This section is not applicable to this SOP.

11.0 HEALTH AND SAFETY

When working with potentially hazardous materials, follow U.S. EPA/OSHA and corporate health and safety procedures.

12.0 REFERENCES

Test Methods for Evaluating Solids Waste (SW-846), Third Edition, Vol. II Field Manual U.S. EPA Office of Solid Waste and Emergency Response, Washington, D.C. November, 1986.

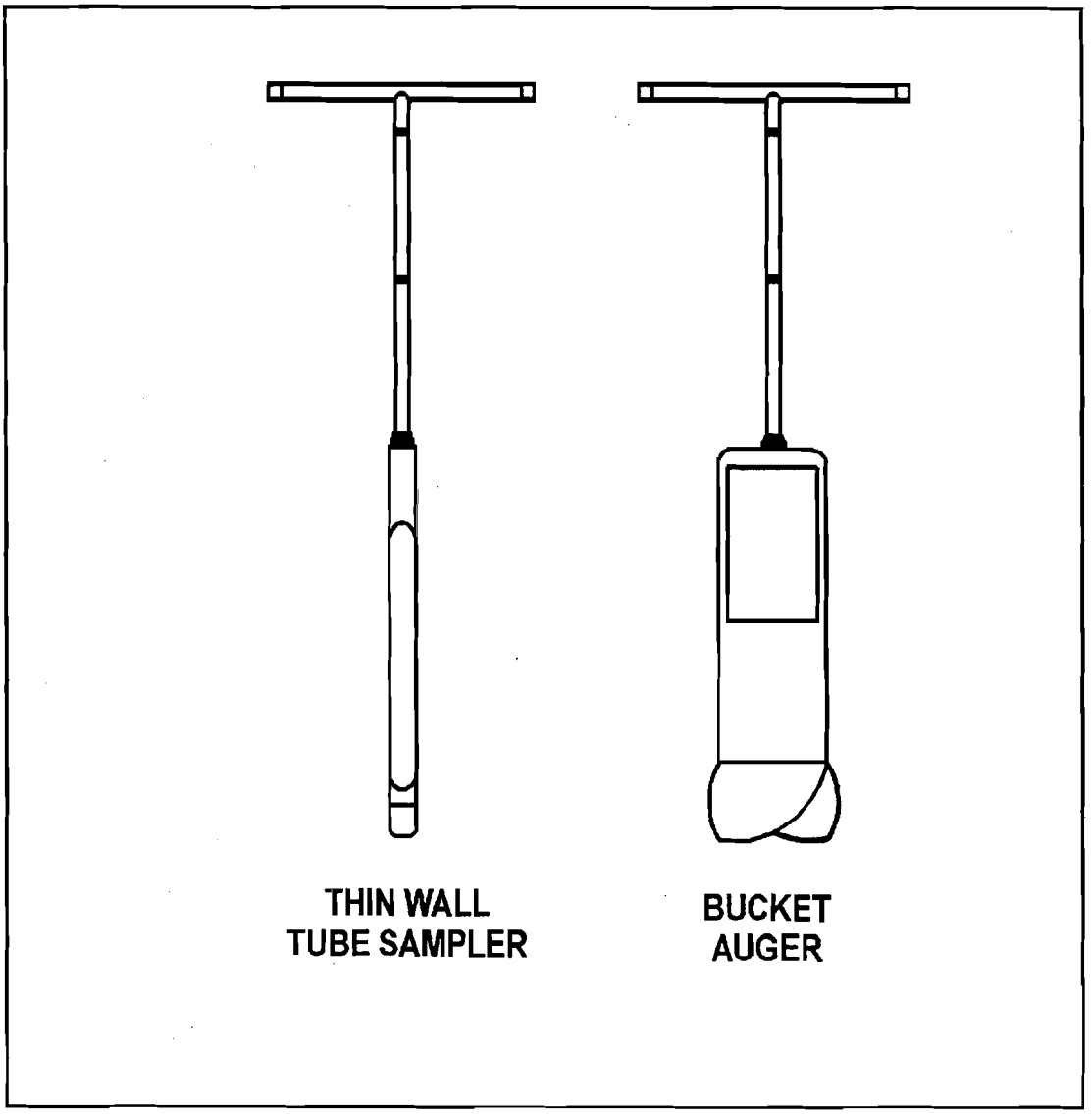
Engineering Support Branch Standard Operating Procedures and Quality Assurance Manual, U.S. Environmental Protection Agency, Region IV, April 1, 1986.

Field Sampling Procedures Manual, New Jersey Department of Environmental Protection, February, 1988.

APPENDIX A

Figures

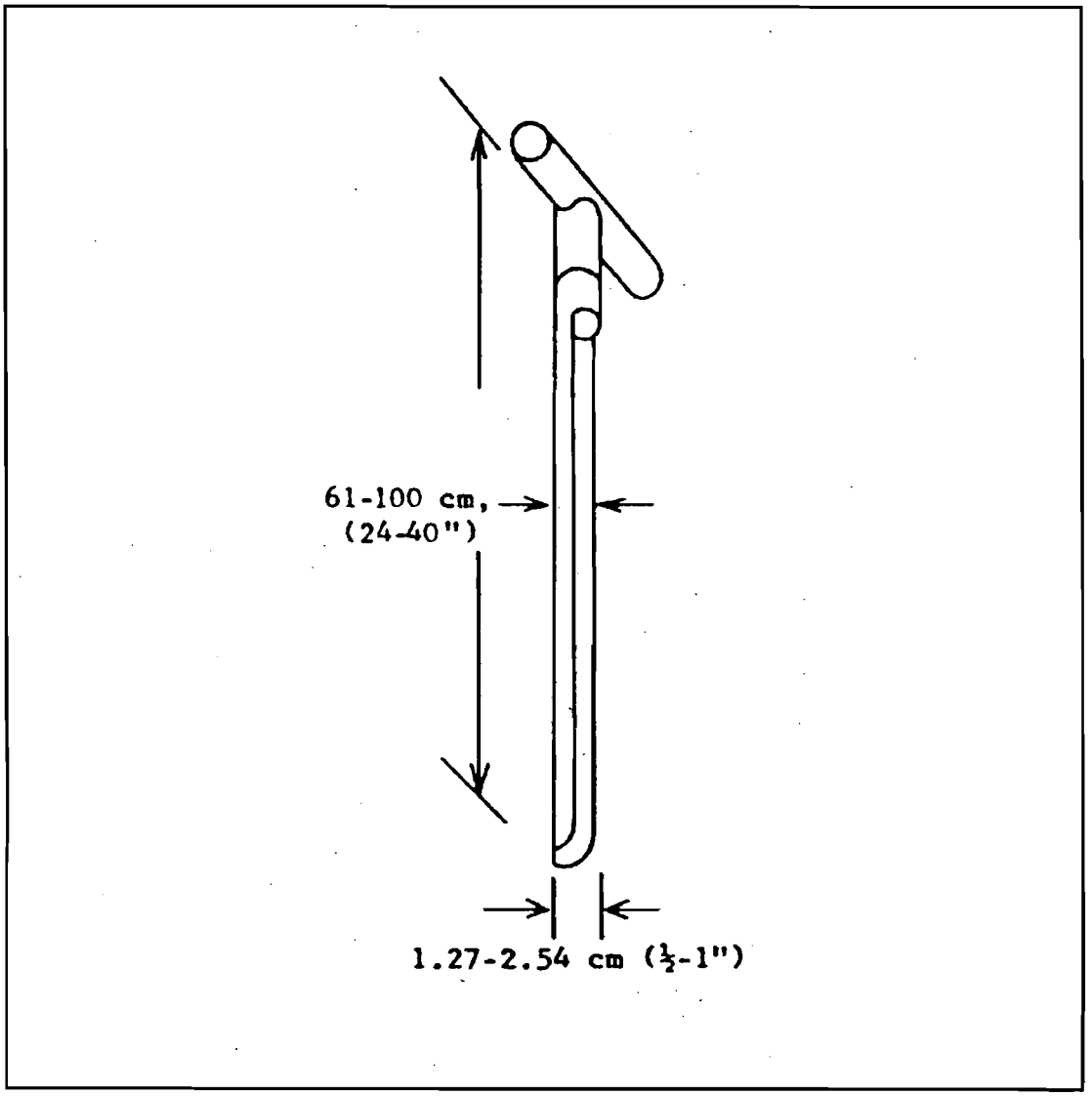
FIGURE 1. Sampling Augers



APPENDIX A (Cont'd)

Figures

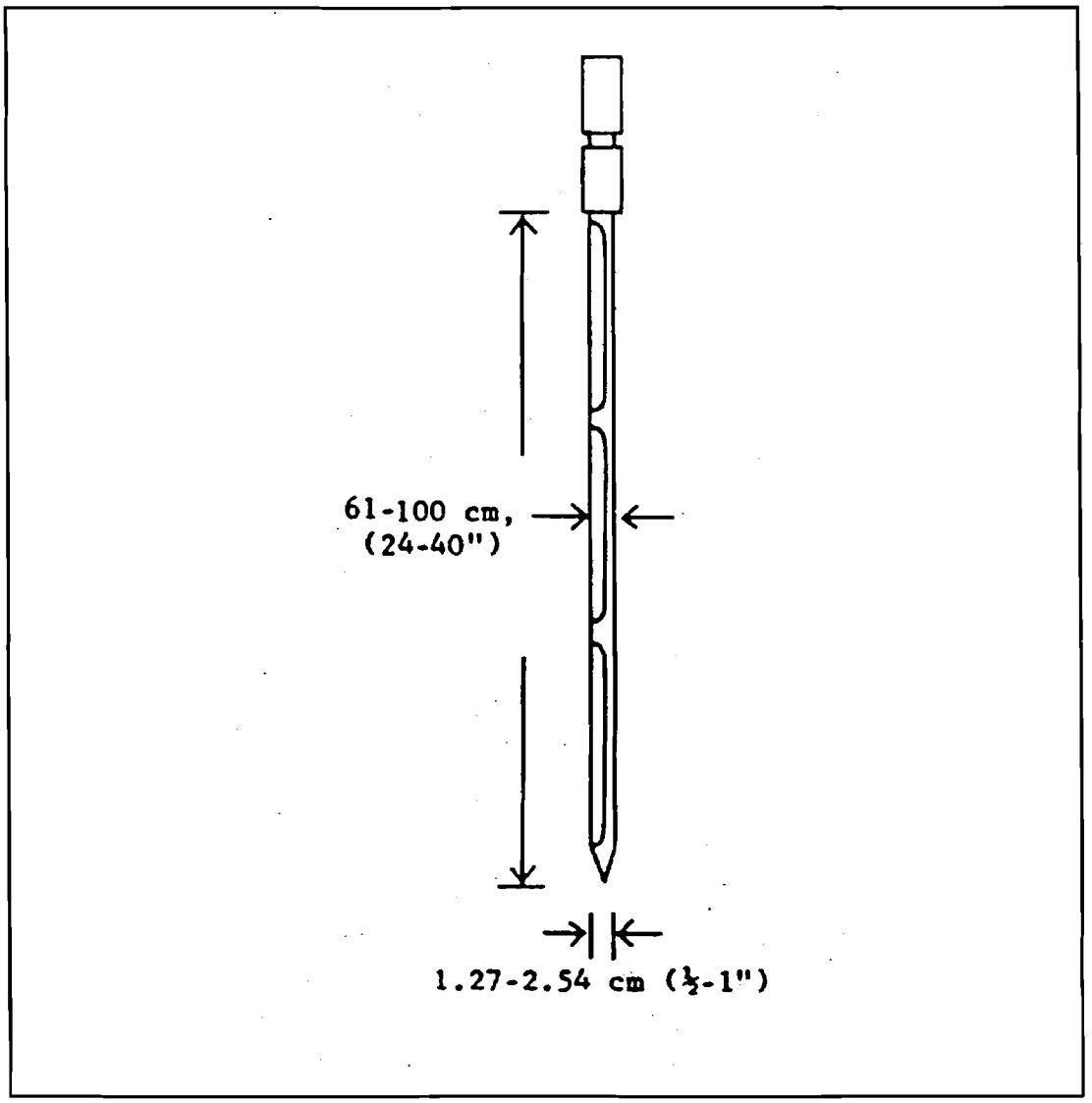
FIGURE 2. Sampling Trier



APPENDIX A (Cont'd)

Figures

FIGURE 3. Grain Sampler



SAMPLE CONTAINERS, PRESERVATION, AND HOLDING TIMES

WESTON will be responsible for collecting and preparing samples for shipment, including necessary paperwork. WESTON will be responsible for shipping the samples and insuring sample preservation and holding time requirements are met.

SAMPLE CONTAINERS

All sample containers to be used during the IMWP will be provided by STAT. The laboratory's sample container preparation coordinates the assembly and shipment of sample containers, preservatives and shipping coolers. The procured sample containers are designated as QC class, which have supporting QC documentation for the purity of each container lot. The lot number is labeled for traceability to a certificate of analysis.

SAMPLE CONTAINER PRESERVATION

STAT will provide the preservatives required for all sampling. STAT uses preservatives that are pre-measured reagents and purchased from suppliers. These preservatives are received with QC documentation to verify purity. These records are maintained by the laboratory and are available for inspection. An identifying lot number is on each preservative to assure traceability.

SAMPLE VOLUME AND SAMPLE HOLDING TIMES

Sample volume required for analysis and sample holding time varies by matrix and sample analyses required.

SAMPLE NUMBERING SYSTEM

The same sample numbering system, developed for confirmation sampling, will also be used for the waste characterization sampling.

DECONTAMINATION PROCEDURES

To provide accurate and reliable analytical data, a strict decontamination program will be implemented during all sampling. All sampling equipment will be decontaminated prior to and subsequent to collecting a sample. The procedures listed below will be followed while decontaminating sampling equipment:

- Spray sampling equipment with a non-phosphatic detergent (e.g., Alconox) and tap water solution (if necessary, scrub sampling equipment with soft-bristle brushes).
- Rinse equipment with deionized water.
- Allow to air dry or wipe dry with clean paper toweling.
- Wrap sampling equipment in polypropylene sheeting or aluminum foil until its next use.

During the excavation activities, the bucket of the excavator will be decontaminated between excavation areas with pressurized steam cleaners. The decontamination process for heavy equipment, tools, and sampling devices/equipment will be performed in one designated area for the entire field program. The wastewater collected during decontamination of sampling equipment will be containerized in 55-gallon drums or larger vessels depending on volume. The heavy equipment decontamination will occur on an established decontamination pad, which is sloped to a sump to collect runoff. The fluids that collect in the sump will also be containerized into 55-gallon drums or larger vessels depending on volume. Containerized decontamination fluids will be moved to a designated storage area while awaiting sample analytical results and disposal.

Personal decontamination procedures will be performed near the heavy equipment decontamination area or in the boundary between exclusion zones and support zones. Protective clothing will be placed in appropriate waste containers and moved to a designated storage area.

In addition, work site and disposal site decontamination certificates will be submitted to NSWC Crane. A decontamination log will also be prepared and maintained for the Site.

SAMPLE PACKAGING AND SHIPMENT

Sample packaging and shipping procedures will be based on state and federal DOT regulations and the International Air Transport Association Dangerous Goods regulations. The procedures will vary according to sample concentrations, type of potential contaminant hazards, and matrix. The procedures have been established to provide adequate protection of samples and to minimize potential risk to the public. All samples collected will typically be sent within 24 hours of their field collection. The sample container exteriors will be cleaned thoroughly and sealed properly in preparation of shipment.

The following standard procedure will be followed for proper sample handling and shipment when samples are to be shipped using a courier service:

- Prepare cooler for delivery by taping the drains of the cooler shut. Affix "This Side Up" arrow labels on all four side and "Fragile" labels on at least two sides of each cooler. Place the mailing label with laboratory address on top of cooler(s).
- Arrange sample containers in groups by sample number.
- Ensure that all bottle labels are completed correctly. Place clear tape over bottle label to prevent moisture accumulation which can cause the label to peel off.
- Determine which samples will be packed into which cooler and complete a chain-of-custody (COC) form for each cooler.
- Seal sample containers within plastic zip-lock bags to prevent vermiculite or other inert packing material from contacting samples. All containers, regardless of size or type, must be placed inside sealed plastic bags (either zip-lock or other type) before packing in vermiculite.
- Place approximately 2 inches of packing material at the bottom of cooler to act as a cushion for the sample container.
- Arrange the containers in the cooler so that they do not touch. Fill remaining spaces with packing material. The VOC vials should be placed in cooler suspended upright in packing material.
- If ice is required to preserve the samples, cubes should be repackaged in double zip-lock bags or other sealed plastic bags and placed within and on top of the packing material.
- Sign the COC form (or obtain signature) and indicate the time and date it was relinquished to the express carrier or other courier service, as appropriate.
- Separate copies of COC forms. Seal proper copies within a large zip-lock bag and tape to inside lid of cooler. Retain copies of all forms in house.
- Close lid and latch cooler. Secure each cooler using custody seals. The seals are provided by the laboratory and operate in one direction only (i.e., when closing or securing) and cannot be removed unless they are torn off. A torn seal indicates that the custody of the cooler has been broken. Clear tape will be put over the custody seals in at least one full rotation of the cooler.

- Tape cooler shut on both ends, making several complete revolutions with strapping tape.
- Relinquish to the express carrier or other courier service. Retain airbill receipt for project records (Note: All samples will be shipped for "NEXT DAY" delivery).
- Telephone laboratory contact and provide them with the following shipment information:
  - Your name, address, and telephone number
  - Project name
  - Number of samples sent, according to matrix and concentration
  - Airbill number and name of carrier
  - Anticipated package arrival time
  - Analytical requirements of the shipment.

Where local personnel are to pick up samples and directly deliver samples to the laboratory, samples only need to be firmly secured and have proper COC guidelines followed.

TRANSPORTATION AND OFFSITE DISPOSAL

All transport and disposal activities will be conducted in accordance with federal, state, and local regulations. All containers will be marked and labeled in accordance with DOT regulations (49 Code of Federal Regulations [CFR] 172), as necessary. Each container will also be affixed with a placard designating the type of waste, as applicable. All appropriate manifests/waste receipts/shipment and delivery certificates will accompany the containers, as necessary, and will be submitted to NSWC Crane.

The following disposal sites for waste will be used:

- Soil waste containing pesticides less than LDR: EQ-Wayne Disposal Landfill
- Soil waste containing pesticides greater than LDR: Clean Harbors Lambton (Sarnia) Landfill
- Soil waste containing TSCA level PCBs: EQ-Wayne Disposal Landfill
- Soil containing no TSCA or RCRA hazardous waste (non-hazardous): Veolia Blackfoot Landfill
- Non-hazardous, non-TSCA water: Ecological Systems, Inc. wastewater treatment plant.

Prior to the transportation of waste offsite, the following decontamination procedures will be conducted:

- Visually inspect all vehicles, equipment, and containers leaving the work site for proper decontamination
- Prepare and maintain a written decontamination log.

Prior to the transportation of waste off site, the following procedures will be conducted:

- Inspect and document all vehicles and containers for proper operation and covering
- Inspect all vehicles and containers for proper markings, manifest documents, and other requirements for waste shipment.

APPENDIX C

LAUCKS TESTING LABORATORY
STANDARD OPERATING PROCEDURES

APPENDIX C

LAUCKS TESTING LABORATORY SOP TABLE OF CONTENTS

LTL-3011	Extraction Method for Chlorinated Herbicides in Soil
LTL-3112	Extraction Method for Total Petroleum Hydrocarbons in Soil
LTL-3303	Extraction Method for Organochlorine Pesticides and Polychlorinated Biphenyls in Soil
LTL-8013	Diesel Range Organics and Residual Range Organics by Modified SW-846 Method 8015
LTL-8084	Analysis of Organochlorine Pesticides and PCBs by SW-846 Methods 8081B and 8082A
LTL-8151	Analysis of Chlorinated Herbicides by SW-846 Method 8151A

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Book: 20 Assigned to: Tetra Tech

Extraction Method for Chlorinated Herbicides in Soil (8151A by Modified 3550C)

Method # LTL-3011

July 6, 2006

Revision Number: #6

Written by: B. O'Neill Date: 7-6-06

Reviewed by: Harry Pontberg Date: 7/19/06

Approved by: Hugh Prentice Date: 7/26/06

Controlled Document
Book: 20 Assigned to: Tetra Tech

1. **PURPOSE** - In this method, samples are first subjected to an alkaline hydrolysis. The sample is extracted while alkaline to remove extraneous materials. It is then acidified, forming the less polar species, which are extracted into ethyl ether. The extracts are derivatized with diazomethane and the methyl esters are isolated for analysis by GC/ECD.

2. **SAFETY** - During the conduct of this method, the extractionist will be exposed to a variety of reagent chemicals and solvents. The health effects of these various chemicals may be ascertained by reading the material safety data sheets (MSDS) available in the general files. Additionally, the samples, by their very nature, may contain significant levels of hazardous materials. It is incumbent on each extractionist to exercise due care and caution executing this method. The company will provide any protective equipment or clothing needed to assure employee safety.

3. **DEFINITIONS**

Method Blank – An analytical control consisting of all reagents and surrogate standards that is carried throughout the entire analytical procedure. The method blank is used to define the level of laboratory, background, and reagent contamination.

Method Blank Spike - An analytical control consisting of all reagents, target analytes, and surrogate standards that is carried throughout the entire analytical procedure.

Matrix Spike – Aliquot of a matrix spiked with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

Matrix Spike Duplicate – A second aliquot of the same matrix as the matrix spike that is spiked in order to determine the precision of the method.

Surrogates – Compounds added to each blank, blank spike, sample, matrix spike and spike duplicate to evaluate analytical efficiency by measuring recovery.

4. **MATERIALS**

4.1. All reagents are to be AR grade or better.

4.2. All solvents are to be distilled in glass unless otherwise noted.

4.3 The following special reagents should be prepared:

4.3.1. 37% Potassium Hydroxide - prepared by dissolving 370 grams potassium hydroxide pellets and diluting to one liter with DIW.

4.3.2. Concentrated Sulfuric Acid

4.3.3. 10% Hydrochloric Acid - measure 100 mL concentrated hydrochloric acid and dilute to 1000 mL with DIW. Note: Observe proper acid preparation techniques.

4.3.4. Anhydrous Sodium Sulfate - prepared by muffling AR grade sodium sulfate for four hours at 400°C.

4.3.5. Acidified Sodium Sulfate - Weigh the muffled anhydrous sodium sulfate in 100 gram increments into a suction flask. Cover the sodium sulfate with ethyl ether containing 0.1 mL concentrated sulfuric acid for each 100 g increment. Swirl the slurry for about two minutes then stopper the flask and apply an aspirator vacuum until the ether is completely removed . Place on a steam bath in a hood to assure that all ether is evaporated. Store in a closed bottle.

4.3.6. 10 M Potassium Hydroxide - prepared by dissolving 56.1 grams potassium hydroxide pellets and diluting to 100 mL with DIW.

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4.3.7. Diethylene Glycol Monoethyl Ether (Carbitol) – (Sigma – catalog # D-1265)

4.3.8. Diazald® (Aldrich - catalog # D2,800-0).

4.3.9. Activated Silicic Acid - activate 100 mesh silicic acid powder by heating for 16 hours at 130°C.

4.3.10. Surrogate solution prepared in methanol:

2,4-Dichlorophenyl Acetic Acid	5.0 µg/mL

4.3.11. Matrix Spiking solution prepared in methanol:

2,4,5-TP	0.8 µg/mL
2,4,5-T	0.8 µg/mL
Dicamba	0.8 µg/mL
Dinoseb	0.8 µg/mL
Picloram	0.8 µg/mL
2,4-DB	0.8 µg/mL
2,4-D	0.8 µg/mL
Dichloroprop	0.8 µg/mL
Dalapon	0.8 µg/mL
MCPP	400 µg/mL
MCPA	400 µg/mL

4.3.12. By request: Matrix Spiking solution for PCP and HCP prepared in methanol:

Pentachlorophenol	0.5 µg/mL
Hexachlorophene	1.0 µg/mL

4.3.13. By request: Matrix Spiking solution for Appendix IX prepared in methanol:

2,4,5-TP	0.8 µg/mL
2,4,5-T	0.8 µg/mL
Dinoseb	0.8 µg/mL
2,4-D	0.8 µg/mL
Hexachlorophene	0.5 µg/mL

5. EQUIPMENT

5.1. Organomations Assoc., Inc. - N-EVAP, (nitrogen evaporator), Model 112

5.2. Standard laboratory glassware to include:

5.2.1. 40 mL Teflon culture tubes

5.2.2. 16 x 100 mm culture tubes

5.3. All glassware to be used shall be rinsed in the following manner:

5.3.1. 10% hydrochloric acid

5.3.1. Reagent grade acetone

5.4. Volumetric measurements are to be made with a calibrated fixed or adjustable volume microdispenser and individually calibrated vials.

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6. **SAMPLE COLLECTION & PRESERVATION** – Samples are normally collected in glass containers with Teflon-lined caps. All samples and sample extracts are stored at 4°C ± 2°C. Soil samples must be extracted within 14 days of collection.

7. **POLLUTION PREVENTION & WASTE MANAGEMENT** – Sample extracts, standards and solvent rinses are disposed of by depositing them in the hazardous waste container located in the solvent locker. Waste segregation and disposal from the point of collection is further covered in LTL-2001.

8. **PERSONNEL QUALIFICATIONS** – This method is restricted to use by, or under the supervision of, experienced chemist/extractionists who have demonstrated the ability to perform the described extraction procedures and techniques.

9. **QUALITY CONTROL** - The normal level of quality control will consist of blank, blank spike, matrix spike and matrix spike duplicate (MS and MSD). This is performed on a per batch basis to include no more than 20 samples. The level of quality control will be indicated to the extractionist at the time the job is assigned. These samples serve to provide a measure of the recovery efficiency for the analyte and to provide data for statistical evaluation of the sample. In those instances that a client requires additional or different quality control measures, the extractionist will be directed accordingly in writing.

10. **METHODOLOGY**

10.1. Sample Extraction:

10.1.1. Mix the sample thoroughly in its original container if there is space available, otherwise mix in solvent rinsed aluminum tray.

10.1.2. Weigh 15.0 grams of soil (wet weight) into an Teflon culture tube. Cover sample with DIW.

10.1.3. Prepare two additional aliquots of one sample, randomly selected or client designated, if quality control is required.

10.1.4. Prepare a blank and a blank spike with 10 mL. DIW.

10.1.5. Pipet 100 µl surrogate solution into each tube.

10.1.6. Pipet 500 µl matrix spiking solution into each QC tube.
(PCP/HCP: 250 µl)

10.1.7. Pipet 1.0 mL 37% potassium hydroxide into each culture tube, mix and loosely cap with Teflon screw cap.

10.1.8. Immerse tubes in a 60-65°C water bath for a minimum of 90 minutes.

10.1.9. Remove from bath and cool to room temperature.

10.1.10. Add 6-7 mL ethyl ether to each culture tube, cap tightly and shake for two minutes. Sonicate in water bath for 5-10 minutes. If emulsions occur, centrifuge tubes.

10.1.11. Draw off and discard ether layer.

10.1.12. Repeat from 10.1.10. two additional times using 3 mL ethyl ether.

10.1.13. Adjust pH to <2 by slowly adding 500µl concentrated sulfuric acid to each tube. Mix and check pH.

10.1.14. Repeat 10.1.10 three times using 3 mL ethyl ether and save ether into a 16 x 100 culture tube.

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10.2. Dehydration of the extract:

10.2.1. Adjust volume to 5-6 mL in the nitrogen blowdown.

10.2.2. Add 3 gm of acidified sodium sulfate to each tube, cap and shake.

10.2.3. Tap the tubes to settle the sodium sulfate and let stand at least 60 minutes and may stand overnight.

10.2.4. Transfer ether extract to 16 x 100 culture tube.

10.2.5. Add 1-2 mL ether to acidified sodium sulfate, cap and shake to break up sodium sulfate.

10.2.6. Transfer rinse to tube containing the ether extract.

10.2.7. Repeat from 10.2.5. two additional times.

10.2.8. Gently reduce the volume to approx. 1 mL in the nitrogen blowdown.

10.2.9. Bring to 2.0 mL with ethyl ether.

10.3. Derivatization:

10.3.1. To tube A (the first tube in the train), add 1.0 mL methanol, and bring to 8.0 mL with ethyl ether.

10.3.2. To tube B add:

10.3.2.1. 2.0 mL 10 M potassium hydroxide

10.3.2.2. 1.4 mL Carbitol (diethylene glycol monoethyl ether)

10.3.3. Place 10 µl micro-pipet in each sample tube from 10.2.9.

10.3.4. Connect nitrogen line to the apparatus and regulate so that tube A bubbles actively but not violently.

10.3.5. Add 2 scoops (approximately 0.1-0.2 grams) of Diazald and 1.4 mL ethyl ether to tube B. Stopper, connecting tube A to tube B.

10.3.6. Bubble the generated diazomethane into the sample tube for 90 seconds. (Extract will turn bright yellow.)

10.3.7. Let extract stand for 15 minutes.

10.3.8. Add 0.1 - 0.2 gm. activated silicic acid to each culture tube. Allow to stand until evolution of nitrogen gas has stopped. This may take several hours and may be stored overnight.

10.3.9. Adjust the final volume to 5.0 mL (as compared to a measured volume) with hexane and centrifuge.

10.3.10. Label the extract and deliver to 940.

10.3.11. Complete all the necessary paperwork and bench sheet Bench sheet should include bottle #, extraction solvent and final solvent lot #s, start and completion (to 940) date and time and extract location. Place folder in GC room extraction folder box.The file folder color will be yellow, and the blank name will be ____GHB.SL_.

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11. **TROUBLESHOOTING** - Please refer to Organic Extractions Troubleshooting Manual for detailed instructions on troubleshooting.

12. **REFERENCES** - The following USEPA methods are the official methods on which this Laucks Testing Laboratory method is based. The primary methods are those which most closely parallel the Laucks procedure and are referenced by their USEPA series and number. In those instances for which there are no official EPA methods, the most suitable reference is given under the miscellaneous references section. The additional reference section cites those methods which contain additional information. These methods will frequently be official methods, which apply in part to, or support the Laucks method.

PRIMARY REFERENCES:

Test Methods for Evaluating Solid Waste, USEPA, SW-846.

3550C (2001), 8151A (1996)

Extraction Method for Total Petroleum Hydrocarbons in Soil
(Modified 8015 by 3545A)

Method # LTL-3112

July 10, 2006

Revision Number: #6

Written by: B. Ogiea Date: 7-10-06

Reviewed by: Harry Romberg Date: 7/20/06

Approved by: Hugh Prentice Date: 7/26/06

UNCONTROLLED

1. **PURPOSE** - In this method, diesel and residual range total petroleum hydrocarbons are extracted from soils with methylene chloride. The extract is dried and concentrated in a Kuderna-Danish (K-D) apparatus. The extract is then screened by GC using a flame ionization detector (FID). This method also includes Low Concentration and silica gel cleanup.

2. **SAFETY** - During the conduct of this method, the extractionist will be exposed to a number of reagent chemicals and solvents. The health effects of these various chemicals may be ascertained by reading the material safety data sheets (MSDS) available in the general files. Additionally, the samples, by their very nature may contain significant levels of hazardous materials. It is incumbent on each extractionist to exercise due care and caution executing this method. The company will provide any protective equipment or clothing needed to assure employee safety.

3. **DEFINITIONS**

Method Blank – An analytical control consisting of all reagents and surrogate standards that is carried throughout the entire analytical procedure. The method blank is used to define the level of laboratory, background, and reagent contamination.

Method Blank Spike - An analytical control consisting of all reagents, target analytes, and surrogate standards that is carried throughout the entire analytical procedure.

Matrix Spike – Aliquot of a matrix spiked with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

Matrix Spike Duplicate – A second aliquot of the same matrix as the matrix spike that is spiked in order to determine the precision of the method.

Surrogates – Compounds added to each blank, blank spike, sample, matrix spike and spike duplicate to evaluate analytical efficiency by measuring recovery.

4. **REAGENTS**

4.1. All reagents are to be AR grade or better.

4.2. All solvents are to be distilled in glass, unless otherwise noted.

4.3. The following special reagents should be prepared:

4.3.1. Anhydrous sodium sulfate - prepared by muffling AR grade sodium sulfate for four hours at 400°C.

4.3.2. Accusand – prepared by soxhleting for 8 hours in methylene chloride to remove color, followed by muffling for four hours at 400°C.

4.3.3. Diesel Range (DRO) surrogate solution prepared in methylene chloride:

2-Fluorobiphenyl	1,000 µg/mL
o-Terphenyl	1,000 µg/mL

4.3.4. Diesel Range (DRO) matrix spiking (MS) solution prepared in methylene chloride:

Diesel	10,000 µg/mL

4.3.5. Residual Range (RRO) surrogate solution prepared in methylene chloride:

n-Octacosane	800 µg/mL

4.3.6. Residual Range (RRO) matrix spiking (MS) solution prepared in methylene chloride:

Motor Oil	50,000 µg/mL

5. **EQUIPMENT**

5.1. Dionex Accelerated Solvent Extractor - Model ASE 200 - Maintain per manufacturer's instructions.

5.1.1. 33 mL sample cells

5.1.2. Cellulose filters

5.2. Organomations Assoc., Inc. - N-EVAP, (nitrogen evaporator), Model 112

5.3. Analytichem International - Vac Elut SPS 24 (Vacuum Manifold)

5.4. Standard laboratory glassware to include:

5.4.1. 8 ounce extraction bottles

5.4.2. Small filling funnels

5.4.3. 60 mL collection vials

5.4.4. K-D apparatus: 250 mL K-D flask, 10 mL or 25 mL ampule and three-ball Snyder column.

5.5. All glassware to be rinsed as follows, prior to use:

5.5.1. Technical grade acetone (if the glassware is wet).

5.5.2. Triple rinsed with methylene chloride.

5.6. Silica SPE columns with teflon frits (1000 mg) – Restek

5.7. Volumetric measurements are to be made with a calibrated fixed or adjustable volume microdispenser and individually calibrated vials.

6. **SAMPLE COLLECTION & PRESERVATION** – Samples are normally collected in glass containers with Teflon-lined caps. All samples and sample extracts are stored at 4°C ± 2°C. Soil samples must be extracted within 14 days of collection.

7. **POLLUTION PREVENTION & WASTE MANAGEMENT** – Sample extracts, standards and solvent rinses are disposed of by depositing them in the hazardous waste container located in the solvent locker. Waste segregation and disposal from the point of collection is further covered in LTL-2001.

8. **PERSONNEL QUALIFICATIONS** – This method is restricted to use by, or under the supervision of, experienced chemist/extractionists who have demonstrated the ability to perform the described extraction procedures and techniques.

9 **QUALITY CONTROL** - The normal level of quality control will consist of blank, blank spike, matrix spike and matrix spike duplicate (MS and MSD). This is performed on a per batch basis to include no more than 20 samples. The level of quality control will be indicated to the extractionist at the time the job is assigned. These samples serve to provide a measure of the recovery efficiency for the analyte and to provide data for statistical evaluation of the sample. In those instances that a client requires additional or different quality control measures, the extractionist will be directed accordingly in writing.

10. METHODOLOGY

10.1. Sample Extraction

10.1.1. Mix sample thoroughly in its original container if there is space available otherwise mix in solvent rinsed aluminum tray.

10.1.2. Weigh 10.0 grams of soil (wet weight) into a extraction bottle.
(Low Conc.: 20.0 grams)

10.1.3. Prepare two additional aliquots of one sample, randomly selected or client designated, if quality control is required. Prepare separate MS/MSD for DRO and RRO.

10.1.4. Add 10 grams sodium sulfate and mix well to give the soil a sandy texture.

10.1.5. Insert cellulose filter into bottom of sample cell.

10.1.6. Using a small filling funnel, add approximately one gram sand to bottom of sample cell

10.1.7. Transfer sample to cell.

10.1.8. Prepare a blank and a blank spike with sodium sulfate. Prepare a separate blank spike for DRO and RRO.

10.1.9. Pipet 100 µl of DRO and/or RRO surrogate solution to each cell.
(Low Conc.: 40 µl of DRO and/or 50 µl RRO surrogate solution)

10.1.10. Pipet 100 µl of DRO and/or RRO matrix spiking solution to each QC cell.
(Low Conc.: 50 µl DRO and/or RRO matrix spiking solution.)

10.1.11. Fill cell to within 1 cm of top with sand or sodium sulfate and cap.

10.1.12. Fill solvent reservoir with methylene chloride.

10.1.13. Align trays and start.

10.2. Solvent dehydration

10.2.1. Prepare a stainless steel funnel by plugging with glass wool and filling 1/4 full with sodium sulfate.

10.2.2. Pre-rinse the sodium sulfate by passing 40 mL methylene chloride through the prepared funnel.

10.2.3. Pass the extract from 10.1.13. through the funnel and collect in an assembled K-D apparatus.

10.2.4. Rinse the collection vessel with several 10 mL methylene chloride rinses.

10.2.5. Rinse the sodium sulfate with 25 mL of methylene chloride.

10.3. Solvent evaporation

10.3.1. Assemble the full K-D apparatus with a Snyder column prewet with 2-3 mL of methylene chloride.

10.3.2. Immerse K-D into a hot water bath using a bath temperature of 90°C, with a long ampule immersed to a depth of 8 mL. Regulate the evaporation time to take approx. 20 minutes.

10.3.3. Reduce the volume to 4-5 mL, remove the apparatus from the water bath, and cool to room temperature.

10.3.4. Rinse joint and remove Snyder column. Allow the rinse solvent to drain into the ampule.

10.3.5. Remove the ampule clamp and wipe the joint with a Kimwipe. Separate the ampule and rinse the joint with a small amount of solvent.

10.3.6. Reduce the extract volume to less than 4 mL in a nitrogen blowdown. Transfer extract to a 16 x 100 mm culture tube and adjust to a final volume of 5.0 mL (as compared to a measured volume) with methylene chloride. Proceed to 10.4.9.

10.3.7. Low Conc.: Reduce the extract volume to less than 2 mL in a nitrogen blowdown. Transfer extract to a 4 mL vial and adjust to a final volume of 2.0 mL (as compared to a measured volume) with methylene chloride. Proceed to 10.4.10.

NOTE: Low Conc.: If client requested cleanup is required, reduce the extract volume to approx. 1 mL in a nitrogen blowdown and proceed to silica gel cleanup.

10.4. Silica Gel Clean Up (3630C) – Client requested only.

10.4.1. Attach the vacuum manifold to the vacuum pump with a trap in between. Place a labeled 16 x 100 mm culture tube in the proper collection slot. Secure the manifold with the straps and move the manifold to the waste position. Adjust the vacuum pressure in the manifold to between five and ten pounds of vacuum.

10.4.2. Place one silica column into the vacuum manifold.

10.4.3. Start the vacuum and prewet the column with methylene chloride by passing at least 5 mL through the column. Do not allow the column to go dry after wetting.

10.4.4. Release the vacuum, and move the manifold to the collect position.

10.4.5. Add 1.0 mL extract from 10.3.6. or 10.3.7. to the top frit of the silica column.

10.4.6. Restore the vacuum, and elute the column with 8-9 mL of methylene chloride. Allow the column to go dry.

10.4.7. Release the vacuum, and move the manifold to the waste position. Remove and discard the used silica column.

10.4.8. Reduce the extract volume to less than 1 mL in a nitrogen blowdown. Transfer extract to a 1.8 mL vial tube and adjust to 1.0 mL. (Final volume will be recorded as 5.0 mL.) Low Conc. final volume is adjusted to 2.0 mL in methylene chloride (as compared to a measured volume).

10.4.9. Label the extract and deliver to 940.

10.4.10. Complete all paperwork and bench sheet. Bench sheet should include bottle #, extraction solvent and final solvent lot #s, sodium sulfate lot #, cleanup method # if indicated, silica lot #, start and completion (to 940) date and time and extract location. Place folder in GC room extraction folder box. The file folder color will be green and the blank name will be ___GSV.SL_.

11. **TROUBLESHOOTING -** Please refer to Organic Extractions Troubleshooting Manual for detailed instructions on troubleshooting.

12. **REFERENCES** - The following USEPA methods are the official methods on which this Laucks Testing Laboratory method is based. The primary methods are those which most closely parallel the Laucks procedure and are referenced by their USEPA series and number. In those instances for which there are no official EPA methods, the most suitable reference is given under the miscellaneous references section. The additional reference section cites those methods which contain additional information. These methods will frequently be official methods, which apply in part to, or support the Laucks method.

PRIMARY REFERENCES:

Test Methods for Evaluating Solid Waste, USEPA, SW-846.

3545A (1998), 3630C (1996)

Controlled Document

Book: 20 Assigned to: Tetra Tech

Extraction Method for Organochlorine Pesticides and Polychlorinated Biphenyls in Soil (8081B/8082A by 3545A)

Method # LTL-3303

July 11, 2006

Revision Number: #5

Written by: B. O'Quiee Date: 7-11-06

Reviewed by: Harry Romberg Date: 7/20/06

Approved by: Hugh Prentice Date: 7/26/06

Controlled Document
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1. **PURPOSE** - In this method organochlorine pesticides and polychlorinated biphenyls are extracted from neutral soil with a mixture of methylene chloride and acetone. The extract is dehydrated and concentrated in a Kuderna-Danish (K-D) apparatus. Pesticide/PCB extracts are GPC cleaned prior to analysis by GC. The PCB only extracts are sulfuric acid cleaned prior to analysis by GC.

2. **SAFETY** - During the conduct of this method, the analyst will be exposed to a variety of reagent chemicals and solvents. The health effects of these various chemicals may be ascertained by reading the material safety data sheets (MSDS) available in the general files. Additionally, the samples, by their very nature, may contain significant levels of hazardous materials. It is incumbent on each analyst to exercise due care and caution executing this method. The company will provide any protective equipment or clothing needed to assure employee safety.

3. **DEFINITIONS**

Method Blank – An analytical control consisting of all reagents and surrogate standards that is carried throughout the entire analytical procedure. The method blank is used to define the level of laboratory, background, and reagent contamination.

Method Blank Spike - An analytical control consisting of all reagents, target analytes, and surrogate standards that is carried throughout the entire analytical procedure.

Matrix Spike – Aliquot of a matrix spiked with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

Matrix Spike Duplicate – A second aliquot of the same matrix as the matrix spike that is spiked in order to determine the precision of the method.

Surrogates – Compounds added to each blank, blank spike, sample, matrix spike and spike duplicate to evaluate analytical efficiency by measuring recovery.

4 **REAGENTS**

4.1. All reagents are to be AR grade or better.

4.2. All solvents are to be distilled in glass, unless otherwise noted.

4.3. The following special reagents should be prepared:

4.3.1. 1:1 methylene chloride/acetone (v/v)- prepared by mixing equal volumes of the solvents.

4.3.2. Anhydrous sodium sulfate - prepared by muffling AR grade sodium sulfate for four hours at 400°C.

4.3.3. Concentrated Sulfuric Acid

4.3.4. Accusand – prepared by soxhleting for 8 hours in methylene chloride to remove color, followed by muffling for four hours at 400°C.

4.3.5. Surrogate solution prepared in acetone:

2,4,5,6-Tetrachloro-m-xylene	1.0 µg/mL
Decachlorobiphenyl	1.0 µg/mL

4.3.6. Pesticide matrix spiking solution prepared in acetone:

4,4'-DDD	2.0 µg/mL
4,4'-DDE	2.0 µg/mL
4,4'-DDT	2.0 µg/mL

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Aldrin	1.0 µg/mL
alpha-BHC	1.0 µg/mL
alpha-Chlordane	1.0 µg/mL
beta-BHC	1.0 µg/mL
delta-BHC	1.0 µg/mL
Dieldrin	2.0 µg/mL
Endosulfan I	1.0 µg/mL
Endosulfan II	2.0 µg/mL
Endosulfan sulfate	2.0 µg/mL
Endrin	2.0 µg/mL
Endrin aldehyde	2.0 µg/mL
Endrin Ketone	2.0 µg/mL
gamma-BHC	1.0 µg/mL
gamma-Chlordane	1.0 µg/mL
Heptachlor	1.0 µg/mL
Heptachlor epoxide	1.0 µg/mL
Methoxychlor	10 µg/mL

4.3.7. PCB (AR1660) matrix spiking solution prepared in acetone:

Aroclor 1016	25 µg/mL
Aroclor 1260	25 µg/mL

Additional matrix spiking solutions such as Toxaphene, Chlordane and other Aroclors available on request.

5. EQUIPMENT

5.1. Dionex Accelerated Solvent Extractor - Model ASE 200 - Maintain per manufacturer's instructions.

5.1.1. 33 mL sample cells

5.1.2. Cellulose filters

5.2. Analytical Biochemical Laboratories, Inc. (ABC) Model 1002B or Model 1000 Gel-Permeation Chromatography (GPC)

5.3. Organomations Assoc., Inc. - N-EVAP (nitrogen evaporator), Model 112

5.4. Standard laboratory glassware to include:

5.4.1. 8 ounce extraction bottles

5.4.2. Small filling funnels

5.4.3. 60 mL collection vials

5.4.4. K-D apparatus: 250 mL K-D flask, 10 mL or 25 mL ampule and three-ball Snyder column.

5.5. All glassware and sample cells to be rinsed as follows, prior to use:

5.5.1. Technical grade acetone (if the glassware is wet).

5.5.2. Triple rinsed with methylene chloride.

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5.6. Volumetric measurements are to be made with a calibrated fixed or adjustable volume microdispenser and individually calibrated vials.

6. **SAMPLE COLLECTION & PRESERVATION** – Samples are normally collected in glass containers with Teflon-lined caps. All samples and sample extracts are stored at 4°C ± 2°C. Soil samples must be extracted within 14 days of collection.

7. **POLLUTION PREVENTION & WASTE MANAGEMENT** – Sample extracts, standards and solvent rinses are disposed of by depositing them in the hazardous waste container located in the solvent locker. Waste segregation and disposal from the point of collection is further covered in LTL-2001.

8. **PERSONNEL QUALIFICATIONS** – This method is restricted to use by, or under the supervision of, experienced chemist/extractionists who have demonstrated the ability to perform the described extraction procedures and techniques.

9. **QUALITY CONTROL** - The normal level of quality control will consist of blanks, blank spikes, matrix spikes and matrix spike duplicates (MS and MSD). This is performed on a per batch basis to include no more than 20 samples. The level of quality control will be indicated to the extractionist at the time the job is assigned. These samples serve to provide a measure of the recovery efficiency for the analyte and to provide data for statistical evaluation of the sample. In those instances that a client requires additional or different quality control measures, the extractionist will be directed accordingly in writing.

   At least once every two years, performance of Toxaphene, Chlordane and all Aroclors, excluding 1016/1260, will be demonstrated with a blank spike, matrix spike and matrix spike duplicate (MS and MSD).

10. **METHODOLOGY**

10.1. Sample Extraction

10.1.1. Mix sample thoroughly in its original container if there is space available otherwise mix in solvent rinsed aluminum tray.

10.1.2. Weigh 15.0 grams of soil (wet weight) into a extraction bottle.

10.1.3. Prepare two additional aliquots of one sample, randomly selected or client designated, if quality control is required. Prepare separate MS/MSD for Pesticides and PCB.

10.1.4. Add 10 grams sodium sulfate and mix well to give the soil a sandy texture.

10.1.5. Insert cellulose filter into bottom of sample cell.

10.1.6. Using a small filling funnel, add approximately one gram sand to bottom of sample cell

10.1.7. Transfer sample to cell.

10.1.8. Prepare a blank and a blank spike with sodium sulfate. Prepare separate blank spike for Pesticides and PCB.

10.1.9. Pipet 100 µl surrogate solution to each cell.

10.1.10. Pipet 100 µl matrix spiking solution to each QC cell.

10.1.11. Fill cell to within 1 cm of top with sand or sodium sulfate and cap.

10.1.12. Fill solvent reservoir with 1:1 methylene chloride/acetone.

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10.1.13. Align trays and start.

10.2. Solvent dehydration

10.2.1. Prepare a stainless steel funnel by plugging with glass wool, and filling 1/4 full with sodium sulfate.

10.2.2. Pre-rinse the sodium sulfate by passing 40 mL methylene chloride through the prepared funnel.

10.2.3. Pass the extract from 10.1.13. through the funnel and collect in an assembled K-D apparatus.

10.2.4. Rinse the collection vessel with several 10 mL methylene chloride rinses.

10.2.5. Rinse the sodium sulfate with 25 mL of methylene chloride.

10.3. Solvent evaporation

10.3.1. Assemble the full K-D apparatus with a Snyder column prewet with 2-3 ml of methylene chloride.

10.3.2. Immerse K-D apparatus into a hot water bath, using a bath temperature of 90°C, with a long ampule immersed to a depth of 12 mL. Regulate the evaporation time to take approx. 30 minutes.

10.3.3. Reduce the volume to 4-5 mL, remove the apparatus from the water bath and cool to room temperature.

NOTE: PCB Only: Reduce the volume to 4-5 mL and proceed to solvent exchange, 10.3.8.1. Bring to final volume of 5.0 mL in hexane. The solvent exchange step must be tested. Take 1 mL extract, 1 ml sulfuric acid and vortex. Check for volume changes between layers. If exchange is complete, proceed to 10.4.

10.3.4. Rinse joint and remove Snyder column. Allow rinse solvent to drain into ampule.

10.3.5. Remove the ampule clamp, and wipe the joint with a Kimwipe. Separate the ampule and rinse the joint with a small amount of solvent.

10.3.6. Pesticides/PCB: Reduce the extract volume to less than 8 mL on a nitrogen blowdown. Transfer extract to a 16 x 100 mm culture tube, and adjust to 10.0 mL intermediate volume (as compared to a measured volume) with methylene chloride.

10.3.7. At this point the extract will be GPC cleaned (3640A) -- see Method # LTL-3692.

10.3.8. K-D the GPC cleaned extract to 4-5 mL and exchange into hexane as follows:

10.3.8.1. Add 2-3 mL hexane through the top of the Snyder column while the ampule is still immersed in the water bath. Reduce to 4-5 mL.

10.3.8.2. Repeat 10.3.8.1. two additional times.

10.3.9. Remove the apparatus from the water bath and cool to room temperature.

10.3.10. Rinse joint with hexane and remove Snyder column. Allow rinse solvent to drain into ampule.

10.3.11. Remove the ampule clamp, and wipe the joint with a Kimwipe. Separate the ampule and rinse the joint with a small amount of hexane.

10.3.12. Reduce the extract to less than 2 mL in a nitrogen blowdown. Transfer extract to a 4.0 mL vial and adjust to a final volume of 2.5 mL (as compared to a measured volume) in hexane. Proceed to 10.4.4. PCB only final volume will be 5.0 mL in a 16 x 100 mm culture tube.

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10.4. Sulfuric Acid Cleanup (3665A) (PCBs only)

10.4.1. Add 2.0 mL concentrated sulfuric acid and vortex for 30 - 60 seconds.

10.4.2. Let stand for a few minutes to allow layers to separate. May be centrifuged.

10.4.3. Label the extract and deliver to 940.

10.4.4. Complete all necessary paperwork and bench sheet. . Bench sheet should include bottle #, extraction solvent and final solvent lot #s, sodium sulfate lot #, cleanup method #, GPC calibration date, start and completion (to 940) date and time and extract location. Place folder in GC room extraction folder box. The file folder color will be purple and the blank name will be ____GPX.SL_. PCB only will be a orange folder and the blank name will be ___GPB.SL_.

11. **TROUBLESHOOTING -** Please refer to Organic Extractions Troubleshooting Manual for detailed instructions on troubleshooting.

12. **REFERENCES** - The following USEPA methods are the official methods on which this Laucks Testing Laboratory method is based. The primary methods are those which most closely parallel the Laucks procedure and are referenced by their USEPA series and number. In those instances for which there are no official EPA methods, the most suitable reference is given under the miscellaneous references section. The additional reference section cites those methods which contain additional information. These methods will frequently be official methods, which apply in part to, or support the Laucks method.

PRIMARY REFERENCES:

Test Methods for Evaluating Solid Waste, USEPA, SW-846

8081B (2001), 8082A (2001), 3545A (1998), 3640A (1994), 3665A (1996)

Uncontrolled Document

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-8013

Title: Diesel Range Organics (DRO) and Residual Range Organics (RRO) by Modified SW 8015B

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1. Introduction and Scope

1.1 Method Description

1.1.1 Modified SW 8015B is used in the determination of Diesel Range Organics (DRO) and Residual Range Organics (RRO), including jet fuels, in soil, sediment and aqueous matrices. Diesel Range Organics are defined as the carbon range of C_{12} to C_{24} alkanes. Residual Range Organics are defined as the carbon range of C_{24} to C_{40} alkanes.

1.1.2 Samples are extracted into solvent, and then analyzed by gas chromatography using a single column to separate all sample components using the flame ionization detector (FID). Quantitation of the DRO and RRO range organics is accomplished by integrating to the baseline as a group, based on the area of the components.

1.1.3 This method is restricted to use by, or under the supervision of analysts experienced in the use of gas chromatography, Flame Ionization Detector (FID), and in the interpretation of chromatograms. Each analyst performing this method must have demonstrated the ability to perform the described chromatographic analysis and data interpretation.

1.2 Deviations

1.2.1 This SOP defines the retention time of DRO to be determined by the retention time of C_{12} and C_{24} alkanes. This is a deviation from the SW 8015 Method as it defines the retention time range of DRO as the retention times of the C_{10} and C_{28} alkanes. This deviation is due to client preference.

1.3 Interferences

1.3.1 In cases where samples contain a significant amount of naturally occurring non-petroleum organics, which may contribute to interferences, the samples may be cleaned with sulfuric acid to assist in the reduction or elimination of the interferences.

1.3.2 Contamination by carryover can occur when low concentration samples are analyzed immediately after a high concentration sample. Whenever an unusually high concentration sample is encountered, it should be followed by an injection of a solvent blank to check for cross contamination.

1.4 Sample Collection, Sample Storage, Holding Times

1.4.1 Waters

1.4.1.1 Samples are collected in glass jars with Teflon-lined lids.

1.4.2 Soils

1.4.2.1 Soils or sediments may be collected in glass jars, with Teflon-lined lids.

1.4.2.2 The samples are stored at 4° ± 2°C. The holding time from collection to extraction is 7 days for waters and 14 days for soils. The holding time for analysis is 40 days from collection.

1.5 Definition of Terms

1.5.1 This section defines terms and acronyms as they are used in this SOP. Other terms, such as MS/MSD or method blank, are not defined here since it is assumed that the user of this SOP already understands their more general meaning.

Blank spike	A background free matrix (DIW for water, clean sand for soils/sediments) to which known amounts of target analytes and surrogates are added each time sample extracts are prepared. In the context of this SOP, a blank spike is the same as a QC check standard. See also QC check standard.
CCV	Continuing calibration verification or also known as the calibration verification standard. This is a standard analyzed at some prescribed frequency during the analysis sequence to verify that the instrument has remained in calibration.
CF	Calibration factor. The ratio of analyte instrument response to nanograms injected. This term is defined in SW 846.
Corr Coef, CC	Correlation coefficient. A measure of the "goodness of fit" of a set of data to a regression model. The closer the value is to 1, the higher the degree of confidence in the correlation.
DCV	Daily Calibration Verification. A standard injected at the start of each QC period that is compared to the initial multi-point calibration to determine whether the instrument is still in calibration.

DIW	Deionized water. Lab reagent water. Organic-free water. Since the systems used to provide DIW at Laucks all contain carbon-polishing filters, they are capable of providing organic-free water for use in method blanks and method blank spikes.
ICV	Initial Calibration Verification. Also known as the second source standard. A standard obtained from a second source that is analyzed subsequent to each initial multi-point calibration to verify the validity of the standards.
MDL	Method detection limit. The lowest concentration in a sample which will yield a positive result that is greater than zero at a known level of confidence. MDLs are empirically determined by Laucks.
PQL or Reporting Limit	Practical Quantitation Limit or Reporting Limit- The value used when reporting a non-detect. It may be administratively, empirically or contractually set.
QC check standard	Quality control check standard. Referred to in this SOP as a blank spike or LFB. A QC check standard is a requirement of SW 846 method 8000 and is used to determine whether the analytical system is in control if MS/MSD recoveries are out of control. See also blank spike.
QC period	Quality control period. An analysis sequence initiated by the analysis of one or more standards, followed by sample or extracts, and terminated with a standard analysis. A QC period can be open-ended chronologically, but calibration verification must be documented using the procedures in this SOP.
RSD or %RSD	Relative standard deviation or percent relative standard deviation. The ratio of the standard deviation of a set of values to the mean of the set of values expressed as a percentage. A measure of the similarity of the values one to another.
RT, Retention time	The time (in minutes) at which a target analyte or surrogate elutes from a chromatography column.

RT window	Retention time window. A range for the semi-volatile petroleum product is determined by the analysis of the Retention Time Standard.
Sequence	A set of samples, QC, and standards introduced into an instrument in a chronologically continuous group. See also QC period.

2. Equipment List and Standards

2.1 Chromatographic System

2.1.1 Gas Chromatograph: Hewlett Packard 5890 I or II including a GROB type split injection port, fitted with "Open-Top-Uniliner" style injection port liner, Restek, or equivalent. Alternatively, a split/splitless injection port (with splitless during injection).

2.1.2 Carrier, Make-up and Detector Gas: Helium 99.995% (high purity grade) or better, nitrogen (high purity), hydrogen (high purity), and air (Balston Zero Air Generator).

2.1.3 Column: 15 m x 0.53 mm x .15 µm film thickness, fused silica capillary column (J&W DB-1 or Restek XTI-5, or equivalent. Alternatively, a 30-m x 0.25 mm x .15 µm film thickness RTX-5 or equivalent.

2.1.4 Autosampler: Hewlett Packard model 7673 or equivalent.

2.1.5 Detectors: FID

2.1.6 Data System: EZChrom data acquisition software, version 6.6. Target analytical software, version 4.03.

2.1.7 Miscellaneous: Assorted calibrated syringes, caps, septa, injection port liners, solvents, ferrules, and assorted supplies.

2.2 Standards

2.2.1 Overview of Standards Preparation

2.2.1.1 Standard information is stored electronically. All standards are assigned a unique identifier to enable cross-referencing of each individual standard back to the supplier's lot number. In addition, all standards are labeled with the standard concentration, the

solvent, date prepared, expiration date, analyst's initials, and the standard reference number. Refer to Laucks' SOP on the traceability, documentation, and preparation of standards.

2.2.1.2 If starting with a neat material, a measured amount of the neat chemical is placed in a glass volumetric and diluted to volume with methylene chloride, then stoppered. For example 250 mg of neat material diluted into 25 mL of methylene chloride yields an intermediate solution of 10,000 µg/mL. Stock solutions are stored for a time period not to exceed one year or the manufacturer's expiration date, whichever is sooner. Working solutions are stored for a time period not to exceed six months or the manufacturer's expiration date, whichever is sooner.

2.2.1.3 All standard solutions are stored in the freezer at -10°C to -20°C. Prior to daily and initial calibration standard preparation, the standard solutions are removed from the freezer and allowed to warm to room temperature.

2.2.1.4 Refer to Appendix II for a listing of the PQL. The ICAL range is described in 2.2.3.2 and 2.2.4.2 below.

2.2.2 Preparation of Surrogates

2.2.2.1 The surrogates are purchased as neat material. 0.1 g of the neat chemical is placed in a 10-mL glass volumetric and diluted to volume with methylene chloride, then stoppered. This solution yields a concentration of 10,000 µg/mL.

Surrogate Standards	Source*	Cat. #	Conc.
2-Fluorobiphenyl	Restek	31096	10,000 PPM
o-Terphenyl	Restek	31097	10,000 PPM
Octacosane	Restek	31672	10,000 PPM
* or equivalent			

2.2.3 Preparation of Initial Calibration Standards (DRO)

2.2.3.1 Certified solutions are purchased at concentration levels of 50,000 µg/mL each.

Standard	Source*	Cat. #	Conc. (µg/mL)
#2 Diesel Composite	Restek	31258	50,000
* or equivalent			

Standard	Second Source*	Cat. #	Conc. (µg/mL)
#2 Diesel Composite	Ultra Scientific	RGO-616	50,000
* or equivalent			

2.2.3.2 The initial calibration standards range from 50 µg/mL to 2000 µg/mL. The standards are prepared by diluting into methylene chloride.

2000 PPM Standard

Diesel Standards	Initial Conc.	Aliquot	Final Volume	Final Concentration
Diesel	50,000 PPM	400 µL	10 mL	2000 PPM
o-Terphenyl	10,000 PPM	200 µL	10 mL	200 PPM
2-Fluorobiphenyl	10,000 PPM	200 µL	10 mL	200 PPM

250 PPM Standard (CCV)

Diesel Standards	Initial Conc.	Aliquot	Final Volume	Final Concentration
Diesel	50,000 PPM	50 µL	10 mL	250 PPM
o-Terphenyl	10,000 PPM	20 µL	10 mL	20 PPM
2-Fluorobiphenyl	10,000 PPM	20 µL	10 mL	20 PPM

Initial Calibration Levels (PPM)

Compound	MDL	1	2	3	4	5	6
Dilution factor → required when using 2000 PPM diesel standard and 200 PPM surrogate standard to obtain concentrations tabulated below.	100	40	20	10	4	2	Full

Compound	MDL	1	2	3	4	5	6
Diesel	20	50	100	200	500	1000	2000
o-Terphenyl	2	5	10	20	50	100	200
2-Fluorobiphenyl	2	5	10	20	50	100	200

2.2.4 Preparation of Initial Calibration Standards (RRO)

2.2.4.1 The RROs are purchased as neat material. An oil composite mixture is prepared by combining 1 mL of each source listed below. The stock standard is prepared by diluting 2.5 gram into 50 mL of methylene chloride. This yields a concentration of 50,000 µg/mL. This standard is stored for a time period not to exceed six months.

Standards*	Conc.
Pennzoil 10W-40	Neat
Valvoline 10W-30	Neat
* or equivalent	

Standard*	Second Source	Catalog #	Concentration
Motor Oil	Restek	31464	50,000 PPM
* or equivalent			

CCV Standard

Oil Standard	Initial Conc.	Aliquot	Final Volume	Final Concentration
Oil	50,000 PPM	400 µL	10 mL	2000 PPM

2.2.4.2 The initial calibration standards for the RROs range from 200 µg/mL to 5,000 µg/mL. The standards are prepared by diluting into methylene chloride as tabulated below.

Initial Calibration Levels (PPM)

Compound	MDL	1	2	3	4	5	6
Oil	100	200	500	1000	2000	2500	5000

2.2.5 Preparation of Continuing Calibration Standards

2.2.5.1 The continuing calibration verification standard (CCV) is prepared at the same concentration level as the mid-range standard in the initial calibration. The continuing calibration standard is used to verify the accuracy of the initial calibration.

2.2.6 Preparation of Retention Time Window Standard

2.2.6.1 The alkanes C_8, C_{10}, C_{12}, C_{14}, C_{16}, C_{18}, C_{20}, C_{22}, C_{24}, C_{26}, C_{28}, C_{30}, C_{32}, C_{34}, C_{36}, C_{38}, and C_{40} are purchased from Restek as a certified composite solution at a concentration level of 500 µg/mL. The alkane C_{25} and toluene are purchased as neat materials. The neats are prepared into stock standards by diluting 1 gram of neat into 100 mL of methylene chloride. This yields a concentration of 10,000 µg/mL. The retention time window standard is prepared by diluting 1.0 mL of the alkanes purchased solution (at 500 µg/mL) and 50 µl of the prepared alkane (at 10,000 µg/mL) into 10 mL of methylene chloride. This yields a concentration of 50 µg/mL. This solution is for qualitative use only and can be stored indefinitely.

2.3 Routine Safety Precautions

2.3.1 All standards and sample extracts should be handled as if they contain hazardous substances.

2.3.2 Refer to the instrument manufacturer's manual for routine instrument precautions.

2.3.3 Routine precautions include an awareness of the moving parts on the instrument you're using. These parts are often charged with power from an electrical component or with high-pressure gas and have the potential to do harm if not used properly.

2.3.4 Electrical shock - All instruments present the possibility of electrical shock. The operator should take all precautions including ensuring that all instruments are operated with fully grounded power outlets, turning off the instrument and disconnecting the instrument from the electrical power supply before working on any electrical components, etc.

2.3.5 Analysts should take the proper precautions such as wearing gloves when working with suspect samples or high level standards or solvents. Additionally, a respirator should be worn and a fume hood utilized for extremely hazardous compounds.

2.4 Waste disposal

2.4.1 Waste solvents and expired standards are disposed of in the appropriate waste solvent container located in the prep area under the hood.

2.4.2 Solid sample matrices are disposed of in appropriate drums labeled for this specific purpose where they are routinely picked up by an approved agency for final disposal.

2.4.3 Waste segregation and disposal from the point of collection is further covered in the Laucks SOP on Waste Segregation and Disposal.

3. Operation procedures

3.1 Analytical Conditions

GC Parameters*		Alternate
Initial GC Temperature:	50°C	50°C
Initial Hold Time:	2 min	1 min
Ramp Rate:	12°C/min	10°C/min
Final Temperature:	360°C	340°C
Final Time:	5.0 min	8.0 min
Run Time:	30.0 min	38.0 min
Injector Temperature:	300°C	300°C
Detector Temperature:	350°C	350°C
Injection Volume:	1 µL	2 µL
Gas Flow Rates (mL/min.)		
Helium:	8-10	1-2
Nitrogen make-up:	15-20	20 -25
Split vent:	20-30	
Hydrogen:	35	35
Air:	250	200

* or equivalent

3.2 Method Detection Limit Study

3.2.1 Prior to the analysis of any samples, it is necessary to establish method detection limits. This procedure is fully described in Laucks SOP LTL-1011. Briefly, it involves the analysis of 7 replicate samples spiked at a concentration near the anticipated method detection limit. A Student's T-test is then applied to these measured values to calculate

the MDL. Current MDL values are found in the iLIMS MDL database and associated raw data are stored in department files. They are also located in Appendix II.

3.3 Method Validation

3.3.1 Prior to the analysis of any samples, it is necessary to validate the method. A method validation study is performed in a similar manner to an MDL study with the exception that a minimum of 4 replicates are required and the concentration levels are typically 10-50 times the MDL. In the absence of criteria for the initial demonstration of proficiency, the limits of 70%- 130% can be used.

3.4 Retention Time Windows

3.4.1 Prior to the analysis of any samples, it is necessary to establish retention times windows for both analytes and surrogates. This is done by analyzing the Retention Time Window Standard over a 72-hour period. Serial injections performed over a time period less than 72 hours may result in retention time windows that are too tight. Refer Laucks SOP on the determination of RT windows.

3.4.2 The retention time window standard consists of $C_{12,}$ and C_{24} for the DRO-type petroleum products. The retention time window standard for the oil-type petroleum products consists of C_{24} and C_{40}. Analysis of the retention time standard is performed daily.

3.5 Initial Multi-Point Calibration

3.5.1 Analyze standard solutions using a minimum of 5 different concentration levels. The lowest concentration should be at a concentration near the reporting limit. The highest concentration should define the upper usable working range of the detector. Inject the standard solutions from the lowest concentration to the highest.

3.6 External Standard Calibration

3.6.1 External standard initial calibration data can be evaluated in one of 3 ways: %RSD of the calibration factors, correlation coefficient of a linear regression analysis, coefficient of determination of a non-linear regression analysis.

CFs are calculated using the equation:

$$CF = \frac{\text{standard amount injected}}{\text{total area of standard}}$$

3.6.2 The distinctions between these methods are: the %RSD method assumes a linear response with the calibration curve passing through the origin, the linear regression method assumes a linear response with a non-zero intercept, and the non-linear method assumes a correlation, but not a linear one.

3.6.3 The calculated CFs are tabulated and the %RSD calculated. If the %RSD is less than 20% over the working range, linearity through the origin can be assumed, and the CF can be used.

3.6.4 The laboratory uses the regression method for semivolatile petroleum products. The correlation coefficient (r) must be 0.99 or greater for SW 846. Laucks adheres to a tighter value of 0.995 in order to meet Agency requirements. An overview of all the correlation coefficient requirements are located in Appendix IV.

3.6.5 Corrective action

3.6.6 If the criteria are not met, the instrument must be re calibrated.

3.7 Continuing and Initial Calibration Verification (CCV/DCV)

3.7.1 Criteria

3.7.1.1 At the beginning of an analysis sequence a mid-range calibration standard is analyzed. The computed calibration factor (CF) or concentration measurement must meet the criteria detailed below.

The DCV or CCV (daily or continuing calibration verification) standards are compared to the initial multi-point calibration. The percent drift is calculated as follows:

$$\%D = \frac{(C_t - C_i)}{C_t} \times 100$$

where:

C_t = True concentration
C_i = Measured concentration

3.7.1.2 The maximum %D allowed is 20%.

3.7.2 Corrective action

3.7.2.1 If the DCV/CCV criteria are not met, no sample extracts can be analyzed. Perform system maintenance and re-check the DCV/CCV. If the criteria still cannot be met, the system must be recalibrated.

3.8 Solvent Blank

3.8.1.1 One or more solvent blanks may precede sample extracts or CCVs in order to minimize carryover.

3.9 Method Blank

3.9.1 Method blanks are used to verify contamination free reagents and apparatus. They are prepared with every set of samples extracted at the same time or one blank every 20 samples which ever is more frequent. Any response above the reporting limit is considered out of control. Refer to Section 6 for method blank acceptance criteria.

3.10 Sample Analysis

3.10.1 The sample extracts are analyzed subsequent to the calibration standard analysis. However, no more than 10 injections are performed in-between calibration verification standards. Once all criteria for the calibration standard have been met, the sample extract analyses are performed.

3.11 Analysis sequence

MeCl2
Retention Time Mixture (RTM)
ICAL
MeCl2
8 injections
MeCl2
CCV
MeCl2
8 injections
MeCl2
CCV

3.12 Qualitative Identification

The quantitation of extractable organics within the retention time as stated does not indicate the presence of specific petroleum products since other extractable organic material may be present in the sample. Qualitative determination of the presence of DRO or oil (or a specific fuel type) based on the characteristic hydrocarbon pattern is noted on the sample result form.

3.13 Compound Quantitation

3.13.1 Target compound concentrations are calculated using the following equations:

Aqueous samples:

The total area of the components is integrated to the baseline as a group. Surrogate areas are subtracted from the gross area. The net area is used for the quantitation by linear regression.

Sa = (x coefficient) * A_x + constant

$$\text{Conc (mg/L)} = \frac{S_a \times D}{V_s / V_t}$$

where:

S_a	=	Sample extract result
V_s	=	Initial sample size (mL).
V_t	=	Volume of total extract (mL).
D	=	Dilution factor. Assume 1.0 for no dilution.
Ax	=	Sample area response
x coefficient	=	Slope m, of the linear regression curve the chromatogram of the sample

y = m *x + b

Non-aqueous samples

Sa = (x coefficient) * A_x + constant

The final result is calculated as follows:

$$\text{Conc (mg/kg)} = \frac{S_a \times D}{(W / Vt) \times (TS / 100)}$$

where:

W = Weight of sample extracted, (g).
TS = Total solids, percent.

3.14 Data Packet Organization

3.14.1 See Appendix I for a checklist detailing data packet organization.

3.15 Quality Control Reports

3.15.1 All results for quality control tests are entered into the lab database. Printouts of all data entered must be included in the data packet. Typically, a method blank report, a blank spike report, and a MS/MSD report are submitted.

3.16 Data Qualifying Flags

3.16.1 Sample report results are qualified with data qualifying flags. These flags have the following definitions:

Code	Definition
U	The analyte of interest was not detected, to the limit of detection indicated.
B	The analyte of interest was detected in the method blank associated with the sample, as well as in the sample itself. The B flag is applied without regard to the relative concentrations detected in the blank and sample.
D	The value reported is derived from the analysis of a diluted sample or sample extract.
E	The value reported is based on a sample or sample extract in which the target analyte concentration exceeded the calibration range. The value reported should be considered an estimate.

3.16.2 Alternate agency-specific flags may be required and will be defined on a project basis.

4. Quality Control

4.1 Initial Calibration

4.1.1 Criteria

4.1.1.1 Initial calibration data are evaluated using linear regression. The correlation coefficient is (r) ≥ 0.99 for SW 846. Laucks uses a tighter value of 0.995 in order to meet Agency requirements. Refer to Appendix IV for an overview of SW-846 as well as the overriding Agency requirements.

4.1.2 Corrective action

4.1.2.1 If the criterion is not met, additional standards may be analyzed or appropriate instrument maintenance and analysis of new standards should be performed.

4.1.3 Documentation

4.1.3.1 Copies of the initial calibration standards and the calculated CFs and Correlation Coefficients are stored with the raw data. If criteria are not met, reanalysis of additional standard(s) are noted in the instrument run log.

4.1.3.2 After completion of a compliant initial calibration curve, a mid-range calibration standard may be analyzed. This standard is from a different source than that of the calibration curve standards. The %D must be ≤ 20 percent of the expected value.

4.2 Continuing Calibration Verification

4.2.1 Criteria

4.2.2 At the beginning of each sequence, after every 10 injections, and at the end of a sequence, a mid-range calibration standard is analyzed. The %D must be ≤ 20 percent.

4.2.3 Corrective action

4.2.3.1 Check calculations, check standard solutions or perform instrument maintenance. Reanalyze the standard. If this fails, analyze a new initial calibration.

4.2.4 Documentation

4.2.4.1 Copies of the continuing calibration standards and the calculated %Ds are stored with the raw data. If criteria are not met, reanalysis of additional standard(s) are noted in the instrument run log.

4.3 Method Blanks

4.3.1 Criteria

4.3.1.1 A method blank is used to verify contamination free reagents and apparatus. The results of the method blank should be less than ½ the laboratory's reporting limit (RL).

4.3.2 Corrective action

4.3.2.1 Corrective action in the form of reanalysis or re-extraction of the method blank is performed when semi-volatile petroleum products are present above ½ the reporting limit.

4.3.2.2 Out-of-control surrogate recoveries in the method blank require at the very least, reanalysis or re-extraction of the method blank. The entire sample set associated with the out of control blank may also require re-extraction and reanalysis. However, if the surrogate recoveries are in control in the associated sample extract analyses, and nothing is detected in the sample extracts, or if the hydrocarbon levels in the samples are greater than 20 times the hydrocarbon levels in the method blank, no further action is required.

4.3.3 Documentation

4.3.3.1 Copies of all method blank analyses are stored with the sample analyses raw data. In addition, the raw data for the method blank analyses are stored in the laboratory for an extended period of time. The results for the method blank analyses are reported electronically via the laboratory's LIMS database. If criteria are not met, reanalysis of additional blank(s) are noted in the instrument run log.

4.4 Blank Spikes

4.4.1 Criteria

4.4.1.1 A blank spike follows the same protocol as a matrix spike analysis except that the spiking solution is added to an aliquot of DIW (or sand for soil samples) instead of an

actual sample. A blank spike is the same as a QC check standard. See Appendix II for control limits. Because control limits are updated often as required by the method, all current control limits are located in the LIMS database.

4.4.2 Corrective action

4.4.2.1 The blank spike is used to determine whether a method is in control during sample preparation and analysis. Sample reanalysis or re-extraction would be triggered by an out of control blank spike.

4.4.3 Documentation

4.4.3.1 The raw data for the blank spike analyses are stored in the laboratory for an extended period of time. The results for the blank spike analyses are reported electronically via the laboratory's LIMS database. If criteria are not met, reanalysis of additional blank spike(s) are noted in the instrument run log

4.5 Matrix Spike

4.5.1 Criteria

4.5.1.1 A sample is chosen at random (unless specified by a client) from the samples to be analyzed, and an aliquot of spiking solution is added to this sample during the extraction procedure. A matrix spike analysis is performed with each preparation batch, up to a maximum of 20 samples. The matrix spike sample is used to evaluate the matrix effect of the sample upon recovery of the analytes. Refer to Appendix II for control limits. Because control limits are updated often as required by the method, all current control limits are located in the LIMS database.

4.5.1.2 The recovery of spike analytes is calculated as follows:

$$\text{Recovery} = \frac{SS - S}{SpikedAmount} \times 100$$

where:

SS = concentration in spiked sample
S = native concentration in unspiked sample

4.5.2 Corrective action

4.5.2.1 Sample reanalysis is not required for a matrix spike that is out of control due to matrix interference, assuming the associated blank spike is in control.

4.5.3 Documentation

4.5.3.1 The raw data for the matrix spike analyses are stored in the laboratory for an extended period of time. The results for the matrix spike analyses are reported electronically via the laboratory's LIMS database. If criteria are not met, this must discussed in the narrative.

4.6 Matrix Spike Duplicate

4.6.1 Criteria

4.6.1.1 A matrix spike duplicate analysis is performed with each batch, up to a maximum of 20 samples. The compound recovery criteria are identical to those for the matrix spike sample. In addition, the matrix spike duplicate is used to measure method precision. This is done by computing the RPD between the matrix spike and matrix spike duplicate recovery values. Refer to Appendix II for control limits. Because control limits are updated often as required by the method, all current control limits are located in the LIMS database.

4.6.1.2 This calculation is as follows:

$$RPD = \frac{S1 - S2}{(S1 + S2) \backslash 2} \times 100$$

where:

S1 = measured concentration for MS sample
S2 = measured concentration for MSD sample

4.6.2 Corrective action

4.6.2.1 If a trend in out-of-control RPD values is observed, the method used must be examined to determine the source of variance. Once this source is identified, the method must be changed so that samples can be analyzed with a predictable reproducibility.

4.6.3 Documentation

4.6.3.1 The raw data for the matrix spike duplicate analyses are stored with the sample analyses raw data. The results for the matrix spike duplicate analyses are reported electronically via the laboratory's LIMS database. Any out-of-control results are documented in the LIMS database and/or analytical narrative.

4.7 Surrogate Recovery

4.7.1 Criteria

4.7.1.1 Surrogates are chemically similar compounds added to every sample, method blank, and QC sample prior to sample processing. They are used to monitor potential sample processing errors and matrix effects. Control limits are located in Appendix II. Because control limits are updated often as required by the method, all current control limits are located in the LIMS database.

4.7.1.2 Surrogate compound recoveries are calculated as follow:

$$\text{Recovery} = \frac{S_m}{S_a} \times 100$$

where:

S_m = concentration of surrogate measured in sample
S_a = concentration of surrogate added

4.7.2 Corrective Action

4.7.2.1 Check calculations for possible error. Reanalysis is required for all surrogate recoveries that exceed the established control limits, unless they are elevated due to matrix interference. Matrix interference occurs when there is organic material present in the sample at levels that interfere with the surrogate recovery. The surrogate recovery values are elevated because the organic extractable material elutes within the retention time window in samples and matrix spike analyses. This can by verified when reviewing the associated sample and/or matrix spike chromatograms. A noticeable presence of material in addition to the surrogate peaks will be evident. Since method blanks and blank spikes are prepared using DIW or clean solid material, these analyses will not exhibit matrix interference. Sample surrogates that exhibit similarly poor recoveries will require reanalysis.

4.7.3 Documentation

4.7.3.1 The surrogate recoveries for all samples, blanks, and QC analyses are reported electronically via the laboratory's LIMS database. If criteria are not met, reanalysis of for out-of-control surrogate recoveries are designated by an "RE" in the instrument run log.

5. References

1) Washington State Department of Ecology Toxics Cleanup Program and The Ecology Environmental Laboratory, Analytical Methods for Petroleum Hydrocarbons, Publication No. ECY 97-602, June 1997.

2) Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, (SW-846), US EPA Office of Solid Waste and Emergency Response, - Method 8000B, 3rd edition, 2nd revision, December 1996.

3) Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, (SW-846), US EPA Office of Solid Waste and Emergency Response, - Method 8015B, 3rd edition, 2nd revision, December 1996.

4) Department of Defense Quality Systems Manual for Environmental Laboratories, , Final Version 3, January 2006

5) Technical Services Quality Assurance Project Plan (QAPP), HQ Air Force Center for Environmental Excellence, Final Version 4.0,.02, May 2006.

6) National Environmental Laboratory Accreditation Program, Ninth NELAC Annual Meeting, June 5, 2003.

APPENDIX I

Data Packet Sequence

I. QC SUMMARY

_____ Analysts 'Client' Comment (hard copy and floppy)
_____ Surrogate Recovery Summary Report
_____ Blank Spike Report
_____ MS/MSD Report
_____ Method Blank Summary

II. SAMPLE DATA:

_____ Organic Analysis Data Sheet
_____ Chromatogram
_____ Quantitation Report

III. STANDARD DATA:

_____ Initial Calibration Verification
_____ DCV/CCV Reports

Continuing Calibration Standards:
_____ Chromatograms
_____ Quantitation Report

Other Standards Used to Support Sample Data and Instrument Blanks

V. Raw QC Data:

_____ Method Blank
_____ Chromatograms
_____ Quantitation Report
_____ Blank Spike
_____ Chromatograms
_____ Quantitation Report
_____ MS/MSD
_____ Chromatograms
_____ Quantitation Report

V. Bench Sheets

_____ Injection Sequence
_____ Extraction Bench Sheets
_____ Miscellaneous Work Sheets. i.e. %TS, SDG summary, calculations, HTVR
_____ Standards Logs
_____ Chain Of Custody

VI. Reject Data:

DO NOT COPY DO NOT PAGINATE

Data not used to support sample results.
All data acquired but rejected on account of QC out of control.
Non-routine standards used to support sample data should be placed at the last of the Standard Data section.

APPENDIX II

Modified 8015B Reporting Limits, MDLs, Control Limits and Carbon Ranges

Reporting Limits

Range	Water (mg/L)		Soil (mg/kg)		Low Level Soil (mg/kg)		Low Level Water (mg/kg)	
	RL	MDL	RL	MDL	RL	MDL	RL	MDL
Jet fuel through #2 Diesel	0.250	0.084	25	6.7	5	0.58	0.05	0.023
Heavy oils	1.0	0.18	100	14	20	1.1	0.2	0.09

Control Limits

Compound	Blank Spike Soil	Blank Spike Water	Matrix Spike Soil	Matrix Spike Water	RPD	Surrogate
Diesel	56 - 124	47 - 123	50 -150	50 -150	50	50 -150

Carbon Ranges

Method	Diesel Range Organics	Oil Range Organics
M8015	C_{12}-C_{24}	C_{24}-C_{40}
California LUFT	C_{10}-C_{24}	C_{24}-C_{40}

APPENDIX III

Laucks Testing Laboratories
Modified 8015B QA Requirements and Corrective Actions

QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
Initial Calibration Curve	Minimum of 5 levels. Corr Coef: 0.99.	Minimum of 5 levels. Corr Coef: 0.995.	Initially.	Reanalysis of out of control standards. Linearity can be assumed if Corr Coef is > 0.995.	
Second Source Standard	None.	Within 20%D.	After every initial calibration.	Reanalysis of standard in order to meet %D criterion. May have to pursue third source to verify all standards.	Copies of raw data filed and noted in instrument logbook.
Continuing Calibration Verification	Mid-level calibration standard run every 10 injections. If not within ≤ 20%D.	Mid-level calibration standard run every 10 injections. If not within ≤ 20%D.	At the beginning of every QC period.	Reanalysis of DCV in order to meet %D criterion. If reanalysis does not meet criterion, analyze initial calibration curve.	Copies of raw data filed and noted in instrument logbook.
Method Blank	One method blank every batch, up to 20 samples. Analysis of the method blank should not contain organic extractable material above the reporting limit.	One method blank every batch, up to 20 samples. Analysis of the method blank should not contain organic extractable material above ½ the reporting limit.	One method blank per batch of up to 20 samples.	Re-extraction and reanalysis of the batch.	Copies of raw data filed, and reported electronically. Daily control charts for all method blanks are recorded.
Surrogate Standards	No method-specified surrogates recommended. Lab-generated control limits.	Recoveries must meet laboratory established control limits in Appendix II.	Surrogates are used in all standards, blanks, samples, and QC.	If surrogate recoveries exceed the limits due to matrix interference, reanalysis is not performed. If method blank surrogate recoveries exceed the limits the samples must be reanalyzed or re-extracted	Any out of control surrogates are documented in associated file.
Blank Spike	Recoveries are suggested to meet the control limits of 70% - 130%.	Recoveries must meet laboratory established control limits in Appendix II.	One blank spike with each batch of samples up to 20 samples.	Reanalysis of QC sample. If still out of control, re-extract and reanalyze.	QC recoveries are stored electronically. Raw data is stored with file. Out of control events are noted in file.
MS/MSD		Recoveries must meet laboratory established control limits in Appendix II.	One MS/MSD with each batch of samples up to 20 samples.	Reanalysis of QC sample. Review LCS recoveries and determine whether matrix interference involved.	Discuss in SDG narrative.
Sample Preservation and Storage	Samples stored at 4°C ± 2°C.	Samples stored at 4°C ± 2°C.			Notify QA and PM personnel immediately.

QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
Holding Time	Waters: 7 days from date of collection to extraction. Soils: 14 days from date of collection to extraction. The holding time for analysis is 40 days from collection.	Waters: 7 days from date of collection to extraction. Soils: 14 days from date of collection to extraction. The holding time for analysis is 40 days from collection.	N/A	Contact client ASAP.	HTVR (holding time violation report) filed with data and noted in file.
Standard Solution Expiration	Refer to SW 8000B. (Stock standards: 12 months. Working solutions: 6 months.)	Refer to SW 8000B. (Stock standards: 12 months. Working solutions: 6 months.)			All standard data recorded in standard logbook.

APPENDIX IV

Agency Requirements

SW 846 Method 8015 DRO			
QC Check	**DoD**	**AFCEE**	**SW 846**
	Acceptance Criteria	Acceptance Criteria	Acceptance Criteria
MDL Study	See 40 CFR 136B. S/N > 3 for MDL verification, Every 12 months, or quarterly for MDL verification checks	Every 12 months. Detection limits ≤ 1/2 RL listed in appropriate AFCEE table.	
Retention Time Window Width calculated for each analyte and surrogate	± 3s over a 72 hour period for each analyte		± 3s over a 72 hour period for each analyte or ± 0.03 minutes, whichever is greater.
Minimum Five Point Initial Calibration	Option 1: RSD ≤ 20%	Option 1: RSD ≤ 20%	Option 1: RSD ≤ 20%
	Option 2: Linear - r ≥ 0.995	Option 2: Linear - r ≥ 0.995	Option 2: Linear - r ≥ 0.99
	Option 3: Non-linear - r^2 ≥ 0.99, minimum of 6 pts for 2nd order	Option 3: Non-linear - r^2 ≥ 0.99, minimum of 6 pts for 2nd order	Option 3: Non-linear - r^2 ≥ 0.99, minimum of 6 pts for 2nd order, 7pts for 3rd order
			AND %D ≤ 20% at each calibration level recommended
Retention time window position establishment for each analyte and surrogate	Once per ICAL and at the beginning of each analytical shift. Position shall be set using the midpoint standard of the calibration curve or the value in the CCV run at the beginning of the analytical shift.		
Retention time window verification for each analyte and surrogate	Each calibration verification standard		
Second Source	%D ≤ 20%	%D ≤ 20%	
Retention Time Range	Set at retention time of midpoint standard of ICAL	Based on retention time of C_{10} and C_{28}	Defined during ICAL. Based on retention time of C_{10} and C_{28} alkanes. Range is from the lower RT of first eluting component to upper RT of last.
Continuing Calibration Verification	%D ≤ 20%	%D ≤ 20%	%D ≤ 20%
	Every 10 field samples, beginning and end of analytical sequence	Every 10 samples, beginning and end of analytical sequence	Beginning and end of each 12 hour analytical shift
Method Blank	No analytes ≥ ½ RL. No common laboratory contaminant analytes ≥ RL.	No TPH ≥ ½ RL. No common laboratory contaminant analytes ≥ RL	Less than the laboratory detection limit OR
			Less than 5% of the regulatory limit OR
			Less than 5% of the sample result WHICHEVER IS GREATER

SW 846 Method 8015 DRO			
QC Check	**DoD**	**AFCEE**	**SW 846**
	Acceptance Criteria	Acceptance Criteria	Acceptance Criteria
Laboratory Control Sample	See appropriate DoD table, or use in-house limits if not listed	See appropriate AFCEE table	Lab-derived. If no lab-derived limits are in place yet, use 70%-130% by default
Matrix Spike	Same as LCS	Same as LCS	Lab-derived
Matrix Spike Duplicate	RPD $\leq$ 30%	See appropriate AFCEE table	Lab-derived
		See appropriate AFCEE table	
Surrogate Spike	Same as LCS	See appropriate AFCEE table	Lab-derived
Results reported between MDL and RL	Apply J flags	Apply F flags	

Agency requirements supercede SW-846.

Controlled Document

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1 Introduction and Scope

1.1 Method Description

1.1.1 This SOP describes the procedures and specifications for instrumental analysis of various organochlorine pesticides and polychlorinated biphenyls (PCBs) in water and soil following SW846 Methods 8081B and 8082A. Analysis is performed by gas chromatography using a single injection port and splitting into dual GC columns with electron-capture detectors. This system provides quantitation and confirmation of pesticides and Aroclors (PCBs) from a single injection. The following table lists the compounds that may be determined by these methods. Additional compounds, listed in Method 8081B, may also be determined. Technical Chlordane will not be reported unless specified by the client.

SW8081B ROUTINE COMPOUNDS	
alpha-BHC	beta-BHC
delta-BHC	gamma-BHC (Lindane)
Heptachlor	Aldrin
Heptachlor epoxide	Endosulfan I
Dieldrin	4,4'-DDE
Endrin	Endosulfan II
4,4'-DDD	Endosulfan sulfate
4,4'-DDT	Methoxychlor
Endrin aldehyde	Endrin ketone
alpha-Chlordane	gamma-chlordane
Toxaphene	
SW8081B OPTIONAL COMPOUNDS	
Chlordane (not otherwise specified)	Isodrin
Simazine	Atrazine

SW8082A COMPOUNDS	
Aroclor-1016	Aroclor-1221
Aroclor-1232	Aroclor-1242
Aroclor-1248	Aroclor-1254
Aroclor-1260	
SW8082A OPTIONAL COMPOUNDS	
Aroclor-1262	Aroclor-1268

1.1.2 This method is restricted to use by, or under the supervision of analysts experienced in the use of gas chromatography and in the interpretation of chromatograms. Each analyst performing this method must have demonstrated the ability to perform the described

chromatographic analysis and/or data interpretation.

1.1.3 In some instances, samples being analyzed for PCBs will require sulfuric acid cleanup. In instances where samples are being analyzed for both pesticides and PCBs, an aliquot is separated prior to the sulfuric acid cleanup step, and is analyzed for pesticides only. The separation of aliquots prior to this cleanup will prevent the potential loss of target pesticide compounds.

1.2 Method Deviations

1.2.1 The analyte list is based on a combination of Method 8081B and 8082A analytes. Additional analytes are only added if requested by the client(s).

1.3 Sample Collection, Sample Storage, Holding Times

1.3.1 Samples are normally collected in glass containers with Teflon-lined caps. All samples and sample extracts are stored at 4°C±2°C. Water samples must be extracted within 7 days of sample collection, soil samples within 14 days of sample collection. All extracts must be analyzed with 40 days of sample preparation.

1.4 Definition of Terms

1.4.1 This section defines terms and acronyms as they are used in this SOP. Other terms, such as MS/MSD or method blank, are not defined here since it is assumed that the user of this SOP already understands their more general meaning.

Batch Identifier	A number given to each preparation or analysis group which uniquely identifies that batch. This number is generally the blank ID for preparation batches and either a sequence number for organic analyses or an analysis number that is similar to the blank ID, only preceded by an "A" rather than a "B" for inorganic batches. The preparation batch IDs are discussed in other documentation.
Blank spike	A background free matrix (DIW for water, clean sand for soils/sediments) to which known amounts of target analytes and surrogates are added each time sample extracts are prepared. In the context of this SOP, a blank spike is the same as a QC check standard. See also QC check standard.
CCV	Continuing calibration verification. This is the same acronym used in the CLP program. This is a standard analyzed at some prescribed frequency during the analysis sequence to verify that the instrument has remained in calibration.

CF	Calibration factor. The ratio of analyte instrument response to nanograms injected. This term is defined in the same way in both the CLP contract and SW 846.
CLP	Contract Laboratory Program. The USEPA program that contracts with laboratories to provide laboratory services. The term has come to mean a much broader set of methods and deliverables. In the context of this SOP, CLP means procedures or operations which are detailed in the CLP contract and which are extended to a broader working definition.
DCC	Daily calibration check. This is the first standard analyzed in the sequence.
DIW	Deionized water. Lab reagent water. Organic-free water. Since the systems used to provide DIW at Laucks all contain carbon-polishing filters, they are capable of providing organic-free water for use in method blanks and blank spikes.
IBLK	Instrument blank. This term is borrowed from CLP. Blank solvent containing the method surrogates is injected into the instrument to monitor for carry over between sample extract injections.
ICV	Initial calibration verification. It is a standard that is injected at the start of each QC period that is compared to the initial multi-point calibration to determine whether the instrument is still in calibration.
IDL	Instrument detection limit. The lowest concentration of a target analyte that will yield a signal:noise ratio of at least 3x. Used as a starting point for selecting MDL study spiking levels.
MDL	Method detection limit. The lowest concentration in a sample which will yield a positive result that is greater than zero at a known level of confidence. MDLs are empirically determined by Laucks.
MDL standard	Method detection limit standard. A standard prepared so that the concentrations of the target analytes are in the range of 1x to 4x the empirically determined MDLs on an extract/digest basis. This standard is used to verify that the instrument is capable of detecting the target analytes on an ongoing basis.

PQL or Reporting Limit	Practical Quantitation Limit or Reporting Limit- The value used when reporting a non-detect. It may be administratively, empirically or contractually set.
QC check standard	Quality control check standard. Referred to in this SOP as a blank spike. A QC check standard is a requirement of SW 846 method 8000 and is used to determine whether the analytical system is in control if MS/MSD recoveries are out of control. See also blank spike.
QC period	Quality control period. An analysis sequence initiated by the analysis of one or more standards, followed by sample extracts/digests, and terminated with a standard analysis. A QC period can be open-ended chronologically, but calibration verification must be documented using the procedures in this SOP.
Reporting Limit (RL)	The reporting limit is defined by the low level standard, also referred to as the practical quantitation limit (PQL).
RSD or %RSD	Relative standard deviation or percent relative standard deviation. The ratio of the standard deviation of a set of values to the mean of the set of values expressed as a percentage. A measure of the similarity of the values one to another.
RT, Retention time	The time (in minutes) at which a target analyte elutes from a chromatography column.
RT window	Retention time window. The +/- value which is applied to the ICV to establish the time range used to make tentative compound identifications.
Sequence	A set of sample extracts/digests and standard solutions introduced into an instrument in a chronologically continuous group. See also QC period.
SRM	Standard Reference Material - A material containing known quantities of target analytes in a homogeneous matrix which approximates the matrix of the samples being analyzed. It is used to establish that the analytical process is in control.

2 Equipment List, Maintenance, and Standards

2.1 Chromatographic and Data System

2.1.1 This analysis requires a gas chromatograph with a programmable oven, heated injection port, dual electron-capture detectors, autosampler and an electronic data-acquisition system.

2.1.2 Equipment list:

- Gas chromatograph (Hewlett-Packard 5890, 5890A, 6890 w/µECDs) or equivalent
- Autosampler (Hewlett-Packard 7673A, 7683) or equivalent
- Electron-capture detectors (Hewlett-Packard) or equivalent
- Capillary columns (J&W DB5, DB608, 30m x 0.45mm, or equivalent)
- 0.45mm megabore, J&W DB-XLB, DB35ms 30m x 0.32mm, or equivalent)
- 5% methane/95% argon detector make-up gas,
- Helium carrier gas
- EZChrom Data Acquisition System version 6.6, Target Analytical Software for NT
- Operating System version 4.02, Pentium PCs, or equivalent.

2.1.3 Maintenance

2.1.1 In order to prevent/reduce endrin breakdown, the following steps are used:

1) use clean and silanized Agilent liners, (splitless, single-taper liners for the 6890)
2) use only gold seals
3) reduce the injection port temperature e.g., from 250°C to 205°C
4) clean inlet with hexane and acetone
5) prime inlet with really high concentration standard
6) make sure syringe does not touch glass wool.

2.2 Standards

2.2.1 Commercially prepared, certified stock standards are used to prepare working solutions for all surrogates, calibration mixes, and spike mixes. The calibration mix (INDAB) contains all of the individual pesticide analytes. All individual pesticides are spiked. Aroclors 1016 and 1260 are spiked. Stock standards must be replaced by the manufacturers expiration date.

2.2.2 Calibration standards are prepared at different concentration levels by dilution of the stock standards with hexane (see table below). High-level INDAB is made at 16 times the PQL concentration. The lower levels are diluted by factors of 2, 4, 5, 8, 16 and 20. The standards must be replaced after 6 months or by the expiration date of the material

they were made from, whichever is earlier.

2.2.3 Multicomponent analyte calibration standards, with the exception of Aroclors 1016 and 1260 (combined are defined as Aroclor 1660), are prepared at a concentration of 1.0 µg/ml, by dilution of commercially purchased stock solutions in hexane (see table below). Toxaphene is made up to a concentration of 0.5 µg/ml and chlordane is made up to a concentration of 0.1 µg/ml by dilution of commercially purchased stock solutions in hexane. Standards of the Aroclors 1016 and 1260 are combined in a mixture and prepared at seven concentration levels: 1.0 µg/ml, 0.75 µg/ml, 0.5 µg/ml, 0.33 µg/ml, 0.25 µg/ml 0.10 µg/ml, and 0.05 µg/ml. These must be replaced after 6 months or by the expiration date of the material they were made from, whichever is earlier.

Standard level	INDAB Mix µg/mL	AR1660 µg/mL	All other Aroclors µg/mL	Toxaphene µg/mL	Chlordane µg/mL
1	0.002-0.004	0.05	N/A	0.005	0.025
2	0.0025-0.005	0.1	N/A	N/A	N/A
3	0.005-0.01	0.20	0.5	N/A	N/A
4	0.008-0.016	0.25	N/A	N/A	N/A
5	0.02-0.4	0.5	N/A	N/A	N/A
6	0.04-0.8	0.75	N/A	N/A	N/A
7	0.04-0.08				

2.2.4 A performance evaluation mixture (PEM) is prepared from a purchased solution of 4,4'-DDT, and endrin in hexane.

2.2.5 A surrogate mix is prepared from separate solutions that contain 2,4,5,6-tetrachloro-meta-xylene (TCMX) and decachlorobiphenyl (DCB). These standards are made in hexane and added to all standard mixes (before dilution if applicable).

2.2.6 Refer to SOP LTL-1013 (Preparation, Storage, Shelf Life and Traceability Documentation of Standards and Reference Materials) for detailed instructions on standards preparation and storage.

2.2.7 Appendix I details the compounds and concentrations contained in all solutions.

3 Safety precautions and Waste Disposal

3.1 Routine Safety Precautions

3.1.1 All standards and sample extracts should be handled as if they contain hazardous substances.

3.1.2 Refer to the instrument manufacturer's manual for routine instrument precautions.

3.1.3 Routine precautions include an awareness of the moving parts on the instrument you're using. These parts are often charged with power from an electrical component or with high-pressure gas and have the potential to do harm if not used properly.

3.1.4 Electrical shock - All instruments present the possibility of electrical shock. The operator should take all precautions including ensuring that all instruments are operated with fully grounded power outlets, turning off the instrument and disconnecting the instrument from the electrical power supply before working on any electrical components, etc.

3.1.5 The electron-capture detectors used in this analysis contain a radioactive source and should not be opened or otherwise tampered with.

3.2 Waste disposal

3.2.1 Solvent wastes generated in using this procedure (expired standards, old sample extracts, rinsates, etc.) should be emptied into the solvent waste container in the fume hood.

3.2.2 Waste segregation and disposal from the point of collection is further covered in the Laucks SOP on Waste Segregation and Disposal.

4 Calibration and Quality Control

4.1 QA Requirements and Corrective Action

4.1.1 Detailed in the following sections are applicable QA requirements and subsequent corrective actions to be applied to this analysis. A summary of these requirements can be found in Appendix IV.

4.2 Method Detection Limit Study

4.2.1 Prior to the analysis of any samples, it is necessary to establish method detection limits. This procedure is fully described in the Laucks SOP on MDLs, located in the SOP manual. Briefly, it involves the analysis of 7 replicate samples spiked at a concentration near the anticipated method detection limit. A Student's T-test is then applied to these measured values to calculate the MDL.

4.3 Method Validation

4.3.1 Prior to the analysis of any samples, it is necessary to validate the method. A method

validation study is performed in a similar manner to an MDL study with the exception that a minimum of 4 replicates are required and the concentration levels are typically higher.

4.3.2 The precision of spike recoveries must meet or exceed the criteria tabulated in SW 846.

4.4 Retention Time Windows

4.4.1 Retention time window studies are conducted following the Laucks SOP on Establishing RTWs and the procedure detailed in SW 846, Method 8000B, which defines a window for each single and multi- component analyte based on the retention times taken from three standard injections over a 72 hour period.

4.4.2 The retention time window half-width is set at 3 times the above calculated standard deviation. This operation must be repeated whenever major equipment changes are made, whenever the chromatographic method is significantly modified, or whenever a column is replaced.

4.4.3 The calculated retention time window half widths are typically unrealistic values. Therefore RT windows have been administratively set at the values listed in OLM04.2 for megabore analyses (see table below) and at ±0.03 for capillary analyses. These values are typically wider than 3 times the standard deviation as determined above, but are more realistic.

Analyte	Megabore	Capillary
alpha-BHC	±0.05	±0.03
beta-BHC	±0.05	±0.03
gamma-BHC (Lindane)	±0.05	±0.03
delta-BHC	±0.05	±0.03
Heptachlor	±0.05	±0.03
Aldrin	±0.05	±0.03
alpha-Chlordane	±0.07	±0.03
gamma-Chlordane	±0.07	±0.03
Heptachlor epoxide	±0.07	±0.03
Dieldrin	±0.07	±0.03
Endrin	±0.07	±0.03
Endrin aldehyde	±0.07	±0.03
Endrin ketone	±0.07	±0.03
4,4'-DDD	±0.07	±0.03
4,4'-DDE	±0.07	±0.03
4,4'-DDT	±0.07	±0.03
Endosulfan I	±0.07	±0.03
Endosulfan II	±0.07	±0.03
Endosulfan sulfate	±0.07	±0.03
Methoxychlor	±0.07	±0.03
Tetrachloro-m-xylene	±0.07	±0.03
Decachlorobiphenyl	±0.10	±0.03
Aroclors	±0.07	±0.03
Toxaphene	±0.07	±0.03

4.5 Breakdown Evaluation (only required when analyzing for pesticides)

4.5.1 At the beginning of each analysis sequence a performance evaluation mixture (PEM) must also be analyzed. This is a separate solution containing 4,4'-DDT and endrin, and is examined for the breakdown products of these analytes (4,4'-DDD, 4,4'-DDE, endrin aldehyde, endrin ketone) which indicate the need for GC system maintenance. The percent breakdown must be less than 15% for both Endrin and 4,4'-DDT.

4.6 Initial Multi-Point Calibration for Pesticides and PCBs

4.6.1 SW 846 allows the use of both linear and non-linear models for the calibration data. The option for non-linear calibration may be necessary to achieve low detection limits or to address specific instrumental techniques.

4.6.2 Analyze single component pesticide standards using at least 5 different concentration levels for linear calibrations. The lowest concentration should be near, but above, the method reporting limit or PQL. The highest concentration should define the upper usable

working range of the detector.

4.6.3 Analyze multi-component pesticides at one concentration level. Initial calibration of Aroclor 1016/1260 is performed using a minimum of five different concentration levels. The more commonly found Aroclors (Aroclors 1248 and 1254) are calibrated using three different calibration levels. The detection of any Aroclor in a sample requires a minimum of three calibration points, followed by re-analysis of the sample extract. Extracts containing toxaphene and chlordane are extremely rare so an initial single point calibration is employed. Single standards of Aroclors, toxaphene, and chlordane are required to aid the analyst in pattern recognition and are also used to determine the initial calibration factor for each analyte. If the sample extract contains toxaphene or chlordane above the reporting limit, a three-point calibration will be analyzed for the target analyte followed by re-analysis of the sample extract. The three point calibration points will be diluted from the stock standard and must be at concentrations that will bracket the concentration of the sample. This three-point calibration method will be used to determine the final calibration factor for the target analyte. The CF is calculated by using a minimum of three to five peaks for the multi-component pesticide and PCB standards.

4.6.4 The choice of a specific calibration model should be made in one of two ways. The first is to begin with the simplest approach, the linear model through the origin, and progressing through the other options until the calibration acceptance criteria are met, or until the analyte is best represented by a calibration model. The second approach is to use *a priori* knowledge of the detector response to choose the calibration model. Such knowledge may come from previous experience, knowledge of physics of the detector, or specific manufacturer's recommendations.

4.7 Linear Calibration

4.7.1 External standard initial calibration data is evaluated by determining the %RSD of the calibration factors.

4.7.2 CFs are calculated using the equation:

$$CF = \frac{\text{response}}{\text{ng injected}}$$

4.7.3 The calculated CFs are tabulated and the %RSD calculated. There are no compound-specific criteria. All %RSDs must be within 15% for each analyte plus recovery of all analytes must be within 80-120%.

4.7.4 Corrective action

4.7.4.1 If the criteria are not met, the instrument must be re-calibrated or if appropriate, an alternative calibration model employed. The appropriate calibration model can be selected through the use of the GC initial calibration exceptions report. This is

available as a template in Microsoft Excel.

4.8 Non-linear Calibration

4.8.1 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 described here have not met the acceptance criteria, a non-linear calibration model may be employed.

4.8.2 When using a calibration model for quantitation, the curve must be continuous, continuously differentiable and monotonic over the calibration range. The model chosen should have no more than four parameters, i.e., if the model is polynomial, it may be no more than third order, as in the equation:

$$y = ax^3 + bx^2 + cx + d$$

4.8.3 The statistical considerations in developing a non-linear calibration model require more data than the more traditional linear approaches. A quadratic (second order) requires a minimum of six standards, and a third order polynomial requires seven standards. Do not force the line through the origin, i.e., do not set the intercept as 0, and do not include the origin (0,0) as a calibration point. The r^2 value must be ≥ 0.990.

4.8.4 Whichever option is employed, a surrogate concentration must fall within the calibration range.

4.8.4.1 A set of three to five major peaks is selected for each multicomponent analyte. These should be characteristic of the multicomponent analyte in question. Retention time windows and calibration factors are generated for each of the peaks chosen.

4.8.5 Corrective action

4.8.5.1 If the criteria are not met, the instrument must be re-calibrated.

4.9 Second Source Standards (Initial Calibration Verification-ICV)

4.9.1 A second source standard containing pesticides and Aroclor 1660, must be analyzed after each initial calibration. The standard should be prepped at a concentration at varied concentration levels. The %D for each second source standard must be within 20%.

4.9.2 Corrective action

4.9.2.1 If the criteria are not met, the second source standard is reanalyzed. Alternatively, a standard from an additional source may be required if there continues to be differences > 15%.

4.10 Daily Calibration Check

4.10.1 Concentration and/or CF Criteria

4.10.1.1 At the beginning of an analysis sequence analyze a mid-range calibration standard. The computed calibration factor (CF) or concentration measurement must meet the criteria detailed below.

4.10.1.2 Using the appropriate calculation technique (average CF) compute either CFs or concentration values. For linear calibrations the DCC standard can be verified by calculating either the percent difference or the percent drift.

4.10.1.2.1 The percent difference calculation compares the DCC CFs to the mean CFs from the initial multi-point calibration. The percent difference is calculated as follows:

$$\%D = \frac{Cv - \overline{CF}}{\overline{CF}} \times 100$$

where:

C_v = Calibration Factor

$\overline{CF}$ = Mean Calibration Factor

4.10.1.2.2 The percent drift calculation compares the DCC calculated concentrations to the theoretical (or actual) concentration of the DCC standard. The percent drift is calculated as follows:

$$\%D = \frac{C_c - C_T}{C_T} \times 100$$

where:

C_c= Calculated Concentration
C_T = Theoretical Concentration

4.10.1.3 There are no compound-specific criteria. The %D results should be within ±15% of the average CF or expected concentration from the initial calibration for each analyte, or averaged across all analytes in the continuing calibration standard.

4.10.2 Corrective action

4.10.2.1 If the DCC criteria are not met, no sample extracts can be analyzed. Perform system maintenance and re-check the DCC. If the criteria still cannot be met, the system must be recalibrated.

4.11 Updating Retention Time Windows

4.11.1 The retention time windows for compound identification are updated using the retention times for each target analyte in the mid-point calibration standard of the initial calibration as the center of the window and the previously determined retention time window half-

width to establish the retention time range to be used for compound identification.

4.12 Instrument Blank

4.12.1 Criteria

4.12.1.1 Any sample that is suspected of containing high concentrations of target analytes should be followed by an IBLK or solvent rinse. This IBLK analysis is used only to make a judgment as to the possibility of carry-over into the sample extract immediately following the IBLK. Evaluation criteria are detailed below.

4.12.2 Corrective action

4.12.2.1 IBLKs used to monitor for possible carryover in high concentration extracts (those IBLKs optionally placed into the sequence following suspected high concentration extracts) are used to flag the possibility of analyte carryover into the following sample extract. The extract immediately following the out of control IBLK may need to be re-analyzed if there is a detectable amount at ½ the reporting limit of the analyte found in the IBLK.

4.13 Continuing Calibration Verification

4.13.1 The continuing calibration is verified each 12 hours by injection of a calibration standard. SW 846 requires that the calibration standard be injected at a frequency of not less than once every 20 samples (the frequency of every 10 samples is recommended to minimize the number of reinjection due to QC failure). Laucks analyzes the continuing calibration standards every 10 samples or every 12 hours, whichever is deemed appropriate by the analyst. In addition, this standard must be the last injection made in the analysis sequence.

4.13.2 Criteria

4.13.3 After 12 hours, a CCV standard is analyzed. The CF or concentration for each analyte is calculated and the percent difference or percent drift is calculated as shown above.

4.13.4 The %D results should be within ±15% of the average CF or expected concentration from the initial calibration for each analyte, or averaged across all analytes in the continuing calibration standard.

4.13.5 The retention times for all target analytes must fall within the RT windows established by the mid-point of the initial calibration.

4.13.6 Corrective Action

4.13.7 Check calculations or perform instrument maintenance. To validate the quantitation of target analytes in analytical samples, the samples must be bracketed by in-control CCVs. However, CCV CFs can be outside the control limits as long as this was due to an increase in response and the corresponding samples contain no detectable levels of the

target analyte for which the CF is out of control.

4.14 Method Blanks

4.14.1 Criteria

4.14.1.1 Method blanks are used to verify contamination free reagents and apparatus. They are prepared with every set of samples extracted at the same time or one blank every 20 samples which ever is more frequent. Any analyte response above ½ the reporting limit is considered out of control.

4.14.2 Corrective action

4.14.2.1 Corrective action may necessitate re-extraction of the sample set. For example, if an analyte were found in the blank but not in any of the associated samples then the sample group may not require re-extraction. In any event it is the laboratory's responsibility to ensure that method interferences caused by contaminants in solvents, reagents, glassware, and other sample processing hardware leading to discrete artifacts and/or elevated baselines in the chromatograms be minimized. In the extreme case of chronic contamination, blanks may have to be analyzed from each stage of the sample processing to determine the contamination source so it can be eliminated. In all cases where blank contamination exceeds the control limit a narrative comment must be made which documents the corrective actions taken.

4.15 Blank Spikes (LCS)

4.15.1 Criteria

4.15.1.1 A blank spike follows the same protocol as with the matrix spike analysis except that the spiking solution is added to a method blank solution instead of an actual sample. A method blank with added analytes is a blank spike. A blank spike is the same as a QC check standard and LCS (Laboratory Control Sample). The single component pesticides and Aroclors 1016/1260 are spiked into the LCS. A subset of the single-component target analytes can be substituted for the full list if specified in project-specific contracts or workplans. The LCS and matrix spike should consist of the same components at the same concentration levels in order to accurately evaluate matrix interference in the MS/MSD samples.

4.15.1.2 Blank spike recoveries must meet the criteria specified in the LIMS.

4.15.2 Corrective action

4.15.2.1 The blank spike is used to determine whether a method is in control during sample preparation and analysis. Sample re- extraction and re-analysis would be triggered by an out of control blank spike only if the sample surrogate recoveries and MS/MSD spike recoveries indicated sample processing errors.

4.16 Matrix Spike

4.16.1 Criteria

4.16.1.1 A sample is chosen at random from the samples to be analyzed, and an aliquot of spiking solution is added to this sample prior to extraction. It is required that a matrix spike analysis be performed with each extraction batch. The minimum frequency for MS analysis is 1 each per 20 samples per matrix. This matrix spike sample is used to evaluate the matrix effect of the sample upon recovery of the analytes. The recovery of spike analytes is calculated as follows:

$$\%\text{Recovery} = \frac{MS - SA}{S} x100$$

where:
MS = concentration in spiked sample
SA = native concentration in unspiked sample
S = spike amount

4.16.1.2 The recovery criteria are detailed in the LIMS. In the instance that the native target analyte concentration is greater than 5x the spike concentration, the MS recovery control limits do not apply. In this case, treat the MS/MSD pair as duplicates and report them as such in the LIMS.

4.16.2 Corrective action

4.16.2.1 Samples with spike recoveries outside control limits will be reviewed for possible corrective action. Corrective action may involve recalculation, re-extraction, and/or reanalysis. This process should also look at the recovery of surrogate compounds in the MS sample and at the recovery of matrix spiking compounds from the extraction batch blank spike analysis. In all cases a narrative explanation of the condition is required to detail the corrective actions taken.

4.17 Matrix Spike Duplicate

4.17.1 Criteria

4.17.1.1 The compound recovery criteria are identical to those for the matrix spike sample. In addition, the matrix spike duplicate is used to measure method precision. This is done by computing the relative percent difference (RPD) between the matrix spike and matrix spike duplicate recovery values. This calculation is as follows:

$$\%\text{RPD} = \frac{|\chi - \delta|}{(\chi + \delta)/2} x100$$

where:

χ = measured concentration for MS sample
δ = measured concentration for MSD sample

4.17.1.2 RPD control limits are detailed in the LIMS.

4.17.2 Corrective action

4.17.2.1 If a trend in out of control RPD values is observed, the methods used must be examined to determine the source of variance. Once this source is identified, the method must be changed so that samples can be analyzed with a predictable reproducibility.

4.18 Surrogate Recovery

4.18.1 Criteria

4.18.1.1 Surrogates are chemically similar compounds added to every sample, method blank, and QC sample prior to sample processing. They are used to monitor for potential sample processing errors and matrix effects. Surrogate compound recoveries are calculated as follows:

$$\% \text{ recovery} = \frac{S_m \times 100}{S_a}$$

where:

S_m = concentration of surrogate measured in extract
S_a = concentration of surrogate added

4.18.1.2 Detailed surrogate recovery control limits are tabulated in the LIMS.

4.18.2 Corrective Action

4.18.2.1 Check calculations for possible error. Low surrogate recoveries are greater potential indicators of poor method performance than high surrogate recovery since non-GC/MS methods cannot separate co-eluting interferences. Hence corrective action is not required for high surrogate recoveries.

4.18.2.2 Low surrogate recoveries in the method blank may require that all the samples in the associated batch be re-extracted and re-analyzed. In any case, it is imperative to identify the problem associated with low recovery so that it can be corrected. It is a requirement that all out of control surrogate recoveries and the corrective action taken be discussed in the narrative.

5 Operation procedures

5.1 Chromatographic Conditions

5.1.1 The following general operating parameters are used on gas chromatographs to perform this method utilizing megabore (0.45 mm) columns:

Carrier gas:	helium
Column flow:	8 mL/min
Make-up gas:	argon/methane (95%/5% High Purity grade)
Make-up flow:	70 mL/min
Injector:	Grob-type, splitless
Injector temperature:	205°C
Injection:	splitless
Injection volume:	2µL (split - 1 µL per column)
Initial temperature:	150°C
Initial hold time:	0.5 min
Temperature ramp:	4.5°C per min
Final temperature:	275°C
Final hold time:	10 min
EC detector temperature:	350°C

5.1.2 The following general operating parameters are used on the 6890 gas chromatograph equipped with 0.32 mm columns for Pesticides:

Carrier gas:	helium
Make-up gas:	argon/methane (95%/5% High Purity grade)
Column flow:	3.6 mL/min
Make-up flow:	30 mL/min
Pulsed pressure:	55.0 psi
Pulsed time:	0.60 min.
Purge flow:	50.0 mL/min
Injector:	splitless, single-taper
Injector temperature:	250°C
Injection:	splitless
Injection volume:	1 µL (split – 0.5 µL per column)
Initial temperature:	110°C
Initial hold time:	0.5 min
Temperature ramp:	15°C per min
Final temperature 1:	320°C
Final time 1:	2 min

The following general operating parameters are used on the 6890 gas chromatograph

equipped with 0.32 mm columns for PCBs:

Carrier gas:	helium
Make-up gas:	argon/methane (95%/5% High Purity grade)
Column flow:	2.6 mL/min
Make-up flow:	35 mL/min
Pulsed pressure:	55.0 psi
Pulsed time:	0.60 min.
Purge flow:	50.0 mL/min
Injector:	splitless, single-taper
Injector temperature:	250°C
Injection:	splitless
Injection volume:	1 µL (split – 0.5 µL per column)
Initial temperature:	150°C
Initial hold time:	0.5 min
Temperature ramp:	25°C per min
Final temperature 1:	250°C
Final time 1:	1 min
Rate 2	15°C per min
Final temperature 2:	340°C
Final time 2:	2.00 min
EC detector temperature:	350°C

These GC conditions should be optimized for analyte separation and sensitivity with a particular pair of columns and detectors. Once optimized, the same conditions must be used for the analysis of all standards, samples, blanks and spikes.

5.2 Sample Analysis

5.2.1 Analysis sequence

5.2.1.1 See Appendix II for a detailed analysis injection sequence.

5.2.2 Compound Identification

5.2.2.1 Compounds are tentatively identified if a peak elutes in the retention time window characteristic of that compound on the column 1. To confirm the presence of that compound in the sample extract, the peak must also elute in its characteristic retention time window on a second column. Retention time windows are established as previously described and the absolute retention times are updated each QC period. Compounds can only be identified if the ICV and CCV criteria previously detailed are strictly adhered to.

5.2.2.2 The experienced analyst's judgment weighs heavily in evaluating chromatograms for compound identification. For instance, the retention times of surrogate compounds may be outside their expected windows due to sample matrix effects. The analyst may

decide to re-adjust the target analyte's retention time windows on an ad hoc basis based on such an observed shift. This can occur only on a sample-specific basis and is used when the analyst examining the data suspects that a retention time shift has occurred. If this is done, it must be fully documented in the case narrative notes.

5.2.2.3 Identification of multicomponent analytes occurs when the retention times and ratios of each of the multicomponent peaks present in the sample match the peaks chosen for the particular multicomponent analyte in the initial calibration. These same conditions must be met on both columns in order to confirm the presence of the multicomponent analyte. The experienced analyst's judgment weighs heavily in evaluating the patterns of multicomponent analytes with regards to weathering and matrix interferences.

5.2.3 Compound Quantitation

Target compound concentrations are calculated using the following equations:

5.2.3.1 Aqueous samples

5.2.3.1.1 The external standard equation, as expressed in SW 846 is:

$$\text{Concentration } (\mu g / L) = \frac{(A_x)(V_t)(D)}{(CF_m)(V_i)(V_s)}$$

where:

A_x = Response for the analyte in the extract, in area or height units.
CF_m = Multi-point average CF
V_i = Volume of extract injected, µL.
D = Dilution factor of extract. The final result of an algebraic multiplication of the ratio of all dilution final volumes to initial volumes. For example, if and extract was diluted 100 µL to 1000 µL and subsequently diluted an additional 100 µL to 1000 µL, the expression would be: (1000/10) * (1000/10) = 100 * 100 = 10,000. If no dilution was made, D = 1.
V_t = Volume of total extract, µL.
V_s = Initial sample size, mL.

The reported concentration for multicomponent analytes calculated is based on an average of the concentrations determined for each of the peaks chosen for calibration.

5.2.3.1.2 To report concentrations in alternate units, apply an appropriate factor:

$$mg/L = \mu g/L * 0.001$$

5.2.3.2 Non-aqueous samples

5.2.3.2.1 The results calculation for non-aqueous samples is very similar to that for aqueous samples. The only difference is the inclusion of a total solids term to calculate the dry weight equivalent of the initial sample size.

$$Conc.(\mu g / kg) = \frac{(A_x)(V_t)(D)}{(CF_m)(V_i)(W)(TS/100)}$$

where:
W = Weight of sample extracted or purged, grams.
TS = Total solids, percent.

The reported concentration for multicomponent analytes is based on an average of the concentrations determined for each of the peaks chosen for calibration.

5.2.4 Sample Dilution

5.2.4.1 If the responses in the sample chromatogram exceed the calibration range of the system, dilute the extract and reanalyze. The dilution should be made so that the concentration of the analyte requiring dilution is in the mid to upper calibration range.

5.2.5 Sample Confirmation

5.2.5.1 When a dual column /dual detector GC technique is employed, a P flag indicates that calculated results from the two determinations differ by more than 40%. If the results from one column is significantly higher (40%) the chromatogram is checked for overlapping peaks, or irregular baseline integration. If no anomalies are discovered, the lower result is reported in order to employ the conservative approach relative to protection of the environment.

6 Reports

6.1 Data Packet Organization

6.1.1 See Appendix III for a checklist detailing data packet organization.

6.2 Quality Control Reports

6.2.1 All results for quality control tests are entered into the quality control database. Printouts of all data entered must be included in the data packet. The routine minimum is a method blank report, a blank spike report, and an MS/MSD report.

6.3 Sample Result Reports

6.3.1 Data Qualifying Flags

6.3.1.1 Sample report results are qualified with data qualifying flags. These flags have the following definitions:

Code	Definition
U	The analyte of interest was not detected, to the reporting limit indicated.
B	The analyte of interest was detected in the method blank associated with the sample, as well as in the sample itself. The flag is applied without regard to the relative concentrations detected in the blank and sample.
J	The analyte of interest was detected below the practical quantification limit. This value should be regarded as an estimate.
D	The value reported is derived from the analysis of a diluted sample or sample extract.
P	When a dual column /dual detector GC technique is employed, this flag indicates that calculated results from the two determinations differ by more than 25%. If the results from one column is significantly higher (25%) the chromatogram is checked for overlapping peaks, or irregular baseline integration. If no anomalies are discovered, the higher result is reported in order to employ the conservative approach relative to protection of the environment.
E	The value reported is based on a sample or sample extract in which the target analyte concentration exceeded the calibration range. The value reported should be considered an estimate.
C	The target analyte's presence was confirmed by GC/MS.

6.4 Control Chart(s)

6.4.1.1 The recovery values for all individual pesticides, Aroclor 1016, Aroclor 1260, TCMX, and DCB in the Blank Spike are plotted on control charts.

7 References

1). U.S. EPA Contract Laboratory Program Contract, Exhibit D, Section III, March 1990

2). U.S. EPA SW846 Test Methods for Evaluating Solid Waste, Method 8000B, Gas Chromatography, Revision 2, December 1996.

3). U.S. EPA SW846 Test Methods for Evaluating Solid Waste, Method , Organochlorine Pesticides by Gas Chromatography, Method 8081B, Revision 2A, May 1999 .

4). U.S. EPA SW846 Test Methods for Evaluating Solid Waste, Method , Polychlorinated Biphenyls, (PCBs) by Gas Chromatography, Method 8082A, Revision 1A, May 1999 .

APPENDIX I

5890 Standard Solution Concentrations, µg/L

Compound	STD1	STD2	STD3	STD4	STD5
alpha-BHC	5.0	10.0	20.0	40.0	80.0
beta-BHC	5.0	10.0	20.0	40.0	80.0
delta-BHC	5.0	10.0	20.0	40.0	80.0
gamma-BHC (Lindane)	5.0	10.0	20.0	40.0	80.0
alpha-Chlordane	5.0	10.0	20.0	40.0	80.0
gamma-Chlordane	5.0	10.0	20.0	40.0	80.0
Heptachlor	5.0	10.0	20.0	40.0	80.0
Aldrin	5.0	10.0	20.0	40.0	80.0
Heptachlor epoxide	5.0	10.0	20.0	40.0	80.0
Endosulfan I	5.0	10.0	20.0	40.0	80.0
Dieldrin	10.0	20.0	40.0	80.0	160
4,4'-DDE	10.0	20.0	40.0	80.0	160
Endrin	10.0	20.0	40.0	80.0	160
Endosulfan II	10.0	20.0	40.0	80.0	160
4,4'-DDD	10.0	20.0	40.0	80.0	160
Endosulfan sulfate	10.0	20.0	40.0	80.0	160
4,4'-DDT	10.0	20.0	40.0	80.0	160
Methoxychlor	50.0	100	200	400	800
Endrin aldehyde	10.0	20.0	40.0	80.0	160
Endrin ketone	10.0	20.0	40.0	80.0	160
Toxaphene			500		
Aroclor-1016	100	250	500	1000	2000
Aroclor-1221			500		
Aroclor-1232			500		
Aroclor-1242			500		
Aroclor-1248			500		
Aroclor-1254			500		
Aroclor-1260	100	250	500	1000	2000
2,4,5,6-tetrachloro-m-xylene	5.0	10.0	20.0	40.0	80.0
Decachlorobiphenyl	10.0	20.0	40.0	80.0	160

6890 Standard Solution Concentrations, µg/L

Compound	STD1	STD2	STD3	STD4	STD5	STD6	STD7
alpha-BHC	4.0	5.0	10.0	16.0	20.0	40.0	80.0
beta-BHC	4.0	5.0	10.0	16.0	20.0	40.0	80.0
delta-BHC	4.0	5.0	10.0	16.0	20.0	40.0	80.0
gamma-BHC (Lindane)	4.0	5.0	10.0	16.0	20.0	40.0	80.0
alpha-Chlordane	4.0	5.0	10.0	16.0	20.0	40.0	80.0
gamma-Chlordane	4.0	5.0	10.0	16.0	20.0	40.0	80.0
Heptachlor	4.0	5.0	10.0	16.0	20.0	40.0	80.0
Aldrin	4.0	5.0	10.0	16.0	20.0	40.0	80.0
Heptachlor epoxide	4.0	5.0	10.0	16.0	20.0	40.0	80.0
Endosulfan I	4.0	5.0	10.0	16.0	20.0	40.0	80.0
Dieldrin	8.0	10.0	20.0	32.0	40.0	80.0	160
4,4'-DDE	8.0	10.0	20.0	32.0	40.0	80.0	160
Endrin	8.0	10.0	20.0	32.0	40.0	80.0	160
Endosulfan II	8.0	10.0	20.0	32.0	40.0	80.0	160
4,4'-DDD	8.0	10.0	20.0	32.0	40.0	80.0	160
Endosulfan sulfate	8.0	10.0	20.0	32.0	40.0	80.0	160
4,4'-DDT	8.0	10.0	20.0	32.0	40.0	80.0	160
Methoxychlor	40.0	50.0	100	160	200	400	800
Endrin aldehyde	8.0	10.0	20.0	32.0	40.0	80.0	160
Endrin ketone	8.0	10.0	20.0	32.0	40.0	80.0	160
Toxaphene				250			
Aroclor-1016	50	100	250	330	500	750	
Aroclor-1221			250				
Aroclor-1232			250				
Aroclor-1242			250				
Aroclor-1248			250				
Aroclor-1254			250				
Aroclor-1260	50	100	250	330	500	750	
2,4,5,6-tetrachloro-m-xylene	4.0	5.0	10.0	16.0	20.0	40.0	80.0
Decachlorobiphenyl	8.0	10.0	20.0	32.0	40.0	80.0	160

Calibration Stock Solutions, mg/L

Compound	Mix	Conc.
alpha-BHC	AB	5.0
beta-BHC	AB	5.0
delta-BHC	AB	5.0
gamma-BHC (Lindane)	AB	5.0
alpha-Chlordane	AB	5.0
gamma-Chlordane	AB	5.0
Heptachlor	AB	5.0
Aldrin	AB	5.0
Heptachlor epoxide	AB	5.0
Endosulfan I	AB	5.0
Dieldrin	AB	10.0
4,4'-DDE	AB	10.0
Endrin	AB	10.0
Endosulfan II	AB	10.0
4,4'-DDD	AB	10.0
Endosulfan sulfate	AB	10.0
4,4'-DDT	AB	10.0
Methoxychlor	AB	50.0
Endrin aldehyde	AB	10.0
Endrin ketone	AB	10.0
Chlordane – technical	TChlor	1000
Toxaphene	Tox	500
Aroclor-1016	AR1660	100
Aroclor-1221	AR1221	100
Aroclor-1232	AR1232	100
Aroclor-1242	AR1242	100
Aroclor-1248	AR1248	100
Aroclor-1254	AR1254	100
Aroclor-1260	AR1660	100
[1]Aroclor-1262	AR1660	100
[1]Aroclor-1268	AR1660	100

[1] These Aroclors are required only for specified DoD projects.

Breakdown Check Solution

Compound	Concentration µg/mL
4,4'-DDT	100
Endrin	100

Surrogate Stock Solution

Compound	Concentration µg/mL
2,4,5,6-tetrachloro-m-xylene	200
Decachlorobiphenyl	200

APPENDIX II

Analysis Sequence-0.45mm ID

Injection	Sample
	hexane rinse
1	breakdown check standard (PEM)
2	ICV standard INDABM
3	ICV standard multi-components(for PCB only analysis - can replace above 3 stds)
4 - 13	up to 10 subsequent sample or QC extracts
14	solvent rinse or IBLK (optional - not required)
15	CCV standard INDABM
16	CCV standard multi-components (for PCB only analysis - can replace above 2 stds)
17 - 26	up to 10 subsequent sample or QC extracts
Last	CCV standard INDABM
Last	CCV standard multi-components (for PCB only analysis - can replace above 2 stds)

Analysis Sequence-0.32mm ID

Injection	Sample
	hexane rinse
1	breakdown check standard (PEM)
2	ICV standard INDABM
3	ICV standard multi-components(for PCB only analysis - can replace above 3 stds)
4 - 13	up to 10 subsequent sample or QC extracts or 12 hours
14	solvent rinse or IBLK (optional - not required)
15	CCV standard INDABM
16	CCV standard multi-components (for PCB only analysis - can replace above 2 stds)
17 - 26	up to 10 subsequent sample or QC extracts or 12 hours
last	CCV standard INDABM
last	CCV standard multi-components (for PCB only analysis - can replace above 2 stds)

APPENDIX III

Data Packet Order

I. QC SUMMARY

_____ Analysts 'Client' Comment (hard copy and floppy)
_____ Surrogate Recovery Summary Report
_____ Blank Spike Report
_____ MS/MSD Report
_____ Method Blank Summary

II. SAMPLE DATA:

_____ Organic Analysis Data Sheet
_____ Sample Confirmation Worksheet
_____ Chromatograms, column 1
_____ Chromatograms, column 2
_____ Chromatographic Report, column 1
_____ Chromatographic Report, column 2

III. STANDARD DATA:

_____ Linearity Report

Linearity Standards:
_____ Chromatograms, column 1
_____ Chromatograms, column 2
_____ Chromatographic Report, column 1
_____ Chromatographic Report, column 2

Second Source Standards:
_____ Chromatograms, column 1
_____ Chromatograms, column 2
_____ Chromatographic Report, column 1
_____ Chromatographic Report, column 2

Continuing Calibration Standards:
_____ CCV Report
_____ Chromatograms, column 1
_____ Chromatograms, column 2
_____ Chromatographic Report, column 1
_____ Chromatographic Report, column 2

APPENDIX III, continued

Other Standards Used to Support Sample Data and Instrument Blanks

V. Raw QC Data:

_____ Method Blank
_____ Chromatograms, column 1
_____ Chromatograms, column 2
_____ Chromatographic Report, column 1
_____ Chromatographic Report, column 2

_____ Blank Spike
_____ Chromatograms, column 1
_____ Chromatograms, column 2
_____ Chromatographic Report, column 1
_____ Chromatographic Report, column 2

_____ Matrix Spike
_____ Chromatograms, column 1
_____ Chromatograms, column 2
_____ Chromatographic Report, column 1
_____ Chromatographic Report, column 2

_____ Matrix Spike Duplicate
_____ Chromatograms, column 1
_____ Chromatograms, column 2
_____ Chromatographic Report, column 1
_____ Chromatographic Report, column 2

APPENDIX III, continued

V. Bench Sheets

_____ SDG Print out
_____ Total Solids, if applicable
_____ Extraction Bench Sheets
_____ Injection Sequence (ICAL Summary, Batch Summary)
_____ calculations, HTVR
_____ Standards Logs

VI. Reject Data:

DO NOT COPY DO NOT PAGINATE

Data not used to support sample results.
All data acquired but rejected due to out of control QC.
Non-routine standards used to support sample data should be placed at the last of the Standard Data section.

APPENDIX IV

Method 8081B QA Requirements and Corrective Actions:

QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
Initial Calibration	5 calibration stds for linear, 6 stds for quadratic, for all single and multi-components, %RSD ≤15% for each analyte.	5 calibration stds for linear, 6 stds for quadratic, for all single and multi-components, %RSD ≤15% for each analyte.	After performing major instrument maintenance or when persistent difficulties meeting CCV criteria occur.	Recalibrate or narrate faults if possible	Narrative
Second Source Standard	All analytes must be within 20%.	All analytes must be within 20%.	Performed after each initial calibration.	Re-analyze or obtain third source.	Kept on file with the ICAL.
Daily Calibration Check	Must be ±15% D for each analyte.	Must be ±15% D for each analyte.	At start of each new analytical sequence, or daily if RTs shift	Rerun with new ICV, instrument maintenance, &/or recalibrate (or narrate if possible)	Narrative
Continuing Calibration Verification	Must be ±15% D for each analyte.	Must be ±15% D for each analyte.	Every 10 samples or every 12 hours.	Rerun with new ICV, instrument maintenance, &/or recalibrate (or narrate if possible)	Narrative
Breakdown	Endrin and DDT breakdown must be <=15%	Endrin and DDT breakdown must be <=15%	At the beginning of each sequence.	Rerun, instrument maintenance	Narrative
Method Blank	Presence of any target analytes must be below MDL	Must be below ½ the reporting limit	Every analytical batch or 1 per 20 samples	Report quantitated contaminants with a "B" flag, or re-extract if necessary	Case narrative and corrective action form if re-extracted

QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
Surrogate Recovery	Limits to be determined by the lab.	Listed in LIMS	Every sample	Where contractually required, all surrogates must be within control limits.	Case narrative and corrective action form if re-extracted
Matrix Spike Recovery	Limits not specified.	Listed in LIMS	Every analytical batch or 1 per 20 samples	If other QC is in control, narrate; otherwise re-extract	Case narrative and corrective action form if re-extracted
MS/MSD RPD	Limits not specified	Listed in LIMS	Every analytical batch or 1 per 20 samples	If other QC is in control, narrate; otherwise re-extract	Case narrative and corrective action form if re-extracted
Blank Spike Recovery	Limits not specified.	Listed in LIMS	Every analytical batch or 1 per 20 samples	If other QC is in control, narrate; otherwise re-extract	Case narrative and corrective action form if re-extracted
Standard Reference Material (SRM) Recovery	Not required.	Not required.	Only if requested	Reanalyze or re-extract and reanalyze SRM	Case narrative and corrective action form if re-extracted

APPENDIX V

Compound Elution order on DB5 and DB608 Megabore (0.45 mm ID) Columns

DB5	DB608
Tetrachloro-m-xylene	Tetrachloro-m-xylene
alpha-BHC	alpha-BHC
beta-BHC	gamma-BHC (Lindane)
gamma-BHC (Lindane)	beta-BHC
delta-BHC	Heptachlor
Heptachlor	delta-BHC
Aldrin	Aldrin
Isodrin	Isodrin
Heptachlor epoxide	Heptachlor epoxide
gamma-Chlordane	gamma-Chlordane
Endosulfan I	alpha-Chlordane
alpha-Chlordane	Endosulfan I
4,4'-DDE	4,4'-DDE
Dieldrin	Dieldrin
Endrin	Endrin
Endosulfan II	4,4'-DDD
4,4'-DDD	Endosulfan II
Endrin aldehyde	4,4'-DDT
Endosulfan sulfate	Endrin aldehyde
4,4'-DDT	Endosulfan sulfate
Endrin ketone	Methoxychlor
Methoxychlor	Endrin ketone
Decachlorobiphenyl	Decachlorobiphenyl

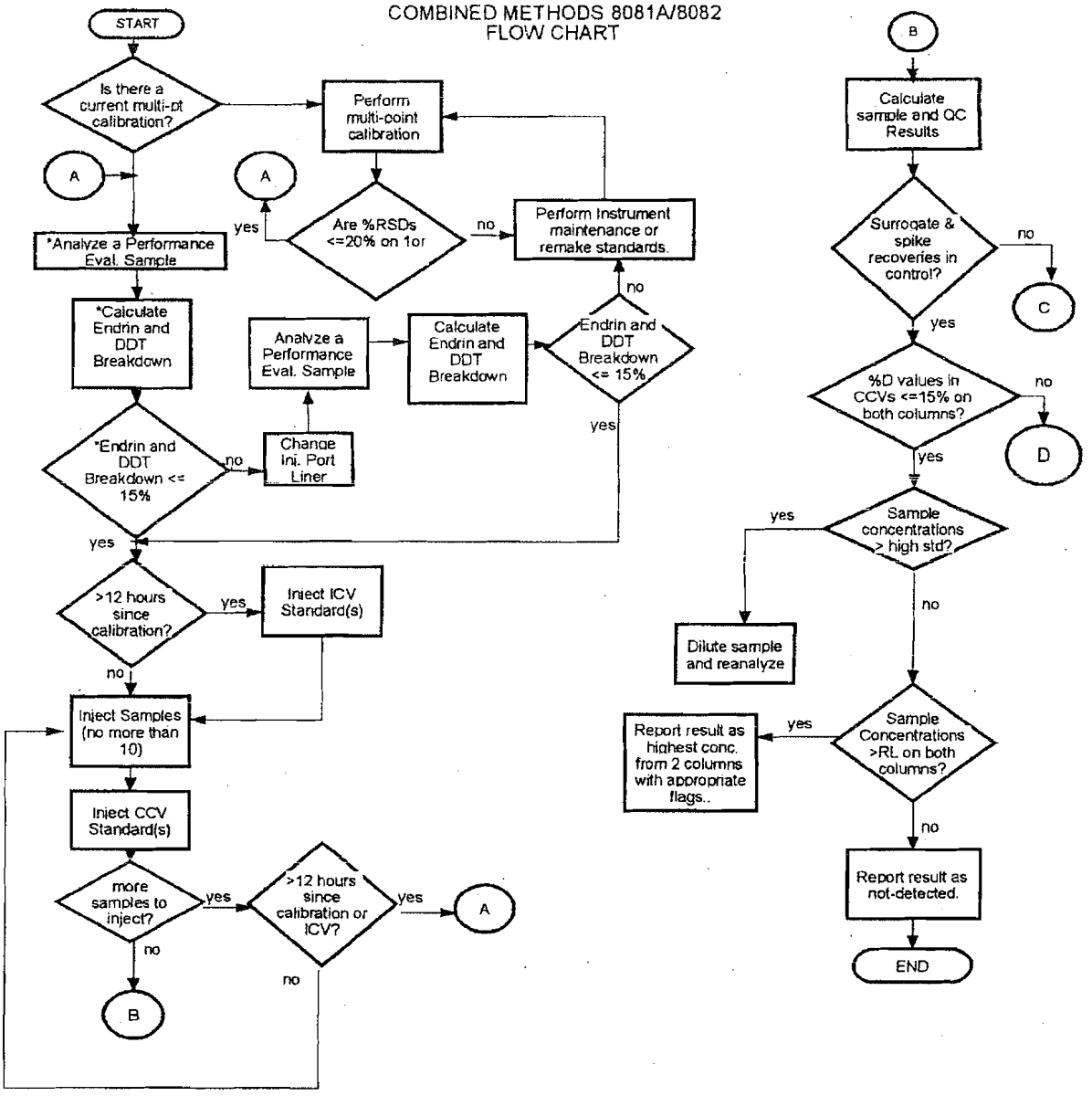
APPENDIX VI

Compound Elution order on DBXLB and DB35ms Capillary (0.32 mm ID) Columns

DBXLB	DB35ms
Tetrachloro-m-xylene	Tetrachloro-m-xylene
alpha-BHC	alpha-BHC
gamma-BHC (Lindane)	gamma-BHC (Lindane)
beta-BHC	beta-BHC
delta-BHC	Heptachlor
Heptachlor	delta-BHC
Aldrin	Aldrin
Heptachlor epoxide	Heptachlor epoxide
gamma-Chlordane	gamma-Chlordane
alpha-Chlordane	alpha-Chlordane
Endosulfan I	Endosulfan I
4,4'-DDE	4,4'-DDE
Dieldrin	Dieldrin
Endrin	Endrin
4,4'-DDD	4,4'-DDD
Endosulfan II	Endosulfan II
Endrin aldehyde	4,4'-DDT
4,4'-DDT	Endrin aldehyde
Endosulfan sulfate	Endosulfan sulfate
Methoxychlor	Methoxychlor
Endrin ketone	Endrin ketone
Decachlorobiphenyl	Decachlorobiphenyl

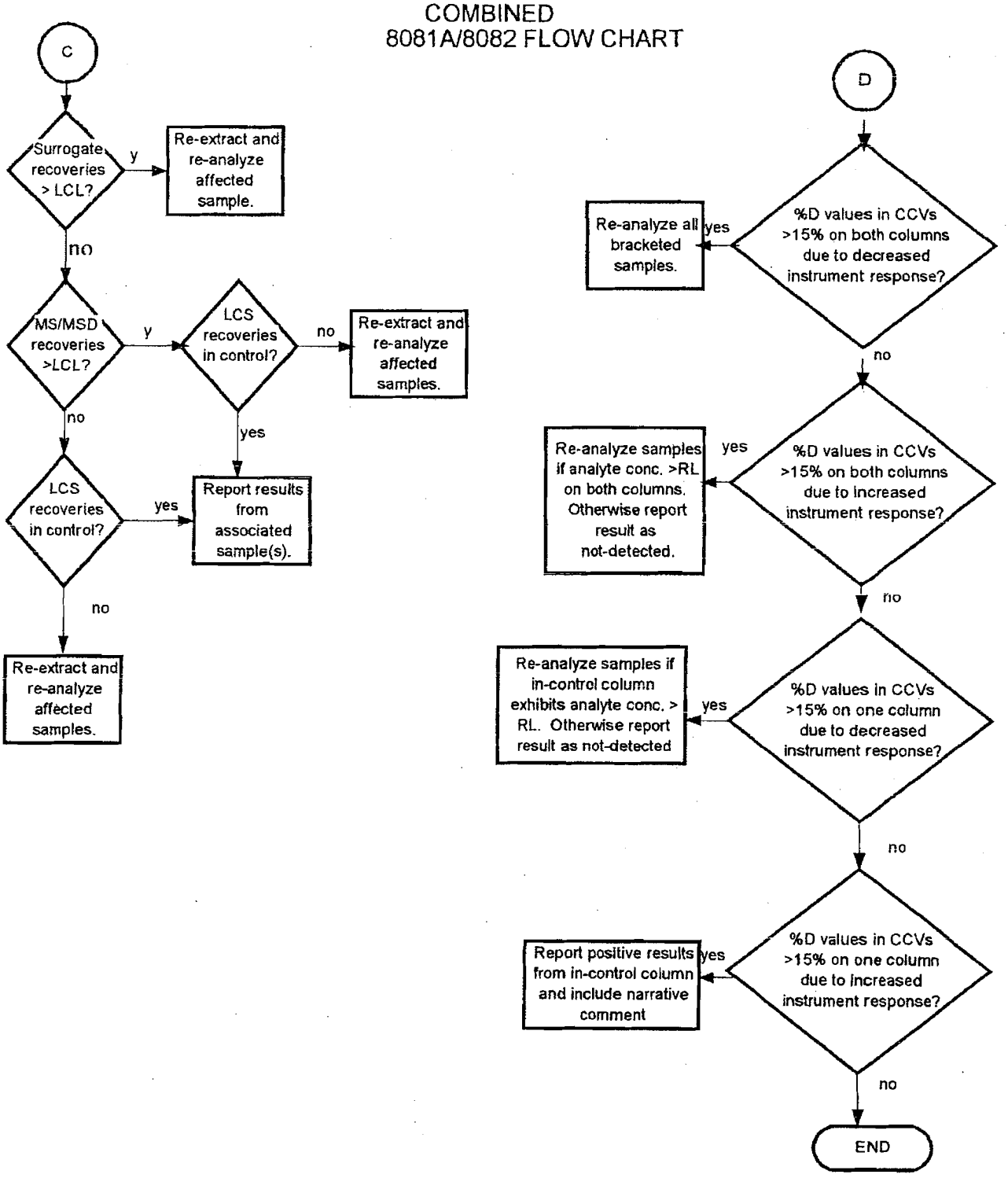
APPENDIX VII

Flow Chart



*These steps can be eliminated if analyzing for SW8082 compounds only

COMBINED
8081A/8082 FLOW CHART



Appendix VIII

Agency Requirements for SW 8081

QC Check	DoD	AFCEE	USACE	SW 846
	Acceptance Criteria	Acceptance Criteria	Acceptance Criteria	Acceptance Criteria
MDL Study	See 40 CFR 136B. S/N > 3 for MDL verification. Every 12 months, or quarterly for MDL verification checks.	Detection limits ≤ 1/2 RL listed in appropriate AFCEE table. Every 12 months.		
Retention Time Window Width	± 3σ over a 72 hour period for each analyte	± 3σ over a 72 hour period for each analyte		± 3σ over a 72 hour period for each analyte or ± 0.03 minutes, whichever is greater.
Minimum Five Point Initial Calibration	Option 1: RSD ≤ 20%	Option 1: Averaged - Grand mean RSD ≤ 20%	Option 1: RSD ≤ 20%	Option 1: Averaged - RSD ≤ 20%
	Option 2: Linear - r ≥ 0.995	Option 2: Linear - r ≥ 0.995	Option 2: Linear - r ≥ 0.995	Option 2: Linear - r ≥ 0.99
	Option 3: Non-linear regression: coefficient of determination r^2 ≥ 0.99	Option 3: Non-linear regression: coefficient of determination r^2 ≥ 0.99	Option 3: Non-linear regression: coefficient of determination r^2 ≥ 0.99	Option 3: Non-linear - r^2 ≥ 0.99, minimum of 6 pts for 2nd order, 7pts for 3rd order AND %D ≤ 20%
Second Source	%D within ± 20%	within ± 15%	within ± 15%	

QC Check	DoD	AFCEE	USACE	SW 846
	Acceptance Criteria	Acceptance Criteria	Acceptance Criteria	Acceptance Criteria
Retention Time	Set at retention time of midpoint standard of ICAL			Set at retention time of first CCV of the analytical sequence, or of the midpoint standard if samples were ran after the ICAL
Continuing Calibration Verification	Within ± 20%.	Within ± 15%.	Within ± 15%.	Within ± 15%.
	Every 10 field samples, beginning and end of analytical run	Every 10 samples, beginning and end of analytical sequence		Beginning and end of each 12 hour analytical shift
				Required after every 20, recommended after 10
Method Blank	No analytes ≥ 1/2 RL. No common laboratory contaminant analytes ≥ RL	No analytes ≥ RL	Analytes < 1/2 MRL	Less than the laboratory detection limit OR Less than 5% of the regulatory limit OR Less than 5% of the sample result WHICHEVER IS GREATER
Laboratory Control Sample	See appropriate DoD table, or use in-house limits if	See appropriate AFCEE table	50%-130% recovery	Lab-derived

QC Check	DoD	AFCEE	USACE	SW 846
	Acceptance Criteria	Acceptance Criteria	Acceptance Criteria	Acceptance Criteria
	not listed			
Matrix Spike	Same as LCS	Same as LCS	40%-140% recovery	Lab-derived
Matrix Spike Duplicate	RPD ≤ 30%	Water: RPD ≤ 30%	RPD ≤ 50%	Lab-derived
		Soil: RPD ≤ 50%		
Surrogate Spike	Same as LCS	Same as LCS	Blank Spike: 50%-130% recovery	Lab-derived
			Matrix Spike: 40%-140% recovery	
Confirmation of positive results	RPD ≤ 40	RPD ≤ 40%, J flag if greater	RPD ≤ 40%	RPD ≤ 40%
Results reported between MDL and RL	Apply J flags	Apply F flags		
Allowable Sporadic ME/Failures	11 - 30 analytes – 1 1 – 10 analytes: 0			

Appendix IX

Control Limits

Water

Target Analyte	RL	MDL	Blank	MS/MSD			BS/BSD		
				LCL	UCL	RPD	LCL	UCL	RPD
alpha-BHC	0.05	0.0032	0.025	45	150	37	25	153	
beta-BHC	0.05	0.0042	0.025	41	166	32	60	144	
delta-BHC	0.05	0.004	0.025	54	175	35	38	174	
gamma-BHC	0.05	0.0037	0.025	35	142	27	43	163	
Heptachlor	0.05	0.0031	0.025	30	127	28	20	129	
Aldrin	0.05	0.0034	0.025	18	147	30	20	133	
Heptachlor epoxide	0.05	0.0035	0.025	41	149	27	39	162	
Endosulfan I	0.05	0.0036	0.025	37	171	9	53	146	
Dieldrin	0.1	0.007	0.05	39	143	27	55	133	
4,4'-DDE	0.1	0.0086	0.05	57	161	11	48	150	
Endrin	0.1	0.0075	0.05	66	159	12	64	168	
Endosulfan II	0.1	0.0079	0.05	61	151	19	67	149	
4,4'-DDD	0.1	0.0072	0.05	53	147	28	47	139	
Endosulfan sulfate	0.1	0.0064	0.05	48	153	37	49	154	
4,4'-DDT	0.1	0.0088	0.05	51	149	14	46	134	
Methoxychlor	0.5	0.0349	0.025	54	149	28	52	135	
Endrin aldehyde	0.1	0.01	0.05	36	141	15	50	136	
alpha-Chlordane	0.05	0.0039	0.025	56	153	30	43	172	
Endrin ketone	0.1	0.0067	0.05	93	138	6	62	155	
gamma-Chlordane	0.05	0.0043	0.025	40	149	31	51	132	
Chlordane	1	0.021	0.5						
Toxaphene	5	0.15	2.5						
Aroclor-1016	0.5	0.043	0.25	60	132	20	46	125	
Aroclor-1221	0.5	0.039	0.25						
Aroclor-1232	0.5	0.084	0.25						
Aroclor-1242	0.5	0.051	0.25						
Aroclor-1248	0.5	0.086	0.25						
Aroclor-1254	0.5	0.16	0.25						
Aroclor-1260	0.5	0.045	0.25	59	139	21	50	143	

Soil

Target Analyte	RL	MDL	Blank	MS/MSD			BS/BSD		
				LCL	UCL	RPD	LCL	UCL	RPD
alpha-BHC	1.7	0.3	0.85	46	141	34	53	136	
beta-BHC	1.7	0.38	0.85	43	158	30	59	146	
delta-BHC	1.7	0.34	0.85	48	162	37	66	156	
gamma-BHC	1.7	0.38	0.85	39	144	29	46	131	
Heptachlor	1.7	0.4	0.85	57	118	25	56	117	
Aldrin	1.7	0.38	0.85	47	139	28	59	126	
Heptachlor epoxide	1.7	0.4	0.85	36	140	52	50	133	
Endosulfan I	1.7	0.39	0.85	19	167	37	42	139	
Dieldrin	3.3	0.75	1.65	44	153	33	52	140	
4,4'-DDE	3.3	0.83	1.65	20	190	47	57	153	
Endrin	3.3	0.86	1.65	55	167	34	48	154	
Endosulfan II	3.3	0.77	1.65	6	179	37	39	162	
4,4'-DDD	3.3	0.74	1.65	49	170	41	29	160	
Endosulfan sulfate	3.3	0.74	1.65	41	155	34	41	150	
4,4'-DDT	3.3	0.74	1.65	38	156	44	41	133	
Methoxychlor	17	3	8.5	67	142	39	61	118	
Endrin aldehyde	3.3	0.59	1.65	28	114	30	45	119	
alpha-Chlordane	1.7	0.44	0.85	19	174	48	38	189	
Endrin ketone	3.3	0.71	1.65	40	165	36	49	154	
gamma-Chlordane	1.7	0.37	0.85	26	150	49	53	132	
Chlordane	17	2.8	8.5						
Toxaphene	170	6.4	85						
Aroclor-1016	17	3.1	8.25	42	128	16	62	130	
Aroclor-1221	17	4.6	8.25						
Aroclor-1232	17	3.9	8.25						
Aroclor-1242	17	4.5	8.25						
Aroclor-1248	17	4.3	8.25						
Aroclor-1254	17	2.6	8.25						
Aroclor-1260	17	3.35	8.25	49	158	31	58	139	

Water

Surrogates	Limits	
	LCL	UCL
Tetrachloro-m-xylene	10	129
Decachlorobiphenyl	32	149

Soil

Surrogates	Limits	
	LCL	UCL
Tetrachloro-m-xylene	61	129
Decachlorobiphenyl	75	158

Controlled Document

Book: 20 Assigned to: Tetra Tech

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-8151

Title: **Analysis of Chlorinated Herbicides by Method 8151A**

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1. Introduction and Scope

1.1 Method Description

1.1.1 This method describes the procedures and specifications for instrumental analysis of various chlorinated herbicides in water and soil per Method 8151A in SW-846 utilizing capillary columns. Analysis is performed by gas chromatography using a single injection port and splitting into dual GC columns with electron-capture detectors. This system provides quantitation and confirmation of herbicides from a single injection. Dinoseb generally yields poor recoveries using this analysis due to difficulty in bringing the analyte through the hydrolysis stage of the extraction procedure. The following table lists the compounds that may be determined by this method:

ABBREVIATION	COMPOUND NAME
2,4-D	2,4-Dichlorophenoxyacetic acid
2,4-DB	4-(2,4-Dichlorophenoxy) butyric acid
2,4,5-T	2,4,5-Trichlorophenoxyacetic acid
2,4,5-TP (Silvex)	2-(2,4,5-Trichlorophenoxy) propionic acid
Dalapon	2,2-Dichloropropionic acid
Dicamba	2-Methoxy-3,6-dichlorobenzoic acid
Dichloroprop (2,4-DP)	2-(2,4-Dichlorophenoxy) propionic acid
Dinoseb	2-(sec-Butyl)-4,6-dinitrophenol
MCPA	(4-Chloro-2-methylphenoxy) acetic acid
MCPP	2,4-(Chloro-2-methylphenoxy) propionic acid
NON-ROUTINE COMPOUNDS	
4-Nitrophenol	4-Nitrophenol
PCP	2,3,4,5,6-Pentachlorophenol
Picloram	4-Amino-3,5,6-trichloropicolinic acid
Hexachlorophene	Hexachlorophene

1.2 Method Summary

1.2.1 Water samples are extracted with ethyl ether and then esterified with either diazomethane or pentafluorobenzyl bromide. The derivatives are determined by gas chromatography with an electron capture detector (GC/ECD). The results are reported as acid equivalents. Refer to Laucks' extraction SOP LTL-3510 for details.

1.2.2 Soil and waste samples are extracted with ethyl ether and esterified with either diazomethane or pentafluorobenzyl bromide. The derivatives are determined by gas chromatography with an electron capture detector (GC/ECD). The results are reported as acid equivalents. Refer to Laucks' extraction SOP LTL-3011 for details.

1.3 Personnel Qualifications

1.3.1 This method is restricted to use by, or under the supervision of analysts experienced in the use of gas chromatography and in the interpretation of chromatograms. Each analyst performing this method must have demonstrated the ability to perform the described chromatographic analysis and/or data interpretation.

1.4 Sample Collection, Sample Storage, Holding Times

1.4.1 Samples are normally collected in glass containers with Teflon-lined caps. All samples and sample extracts are stored at 4°C. Water samples must be extracted within 7 days of sample collection, soil samples within 14 days of sample collection. All extracts must be analyzed with 40 days of sample extraction.

1.5 Definition of Terms

1.5.1 This section defines terms and acronyms as they are used in this SOP. Other terms, such as MS/MSD or method blank, are not defined here since it is assumed that the user of this SOP already understands their more general meaning.

Batch Identifier	A number given to each preparation or analysis group which uniquely identifies that batch. This number is generally the blank ID for preparation batches and either a sequence number for organic analyses or an analysis number which is similar to the blank ID, only preceded by an "A" rather than a "B" for inorganic batches. The preparation batch IDs are discussed in other documentation.
Blank spike	A background free matrix (DIW for water, clean sand for soils/sediments) to which known amounts of target analytes and surrogates are added each time sample extracts are prepared. In the context of this SOP, a blank spike is the same as a QC check standard. See also QC check standard.
CCV	Continuing calibration verification. This is the same acronym used in the CLP program. This is a standard analyzed at some prescribed frequency during the analysis sequence to verify that the instrument has remained in calibration.

CF	Calibration factor. The ratio of analyte instrument response to nanograms injected. This term is defined in the same way in both the CLP contract and SW 846.
CLP	Contract Laboratory Program. The USEPA program that contracts with laboratories to provide laboratory services. The term has come to mean a much broader set of methods and deliverables. In the context of this SOP, CLP means procedures or operations which are detailed in the CLP contract and which are extended to a broader working definition.
Corr Coef, CC	Correlation coefficient. A measure of the "goodness of fit" of a set of data to a regression model. The closer the value is to 1, the higher the degree of confidence in the correlation.
DIW	Deionized water. Lab reagent water. Organic-free water. Since the systems used to provide DIW at Laucks all contain carbon polishing filters, they are capable of providing organic-free water for use in method blanks and method blank spikes.
IBLK	Instrument blank. This term is borrowed from CLP. Blank solvent containing the method surrogates is injected into the instrument to monitor for carry over between sample extract injections.
ICV	Initial calibration verification. This refers to a second source standard that is analyzed following each initial calibration.
IDL	Instrument detection limit. The lowest concentration of a target analyte that will yield a signal:noise ratio of at least 3x. Used as a starting point for selecting MDL study spiking levels.
MDL	Method detection limit. The lowest concentration in a sample which will yield a positive result that is greater than zero at a known level of confidence. MDLs are empirically determined by Laucks.
MDL standard	Method detection limit standard. A standard prepared so that the concentrations of the target analytes are in the range of 1x to 4x the empirically determined MDLs on an extract/digest basis. This standard is used to verify that the instrument is capable of detecting the target analytes on an ongoing basis.

PQL or Reporting Limit	Practical Quantitation Limit or Reporting Limit- The value used when reporting a non-detect. It may be administratively, empirically or contractually set.
QC check standard	Quality control check standard. Referred to in this SOP as a blank spike. A QC check standard is a requirement of SW 846 method 8000 and is used to determine whether the analytical system is in control if MS/MSD recoveries are out of control. See also blank spike.
QC period	Quality control period. An analysis sequence initiated by the analysis of one or more standards, followed by sample extracts/digests, and terminated with a standard analysis. A QC period can be open-ended chronologically, but calibration verification must be documented using the procedures in this SOP.
RRF	Relative Response Factor. A measure of the relative response of an analyte compared to its internal standard. Relative response factors are determined by analysis of standards and are used in the calculation of concentrations of analytes in samples. RRF is determined by the following equation: $$RRF = \frac{A_x}{A_{is}} \times \frac{C_{is}}{C_x}$$ Where A = area of response measured C = concentration is = internal standard x = analyte of interest
RSD or %RSD	Relative standard deviation or percent relative standard deviation. The ratio of the standard deviation of a set of values to the mean of the set of values expressed as a percentage. A measure of the similarity of the values one to another.
RT, Retention time	The time (in minutes) at which a target analyte elutes from a chromatography column.
RT window	Retention time window. The +/- value which is applied to the first CCV to establish the time range used to make tentative compound identifications.

Sequence — A set of sample extracts/digests and standard solutions introduced into an instrument in a chronologically continuous group. See also QC period.

2. Equipment List and Standards

2.1 Chromatographic System

2.1.1 This analysis requires a gas chromatograph with a programmable oven, heated injection port, dual electron-capture detectors, autosampler and an electronic data-acquisition system.

2.1.2 **Equipment list:**

Gas chromatograph:	Hewlett-Packard 5890, Agilent 6890 or equivalent
Autosampler:	Hewlett-Packard 7673, Agilent 7683 or equivalent
Electron-capture detectors:	Hewlett-Packard, Agilent or equivalent
Capillary chromatographic columns of dissimilar phase:	J&W DB5, DB608 or DB1701, 30m x 0.45mm, 0.53mm, 0.85mm or 0.25mm megabore; DB-35ms 30m x 0.32mm x 0.25 µm; DB-XLB 20m x 0.32mm x 0.5 µm or equivalent
Carrier gas:	Ultra high purity Helium (99.999%)
Make-up gas:	5% methane/95% argon
Data System:	Pentium PCs, or equivalent, EZChrom Data Acquisition System version 6.6
Analytical Software:	Target for NT Operating System version 4.02

2.2 Troubleshooting

2.2.1 Please refer to Organics' Troubleshooting Manual for detailed instructions on instrumentation.

2.3 Standards

2.3.1 Commercially prepared and certified standard solutions are used. Suppliers may change without notice or immediate update to this Standard Operating Procedure. Refer to Laucks' SOP on the traceability, documentation, and preparation standards.

2.3.2 Working standards are prepared in hexane from these stocks. Those which are prepared in the free acid form (not prepared from methyl esters) are methylated by

derivatization using diazomethane. At this stage all working standards are in methyl ester or ether form. They must be replaced after six months or by the expiration date of the parent standard, whichever is earlier.

2.3.3 Calibration standards are prepared by combining the stock standards and diluting with hexane to prepare the calibration standard which defines the upper and lower range of the ECD. All calibration standards must be replaced after 6 months or by the expiration date of the parent standard, whichever is earlier.

2.3.4 Appendix I details the compounds and concentrations contained in all solutions.

Primary	**Manufacturer**	**Catalog Number**	**Comments**
7 cmpds	Restek	32055	Methyl Ester
MCPA, MCPP*	Restek	32059	Methyl Ester
PCP	Restek	31297	Acid
4-Nitrophenol	Restek	31296	Acid
Picloram	Restek	32266	Methyl Ester
Hexachlorophene	Ultra	PH270	Acid
2,4-DCPAA(surr)	Restek	32050	Methyl Ester
Dalapon	Restek	32057	Methyl Ester
Second Source	**Manufacturer**	**Catalog Number**	**Comments**
10 cmpds	Crescent	CC2229	Methyl Ester
PCP	Absolute	30038	Methyl Ester
4-Nitrophenol	Supelco	48695	Methyl Ester
Picloram	Ultra	PS1108	Methyl Ester
Hexachlorophene	Crescent	3233M	Acid
2,4-DCPAA(surr)	Crescent	CC2064A	Methyl Ester

*MCPA and MCPP must be spiked separately due to interfering compounds in the standards. The vendors are aware of this and are trying to resolve this issue.

3. Safety precautions and Waste Disposal

3.1 Routine Safety Precautions

3.1.1 All standards and sample extracts should be handled as if they contain hazardous substances.

3.1.2 Refer to the instrument manufacturer's manual for routine instrument precautions.

3.1.3 Routine precautions include an awareness of the moving parts on the instrument you're using. These parts are often charged with power from an electrical component or with high pressure gas and have the potential to do harm if not used properly.

3.1.4 Electrical shock - All instruments present the possibility of electrical shock. The operator should take all precautions including ensuring that all instruments are operated with fully grounded power outlets, turning off the instrument and disconnecting the instrument from the electrical power supply before working on any electrical components, etc.

3.1.5 The electron-capture detectors used in this analysis contain a radioactive source and should not be opened or otherwise tampered with.

3.1.6 Ensure that all gas cylinders are either fastened to an immovable object or capped securely at all times.

3.2 Waste disposal

3.2.1 Solvent wastes generated in using this procedure (expired standards, old sample extracts, rinsates, etc.) should be emptied into the solvent waste container in the fume hood.

3.2.2 Waste segregation and disposal from the point of collection is further covered in the Laucks SOP on Waste Segregation and Disposal.

4. Calibration and Quality Control

4.1 QA Requirements and Corrective Action

4.1.1 Detailed in the following sections are applicable QA requirements and subsequent corrective actions to be applied to this analysis. A summary of these requirements can be found in Appendix IV.

4.2 Method Detection Limit Study

4.2.1 Prior to the analysis of any samples, it is necessary to establish method detection limits. This procedure is fully described in the Laucks SOP on MDL Studies. Briefly, it involves the analysis of 7 replicate samples spiked at a concentration near the anticipated method detection limit. A Student's T-test is then applied to these measured values to calculate the MDL. Refer to Appendix VII for MDLs (at the time of this writing). Most current MDL values are found in the LIMS MDL database and associated raw data are stored in department files

4.3 Method Validation

4.3.1 Prior to the analysis of any samples, it is necessary to validate the method. A method validation study is performed in a similar manner to an MDL study with the exception

that a minimum of 4 replicates are required and the concentration levels must be similar to those found in SW-846.

4.3.2 The results must be equal to or better than the spike recoveries tabulated in SW 846. These criteria and recommended spiking concentrations for method validation are tabulated in SW 846.

4.4 Retention Time Windows

4.4.1 Prior to the analysis of any samples, it is necessary to establish retention times windows for the method by analyzing standards for all target analytes over at least a 72-hour period. This need not be a single 72 hour sequence but can be 3 chronologically contiguous sequences. These standards should be inter-mixed with real sample extracts in order to mimic actual instrument operating conditions. Tabulate the retention times for all standard compounds and compute the standard deviations of all the retention times. Retention time normalization techniques may be applied if appropriate. For megabore capillary columns, a default RT window of ± 0.05 minutes may be used. Details of the procedure for determining retention time windows can be found in Laucks SOP on establishing retention time windows.

4.5 Initial Multi-Point Calibration

4.5.1 Analyze herbicide standards using at least 5 different concentration levels for linear calibrations. The lowest concentration should define the reporting limit (RL). The highest concentration should define the upper usable working range of the detector. In addition, an instrument blank is analyzed as part of the initial calibration. Subsequent to the initial calibration, an additional calibration standard is analyzed using standards obtained from a second source. The second source standard must be from a different manufacturer unless one is not available. The acceptance criteria for the second source standards are tabulated below and are located in Appendix VIII.

Agency	% Criterion
AFCEE	± 15
USACE	N/A
DoD	± 20
SW 846	N/A

4.5.2 SW 846 allows the use of both linear and non-linear models for the calibration data. The option for non-linear calibration may be necessary to achieve low detection limits or to address specific instrumental techniques.

4.5.3 The choice of a specific calibration model should be made in one of two ways. The first is to begin with the simplest approach, the linear model through the origin, and progressing through the other options until the calibration acceptance criteria are met. The second approach is to use *a priori* knowledge of the detector response to choose the calibration model. Such knowledge may come from previous experience, knowledge of physics of the detector, or specific manufacturer's recommendations.

4.6 Linear Calibration

4.6.1 External standard initial calibration data is evaluated by determining the %RSD of the calibration factors.

4.6.2 CFs are calculated using the equation:

$$CF = \frac{\text{response}}{\text{ng injected}}$$

4.6.3 The calculated CFs are tabulated and the %RSD calculated. All %RSDs must be within 20% for each analyte.

4.6.4 Corrective action

4.6.4.1 If the criteria are not met, the instrument must be re-calibrated.

4.7 Non-linear Calibration

4.7.1.1 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 described here have not met the acceptance criteria, a non-linear calibration model may be employed.

4.7.1.2 When using a calibration model for quantitation, the curve must be continuous, continuously differentiable and monotonic over the calibration range.

4.7.1.3 The statistical considerations in developing a non-linear calibration model require more data than the more traditional linear approaches. A quadratic (second order) requires a minimum of six standards. Do not force the line through the origin, i.e., do not set the intercept as 0, and do not include the origin (0,0) as a calibration point. The R^2 value must be greater than 0.99.

4.7.1.4 Whichever option is employed, a surrogate concentration must fall within the calibration range.

4.7.2 Corrective action

4.7.2.1 If the criteria are not met, the instrument must be re-calibrated.

4.8 Calibration Verification

4.8.1 Concentration and/or CF Criteria

4.8.1.1 At the beginning of an analysis sequence analyze a calibration standard. A mid-range calibration standard is also analyzed at the frequency of every 12 hours. In addition, this standard must be the last injection made in the analysis sequence. The concentration of the calibration standard is most often the mid-range. However, the concentration of the calibration standard must be varied from time to time. The computed calibration factor (CF) or concentration measurement must meet the criteria detailed below.

4.8.1.2 Using the appropriate calculation technique (average CF) compute either CFs or concentration values. For linear calibrations the CCV standard can be verified by calculating either the percent difference or the percent drift.

4.8.1.2.1 The percent difference calculation compares the CCV CFs to the mean CFs from the initial multi-point calibration. The percent difference is calculated as follows:

$$\%D = \frac{Cv - \overline{CF}}{\overline{CF}} \times 100$$

where:

C_v = Calibration Factor

$\overline{CF}$ = Mean Calibration Factor

4.8.1.2.2 The percent drift calculation compares the CCV calculated concentrations to the theoretical (or actual) concentration of the CCV standard. The percent drift is calculated as follows:

$$\%D = \frac{C_c - C_T}{C_T} \times 100$$

where:

C_c= Calculated Concentration
C_T = Theoretical Concentration

4.8.1.3 If the response (or calculated concentration) for an analyte is ±15% of the response obtained during the initial calibration, then the initial calibration is considered still valid.

4.8.2 Corrective action

4.8.2.1 If the CCV criteria are not met, no sample extracts can be analyzed. Perform system maintenance and re-check the CCV. If the criteria still cannot be met, the system must be recalibrated.

4.9 Method Blanks

4.9.1 Criteria

4.9.1.1 Method blanks are used to verify contamination free reagents and apparatus. They are prepared with every set of samples extracted at the same time or one blank every 20 samples which ever is more frequent. Any analyte response above 1/2 the reporting limit is reported. Method blank control limits are detailed in the LIMS database and Appendix VII.

4.9.2 Corrective action

4.9.2.1 Corrective action may necessitate re-extraction of the sample set. For example if an analyte were found in the blank but not in any of the associated samples then the sample group may not require re-extraction. In any event it is the laboratory's responsibility to ensure that method interferences caused by contaminants in solvents, reagents, glassware, and other sample processing hardware leading to discrete artifacts and/or elevated baselines in the chromatograms be minimized. In the extreme case of chronic contamination, blanks may have to be analyzed from each stage of the sample processing to determine the contamination source so it can be eliminated. In all cases where blank contamination exceeds the control limit a narrative comment must be made which documents the corrective actions taken.

4.10 Blank Spikes

4.10.1 Criteria

4.10.1.1 A blank spike follows the same protocol as with the matrix spike analysis except that the spiking solution is added to a method blank solution instead of an actual sample. A method blank with added analytes is a blank spike. A blank spike is similar to a QC check standard. Refer to Appendix VII for control limits. Because control limits are updated often as required by the method, all current control limits are located in the LIMS database. Additional requirements for each Agency are located in Appendix VIII.

4.10.2 Corrective action

4.10.2.1 The method blank spike is used to determine whether a method is in control during sample preparation and analysis. Sample re- extraction and re-analysis would be triggered by an out of control method blank spike only if the sample surrogate recoveries and MS/MSD spike recoveries indicated sample processing errors.

4.11 Matrix Spike

4.11.1 Criteria

4.11.1.1 A sample is chosen at random from the samples to be analyzed, and an aliquot of spiking solution is added to this sample prior to extraction. It is required that a matrix spike analysis be performed with each extraction batch. The minimum frequency for MS analysis is 1 each per 20 samples per matrix. This matrix spike sample is used to evaluate the matrix effect of the sample upon recovery of the analytes. The recovery of spike analytes is calculated as follows:

$$\%\,\text{recovery} = \frac{SS - S}{SA} \times 100$$

where:

SS = spiked sample result
S = unspiked sample result
SA = amount spiked

4.11.1.2 Refer to Appendix VII for control limits. Because control limits are updated often as required by the method, all current control limits are located in the LIMS database. Additional requirements for each Agency are located in Appendix VIII.

4.11.1.3 In the instance that the native target analyte concentration is greater than 5x the spike added concentration, the MS recovery control limits do not apply. In this case, treat the MS/MSD pair as duplicates and report them as such in the LIMS database.

4.11.2 Corrective action

4.11.2.1 Samples with spike recoveries outside control limits will be reviewed for possible corrective action. Corrective action may involve recalculation, re-extraction, and/or reanalysis. This process should also look at the recovery of surrogate compounds in the MS sample and at the recovery of spiking compounds from the extraction batch blank spike analysis. In all cases a narrative explanation of the condition is required to detail the corrective actions taken.

4.12 Matrix Spike Duplicate

4.12.1 Criteria

4.12.1.1 The compound recovery criteria are identical to those for the matrix spike sample. (A sample is chosen at random from the samples to be analyzed.) In addition, the matrix spike duplicate is used to measure method precision. This is done by computing the

relative percent difference (RPD) between the matrix spike and matrix spike duplicate recovery values.

4.12.1.2 This calculation is as follows:

$$\% RPD = \frac{|S_1 - S_2|}{(S_1 + S_2)/2} \times 100$$

where:

S_1 = measured concentration for MS sample
S_2 = measured concentration for MSD sample

4.12.1.3 RPD control limits are detailed in the LIMS database and Appendix VII.

4.12.2 Corrective action

4.12.2.1 If a trend in out of control RPD values is observed, the methods used must be examined to determine the source of variance. Once this source is identified, the method must be changed so that samples can be analyzed with a predictable reproducibility.

4.13 Surrogate Recovery

4.13.1 Criteria

4.13.1.1 Surrogates are chemically similar compounds added to every sample, method blank, and QC sample prior to sample processing. They are used to monitor for potential sample processing errors and matrix effects. Surrogate compound recoveries are calculated as follows:

$$\% \text{ recovery} = \frac{S_m \times 100}{S_a}$$

where:

S_m = concentration of surrogate measured in extract
S_a = concentration of surrogate added

4.13.1.2 Refer to Appendix VII for control limits. Because control limits are updated often as required by the method, all current control limits are located in the LIMS database. Additional requirements for each Agency are located in Appendix VIII.

4.13.2 Corrective Action

4.13.2.1 Check calculations for possible error. Low surrogate recoveries are greater potential indicators of poor method performance than high surrogate recovery since non-GC/MS methods cannot separate co-eluting interferences. Hence corrective action is not usually required for high surrogate recoveries. These cases should be evaluated for other possible causes (such as double surrogate spiking or incorrect dilution factors).

4.13.2.2 Low surrogate recoveries in the method blank may require that all the samples in the associated batch be re-extracted and re-analyzed. In any case, it is imperative to identify the problem associated with low recovery so that it can be corrected. It is a requirement that all out of control surrogate recoveries and the corrective action taken be discussed in the narrative.

5. Operation procedures

5.1 Chromatographic Conditions

5.1.1 The following are typical operating parameters used to perform this method. There may be times when adjustments are made in order to optimize the analysis.

	5890	**6890**
Column flow	7-8 mL/min	3.0 mL/min
Make-up gas	argon/methane (95%/5% High Purity Grade)	Argon/methane (95%/5% High Purity Grade)
Make-up flow	60 - 65 mL/min	30 mL/min
Injector	grob-type, split/splitless with 4mm wide bore deactivated liner	Grob-type, split/splitless with 4mm wide bore deactivated liner
Injector temperature	205°C	250°C
Injection	on-column	on-column
Injection volume	1µl per column (2µl total)	0.5 µl per column (1µl total)
Initial temperature	45°C	50°C
Initial hold time	1.0 min	0.5 min
Temperature ramp	25°C per min to 150°C	25°C per min to 100°C
Hold time	1 min	0 min
Temperature ramp	5°C per min to 240°C	12°C per min to 320°C
Hold time	0 min	2 min
Temperature ramp	25°C per min to 280°C	None

	5890	6890
Final hold time	0 min (10 min. if hexachlorophene is a target analyte)	
Detector temperature	325°C	325°C

5.2 Sample Analysis

5.2.1 Analysis sequence

5.2.1.1 See Appendix II for a detailed analysis injection sequence.

5.2.2 Compound Identification

5.2.2.1 Compounds are tentatively identified if a peak elutes in the retention time window characteristic of that compound on the primary column. To confirm the presence of that compound in the sample extract, the peak must also elute in its characteristic retention time window on a second column. Compounds can only be identified if the CCV criteria previously detailed are strictly adhered to.

5.2.2.2 The experienced analyst's judgment weighs heavily in evaluating chromatograms for compound identification. For instance, the retention times of surrogate compounds may be outside their expected windows due to sample matrix effects. The analyst may decide to re-adjust the target analyte's retention time windows on an ad hoc basis based on such an observed shift. This can occur only on a sample-specific basis and is used when the analyst examining the data suspects that a retention time shift has occurred. If this is done, it must be fully documented in the case narrative notes. If the concentration of any target analyte exceeds the calibration range, the sample extract must be diluted and reanalyzed.

5.2.3 Compound Quantitation

Target compound concentrations are calculated using the following equations:

5.2.3.1 Aqueous samples

The external standard equation, as expressed in SW 846 is:

$$\text{Concentration } (\mu g / L) = \frac{As \times Vt \times D}{\overline{CF} \times Vi \times Vs}$$

where:

A_S = Area or height of the peak for the analyte in the sample.
V_i = Volume of extract injected, µL.
D = Dilution factor of extract. The final result of an algebraic multiplication of the ratio of all dilution final volumes to initial volumes. For example, if and extract was diluted 10 µL to 1000 µL and subsequently diluted an additional 10 µL to 1000 µL, the expression would be: (1000/10) * (1000/10) = 100 * 100 = 10,000.
If no dilution was made, D = 1.
V_t = Volume of total extract, µL.
V_S = Initial sample size, mL.
$\overline{CF}$ = Mean calibration factor.

To report concentrations in alternate units, apply an appropriate factor:

mg/L = µg/L * 0.001

5.2.3.2 Non-aqueous samples

The results calculation for non-aqueous samples is very similar to that for aqueous samples. The only difference is the inclusion of a total solids term to calculate the dry weight equivalent of the initial sample size.

$$Conc.(\mu g / kg) = \frac{Vt \times As \times D}{\overline{CF} \times Vi \times Ws}$$

where:
Ws = Weight of sample extracted or purged, grams. Either the wet weight or dry weight..

6. Reports

6.1 Data Packet Organization

See Appendix III for a check list detailing data packet organization.

6.2 Quality Control Reports

All results for quality control tests are entered into the lab quality control data base. Printouts of all data entered must be included in the data packet. The routine minimum is a method blank report, a method blank spike report, and an MS/MSD report.

6.3 Sample Result Reports

6.3.1 Data Qualifying Flags

Sample report results are qualified with data qualifying flags. These flags have the following definitions:

Code	Definition
U	The analyte of interest was not detected, to the reporting limit indicated.
B	The analyte of interest was detected in the method blank associated with the sample, as well as in the sample itself. The B flag is applied without regard to the relative concentrations detected in the blank and sample.
J	The analyte of interest was detected below the practical quantification limit. This value should be regarded as an estimate.
D	The value reported is derived from the analysis of a diluted sample or sample extract.
P	When a dual column /dual detector GC technique is employed, this flag indicates that calculated results from the two determinations differ by more than 25%. Generally, we report the lower value.
E	The value reported is based on a sample or sample extract in which the target analyte concentration exceeded the calibration range. The value reported should be considered an estimate.
C	The target analyte's presence was confirmed by GC/MS.

7. References

1) *SW846 Test Methods for Evaluating Solid Waste*, Method 8000B Gas Chromatography, US EPA Office of Solid Waste and Emergency Response, Revision 2, December 1996.

2) *SW846 Test Methods for Evaluating Solid Waste*, Method 8151A Chlorinated Herbicides by GC Using Methylation or Pentafluorobenzylation Derivatization, US EPA Office of Solid Waste and Emergency Response, Revision 1, December 1996.

3) *Department of Defense Quality Systems Manual for Environmental Laboratories*, Department of Navy, Final Version 3, March 2005

4) *Technical Services Quality Assurance Project Plan (QAPP)*, HQ Air Force Center for Environmental Excellence, Draft Final Version 4.0.01, May 2005

5) *The Shell for Analytical Chemistry Requirements for USACE Projects*, U.S. Army Corps of Engineers, EM 200-1-3, February 1, 2001

APPENDIX I

Calibration Levels, µg/mL

Compound	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7	RL Water (µg/L)	RL Soil (ug/kg)
2,4-D	0.008	0.016	0.02	0.04	0.08	0.10	0.160	.08	2.67
2,4-DB	0.008	0.016	0.02	0.04	0.08	0.10	0.160	.08	2.67
2,4,5-T	0.008	0.016	0.02	0.04	0.08	0.10	0.160	.08	2.67
2,4,5-TP (Silvex)	0.008	0.016	0.02	0.04	0.08	0.10	0.160	.08	2.67
Dalapon	0.008	0.016	0.02	0.04	0.08	0.10	0.160	.08	2.67
Dicamba	0.008	0.016	0.02	0.04	0.08	0.10	0.160	.08	2.67
Dichloroprop (2,4-DP)	0.008	0.016	0.02	0.04	0.08	0.10	0.160	.08	2.67
Dinoseb	0.008	0.016	0.02	0.04	0.08	0.10	0.160	.08	2.67
MCPA	4.00	8.00	10.00	20.00	40.00	50.00	80.00	40	1334
MCPP	4.00	8.00	10.00	20.00	40.00	50.00	80.00	40	1334
Surrogate									
2,4-DCPAA	0.008	0.016	0.02	0.04	0.08	0.10	0.160	N/A	N/A
Non-routine Compounds									
PCP	0.0027	0.0054	0.00675	0.0135	0.027	0.03375	0.054	0.027	0.90
Hexachlorophene	0.005	0.010	0.0125	0.0250	0.05	0.0625	0.1	0.05	1.67
4-Nitrophenol	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Picloram	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A

At the time of this writing these are the current calibration concentration levels. However, these levels may change due to project-specific requirements, or a change in standard suppliers.

Spiking Compounds

2,4-D	Dichlorprop (2,4-DP)
2,4-DB	Dinoseb
2,4,5-T	Dalapon
2,4,5-TP (silvex)	MCPA
Dicamba	MCPP
Hexachlorophene	Pentachlorophenol

APPENDIX II

Analysis Sequence

Injection	Sample
	rinse
1	CCV standard
2	up to 10 subsequent sample or QC extracts
12	CCV standard
13	up to 10 subsequent sample or QC extracts
last	CCV standard

APPENDIX III

Data Packet Sequence

I. QC SUMMARY

Surrogate Recovery Summary Report
Blank Spike Report
MS/MSD Report
Method Blank Summary

II. SAMPLE DATA:

Organic Analysis Data Sheet
Sample Confirmation Worksheet
Chromatograms, primary column
Chromatograms, secondary column
Chromatographic Report, primary column
Chromatographic Report, secondary column

III. STANDARD DATA:

Initial Calibration
Surrogate
RT Evaluation Report
CCV Reports
Confirmation Reports

Linearity Standards:
Chromatograms, primary column
Chromatograms, secondary column
Chromatographic Report, primary column
Chromatographic Report, secondary column

Continuing Calibration Standards:
Chromatograms, primary column
Chromatograms, secondary column
Chromatographic Report, primary column
Chromatographic Report, secondary column
Other Standards Used to Support Sample Data and Instrument Blanks

IV. Raw QC Data:

Method Blank
Chromatograms, primary column
Chromatograms, secondary column
Chromatographic Report, primary column
Chromatographic Report, secondary column

Blank Spike
Chromatograms, primary column
Chromatograms, secondary column
Chromatographic Report, primary column
Chromatographic Report, secondary column

Matrix Spike
Chromatograms, primary column
Chromatograms, secondary column
Chromatographic Report, primary column
Chromatographic Report, secondary column

Matrix Spike Duplicate
Chromatograms, primary column
Chromatograms, secondary column
Chromatographic Report, primary column
Chromatographic Report, secondary column

V. Bench Sheets

Injection Sequence
Extraction Bench Sheets
Miscellaneous Work Sheets. i.e. %TS, SDG summary, calculations, HTVR
Standards Logs

VI. Reject Data:

Data not used to support sample results.
All data acquired but rejected on account of QC out of control.
Non-routine standards used to support sample data should be placed at the last of the Standard Data section.

APPENDIX IV

Method 8151 QA Requirements and Corrective Actions:

QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
Initial Calibration	5 calibration std. for linear, 6 std. for quadratic, for all single and multi-components, %RSD ≤20% for each analyte.	5 calibration std. for linear, 6 std. for quadratic, for all single and multi-components, %RSD ≤20% for each analyte.	After performing major instrument maintenance or when persistent difficulties meeting CCV criteria occur.	Recalibrate.	Narrative
Second source standard	None	Refer to table in section 4 and Appendix VIII.	Once per initial calibration.	Reanalyze or narrate if possible	Narrative
Continuing Calibration Verification	Must be ±15% D for all quantitated analytes.	Must be ±15% D for all quantitated analytes.	Every 12 hours.	Reanalyze new CCV, perform instrument maintenance, &/or recalibrate (or narrate if possible)	Narrative
Method Blank	Must be below MDL.	Must be below 1/2 reporting limit.	Every analytical batch or 1 per 20 samples.	Report quantitated contaminants with a "B" flag, or re-extract if necessary	Case narrative and corrective action form if re-extracted
Surrogate Recovery	Limits to be determined by lab.	Listed in LIMS database.	Every sample.	If other QC is in control, narrate; otherwise re-extract.	Case narrative and corrective action form if re-extracted.

QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
Matrix Spike Recovery	Every analytical batch or 1 per 20 samples, limits to be determined by lab.	Listed in LIMS database.	Every analytical batch or 1 per 20 samples.	If other QC is in control, narrate; otherwise re-extract.	Case narrative and corrective action form if re-extracted.
MS/MSD RPD	Every analytical batch or 1 per 20 samples, limits to be determined by lab.	Listed in LIMS database.	Every analytical batch or 1 per 20 samples.	If other QC is in control, narrate; otherwise re-extract.	Case narrative and corrective action form if re-extracted.
Blank Spike Recovery	Every analytical batch or 1 per 20 samples, limits to be determined by lab.	Listed in LIMS database.	Every analytical batch or 1 per 20 samples.	If other QC is in control, narrate; otherwise re-extract.	Case narrative and corrective action form if re-extracted.

APPENDIX V

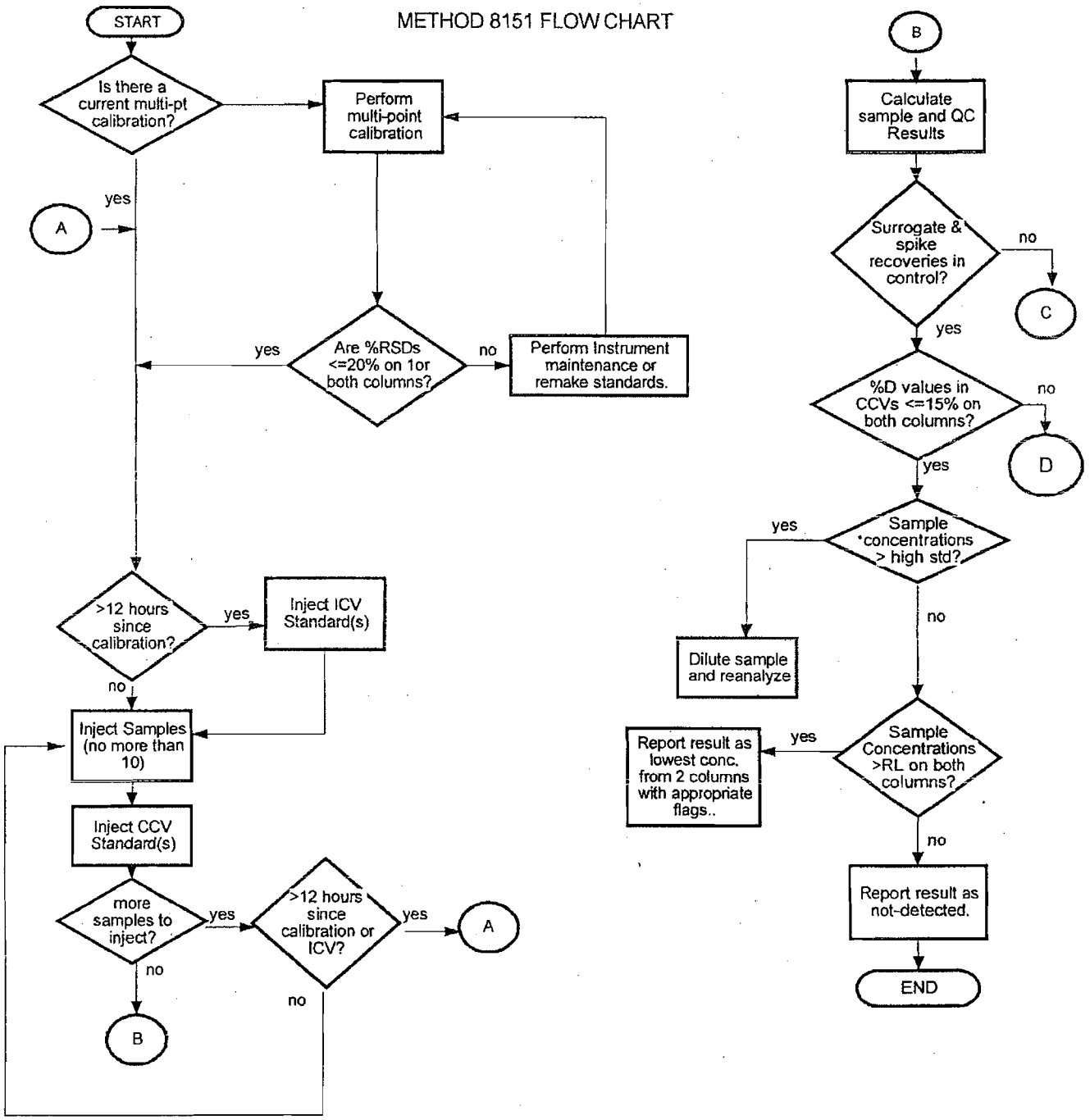
Compound Elution Order

Column DB-5	Column DB-608	Column DB-1701
Dalapon	Dalapon	Dalapon
4-Nitrophenol	4-Nitrophenol	
2,4-DCPAA (surr)	2,4-DCPAA (surr)	2,4-DCPAA (surr
Dicamba	MCPP	Dicamba
MCPP	Dicamba	MCPP
MCPA	MCPA	MCPA
Dichloroprop (2,4-DP)	Dichloroprop (2,4-DP)	Dichloroprop (2,4-DP)
2,4-D	2,4-D	2,4-D
Pentachlorophenol	Pentachlorophenol	Pentachlorophenol
2,4,5-TP (Silvex)	2,4,5-TP (Silvex)	2,4,5-TP (Silvex)
2,4,5-T	2,4,5-T	2,4,5-T
2,4-DB	Dinoseb	2,4-DB
Dinoseb	2,4-DB	Dinoseb
Picloram	Picloram	
Hexachlorophene	Hexachlorophene	Hexachlorophene

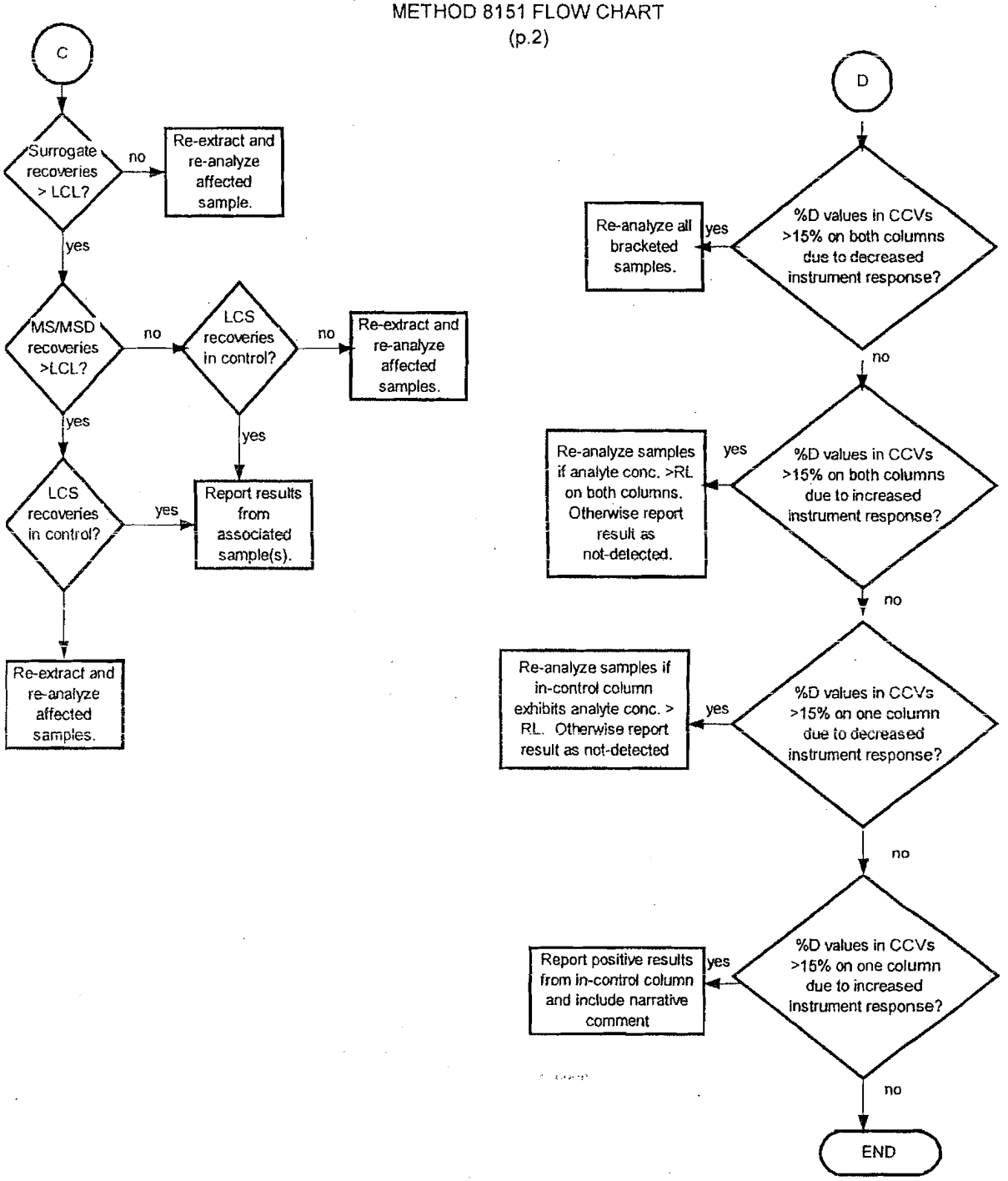
Column DB-35ms	Column DB-XLB
Dalapon	Dalapon
2,4-DCPAA (surr)	2,4-DCPAA (surr)
Dicamba	Dicamba
MCPP	MCPP
MCPA	MCPA
Dichloroprop (2,4-DP)	Dichloroprop (2,4-DP)
2,4-D	2,4-D
Pentachlorophenol	Pentachlorophenol
2,4,5-TP (Silvex)	2,4,5-TP (Silvex)
2,4,5-T	2,4,5-T
Dinoseb	2,4-DB
2,4-DB	Dinoseb
Hexachlorophene	Hexachlorophene

APPENDIX VI

Flow Chart



METHOD 8151 FLOW CHART
(p.2)



APPENDIX VII

MDL, RLS, and Control Limits

Waters (ug/L)

Target Analyte*	CAS#	PQL	MDL	Blank	Matrix Spike/Matrix Spike Duplicate			Blank Spike/Blank Spike Duplicate	
					LCL	UCL	RPD	LCL	UCL
2,4,5-T	93-76-5	0.08	0.0033	0.04	18	167	40	10	178
2,4,5-TP	93-72-1	0.08	0.019	0.04	34	148	36	17	137
2,4-D	94-75-7	0.08	0.014	0.04	21	165	35	30	130
2,4-DB	94-82-6	0.08	0.026	0.04	30	128	35	10	152
Dalapon	75-99-0	0.08	0.0018	0.04		99	47	10	158
Dicamba	1918-00-9	0.08	0.021	0.04	21	156	34	10	155
Dichloroprop	120-36-5	0.08	0.038	0.04		168	34	10	137
Dinoseb	88-85-7	0.08	0.013	0.04	29	113	40	15	123
MCPA	94-74-6	40	3	10	21	131	24	32	149
MCPP	93-65-2	40	2	10	28	117	46	29	134
Non-routine analytes									
4-Nitrophenol		1			20	160	50	20	160
PCP		0.027			20	160	50	20	160
Picloram		1			20	160	50	20	160
Hexachlorophene		0.05			20	160	50	20	160

Surrogate	CAS#	Limits	
		LCL	UCL
2,4-Dichlorophenyl Acetic Acid	19719-28-9	33	138

Soils (ug/Kg)

Target Analyte*	CAS#	PQL	MDL	Blank	Matrix Spike/Matrix Spike Duplicate			Blank Spike/Blank Spike Duplicate	
					LCL	UCL	RPD	LCL	UCL
2,4,5-T	93-76-5	2.67	0.21	1.34	22	155	43	20	160
2,4,5-TP	93-72-1	2.67	0.35	1.34	12	132	51	20	160
2,4-D	94-75-7	2.67	0.3	1.34		119	44	20	160
2,4-DB	94-82-6	2.67	0.4	1.34	39	134	47	20	160
Dalapon	75-99-0	2.67	1.2	1.34		142	61	20	160
Dicamba	1918-00-9	2.67	0.45	1.34		144	37	20	160
Dichloroprop	120-36-5	2.67	0.88	1.34		157	70	20	160
Dinoseb	88-85-7	2.67	0.46	1.34	7	99	65	20	160
MCPA	94-74-6	1333	160	334	23	137	43	20	160
MCPP	93-65-2	1333	150	334	18	149	58	20	160
Non-routine analytes									
4-Nitrophenol		N/A	N/A		20	160	50	20	160
PCP		0.9	N/A	0.5	20	160	50	20	160
Picloram	1918-02-1	1	N/A	0.5	20	160	50	20	160
Hexachlorophene	70-30-4	1.67	0.054	0.42	20	160	50	20	160

Surrogate Analyte	CAS#	Limits	
		LCL	UCL
2,4-Dichlorophenyl Acetic Acid	19719-28-9	20	160

APPENDIX VIII

Agency Requirements

SW 846 Method 8151			
QC Check	**DoD*** Acceptance Criteria	**AFCEE** Acceptance Criteria	**SW846** Acceptance Criteria
MDL Study	See 40 CFR 136B. S/N > 3 for MDL verification. Every 12 months, or quarterly for MDL verification checks.	Detection limits ≤ 1/2 RL listed in appropriate AFCEE Table. Every 12 months.	
Retention Time Window Width	± 3s over a 72 hour period for each analyte	± 3s over a 72 hour period for each analyte	± 3s over a 72 hour period for each analyte or ± 0.03 minutes, whichever is greater.
Minimum Five Point Initial Calibration	Option 1: : Averaged - RSD ≤ 20%	Option 1: Averaged - Grand mean RSD ≤ 20% and no RSD > 30%	Option 1: Averaged - RSD ≤ 20%
	Option 2: Linear - r ≥ 0.995	Option 2: Linear - r ≥ 0.995	Option 2: Linear - r ≥ 0.99
	Option 3: Non-linear - r^2 ≥ 0.99, 6 pts for 2nd order	Option 3: Non-linear - r^2 ≥ 0.990, minimum of 6 pts for 2nd order, 7pts for 3rd order	Option 3: Non-linear - r^2 ≥ 0.99, minimum of 6 pts for 2nd order, 7pts for 3rd order
	Option 4: Non-linear – r^2 ≥ 0.990, minimum of 6 pts for 2nd order, 7pts for 3rd order		AND %D ≤ 20% at each calibration level recommended
Second Source	%D ≤ 20%	%D ≤ 15%	
Retention Time	Set at retention time		Set at retention time of

SW 846 Method 8151			
QC Check	**DoD*** Acceptance Criteria	**AFCEE** Acceptance Criteria	**SW846** Acceptance Criteria
	of midpoint standard of ICAL		first CCV of the analytical sequence, or of the midpoint standard if samples were ran after the ICAL
Continuing Calibration Verification	%D ≤ 20%	%D ≤ 15%	%D ≤ 20%
	Every 10 field samples, beginning and end of analytical run		Beginning and end of each 12 hour analytical shift
			Every 10 samples
Method Blank	No analytes ≥ 1/2 RL. No common laboratory contaminant analytes ≥ RL	No analytes ≥ RL	Less than the laboratory detection limit OR
			Less than 5% of the regulatory limit OR
			Less than 5% of the sample result WHICHEVER IS GREATER
Laboratory Control Sample	See appropriate tables D-8, D-9 listed DoD Quality Systems	See appropriate AFCEE table	Lab-derived. If no lab-derived limits are in place yet, use 70%-130% by default
Matrix Spike	Same as LCS	Same as LCS	Lab-derived

SW 846 Method 8151			
QC Check	**DoD***	**AFCEE**	**SW846**
	Acceptance Criteria	Acceptance Criteria	Acceptance Criteria
Matrix Spike Duplicate	RPD ≤ 30%	Water : RPD ≤ 30%	Lab-derived
		Soil : RPD ≤ 50%	
Surrogate	No DoD limits at this time for this method	See appropriate AFCEE table	Lab-derived
Confirmation of positive results	RPD ≤ 40%. Apply J flag if RPD > 40%	RPD ≤ 40%, J flag if greater	RPD ≤ 40%
Results reported between MDL and RL	Apply J flags	Apply F flags	
Allowable Sporadic Marginal Excedences/Failures	> 90 analytes - 5		
	71 - 90 analytes - 4		
	51 - 70 analytes - 3		
	31 - 50 analytes - 2		
	11 - 30 analytes - 1		
	< 11 analytes - 0		

*For non-DoD clients, generated in-house limits will be used, unless otherwise specified in project-specific documents. This information is located in the laboratory LIMS.

± Agency control limits for each analytical method are located in the laboratory LIMS.

APPENDIX D

STAT ANALYSIS LABORATORY
STANDARD OPERATING PROCEDURES

APPENDIX D

STAT ANALYSIS LABORATORY SOP TABLE OF CONTENTS

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STAT Analysis Corporation:

STANDARD OPERATING PROCEDURE 2125

LEACHING PROCEDURES

TOXICITY CHARACTERISTIC LEACHING PROCEDURE (EPA METHOD 1311)

SYNTHETIC PRECIPITATION LEACHING PROCEDURE (EPA METHOD 1312)

ASTM D3987-85 LEACHING PROCEDURE

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Flowchart 2: Leaching Procedure Flowchart from Method 1312, Revision 0; U.S. EPA SW-846 "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods" Update III, December 1996 28

1.0 Identification of Test Method

SOP Title: Leaching Procedures is abbreviated LP in this SOP. This SOP incorporates three leaching procedures.
SOP Title: Toxicity Characteristic Leaching Procedure (EPA 1311) is abbreviated as TCLP in laboratory records.
SOP Title: Synthetic Precipitation Leaching Procedure (EPA 1312) is abbreviated as SPLP in laboratory records.
SOP Title: ASTM Leaching Procedure (ASTM D3987-85) is abbreviated as ASTM in this SOP.
All references which apply to all three leaching procedures listed is abbreviated LP in this SOP. If a section refers to a specific leaching procedure, it will be abbreviated accordingly.

2.0 Applicable Matrix or Matrices

This method is applicable to the following matrices: liquid, solid and multiphasic wastes.

3.0 Detection Limits

See specific analytical SOPs for MDLs and Reporting limits for specific matrices.

4.0 Scope and Application

4.1 The LP method is designed to determine the mobility of organic and inorganic analytes present in liquid, solid and multiphasic wastes.

4.2 If a total analysis of the waste demonstrates that individual analytes are not present in the waste, or that they are present, but at such low concentrations that the appropriate regulatory levels could not possibly be exceeded, the LP need not be run.

4.3 If an analysis of any one of the liquid fractions of the LP extract indicates that a regulated compound is present at such a high concentration that, even after accounting for dilution from other fractions of the extract, the concentration would be equal to or above the regulatory level for that compound, then the waste is hazardous and it is not necessary to analyze the remaining fractions of the extract.

4.4 If an analysis of extract obtained using a bottle extractor shows that the concentration of any regulated volatile analyte equals or exceeds the regulatory level for that compound, then the waste is hazardous and extraction using the Zero Headspace Extractor (ZHE) is not necessary. However, extract from a bottle extractor cannot be used to determine that the concentration of volatile compounds is below the regulatory limit.

5.0 Summary of Test Method

5.1 For liquid wastes (i.e., those containing less than 0.5% dry solid material), the waste, after filtration through a 0.6 to 0.8 μm glass fiber filter, is defined as the LP extract.

5.2 For wastes containing greater than or equal to 0.5% solids, the liquid, if any is separated from the solid phase and stored for later analysis. The particle size of the solid phase is reduced, if necessary. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. The extraction fluid employed:

- is reagent water for ASTM samples.
- is a function of the alkalinity of the solid phase of the waste for TCLP samples.
- is a function of the region of the country where the sample site is located if the SPLP sample is a soil.

If the SPLP sample is a waste or wastewater, the extraction fluid employed is a pH 4.2 solution.

A special extractor vessel is used when testing for volatile analytes. Following extraction, the liquid is separated from the solid phase by filtration through a 0.6 to 0.8 µm glass fiber filter.

5.3 If compatible (i.e., multiple phases will not form on combination), the initial liquid phase of the waste is added to the liquid extract, and these are analyzed together. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume-weighted average concentration.

5.4 Method Modifications from Reference – This SOP incorporates options for three methods; based on SW-846 (1311 and 1312) and ASTM method D3987-85.

5.4.1 Sample amounts used are varied based upon analytical tests required.

5.4.2 Sample extracts for volatile organic analysis are expressed directly into 40 mL VOA vials according to criteria in Section 9.6.2.

5.4.3 Samples for ASTM are rotated at 30 ± 2 rpm and filtered through a 0.6 to 0.8 µm glass fiber filter.

5.4.4 Preliminary evaluations are not done using a minimum 100 g aliquot.

6.0 Definitions

The STAT Analysis Quality Assurance Manual Section 19.0 contains all the definitions of standard terms used in SOPs.

7.0 Interferences

Potential interferences that may be encountered during analysis are discussed in the individual analytical methods.

8.0 Safety

8.1 Safety glasses, gloves, lab coats and closed toe shoes, are to be used during this procedure.

8.2 Tumbling apparatus' must be covered or located away from direct contact with lab personnel.

8.3 Venting and pressurizing should be conducted in a hood or shielded area if possible.

8.4 Other safety precautions must be conducted in accordance with the Chemical Hygiene Plan. Other actions can also be applied if deemed necessary. A reference file of material safety data sheets (MSDS) is available in each room for personnel involved in an analysis using chemicals.

9.0 Equipment and Supplies

The following apparatus is recommended for performing this procedure. Equivalent items can be used, if with their use, the analytical and QA/QC requirements in this SOP can be met. All catalog numbers in this SOP are current as of the effective date and thereafter subject to change.

9.1 Agitation Apparatus: Millipore four space Rotary Agitator and Environmental Express 12 space Rotary Agitator.

The agitation apparatus must be capable of rotating the extraction vessel in and end-over-end fashion at 30 ± 2 rpm.

9.2 Extraction Vessels

9.2.1 Zero-Headspace Extraction Vessel (ZHE): MilliporeYT30090HW Zero Headspace Extractor.

This device is for use only when the waste is being tested for the mobility of volatile analytes. The ZHE allows for liquid/solid separation within the device, and effectively precludes headspace. This type of vessel allows for initial liquid/solid separation, extraction, and final extract filtration without opening the vessel. The vessels shall have an internal volume of 500-600 mL, and be equipped to accommodate a 90-110 mm filter. The devices contain VITON® O-rings, which should be replaced frequently.

For the ZHE to be acceptable for use, the piston within the ZHE should be able to be moved with approximately 15 psi or less. If it takes more pressure to move the piston, the O-rings in the device should be replaced. If this does not solve the problem, the ZHE is unacceptable for LP analyses and the manufacturer should be contacted.

The ZHE should be checked for leaks before every extraction. Pressurize the device to 50 psi, allow it to stand unattended for 1 hour, and recheck the pressure. If pressure is lost, check all fittings and inspect and replace O-rings, if necessary. Retest the device. If leakage problems cannot be solved, the manufacturer should be contacted.

9.2.2 Bottle Extraction Vessel: ESS 32 oz Amber Wide Mouth Glass Jars (UC0950-0050 or UC0950-0010), for Metals, ESS 250 ml and 500 ml plastic bottles and Silgan 500 or 950 ml HDPE Jars.

When the waste is being evaluated using the non-volatile extraction, a jar with sufficient capacity to hold the sample and the extraction fluid is needed. Headspace is allowed in this vessel.

The extraction bottles may be constructed from various materials, depending on the analytes to be analyzed and the nature of the waste (see Section 9.3.3). It is recommended that borosilicate glass bottles be used instead of other types of glass, especially when inorganics are of concern. Plastic bottles, other than polytetrafluorethylene, shall not be used if organics are to be investigated. When this type of extraction vessel is used, the filtration device discussed in Section 9.3.2 is used for initial liquid/solid separation and final extract filtration.

9.3 Filtration Devices: It is recommended that all filtrations be performed in a hood.

9.3.1 Zero-Headspace Extractor Vessel (ZHE): When the waste is evaluated for volatiles, the ZHE described in Section 9.2.1 is used for filtration. The device shall be capable of supporting and keeping in place the glass fiber filter and be able to withstand the pressure needed to accomplish separation (50 psi).

NOTE: When it is suspected that the glass fiber filter has been ruptured, an in-line glass fiber filter may be used to filter the material within the ZHE.

9.3.2 Filtration Devices: Millipore YT30142HW Hazardous Waste Filtration System.

Filter Holder: When the waste is evaluated for other than volatile analytes, any filter holder capable of supporting a glass fiber filter and able to withstand the pressure needed to accomplish separation may be used. Suitable filter holders range from simple vacuum units to relatively complex systems capable of exerting pressures of up to 50 psi or more. The type of filter holder used depends on the properties of the material to be filtered (see Section 9.3.3). These devices shall have a minimum internal volume of 300 mL and be equipped to accommodate a minimum filter size of 47 mm (filter holders having an internal capacity of 1.5 L or greater, and equipped to accommodate a 142 mm diameter filter, are recommended). Vacuum filtration can only be used for wastes with low solids content (<10%) and for highly granular, liquid-containing wastes. All other types of wastes should be filtered using positive pressure filtration.

9.3.3 Materials of Construction: Extraction vessels and filtration devices shall be made of inert materials, which will not leach or absorb waste components. Glass, polytetrafluorethylene (PTFE), or type 316 stainless steel equipment may be used when evaluating the mobility of both organic and inorganic components. Devices made of high-density polyethylene (HDPE), polypropylene (PP), or polyvinyl chloride (PVC) may be used only when evaluating the mobility of metals. Borosilicate glass bottles are recommended for use over other types of glass bottles, especially when organics are analytes of concern.

9.4 Filters: Gelman Sciences TCLP/SPLP Glass Fiber Filter 90 and 142 mm

Filters shall be made of borosilicate glass fiber, shall contain no binder materials, and shall have an effective pore size of 0.6 to 0.8 μm, or equivalent. Pre-filters must not be used. When evaluating the

mobility of metals, filters shall be acid washed prior to used by rinsing with 1.1 nitric acid followed by three consecutive rinses with de-ionized water (a minimum of 1 L per rinse is recommended). Glass fiber filters are fragile and should be handled with care.

9.5 pH Meter: Beckman 340 pH Meter, Orion/VWR or equivalent 4, 7 and 10 Buffer solution.

The meter should be accurate to ± 0.05 units at 25°C.

9.6 ZHE Extract Collection Container (ECC):

- 40 mL pre-cleaned HCl preserved glass VOA vials.
- TEDLAR® bags.

The ECCs listed are recommended for use under the following conditions:

9.6.1 If the waste contains a significant amount of liquid in the initial phase and has ≥ 0.5% dry solids a TEDLAR® bag is used for both the initial solid/liquid separation and the final extract filtration.

9.6.2 If the waste is:
1) 100% solid (no initial liquid phase) or
2) Has <0.5% dry solids and the liquid is greater than 99% aqueous

40 mL HCl preserved VOA vials may be used.

9.7 ZHE Extraction Fluid Transfer Devices: Any device capable of transferring the extraction fluid into the ZHE without changing the nature of the extraction fluid is acceptable [e.g., a positive displacement or peristaltic pump, pressure filtration unit (see Section 9.3.2), glass, stainless steel or PTFE gas tight syringe, or other ZHE device].

9.8 Laboratory Balance: Mettler BD1201, Mettler PM300
Any laboratory balance accurate to within ± 0.01 grams may be used (all weight measurements are to be within ± 0.1 grams).

9.9 Beakers: plastic or glass 150, 400 and 500 mL

9.10 Parafilm, appropriate diameter to cover beaker.

9.11 Magnetic Stirrer: VWR Model 200 Magnetic Stirrer

9.12 Hot Plate: VWR Dylatherm

9.13 Wooden spatulas

9.14 Syringes: 100 or 250 mL glass, stainless steel, or PTFE gas tight.

9.15 Standard Seive 9.5 mm.

10.0 Reagents and Standards

The following reagents and standards are required to perform this procedure. When instructions are given on how to prepare a specific volume of a reagent or standard, larger or smaller volumes can be prepared as needed so long as the final concentrations remain the same. Any other deviations from the reagents or standards listed in this SOP could be detrimental to the quality of the data produced. Such deviations would have to be approved and documented (see 230 Corrective Action SOP).

10.1 Instructions for labeling and record keeping of reagents and standards are contained in SOP 1010 Standard and Reagent Preparation.

10.2 Reagents - In methods where the purity of reagents is not specified, analytical reagent grade shall be used. Reagents of lesser purity than those specified by the test method shall not be used.

10.2.1 Reagent Water: Reagent water is defined as water in which an interferant is not observed at or above the method detection limit.

10.2.2 Hydrochloric Acid (1N), HCl, made from ACS reagent grade. Dilute 83.3 ml of concentrated HCl to 1 L with de-ionized reagent water.

10.2.3 Nitric acid, HNO_3, concentrated, ACS reagent grade.

10.2.4 1:1 Nitric Acid, HNO_3. Dilute 500 ml of HNO_3 to 1L with reagent water.

10.2.5 Sodium Hydroxide, NaOH, ACS reagent grade pellets.

10.2.6 Glacial Acetic Acid, CH3CH2OOH, ACS reagent grade.

10.2.7 Sulfuric Acid, concentrated ACS reagent grade.

10.2.8 Extraction Fluid:

10.2.8.1 Extraction fluid #1: Add 5.7 mL Glacial Acetic Acid to 500 mL of reagent water, dissolve 2.57 g of NaOH, and dilute to a volume of 1 liter. When correctly prepared, the pH of this fluid will be 4.93 ± 0.05. (TCLP)

10.2.8.2 Extraction Fluid #2: Dilute 5.7 mL Glacial Acetic Acid with reagent water to a volume of 1 liter. When correctly prepared, the pH of this fluid will be 2.88 ± 0.05. (TCLP)

10.2.8.3 Extraction Fluid #3: This fluid is reagent water and is used to determine cyanide, and for ASTM and SPLP volatiles extractions.

10.2.8.4 Extraction Fluid #4: Sulfuric Acid/Nitric Acid (60/40 weight percent mixture) H_2SO_4/HNO_3. Cautiously mix 60 mL of concentrated sulfuric acid with 40 mL of concentrated nitric acid. If preferred, a more dilute H_2SO_4/HNO_3 acid mixture may be prepared and used in steps 10.2.3.1 and 10.2.3.2 making it easier to adjust the pH of the extraction fluids. This fluid is used to determine the leachability of samples from sites east of the Mississippi River. (SPLP method)

10.2.8.5 Extraction Fluid #5: Made by adding the 60/40 weight percent mixture of sulfuric acids (or a suitable dilution) to reagent water until the pH is 5.00 ± 0.05. The fluid is used to determine the leachability of soil from sites west of the Mississippi River. (SPLP method)

NOTE: These extraction fluids should be monitored frequently for impurities. The pH must be checked prior to use to ensure that these fluids are made up accurately. If impurities are found or the pH is not within the above specifications, the fluid shall be discarded and fresh extraction fluid prepared. The pH of the extraction fluid must be checked before rotation. Record this in the TCLP Prep logbook.

11.0 Sample Collection, Preservation and Handling

All samples are stored away from all standards, reagents, food and other potentially contaminating sources in order to prevent cross contamination.

SAMPLE MAXIMUM HOLDING TIMES (days)

If sample holding times are exceeded, the values obtained will be considered minimal concentrations.

Matrix	Bottle Type	From: Field Collection To: SPLP Extraction	From: SPLP Extraction To: Preparative Extraction	From: Preparative Extraction To: Determinative Analysis	Total Elapsed Time
Volatiles	G, AG	14	NA	14	28
Semi-Volatiles	G, AG	14	7	40	61
Mercury	G, AG, P	28	NA	28	56
Metals, except Mercury	G, AG, P	180	NA	180	360

[P= Polyethylene, G = Glass, AG = Amber Glass, etc.].

All samples and extracts are stored at 0.1-6 degrees C.
Metals extracts will be preserved to pH < 2 with 1:1 HNO_3.
Volatiles extracts will be preserved with HCl.

11.1 All samples shall be collected using an appropriate sampling plan.

11.2 The LP may place requirements on the minimal size of the field sample, depending upon the physical state or states of the waste and the analytes of concern. An aliquot is needed for preliminary evaluation of which extraction fluid is to be used for the non-volatile analyte extraction procedure (TCLP/SPLP). Another aliquot may be needed to actually conduct the non-volatile extraction. If volatile organics are of concern, another aliquot may be needed. Quality control measures may require additional aliquots. Further, it is always wise to collect more sample just in case something goes wrong with the initial attempt to conduct the test.

11.3 Preservatives shall not be added to samples before extraction.

11.4 Samples are refrigerated unless refrigeration results in irreversible physical damage to the waste. If precipitation occurs, the entire sample (including precipitate) is extracted.

11.5 When the waste is to be evaluated for volatile analysis, care shall be taken to minimize the loss of volatiles. Samples shall be collected and stored in a manner intended to prevent the loss of volatile organics (e.g., samples are collected in Teflon-lined septum capped vials and stored at 0.1-6°C. Samples should be opened only immediately prior to extraction).

11.6 LP extracts are prepared for analysis and analyzed as soon as possible following extraction. Extracts or portions of extracts for metallic analyte determinations must be acidified with Nitric Acid to a pH < 2, unless precipitation occurs (see Section 14.2.14 if precipitation occurs). Extracts are preserved for other analytes according to the guidance given in the individual analysis methods. Extracts or portions of extracts for organic analyte determinations shall not be allowed to come into contact with the atmosphere (i.e., no headspace) to prevent losses. See Section 12.0 (Quality Control) for acceptable sample and extract holding times.

12.0 Quality Control

The following details the QC requirements that apply to this analysis. Each Quality Control Indicator (QCI) provides information pertaining to either method or individual sample performance. Our goal is to produce defensible data of known and documented quality. The results of these Quality Control Indicator (QCI) samples are used to assess the acceptability of data.

12.1 Blanks

12.1.1 A method blank shall be prepared once per preparation batch of 20 or less samples per matrix type. If more than 20 samples are prepared a second blank shall be prepared after the twentieth sample.

12.1.2 The method blank shall be processed through all preparatory steps used for the samples. The blank shall be analyzed using the same instrument and conditions as the samples. The Method Blank analysis is performed to determine if any contamination is present in the analytical process and is used to evaluate acceptance of the batch of samples. For ZHE extraction, alternate which ZHE unit is used for the blank, rotating all units through the process over time.

12.2 Matrix Spike and Matrix Spike Duplicate (MS/MSD)

One matrix spike shall be performed for each batch of twenty samples or less if preparing TCLP or SPLP extractions. TCLP and SPLP samples are separate extractions and must each have a unique matrix spike.

MS/MSDs are prepared according to individual analytical SOPS and are not part of this method.

For metals analysis, if percent recovery is less than 50% and the metal concentration is within 20% of the regulatory level, the method of standard additions may be used to determine metal concentrations.

13.0 Calibration and Standardization

13.1 Balances – Be sure the balance is checked prior to use and performance criteria are met (see SOP 1040 for calibration of balances.

13.2 pH Meter – Calibrate the pH meter prior to use (see SOP 4210 for pH meter calibration).

13.3 Thermometer – Check the thermometer to ensure the calibration has not expired (see SOP 1040 for thermometer calibration). Check the thermometer during the analysis and record the corrected temperature in the preparation logbook.

14.0 Procedure

14.1 Preliminary Evaluations:

Perform preliminary LP evaluations on an aliquot of waste. Size used may vary depending on amount of sample available for testing. This aliquot may not actually undergo LP extraction. These preliminary evaluations include: (1) determination of the percent solids (Section 14.1.1); (2) determination of whether the waste contains insignificant solids and is, therefore, its own extract after filtration (Section 14.1.2); (3) determination of whether the solid portion of the waste requires particle size reduction (Section 14.1.3); and (4) determination of which of the extraction fluids are to be used for the non-volatile LP extraction of the waste (Section 14.1.4 and 14.1.5).

14.1.1 Preliminary determination of percent solids: Percent solids is defined as that fraction of a waste sample (as a percentage of the total sample) from which no liquid may be forced out by an applied pressure, as described below.

14.1.1.1 If the waste will obviously yield no liquid when subjected to pressure filtration (i.e., is 100% solids) proceed to Section 14.1.3.

14.1.1.2 If the sample is liquid or multiphasic, liquid/solid separation to make a preliminary determination of percent solids is required. This involves the filtration device described in Section 9.3.2 and is outlined in Sections 14.1.1.3 through 14.1.1.9.

14.1.1.3 Pre-weigh the filter and the container that will receive the filtrate, record the weight.

14.1.1.4 Assemble the filter holder and filter following the manufacturer's instructions.

14.1.1.5 Weigh out a subsample of the waste and record the weight.

14.1.1.6 Allow slurries to stand to permit the solid phase to settle. Wastes that settle slowly may be centrifuged prior to filtration. Centrifugation is to be used only as an aid to filtration. If used, the liquid should be decanted and filtered followed by filtration of the solid portion of the waste through the same filtration system.

14.1.1.7 Quantitatively transfer the waste sample to the filter holder (liquid and solid phases). Spread the waste sample evenly over the surface of the filter.

NOTE: If waste material (>1% of original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Section 14.1.1.5 to determine the weight of the waste sample that will be filtered.

14.1.1.8 Gradually apply pressure of 1-10 psi, until air or pressurizing gas moves through the filter. If this point is not reached under 10 psi, and if no additional liquid has passed through the filter in any 2-minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter, or when liquid flow has ceased at 50 psi (i.e., filtration does not result in any additional filtrate within any 2 minute period), stop the filtration.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

14.1.1.9 The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase.

NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying pressure filtration, as outlined in Section 14.1.1.8, this material may not filter. If this is the case, the material within the filtration device is defined as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.

14.1.1.10 Determine the weight of the liquid phase by subtracting the weight of the filtrate container (see Section 14.1.1.3) from the total weight of the filtrate-filled container. Determine the weight of the solid phase of the waste sample by subtracting the weight of the liquid phase from the weight of the total waste sample, as determined in Section 14.1.1.5 or 14.1.1.7. Record the weight of the liquid and solid phases. Calculate the percent solids:

$$\text{Percent solids} = \frac{\text{Weight of solid (Section 14.1.1.9)}}{\text{Total weight of waste (Section 14.1.1.5 or 14.1.1.7)}} \times 100$$

14.1.2 If the percent solids determined in Section 14.1.1.10 is equal to or greater that 0.5%, then proceed either to Section 14.1.3 to determine whether the solid material requires particle size reduction or to

the next section 14.1.2.1 if it is noticed that a small amount of the filtrate is entrained on the filter. If the percent solids determined in Section 14.1.1.10 is less than 0.5%, then proceed to Section 14.2.13 if the non-volatile LP is to be performed and to Section 14.3 with a fresh portion of the waste if the volatile LP is to be performed.

14.1.2.1 Remove the solid phase and the filter from the filtration apparatus.

14.1.2.2 Dry the filter and solid phase at 100 ± 20°C until two successive weighings yield the same value within ± 1%. Record the final weight.

14.1.2.3 Calculate the percent dry solids as follows:

$$\text{Percent dry solids} = \frac{\text{(Weight of dry waste + filter) – tared weight of filter}}{\text{Initial weight of waste (Section 14.1.1.5 or 14.1.1.7)}} \times 100$$

14.1.2.4 If the percent dry solids is less than 0.5%, then proceed to Section 14.2.13 if the non-volatile LP is to be performed, and to Section 14.3 if the volatile LP is to be performed.

If the percent dry solids is greater than or equal to 0.5%, and if the non-volatile LP is to be performed, return to the beginning of Section 14.1 and, with a fresh portion of waste, determine whether particle size reduction is necessary (Section 14.1.3) then determine the appropriate extraction fluid for TCLP or SPLP (Section 14.1.4 and 14.1.5).
For ASTM always use extraction fluid #3

If only the volatile LP is to be performed, proceed to section 14.3 and use extraction fluid #1 for TCLP and extraction fluid #3 for SPLP.

14.1.3 Determination of whether the waste requires particle size reduction (particle size is reduced during this step): Using the solid portion of the waste, evaluate the solid for particle size. Particle size reduction is required, unless the solid has a surface area per gram of material equal to or greater that 3.1 cm^2, or is smaller than 1 cm in its narrowest dimension (i.e., is capable of passing through a 9.5 mm (0.375 inch standard sieve). If the surface area is smaller or the particle size larger than described above, prepare the solid portion of the waste for extraction by crushing, cutting, or grinding the waste to a surface area or particle size as described above. If the solids are prepared for organic volatiles extraction, special precautions must be taken (see Section 14.3.6).

NOTE: Surface area criteria are meant for filamentous (e.g., paper, cloth, and similar) waste materials. Actual measurement of surface area is not required, nor is it recommended. For materials that do not obviously meet the criteria, sample-specific methods would need to be developed and employed to measure the surface area. Such methodology is currently not available.

14.1.4 Determination of appropriate extraction fluid for TCLP.

If the solid content of the waste is greater than or equal to 0.5% and if the sample will be extracted for non-volatile constituents (Section 14.2), determine the appropriate fluid (Section 10.2.8) for the non-volatiles extraction as follows:

14.1.4.1 Weigh out a small subsample of the solid phase of the waste, reduce the solid (if necessary) to a particle size of approximately 1 mm in diameter or less, and transfer 5.0 grams of the solid phase of the waste to a beaker.

14.1.4.2 Add 96.5 mL of reagent water to the beaker and stir vigorously for 5 minutes using a magnetic stirrer. Measure and record the pH. If the pH is <5.0, use extraction fluid #1. Proceed to Section 14.2.

14.1.4.3 If the pH from section 14.1.4.2 is >5.0, add 3.5 mL 1N HCl, slurry briefly, heat to 50°C, and hold at 50°C for 10 minutes.

14.1.4.4 Let the solution cool to room temperature and record the pH. If the pH is <5.0, use extraction fluid #1. If the pH is >5.0, use extraction fluid #2. Proceed to section 14.2.

14.1.5 For Determination of the appropriate extraction fluid for SPLP:

14.1.5.1 For soils, if the sample is from a site that is east of the Mississippi, extraction fluid #4 should be used. If the sample is from a site that is west of the Mississippi River, extraction fluid #5 should be used.

14.1.5.2 For wastes and wastewater, extraction fluid #4 should be used.

14.1.5.3 For cyanide-containing wastes and/or soils, extraction fluid #3 (reagent water) must be used because leaching of cyanide-containing samples under acidic conditions may result in the formation of hydrogen cyanide gas.

14.1.6 If the aliquot of the waste used for the preliminary evaluation (Sections 14.1.1 – 14.1.5) was determined to be 100% solid at Section 14.1.1.1, then it can be used for the Section 14.2 extraction. If the aliquot was subjected to the procedure in Section 14.1.1.7, then another aliquot shall be used for the volatile extraction procedure in Section 14.3. The aliquot of the waste subjected to the procedure in 14.1.1.7 might be appropriate for use for the Section 14.2 extraction if an adequate amount of solid (determined by Section 14.1.1.10) was obtained. The amount of solid necessary is dependent upon whether a sufficient amount of extract will be produced to support the analyses. If an adequate amount of solid remains, proceed to section 14.2.10 of the non-volatile LP extraction.

14.2 Procedure When Volatiles Are Not Involved

A sample size up to 45 grams is recommended. In some cases, a larger sample size may be appropriate, depending on the solids content of the waste sample (percent solids, See Section 14.1.1), whether the initial liquid phase of the waste will be miscible with the aqueous extract of the solid, and whether inorganics, semi-volatile organics, pesticides, and herbicides are all analytes of concern. Enough solids should be generated for all extraction such that the volume of LP extract will be sufficient to support all of the analyses required. If the amount of extract generated by a single LP extraction will not be sufficient to perform all of the analyses, more than one extraction may be performed and the extracts from each combined and aliquoted for analysis.

14.2.1 If the waste will obviously yield no liquid when subjected to pressure filtration (i.e., is 100% solid, see Section 14.1.1), weigh out a subsample of the waste and proceed to Section 14.2.10.

14.2.2 If the sample is liquid or multiphasic, liquid/solid separation is required. This involves the filtration device described in Section 9.3.2 and is outlined in Section 14.2.3 to 14.2.8.

14.2.3 Pre-weigh the container that will receive the filtrate.

14.2.4 Assemble the filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure. Acid wash the filter if evaluating the mobility of metals (see Section 9.4)

NOTE: Acid washed filters may be used for all non-volatile extractions even when metals are not of concern.

14.2.5 Weigh out a subsample of the waste and record the weight. If the waste contains <0.5% dry solids (Section 14.1.2) the liquid portion of the waste, after filtration, is defined as the LP extract. Therefore, enough of the sample should be filtered so that the amount of filtered liquid will support all of the analyses required of the LP extract. For wastes containing ≥0.5% dry solids (Sections 14.1.1 or 14.1.2), use the percent solids information obtained in Section 14.1.1 to determine the optimum sample size for filtration. Enough solids should be generated by filtration to support the analyses to be performed on the LP extract.

14.2.6 Allow slurries to stand to permit the solid phase to settle. Wastes that settle slowly may be centrifuged prior to filtration. Use centrifugation only as an aid to filtration. If the waste is centrifuged, the liquid should be decanted and filtered followed by filtration of the solid portion of the waste through the same filtration system.

14.2.7 Quantitatively transfer the waste sample (liquid and solid phases) to the filter holder (Section 9.3.2). Spread the waste sample evenly over the surface of the filter.

NOTE: If waste material (>1% of the original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Section 14.2.5, to determine the weight of the waste sample that will be filtered.

14.2.8 Gradually apply a pressure of 1-10 psi, until air or pressurizing gas moves through the filter. If this point is not reached under 10 psi, and if no additional liquid has passed through the filter in any 2-

minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter, or when liquid flow has ceased at 50 psi (i.e., filtration does not result in any additional filtrate within any 2 minute period), stop the filtration.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

14.2.9 The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase. Weigh the filtrate. The liquid phase may now be either analyzed (see Section 14.2.12) or stored at 0.1-6°C until time of analyses.

NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying pressure filtration, as outlined in Section 14.2.8, this material may not filter. If this is the case, the material within the filtration device is defined as a solid and is carried through the extraction as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.

14.2.10 Transfer the solid material into the extractor bottle (after particle size reduction, if needed) along with the filter used to separate the initial liquid from the solid phase, and proceed to Section 14.2.11.

14.2.11 Determine the amount of extraction fluid to add to the extractor vessel as follows:

$$\text{Weight of extraction fluid} = \frac{20 \times \text{percent solids (Section 14.1.1)} \times \text{weight of waste filtered (Section 14.2.5 or 14.2.7)}}{100}$$

Slowly add this amount of appropriate extraction fluid (see Section 14.1.4 or 14.1.5) to the extractor vessel. Close the extractor bottle tightly (it is recommended that Teflon tape be used to ensure a tight seal), secure in rotary agitation device, and rotate at 30 ± 2 rpm for 18 ± 2 hours. Ambient temperature (i.e., temperature of room in which extraction takes place) shall be maintained at 23 ± 2°C during extraction period.

NOTE: For ASTM rotate for 18 hours ± 15 minutes.

NOTE: As agitation continues, pressure may build up within the extractor bottle for some types of wastes (e.g., limed or calcium carbonate containing waste may evolve gases such as carbon dioxide). To relieve excess pressure, the extractor bottle may be periodically opened (e.g., after 15 minutes, 30 minutes, and 1 hour) and vented into a hood.

14.2.12 Following the extraction, separate the material in the extractor vessel into its component liquid and solid phases by filtering through a new glass fiber filter, as outlined in Section 14.2.7. For final filtration of the LP extract, the glass fiber filter may be changed, if necessary, to facilitate filtration. Filter(s) shall be acid washed (see Section 9.4) if evaluating the mobility of metals.

14.2.13 Prepare the LP extract as follows:

14.2.13.1 If the waste contained no initial liquid phase, the filtered liquid material obtained after rotation (section 14.2.11) is defined as the LP extract. Proceed to section 14.2.14.

14.2.13.2 If compatible (e.g., multiple phases will not result on combination), combine the filtered liquid after rotation (section 14.2.11) with the initial liquid phase of the waste obtained in Section 14.2.9. This combined liquid is defined as the LP extract. Proceed to Section 14.2.14.

14.2.13.3 If the initial liquid phase of the waste as obtained in Section 14.2.9, is not or may not be compatible with the filtered liquid resulting from Section 14.2.12, do not combine these liquids. Analyze these liquids separately (they are collectively defined as the LP extract), and combine the results mathematically, as described in Section 14.2.14.

14.2.14 Following collection of the LP extract, the pH of the extract should be recorded. Immediately aliquot and preserve the extract for analysis. Metals aliquots must be acidified with nitric acid to pH <2. If precipitation is observed upon addition of nitric acid to a small aliquot of the extract, then the remaining portion of the extract for metals analysis shall not be acidified and the extract shall be analyzed as soon as possible. All other aliquots must be stored under refrigeration (0.1-6°C) until analyzed. The LP extract shall be prepared and analyzed according to appropriate analytical methods. LP extracts to be analyzed for metals shall be acid digested except in those instances where digestion causes loss of metallic analytes. If an analysis of the undigested extract shows that the concentration of any regulated metallic analyte exceeds the regulatory level, then the waste is hazardous and digestion of the extract is not necessary. However, data on undigested extracts alone cannot be used to demonstrate that the waste is not hazardous. If the individual phases are to be analyzed separately, determine the volume of the individual phases (to ± 0.5%), conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted average:

$$\text{Final Analyte Concentration} = \frac{(V_1)(C_1) + (V_2)(C_2)}{V_1 + V_2}$$

Where:

V_1 = The volume of the first phase (L).
C_1 = The concentration of the analyte of concern in the first phase (mg/L).
V_2 = The volume of the second phase (L).
C_2 = The concentration of the analyte of concern in the second phase (mg/L).

14.3 Procedure When Volatiles are Involved

Use the ZHE to obtain LP extract for analysis of volatile compounds only. Extract resulting from the use of the ZHE shall not be used to evaluate the mobility of non-volatile analytes (e.g., metals, pesticides, etc.).

The ZHE device has approximately 500 mL internal capacity. The ZHE can thus accommodate a maximum of 25 grams of solid (defined as that fraction of a sample from which no additional liquid may be forced out by an applied pressure of 50 psi), due to the need to add an amount of extraction fluid equal to 20 times the weight of the solid phase.

Charge the ZHE with sample only once and do not open the device until the final extract (of the solid) has been collected. Repeated filling of the ZHE to obtain 25 grams of solid is not permitted.

Do not allow the waste, the initial liquid phase, or the extract to be exposed to the atmosphere for any more time than is absolutely necessary. Any manipulation of these materials should be done when cold (0.1-6°C) to minimize loss of volatiles.

14.3.1 Pre-weigh the extract collection container ECC (see Section 9.6) and set aside. Express an appropriate amount of liquid from the ZHE device into the ECC whether for the initial or final liquid/solid separation, and take an aliquot from the liquid for analysis. The ECCs listed in Section 9.6 are recommended for use under the conditions stated in Sections 9.6.1 – 9.6.2.

14.3.2 Place the ZHE piston within the body of the ZHE (it may be helpful to first moisten the piston O-rings slightly with extraction fluid). Adjust the piston within the ZHE body to a height that will minimize the distance the piston will have to move once the ZHE is charged with sample (based upon sample size requirements determined from Section 14.3, Section 14.1.1 and/or 14.1.2). Secure the gas inlet/outlet flange (bottom flange) onto the ZHE body in accordance with the manufacturer's instructions. Secure the glass fiber filter between the support screens and set aside. Set liquid inlet/outlet flange (top flange) aside.

14.3.3 If the waste is 100% solid, (see Section 14.1.1), weigh out a subsample (25 gram maximum) of the waste, record weight, and proceed to Section 14.3.5.

14.3.4 If the waste contains < 0.5% dry solids (Section 14.1.2), the liquid portion of waste after filtration, is defined as the LP extract. Filter enough of the sample so that the amount of filtered liquid will support all of the volatile analyses required. For wastes containing ≥ 0.5% dry solids (Sections 14.1.1 and/or 14.1.2), use the percent solids information obtained in Section 14.1.1 to determine the optimum sample size to charge into the ZHE. The recommended sample size is as follows:

$$\text{Weight of waste to charge ZHE} = \frac{25}{\text{Percent solids (Section 14.1.1)}} \times 100$$

Weigh out a subsample of the waste of the appropriate size and record the weight.

14.3.5 If particle size reduction of the solid portion of the waste was required in Section 14.1.3, proceed to Section 14.3.6. If particle size reduction was not required in Section 14.1.3, proceed to Section 14.3.7.

14.3.6 Prepare the waste for extraction by crushing, cutting, or grinding the solid portion of the waste to a surface area or particle size as described in Section 14.1.3. Wastes and appropriate reduction

equipment should be refrigerated, if possible, to 0.1-6°C prior to particle size reduction. The means used to effect particle size reduction must not generate heat in and of itself. If reduction of the solid phase of the waste is necessary, exposure of the waste to the atmosphere should be avoided to the extent possible.

NOTE: Sieving of the waste is not recommended due to the possibility that volatiles may be lost. The use of an appropriately graduated ruler is recommended as an acceptable alternative. Surface area requirements are meant for filamentous (e.g., paper, cloth) and similar waste materials. Actual measurement of surface area is not recommended.

When the surface area or particle size has been appropriately altered, proceed to Section 14.3.7.

14.3.7 Waste slurries need not be allowed to stand to permit the solid phase to settle. Do not centrifuge wastes prior to filtration.

14.3.8 Quantitatively transfer the entire sample (liquid and solid phases) quickly to the ZHE. Secure the filter and support screens onto the top flange of the device and secure the top flange to the ZHE body in accordance with the manufacturer's instructions. Tighten all ZHE fittings and place the device in the vertical position (gas inlet/outlet flange on the bottom). Do not attach the extract collection device to the top plate.

NOTE: If waste material (>1% of original sample weight) has obviously adhered to the container used to transfer the sample to the ZHE, determine the weight of this residue and subtract it from the sample weight determined in Section 14.3.4 to determine the weight of the waste sample that will be filtered.

Attach a gas line to the gas inlet/outlet valve (bottom flange) and, with the liquid inlet/outlet valve (top flange) open, begin applying gentle pressure of 1-10 psi (or more if necessary) to force all headspace slowly out of the ZHE device into a hood. At the first appearance of liquid from the liquid inlet/outlet valve, quickly close the valve and discontinue pressure. If the waste is 100% solid (see Section 14.1.1), slowly increase the pressure to a maximum of 50 psi to force most of the headspace out of the device and proceed to Section 14.3.12.

14.3.9 Place the pre-weighed ECC under the liquid inlet/outlet valve and open the valve. Begin applying gentle pressure of 1-10 psi to force the liquid phase of the sample into the filtrate collection container. If no additional liquid has passed through the filter in any 2-minute interval, slowly increase the pressure in 10 psi increments to maximum of 50 psi. After each incremental increase of 10 psi, if no additional liquid has passed through the filter in any 2 minute interval, proceed to the next 10 psi increment. When liquid flow has ceased such that continued pressure filtration at 50 psi does not result in any additional filtrate within any 2-minute period, stop the filtration. Close the liquid inlet/outlet valve, discontinue pressure to the piston, and disconnect and weigh the filtrate collection container.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

14.3.10 The material in the ZHE is defined as the solid phase of the waste and the filtrate is defined as the liquid phase.

NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying pressure filtration, this material will not filter. If this is the case, the material within the filtration device is defined as a solid and is carried through the LP extraction as a solid.

If the original waste contained <0.5% dry solids (see Section 14.1.2), this filtrate is defined as the LP extract and is analyzed directly. Proceed to section 14.3.16.

14.3.11 The liquid phase may now be either analyzed immediately (see Sections 14.3.13 through 14.3.15) or stored at 0.1-6°C under minimal headspace conditions until time of analysis.

Determine the weight of extraction fluid #1 to add to the ZHE for TCLP,

or

determine the weight of extraction fluid #3 to add to the ZHE for SPLP as follows:

$$\text{Weight of extraction fluid} = \frac{20 \times \text{percent solids (Section 14.1.1)} \times \text{weight of waste to charge the ZHE (Section 14.3.4 or 14.3.8)}}{100}$$

14.3.12 The following sections detail how to add the appropriate amount of extraction fluid to the solid material within the ZHE and agitation of the ZHE vessel. Extraction fluid #1 is used in all cases for TCLP. Extraction fluid #3 is used in all cases for SPLP.

14.3.12.1 With the ZHE in the vertical position, attach a line from the extraction fluid reservoir to the liquid inlet/outlet valve. The line used shall contain fresh extraction fluid and should be pre-flushed with fluid to eliminate any air pockets in the line. Release gas pressure on the ZHE piston (from the gas inlet/outlet valve), open the liquid inlet/outlet valve, and begin transferring extraction fluid (by pumping or use of a syringe or similar means) into the ZHE. Continue pumping extraction fluid into the ZHE until the appropriate amount of fluid has been introduced into the device.

14.3.12.2 After the extraction fluid has been added, immediately close the liquid inlet/outlet valve and disconnect the extraction fluid line. Check the ZHE to ensure that all valves are in their closed positions. Reposition the ZHE in the vertical position with the liquid inlet/outlet valve on top. Pressurize the ZHE to 5-10 psi (if necessary) and slowly open the liquid inlet/outlet valve to bleed out any headspace (into a hood) that may have been introduced due to the addition of extraction fluid. This bleeding shall be done quickly and shall be stopped at the first appearance of liquid from the valve.

14.3.12.3 Re-pressurize the ZHE to 50 psi and check all ZHE fittings to ensure that they are closed and record the pressure. Let stand for 1 hour. Check and record the pressure again. If the pressure has not changed, depressurize to 5-10 psi and proceed to the next step. If the pressure has changed, check the fittings to determine the source of the leak and try to correct. If the problem was corrected repeat this step (Section 14.3.12.3).

14.3.12.4 Place the ZHE in the rotary agitation apparatus (if it is not already there) and rotate at 30 ± 2 rpm for 18 ± 2 hours. Ambient temperature shall be maintained at 23 ± 2°C during agitation.

14.3.13 Following the agitation period, check and record the pressure behind the ZHE piston. If pressure has not been maintained (i.e., pressure on the gauge has dropped or no gas release is observed), the device is leaking. Check the ZHE for leaking as specified in Section 9.2.1 and perform the extraction again with a new sample of waste. If the pressure within the device has been maintained, the material in the extractor vessel is once again separated into its component liquid and solid phases.

14.3.14 If the waste contained an initial liquid phase, filter the liquid into the TEDLAR® bag that contains the initial liquid before agitation. A separate TEDLAR® bag must be used if combining would create multiple phases, or there is not enough volume left within the TEDLAR® bag. Filter through the glass fiber filter. These liquids are collectively defined as the LP extract.

If the original waste contained no initial liquid phase, filter through the glass fiber filter into 40 mL HCl preserved VOA vials. This filtered liquid is defined as the LP extract.

NOTE: An in-line glass fiber filter may be used to filter the material within the ZHE if it is suspected that the glass fiber filter has been ruptured.

14.3.15 Following collection of the LP extract, immediately prepare the extract for analysis and store with minimal headspace at 0.1-6°C until analyzed. Analyze the LP extract according to the appropriate analytical methods. If the individual phases are to be analyzed separately (i.e., are not miscible), determine the volume of the individual phases (to ± 0.5%), conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted average:

$$\text{Final Analyte Concentration} = \frac{(V_1)(C_1) + (V_2)(C_2)}{V_1 + V_2}$$

where:

V_1 = The volume of the first phase (L).
C_1 = The concentration of the analyte of concern in the first phase (mg/L).
V_2 = The volume of the second phase (L).
C_2 = The concentration of the analyte of concern in the second phase (mg/L).

15.0 Data Reduction, Calculations and Loading

Not Applicable to the SOP

16.0 Method Performance

Not Applicable to the SOP

17.0 Pollution Prevention

The preparation of excessive volumes of laboratory reagents and standards shall be avoided so that waste and potential for pollution are minimized. Samples, reagents and standards shall be disposed in compliance with the lab waste disposal program, SOP 1130. With the consent of the client, the samples may be returned to their origin for treatment.

Uncontaminated paper waste, glass and cans should be separated for recycling. Laboratory staff are required to protect the laboratory's and our clients' business information when disposing of recycled paper or waste from the facility.

18.0 Data Assessment and Criteria for Quality Control Measures

Demonstration of Capability (DOC)

DOCs are not applicable to this procedure.

19.0 Corrective Actions for Out-Of-Control Data

The process for handling unacceptable and out of control data is found in SOP 230 Corrective Action.

20.0 Contingencies for Handling Out-Of-Control Or Unacceptable Data

Every effort is made to prevent problems from occurring. When out of control or unacceptable data occurs the first option is to identify the problem and reanalyze the samples within the holding times. When this is not possible, the QA Manager and/or the Laboratory Director reviews data and discusses options with the client. Reanalysis or reporting the data with qualification are alternatives. Out of control or unacceptable data reported to the client must include the data qualifier, flag and discussion on the rationale for reporting.

Holding time exceedance, improper preservation and improper sample condition or storage are noted on the corrective action form and included on the final report.

20.1 The process for handling unacceptable and out of control data is found in the Laboratory QAM Section 11. The reporting of data that is out of control must be approved and documented by Quality Assurance Manager and either the Technical Manager or the Laboratory Director.

20.2 Client Requested Modifications:

20.2.1 Clients must request modifications from the laboratory SOP in writing to the lab.

20.2.2 The lab director, technical manager and quality assurance manager will evaluate the requested client deviations, determine the feasibly of the deviation and the potential effects on the data.

20.2.3 If it is determined that the lab will perform the requested deviations, lab director, technical manager and quality assurance manager will decide if a method validation study is required.

20.2.4 The designated project manager will retain all documentation concerning the requested deviation, including all correspondence with the client, in the client folder.

20.2.5 The final analytical report must include the statement "*This report has analyses performed using client requested modifications* ".

21.0 Waste Management

The STAT Analysis Corporation Waste Disposal SOP 1130 identifies proper waste management practices for the chemicals used in this procedure. Samples are stored and discarded accordance with SOP 1130 Waste Disposal.

22.0 References

22.1 Method 1311, Revision 0; U.S. EPA SW-846 "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods" Update III, December 1996
22.2 Method 1312, Revision 0; U.S. EPA SW-846 "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods" Update III, December 1996
22.3 ASTM Method D 3987-85 Re-approved 1992
22.4 SOP 230 Corrective Actions
22.5 SOP 1010 Standard and Reagent Preparation
22.6 SOP 1400 LIMS
22.7 SOP 1130 Waste Disposal
22.8 SOP 003 Chemical Hygiene Plan
22.9 SOP 1250 Data Review
22.10 Manufacturers' Equipment Instruction Manuals
22.11 SOP 1230 Training
22.12 SOP 4210 pH of Aqueous, Soil, and Waste Samples by EPA 9040B, 9045C, 150.1
22.13 SOP 1040 General Laboratory Procedures

23.0 Forms, Figures, Tables, Diagrams, Flowcharts, Attachments or Validation Data

23.1 Figure 1 and Figure 2: Agitation Apparatus and Zero Headspace Extractor (ZHE).

23.2 Flowchart 1: Leaching Procedure Flowchart from Method 1311, Revision 0; U.S. EPA SW-846 "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods" Update III, December 1996

23.3 Flowchart 2: Leaching Procedure Flowchart from Method 1312, Revision 0; U.S. EPA SW-846 "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods" Update III, December 1996

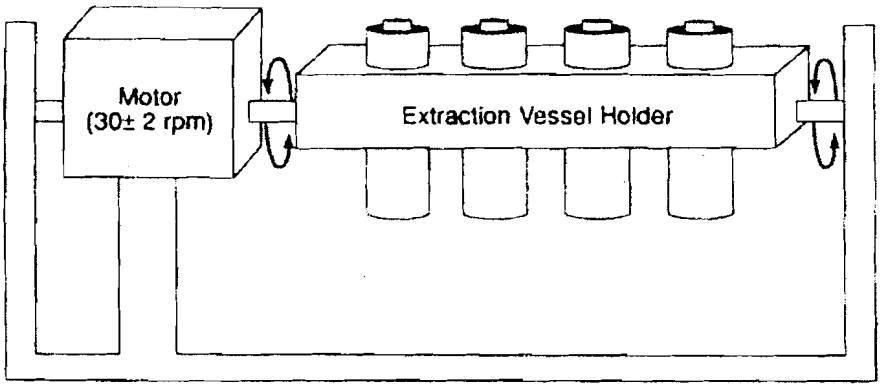


Figure 1. Rotary Agitation Apparatus

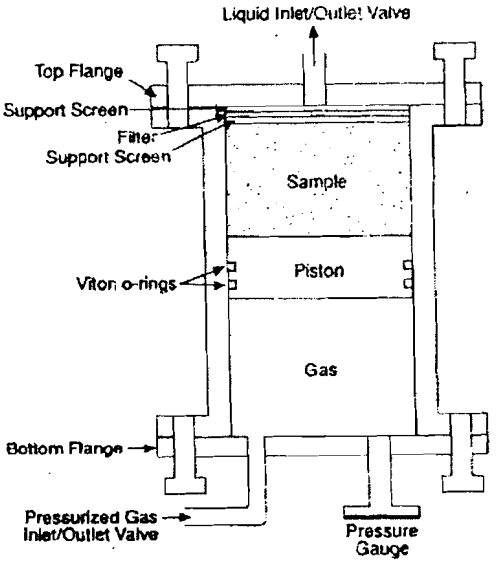
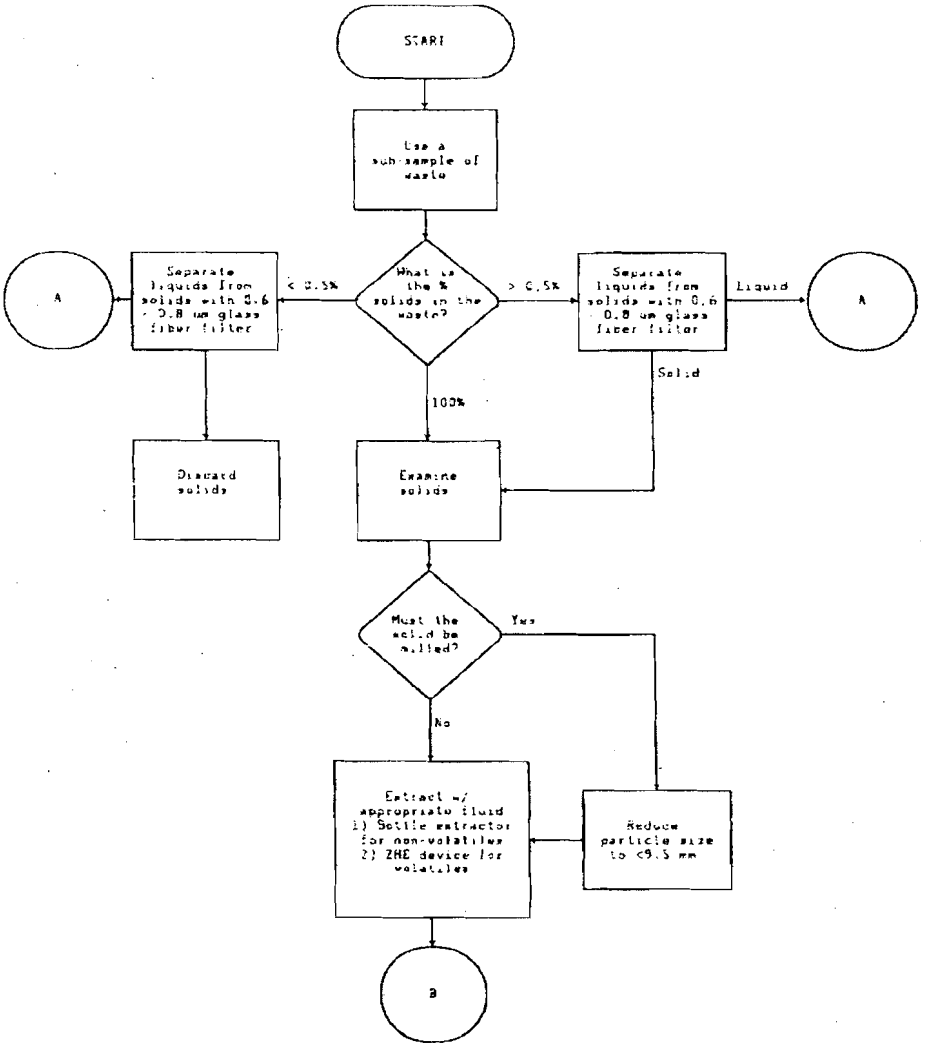


Figure 2. Zero-Headspace Extractor (ZHE)

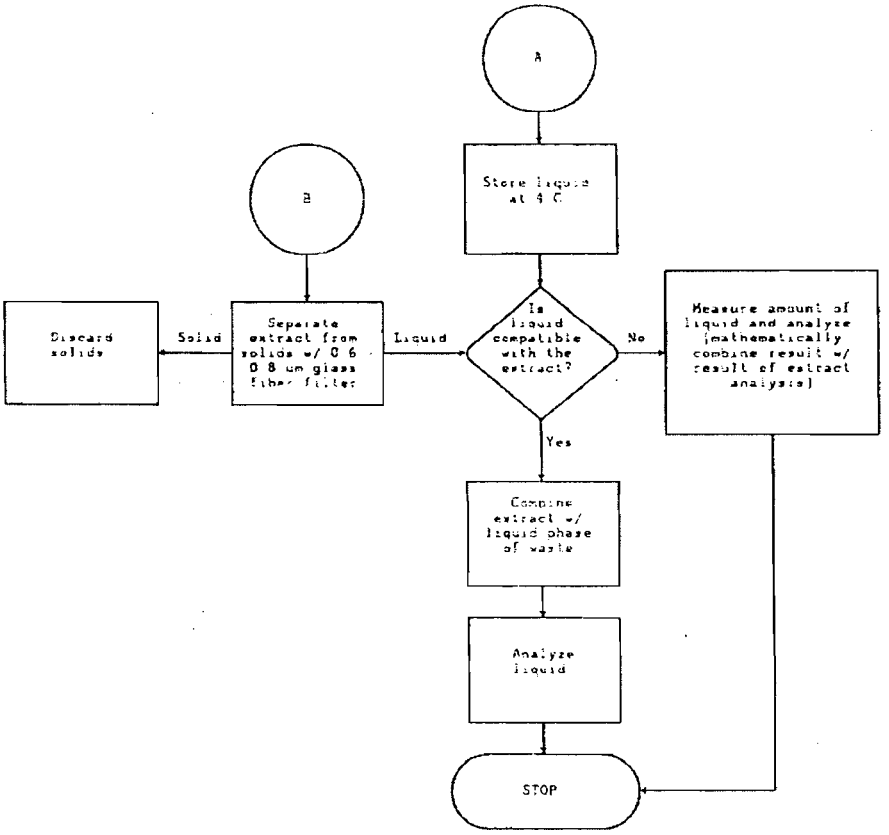
METHOD 1311

TOXICITY CHARACTERISTIC LEACHATE PROCEDURE



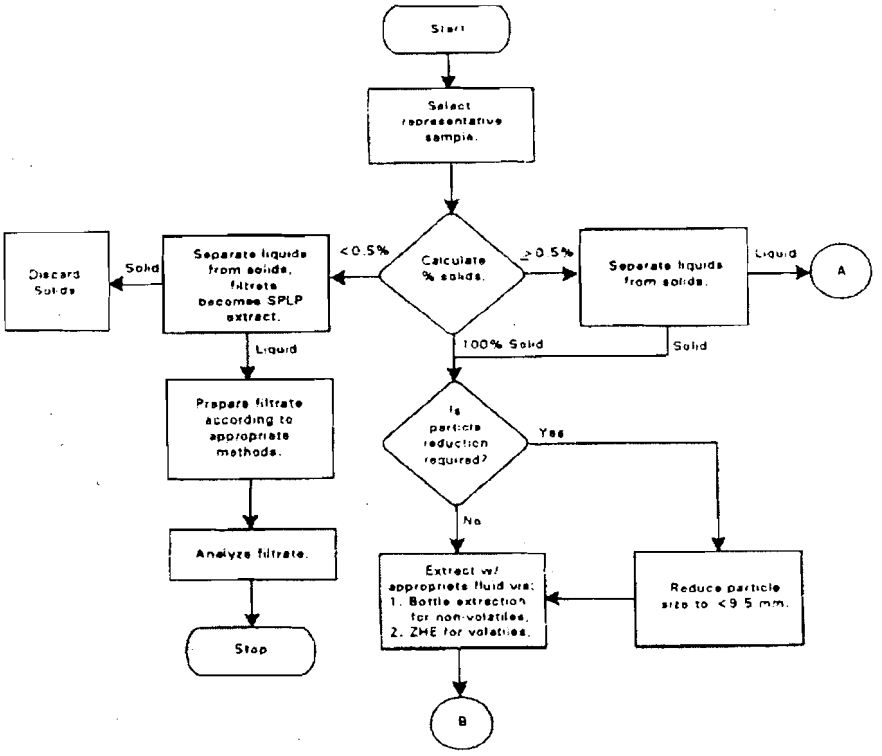
METHOD 1311 (CONTINUED)

TOXICITY CHARACTERISTIC LEACHATE PROCEDURE



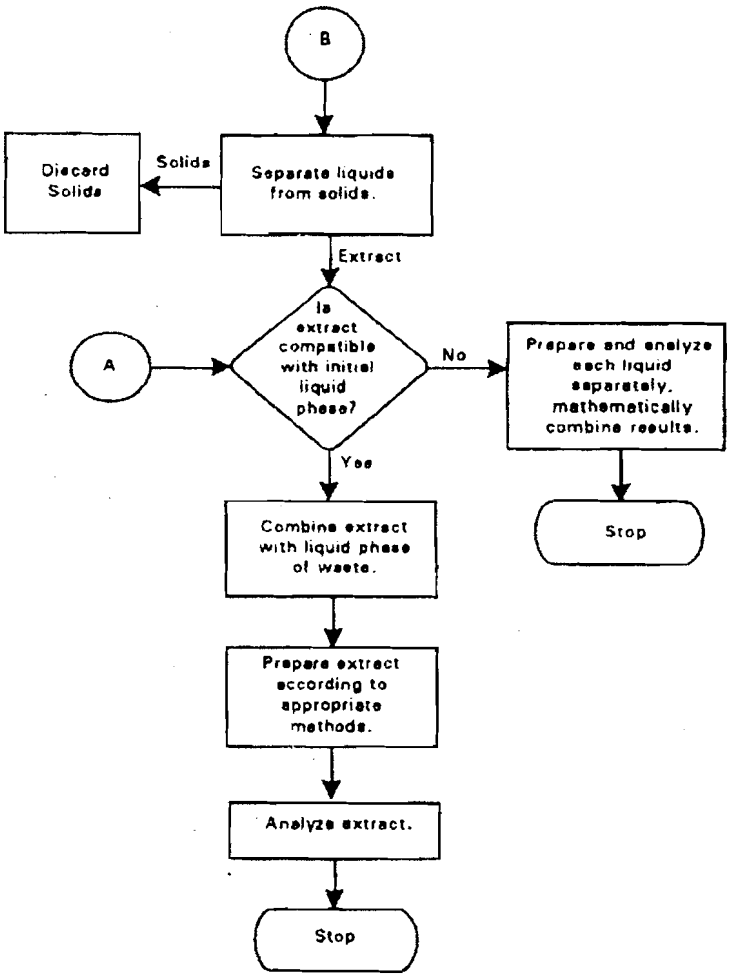
METHOD 1312

SYNTHETIC PRECIPITATION LEACHING PROCEDURE



METHOD 1312

SYNTHETIC PRECIPITATION LEACHING PROCEDURE (continued)



SOP ADDENDUM

SOP TITLE: SOP 2125 Leaching Procedures
Revision 00, Effective Date: 6/2/03.

Issued by Laurie Fetterman, QA Manager LF 10/31/03

Approved by: Dennis Jachim, Technical Manager DJ 10/31/03

Date of Issue: October 31, 2003

The following information is added to the SOP:

Section 2. (edit this section, additions are *italicized*)

This method is applicable to the following matrices: aqueous, drinking waters, Saline/Estuarine, non-aqueous liquid, biological tissue, solids (including soils, sediments, sludges and other matrices with >15% settleable solids), chemical waste, and air and emissions.

Section 5. (edit this section, additions are *italicized*)

5.4.1 Sample amounts used are varied based upon analytical tests requirements. *The laboratory tumbles enough sample to generate extract to support the analyses requested. Waste, minimizing the amount of laboratory waste. If additional analyses are requested or upon customer request, the laboratory can leach more sample.* Sample extracts for volatile organic analysis are expressed directly into 40 mL VOA vials according to criteria in Section 9.6.2. *These vials allow for automated analysis of the sample. If the leachate were first expressed into a TEDLAR® bags, then it would need to be transferred into a 40 mL vial. This step minimizes sample handling.*

5.4.2 Samples for ASTM are rotated at 30±2 rpm and filtered through a 0.6 to 0.8 um glass fiber filter. *The filters are used to comply with the TCLP standards.*

5.4.3 Preliminary evaluations are not done using a minimum 100 g aliquot. *There is usually not enough sample for this preliminary step. Thus, samples are leached and analyzed directly. This also minimizes the amount of waster generated.*

5.4.4 Preliminary evaluations are not done using a minimum 100g aliquot. *This modification is only performed when there is insufficient sample. Otherwise, 100g sample is used for preliminary evaluation.*

Section 14.4 Procedure (edit this section, additions are italicized

Records: Leaching Procedure Records will contain, at a minimum, the following:

1) *Lab sample ID code*
2) *Date and Time of analysis*
3) *ZHE vessel number*
4) *Analysis type*
5) *All manual calculations*
6) *Analyst's initials or signature.*

The initials/signature of the QA Manager and the Technical Manager indicate that this is a controlled document.

Section 16.0 Method Performances (edit this section, additions are *italicized*)

16.1 Ruggedness. The Laboratory has relied on the ruggedness testing listed in Method 1311 of SW-846. Two ruggedness studies have been performed by EPA to determine the effect of various perturbations on specific elements of the leaching procedure protocol. (The Laboratory has relied on the ruggedness testing listed in Method 1311 of SW-846.) Ruggedness testing determines the sensitivity of small procedural variations, which might be expected to occur during routine laboratory application.

16.1.1 Metals – The following conditions were used when leaching a waste for metals analysis:

Varying Conditions

Liquid/Solid Ratio	*19:1 vs. 21:1*
Extraction time	*16 hours vs. 18 hours*
Headspace	*20% vs. 60%*
Buffer #2 acidity	*190 meq vs. 210 meq*
Acid-washed filters	*yes vs. no*
Filter type	*0.7 um glass fiber vs. 0.45 um vs. polycarbonate*
Bottle type	*borosilicate vs. flint glass*

Of the seven method variations examined, acidity of the extraction fluid had the greatest impact on the results. Four of 13 metals from an API separator sludge/electroplating waste (API/EW) mixture and two of three metals from an ammonia lime still bottom were extracted at higher levels by the more acidic buffer. Because of the sensitivity to pH changes, the method requires that the extraction fluids be prepared so that the final pH is within ±0.05 pH units as specified.

16.1.2 Volatile Organic Compounds – The following conditions were used when leaching a waste for VOC analysis:

Varying Conditions

Liquid/Solid Ratio	*19:1 vs. 21:1*
Headspace	*0% vs. 5%*
Buffer #1 acidity	*60 meq vs. 80 meq*
Method of storing extract	*Syringe vs. Tedlar bag*
Aliquotting	*yes vs. no*
Pressure behind piston	*0 psi vs. 20 psi*

None of the parameters had a significant effect on the results of the ruggedness test.

23. Attachments. (edits this section, additions are *italicized*

Attachment 1: Leaching Procedures Prep Logbook Page

END OF ADDENDUM

The initials/signature of the QA Manager and the Technical Manager indicate that this is a controlled document.

TCLP Preparation Logbook

Reviewed by: _____

Stat Sample ID:										
Jar Number:										
Matrix:										
Analyst:										
% SOLIDS DETERMINATION:										
Weight of Sample (g.) (A):										
Weight of Dry Filter (E):										
Wt. of Dry Filter + % Dry Solids (F):										
Weight of Empty Beaker (B):										
Weight of Beaker + Filtrate (C):										
% Solids (D): (A-(C-B))/A) x 100:										
or % Dry Solids (G): ((F-E)/A) x100:										
Primary Leachate Volume (mL):										
EXTRACTION FLUID DETERMINATION:										
pH 1: 5 g sample + 96.5 mL DI, stir 5 min., if pH <5 use fluid #1, if >5 add 3.5 mL 1M HCl, heat to 50°C and hold for 10 min., cool to 25°C, measure pH (=pH 2)										
pH 2: If pH 2 <5, use fluid #1, if pH2 >5, use fluid #2										
Extraction Fluid Used (1or 2) and pH: (pH of Fluid 1 = 4.88-4.98, Fluid 2 = 2.83-2.93)										
ACTUAL TCLP SET-UP:										
Weight of sample (g.):										
Amount of Extraction Fluid used = (20 x D x g)/100:										
Date/Time Started:										
Date/Time Stopped:										
Temperature Range (°C):	-	-	-	-	-	-	-	-	-	-
ZHE Pressure (psi) Initial/Post Rotation/Final										
Vessel Number or Disposable:										
Filtration Unit #										
pH before Filtration										
Acid Preserved (Initials)										

Comments: _____

STAT Analysis Corporation:

STANDARD OPERATING PROCEDURE 4000

VOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS) (EPA Methods 5030B/5035/8260B)

Revision 04
Effective Date: February 11, 2003

Authors: Petra Svacha/ Thomas Bauer

Printed Name	Signature/Date
Jeremiah J. Favero Organic Manager	_____
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Thomas M. Bauer Laboratory Director	_____

This Standard Operating Procedure has been prepared for the sole use of STAT Analysis Corporation.

Copy Number: _____

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1.0 IDENTIFICATION OF TEST METHOD

SOP Title: Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS) is abbreviated as VOC in laboratory records.

2.0 APPLICABLE MATRICES

This method is also applicable to nearly all types of samples, regardless of water content, including, but not limited to, ground and surface water, mobility extracts, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments. Purge-and-trap by Methods SW-846 5030 (aqueous samples) and SW-846 5035 (solid and waste oil samples) are the preparation techniques used in this SOP.

In addition, other preparation techniques are also appropriate and necessary for some additional compounds not routinely analyzed using this SOP (see Method SW-846 8260B). These additional preparation techniques and non-routine compounds are not addressed in this SOP.

3.0 DETECTION LIMITS

The lab follows the procedure found in 40CFR Part 136B to determine the MDL for each matrix type on an annual basis. See the STAT Analysis SOP 1210 for the MDL procedure, frequency and acceptance criteria. The MDLs measured by the lab and all supporting documentation are in the laboratory QA files for review.

The laboratory determined MDL must always be less than the reporting limit (RL), which is determined by the lowest calibration standard. The RLs will usually range from three to ten times the laboratory measured MDLs but this relationship may vary dependent on dilution of sample aliquots, matrix interferences, moisture adjustments (in solid samples), or method-specified requirements. Attachment 1 contains the current MDLs and reporting limits (RLs) for this SOP.

4.0 SCOPE AND APPLICATION

4.1 This standard operating procedure describes in detail the precise methods used at STAT Analysis Corporation for the analysis of environmental samples for Volatile Organic Compounds (VOCs) by GC-MS. This SOP as written is to be applied when Method SW-846 8260B is requested. This SOP is used to determine the concentration of VOC's in all types of solid waste matrices, soils, and various types of water.

4.2 SOP 4000 can be used to quantify most VOCs that have both boiling points below 200°C and are either insoluble or slightly soluble in water. Volatile water-soluble compounds can be included in this analytical technique; however, for more soluble compounds, quantitation limits are approximately ten times higher due to poor extraction efficiencies from water. The SOP is also limited to compounds that elute as sharp peaks from a GC non-polar capillary column. Such compounds include low-molecular weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides. See Attachment 2 for a list of compounds and their characteristic ions that have been evaluated on the specified GC/MS system.

4.3 The reporting limits (RLs) for this SOP are shown in Attachment 1 for soils and water. RLs will be proportionately higher for sample extracts and samples that require dilution or reduced sample size to avoid saturation of the detector.

4.4 This method is restricted to use by or under the supervision of analysts experienced in the use of a Gas Chromatograph/Mass Spectrometer (GC/MS) and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

5.0 SUMMARY OF TEST METHOD

5.1 Prior to using this method, the samples must be prepared for the GC/MS using the appropriate sample preparation technique (see Section 14.1). Volatile compounds (VOCs) are introduced into a Gas Chromatograph (GC) by the purge-and-trap method or by direct injection. Purge and Trap: An inert gas (Helium) is bubbled through the water at ambient temperature (Method SW-846 5030) and at 40°C for soils (Method SW-846 5035). The volatile components are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through an adsorbent column where the volatile components are trapped. After purging is completed, the adsorbent column is heated and back flushed with Helium desorbing the components into a GC column. If the above sample introduction techniques are not applicable, a portion of sample is dispersed in methanol to dissolve the volatile organic constituents. A portion of the methanol solution is combined with water in the purging chamber. It is then analyzed by purge-and-trap GC/MS following the normal soil method.

5.2 This method describes chromatographic conditions that will allow for the separation of the compounds and for their qualitative and quantitative analysis by Gas Chromatography/Mass Spectrometry (GC/MS). Identification of target compounds is accomplished by comparing component retention times to those of authentic standards and by comparing their mass spectra with the electron impact (or electron impact-like) spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using a five-point calibration curve.

5.3 **Method Modifications from Reference** – This SOP is based on Methods SW-846 8260B, 5030B, and 5035. The 4-Bromofluorobenzene (BFB) mass spectrometer tuning criteria used in this SOP is referenced in the CLP Statement of Work (SOW) for Organic Analyses Revision OLM04.2 May 1999. This is an option in Method SW-846 8260B. Soil samples received in Encore (or equivalent) are prepped according to CLP Statement of Work (SOW) for Organic Analyses Revision OLM04.2 May 1999. Medium level dilutions are prepared from an aliquot of the methanol preserved sample that is transferred into 5 ml of reagent water and analyzed using the soil Archon procedure.

6.0 DEFINITIONS

The STAT Analysis Quality Manual Section 19.0 contains all the definitions of standard terms used in SOPs.

7.0 INTERFERENCES

7.1 GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. Interferences purged or co-extracted with methanol from the samples, will vary from source to source depending upon the particular sample or extract being tested. Determine if the source of interference is laboratory induced. If the source of the interference is laboratory induced, take corrective action to eliminate the problem.

7.2 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. Reagent blanks must be analyzed to demonstrate that carryover has been eliminated. Reanalysis must be performed on all affected samples to demonstrate that the compound concentration is from the sample and not due to carryover. The purge-and-trap system may require extensive bake out and cleaning after a high-level sample. Cleaning may include trap replacement, purge gas filter replacement, frit cleaning/replacement and/or transfer line cleaning/replacement.

7.3 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride, acetone, and fluorocarbons) through the septum seal into the sample during shipment and storage. A refrigerator blank, consisting of preserved reagent water, is stored under the same conditions as the samples. It is analyzed weekly to ensure that samples are not cross-contaminated during the storage process. Clients may specify trip blanks and field blanks for additional contamination checks to monitor for cross contamination during the shipping and sample collection processes.

7.4 The laboratory where volatile analysis is performed must be kept completely free of solvents (except P&T Grade Methanol). Storage of sprays, neat standards, and white out (for capillary column marking only) is forbidden.

7.5 Impurities in the purge gas and from organic compounds out-gassing from the plumbing ahead of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free of contamination under the conditions of analysis by running calibration and reagent blanks. The use of non-PTFE plastic coating, non-PTFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

7.6 Laboratory clothing worn by the analyst should be kept only in the VOA laboratory since the clothing exposed to solvents can cross contaminate samples. Lab coats used in other areas the lab, i.e. liquid/liquid extractions, soil extractions, dishwashing and PCM prep, etc., are forbidden.

8.0 SAFETY

Numerous compounds analyzed by this method are known or suspected carcinogens. Proper personal protective equipment including safety glasses, nitrile gloves and a lab coat are required during different parts of this method. Other safety precautions must be conducted in accordance with the Chemical Hygiene Plan. Other actions can also be applied if deemed necessary. A reference file of Material Safety Data Sheets (MSDS) is available to all personnel involved in this method.

9.0 EQUIPMENT AND SUPPLIES

The following apparatus is recommended for performing this procedure. Equivalent items can be used, if with their use, the analytical and QA/QC requirements in this SOP can be met. All catalog numbers in this SOP are current as of the effective date and thereafter subject to change.

9.1 Gas Chromatograph/Mass Spectrometer system (GC/MS)

9.1.1 Gas chromatograph(GC) – Agilent 6890 or 5890/ HP 5890 with electronic flow control gas chromatograph with a split flow injection port used to reduce Helium flow. The column is directly coupled to the source.

9.1.2 Column – 20 m X 0.180 mm ID J&W DB-624 column with 1 µm film thickness.

9.1.3 Mass spectrometer(MS) - Agilent 5971 and 5973

9.1.4 Data system – A computer system using Agilent 3365 Chemstation Software (G1701AA Version C.03.00, G1701BA Version B.00.01, and G1701CA Version C.01.08) is used to collect and process data.

9.1.5 NIST Library of Reference Spectra, Edition NIST98.L

9.2 Purge-and-Trap device: Tekmar Model 3000/3100 (or equivalent) equipped with a 5 mL (or 25 mL) glass frit sampler and an VOC trap, Vocarb 3000.

9.3 Archon Auto Sampler

9.4 Microliter syringes - 10 µL, 25 µL, 100 µL, 250 µL, 500 µL and 1,000 µL. These syringes should be equipped with a 20-gauge needle having a length sufficient to extend into a volumetric flask

9.5 Glass Vials – 40 mL VOA vials with Teflon faced septum and screw cap

9.6 EnCore (or equivalent) samplers for soil samples

9.7 Gas tight glass syringes - 5mL and 10 mL

9.8 Syringe valve: two way, Luer ends

9.9 Volumetric flasks, Class A - 10 mL, 50 mL, 250 mL with ground glass stoppers

9.10 Balance: Analytical, capable of accurately weighing 0.0001g and a top loading balance capable 0.001g

9.11 Spatula - Stainless steel

9.12 Disposable pipettes: Pasteur

9.13 Amber glass vials - 10 mL with Teflon-lined mininert screw caps

9.14 pH strips, wide range

9.15 Magnetic Stirring bars – Teflon coated

9.16 EnCore extrusion tool.

9.17 Adjustable autopipette dispenser – 10 mL

10.0 REAGENTS AND STANDARDS

The following reagents and standards are required to perform this procedure. When instructions are given on how to prepare a specific volume of a reagent or standard, larger or smaller volumes can be prepared as needed so long as the final concentrations remain the same. Any other deviations from the reagents or standards listed in this SOP could be detrimental to the quality of the data produced. Such deviations would have to be approved and documented (see 230 Corrective Action SOP).

Instructions for labeling and record keeping of reagents and standards are contained in SOP 1010 Standard and Reagent Preparation.

10.1 Analytical reagent grade chemicals shall be used in all tests. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.

10.2 Organic-free reagent water - All references to water in this SOP refers to Type II reagent water (in-house system). Note: Reagent water may be de-gassed with High Purity Helium to remove trace impurities.

10.3 Stock Standard solutions - Standard solutions can be prepared from pure standard materials or purchased as certified solutions (e.g. Supelco). The routine laboratory practice is to purchase these standards from approved vendors. The standards used are purchased from: Protocol, Aldrich, Supelco, Restek, and AccuStandard. All purchased standards are stored at manufacturer's recommended conditions. Stock solutions prepared from neat compounds expire six months from preparation date. Working Standard solutions and Working Quality Control (QC) solutions are stored at < -10°C and must be replaced monthly or sooner if comparison with quality control check samples indicates a problem. Quality Control Standards must be from different source (lot numbers) than Calibration Standards.

10.3.1 Primary Stock Standard Solutions – These solutions are made using the individual Stock Standard solutions. Using microliter syringes, the following amounts of each Stock Standard solution are injected into 10 mL volumetric flasks. Each solution is brought to volume with P&T methanol, capped and mixed. The final concentration of each component is listed in Table 1. These are the primary stock standard solutions used to prepare the Working standard solutions in Section 10.3.2. These standards are stored at < -10°C in 10 mL amber vials equipped with Teflon lined mininert screw caps. They are freshly prepared every 6 months, or sooner if check standards indicate a problem. Note: The 50000 µg/mL 2-methylnaphthalene Primary Stock solution is made from pure solution by diluting 0.5000g in a 10.0mL Volumetric Flask with P&T methanol. Once a purchased Stock Standard solution has been opened, it is stored as a Primary Stock Standard Solution.

Table 1 Primary Stock Standard Solutions

Solution ID	Stock Solution	Conc. Stock (µg/ml)	Vol. Stock (µl)	Final Conc. (µg/ml)
VOC-Cyclohexanone	Cyclohexanone	Neat	422	40,000
VOC-2-methylnaphthalene	2-methylnaphthalene	50000	1000	5000

10.3.2 Working Standard Solutions – These solutions are made using the Stock Standard solutions and Primary Stock Standards solutions. Using microliter syringes, the following amounts of each Stock Standard solution are injected into 10 mL volumetric flasks. Each solution is brought to volume with Methanol, capped and mixed. The final concentration of each component is listed in Table 2. These are the Working Standard solutions used to prepare the calibration standards in Section 10.4. These standards are stored at < -10°C in 10 mL amber vials equipped with Teflon lined mininert screw caps. Note: the 1,4-dioxane is stored in an 1ml vial with no dilution. Working Standard Solutions are freshly prepared every month, or sooner if check standards indicate a problem. The Working standard for gases, M-502B-GASES, has been found to be stable for one month when stored at the listed concentration and final volume (Table 2). This solution is replaced if Continuing Calibration Verification (CCV) or Laboratory Control Sample (LCS) outliers exist.

Table 2 Working Standard Solutions

Solution ID	Stock Solution	Vendor/Catalog No.*	Conc. Stock (µg/ml)	Vol. Stock (µl)	Final Conc. (µg/ml)
VOC-MOR	Custom VOA Mix	Restek / 553515	2000 - 40000	1250	250 - 5000
VOC-EH	M-8260-ADD-10X	AccuStandard/ M-8260-ADD-10X	2000	1250	250
	1,3-Butadiene	AccuStandard/ S-406A-10X	2000	1250	250
	2-Ethyltoluene	Aldrich/E4,940-1	2000	1250	5000
Solution ID	Stock Solution	Vendor/Catalog No.*	Conc. Stock (µg/ml)	Vol. Stock (µl)	Final Conc. (µg/ml)
VOC-VCX	M-502A-R-10X	AccuStandard/ M-502A-R-10X	2000	1250	250
VOC-GAS	GASES/M-502B-10X	AccuStandard/ M-502B-10X	2000	1250	250
VOC-F.LIST	2-Nitropropane	Restek/30403-510	2000	1250	250
	Cyclohexanone	Supelco/44-2532	40,000	1250	5000
	Ethyl Acetate	Supelco/4-7947	2000	1250	250
	Ethyl Ether	Supelco/4-7948	2000	1250	250
VOC-1,2-Methylnaphthalene	2-methylnaphthalene	Supelco/44-2359	5000	500	250
	1-methylnaphthalene	Supelco/4-8162	2000	1250	250
1,4-Dioxane	1,4-Dioxane	Supelco/4-8367	2000	No dilution	2000

* or equivalent

10.4 Calibration Standards - A minimum of five calibration standards are prepared. The low standard is the RL and above the MDL. The others define the working range of the GC/MS system. Calibration standards in current use: 5, 20, 50, 100, 200 and 300 µg/L. See Table 3 for Soil and Table 4 for Water standards.

10.4.1 Using microliter syringes, the following amounts of the Working solutions are injected into a volumetric flask. The flask contains water within 1 mL of the mark. After all Working solutions are injected into the water, the solution is brought to volume with water and capped. The flask is gently inverted three times to mix the solution. The contents of the neck portion of the flask are discarded prior to taking an aliquot. The final concentration of each component is listed in Table 3 and Table 4. The solution may be stored in a gas tight syringe or a 40 mL VOA vial (with no headspace in the storage container) at 4°C for up to 24 hours. The continuing calibration verification standards (CCVs) are prepared daily. Levels 2, 3 and 4 (10, 50, and 100 µg/L) are used for the CCVs.

10.4.2 For soil calibration: A 5 mL gas tight syringe is used, the plunger from the syringe is removed. The calibration standard solution from the volumetric flask is gently decanted into the syringe until the syringe is filled to almost overflowing. The plunger is carefully placed into the syringe barrel; no air bubbles are trapped in solution. The solution volume is adjusted to 5 mL. The 5 mL aliquot of each calibration solution is then transferred to an individual 40 mL VOA vial containing a stir bar. The vial is sealed with a screw cap with Teflon faced septum.

Table 3 Soil Calibration Standards

Level	Volume (µL) Secondary Stock	Volumetric Flask (mL)	Final Concentration (µg/L)
1	1.0/1.25*	50	5
2	2.0/2.5*	50	10
3	2.0/2.5*	10	50
4	4.0/5.0*	10	100
5	8.0/10.0*	10	200
6	12.0/15.0*	10	300

* Second Volume is for 1,4-Dioxane only.

10.4.3 For water calibration: The calibration standard solution from the volumetric flask is gently decanted into an individual 40 mL VOA vial until the vial is filled to almost overflowing. The screw cap with Teflon faced septum is carefully placed on the vial; no air bubbles are trapped in solution.

10.4.4 A 200 ppb Gas Only (GASES/M-502B-10X) Calibration Standard may be prepared if bromomethane and/or chloroethane response is suppressed due to an excessive volume of P&T methanol needed to prepare the 200 ppb standard. Methanol will co-elute with bromomethane and/or chloroethane causing their signal to be suppressed if excessive methanol is present.

Table 4 Water Calibration Standards

Level (5mLpurge)	Volume (µL) Secondary Stock	Volumetric Flask (mL)	Final Concentration (µg/L)
1	1.00/1.250*	50	5
2	2.0/25*	50	10
3	10.0/12.5*	50	50
4	20.0/25.0*	50	100
5	40.0/50.0*	50	200
6	60.0/75.0*	50	300
Level (25mL purge)	Volume (µL) Secondary Stock	Volumetric Flask (mL)	Final Concentration (µg/L)
1	0.40/0.50*	500	0.2
2	2.0/2.5	500	1
3	1.00/1.250*	50	5
4	2.0/2.5*	50	10
5	4.0/5.0*	50	20
6	8.0/10.0*	50	40

* Second Volume is for 1,4-Dioxane only.

10.5 Internal Standards/Surrogate Standards Solution: The internal standards used are Chlorobenzene-d_5, Pentafluorobenzene, 1,4-Dichlorobenzene-d_4, and 1,4-Difluorobenzene. The surrogates are Toluene-d_8, 4-Bromofluorobenzene, Dibromofluoromethane, and 1,2-Dichloroethane-d_4. A commercially prepared stock solution, 2000 µg/ml, is purchased from Supelco (Cat. No. 4-8958/4-7778). The Working Standard solution is prepared by injecting 6.25 ml of stock standard into a 50 mL volumetric flask and diluting to mark with Methanol. The concentration of the Spiking solution is 250 µg/mL. This Working Standard solution is added to the standard reservoir of the Archon Autosampler. One microliter (1.0 µL) is added to each sample aliquot that is analyzed by the system. The concentration in the sample is 50 µg/L for all Internal Standard and Surrogate compounds. This solution expires after one month. The internal standards permit most of the compounds of interest in a chromatogram to have retention times of 0.80-1.20 relative to one of the internal standards. Use the base peak ion from the specific internal standard as the primary ion for quantitation (see Attachment 2, i.e. for 1,4-dichlorobenzene-d_4, use 152 m/z for quantitation). If interferences are noted, use the next most intense ion as the quantitation ion.

10.6 GC/MS tuning standard - A standard solution containing 25 µg/mL of BFB in methanol is prepared. Dilute the Protocol 2000 µg/mL BFB standard (125 µL) in a 10.0 ml Volumetric Flask with P&T methanol. Inject 2 µL of this working solution onto the column every 12 hours. This solution will expire after six months. A methanol solution containing 25 ng/µL of 4-Bromofluorobezene (BFB) is used to tune the mass spec. The VOC tuning standard is purchased from Protocol (Cat. No. 5242-S1). Store at < -10°C when not being used. Inject 2 µL of this standard at the start of every 12 hours of operation.

10.7 The Laboratory Control Sample (LCS) is also used as an Initial Calibration Verification Standard (ICV). Spiking solutions are prepared from certified analytical stock standard solutions purchased independently from the Calibration Standards. The LCS stock standards are purchased from Supelco and Restek.

10.7.1 The LCS Spiking Solutions are prepared according to Table 5. These solutions are made using the LCS stock standard solutions. Using a microliter syringe, the following amounts of each solution are injected into a single 10 mL volumetric flask. The solution is brought to volume with Methanol, capped and mixed. The final concentration of each component is listed in Table 5. These are the source solutions used to prepare the LCS for both soil and water samples. These solutions are stored at < -10°C in a 10 mL amber vial equipped with a Teflon lined mininert screw cap. It is freshly prepared every month, or sooner if check standards indicate a problem. Note: The 2000 µg/mL Acrolein Stock solution is made from pure solution by diluting 25µL in a 10.0mL Volumetric Flask with methanol.

Table 5 LCS Spiking Solutions

Solution ID	Stock Solution	Vendor/Catalog No.*	Conc. Stock (µg/ml)	Vol. Stock (µL)	Final Conc. (µg/ml)
LCS-MIX	8260 VC Mix	Supelco/5-00607	2000	250	50
	VOC Mix #6	Supelco/48799-U	2000	250	50
	8240B Mix #2	Supelco/4-7364	2000	250	50
LCS-CM	Acrolein	Supelco/4-8501	2000	250	50
	Custom Mix	Supelco/20283002	2000 - 40000	250	50 - 1000
	Vinyl Acetate	Restek/30216	2000	250	50

* or equivalent

10.7.2 Soil LCS preparation: Using a 10 µL microliter syringe, inject 10 µL of each LCS Spiking Solutions into a 10 ml volumetric flask filled to the mark with water. The flask is capped and is gently inverted three times to mix the solution. The contents of the neck portion of the flask are discarded prior to taking an aliquot. A 5 mL gas tight syringe is used, the plunger from the syringe is removed and the LCS working solution from the volumetric flask is gently decanted into the syringe until the syringe is filled to almost overflowing. The plunger is carefully placed into the syringe barrel; ensure that no air bubbles are trapped in solution. The solution volume is adjusted to 5 mL. The 5 mL aliquot of the LCS solution is then transferred to an individual 40 mL VOA vial containing a stir bar and standard Ottawa sand. The vial is sealed with a screw cap with Teflon faced septum

10.7.3 Water LCS preparation: Using a 100 µL syringe, inject 50 µL of each LCS Spiking Solution into a 50 ml volumetric flask filled to the mark with water. The flask is capped and is gently inverted three times to mix the solution. The contents of the neck portion of the flask are discarded prior to taking an aliquot. The LCS solution from the volumetric flask is gently decanted into an individual 40 mL VOA vial until the vial is filled to almost overflowing. The screw cap with Teflon faced septum is carefully placed on the vial. Ensure that no air bubbles are trapped in the vial.

10.8 Matrix Spike standards - The LCS Spiking solutions are also used for the Matrix Spiking solution. For soil samples, prepare the LCS Spiking solution (50µg/L) as in Section 10.7.3. The LCS solution from the volumetric flask is gently decanted into a 10 mL gas tight syringe with removable needle, and injected into each vial already containing the soil sample. For water samples, transfer the water sample into a 50 ml volumetric flask and follow the procedure in Section 10.7.3

10.9 Methanol - Purge & Trap (P&T) Grade quality. Due to possible cross contamination, store in VOA room only.

10.10 Helium - UHP grade for purge gas and carrier gas.

10.11 Helium - HP grade for optional reagent water degassing .

10.12 Ottawa Sand.

11.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

11.1 Containers used to collect samples for the determination of volatile organic compounds: For water samples, use 40 mL VOA glass vials equipped with Teflon faced septum and screw cap, no headspace and preserved with concentrated HCl to pH <2. Water samples containing residual chlorine should be field treated to remove the chlorine prior to collection. Soil samples may be collected in either a 40 mL VOA vial, a 40 mL VOA vial preserved with sodium bisulfate, a 40 mL VOA vial with 5.0 ml methanol, or EnCore (or equivalent) samplers. Plastic containers or lids must NOT be used for the storage of samples due to the possibility of sample loss. A separate 4 oz jar should be supplied for percent moisture determination for soil and sediment analysis. Soils analyzed from a glass jar will NOT be reported by Method 5035 .

11.2 Water samples, soil samples preserved with sodium bisulfate, and soil samples preserved with 5.0 ml methanol must be stored under refrigeration at between 0.1°C and 6.0°C. Analysis must be within 14 days from sampling date for water preserved with HCl (7 days for unpreserved water samples) and 14 days for soils. Soil samples collected in 40 mL VOA vials or EnCore (or equivalent) samplers that are transferred to a close-system 40 mL VOA vial, that may contain reagent water; must be frozen within 48 hours of collection are held at <–10°C until analysis.

11.3 All samples are stored away from all standards, reagents, food, and other potentially contaminating sources in order to prevent cross contamination.

12.0 QUALITY CONTROL

The following details the QC requirements that apply to this analysis. Each Quality Control Indicator (QCI) provides information pertaining to either method or individual sample performance. Our goal is to produce defensible data of known and documented quality. The results of these Quality Control Indicator (QCI) samples are used to assess the acceptability of data.

12.1 Calibration Verification

An Initial Calibration Verification (ICV) standard containing all of the target compounds reported in this method (refer to section 10.7) shall be analyzed immediately after the completion of the initial calibration. The ICV shall be purchased from a second source to verify compound concentrations.

12.2 Blanks

Method Blank analysis is performed to determine if any contamination is present in the analytical process and is used to evaluate acceptance of the batch of samples. A method blank shall be prepared once per preparation batch of 20 or less samples per matrix type. If more than 20 samples are prepared a second blank shall be prepared after the twentieth sample. The method blank shall be processed through all preparatory steps used for the samples, including cleanup procedures. The blank shall be analyzed using the same instrument and conditions as the samples.

12.3 Laboratory Control Sample (LCS)

The LCS is used to evaluate the performance of the total analytical system, including all preparation and analysis steps. The LCS shall be prepared once per preparation batch of 20 or less samples per matrix type. If more than 20 samples are prepared a second LCS shall be prepared after the twentieth sample. The LCS shall be processed through all preparatory steps used for the samples, including cleanup procedures. The LCS shall be analyzed using the same instrument and conditions as the samples. Refer to section 10.7 for LCS compounds and concentrations.

12.4 Surrogates

The surrogates used for this method are added to all samples, standards, and blanks. Refer to section 10.5 for preparation and concentration instructions.

12.5 Duplicates

Duplicates of field samples or of the LCS must be prepared in compliance with the method requirements and client directives. Duplicate LCSs are prepared for cases in which there is insufficient sample to perform a matrix spike and matrix spike duplicate. Reproducibility performance would be the same as for a matrix spike/matrix spike duplicate.

12.6 Matrix Spike and Matrix Spike Duplicate (MS/MSD)

MS/MSDs indicate the effect of the sample matrix on the precision and accuracy of the results generated using the selected method. This information does not determine the validity of the entire batch. MS/MSDs must be analyzed at a minimum of 1 per 20 samples per matrix per preparation procedure, or as specified by the required test method. If an MS/MSD pair is not analyzed in the preparation batch, an LCS/LCSD pair is analyzed. Samples chosen for matrix spiking are rotated among different clients and/or different client projects. This is accomplished through communication between the Department Manager and the analyst. In addition, designated samples, as indicated by client request or contract requirement, are matrix spiked. The MS/MSD pair shall be processed through all preparatory steps used for the samples. They shall be analyzed using the same instrument and conditions as the samples. The LCS solutions in Section 10.7 are used for matrix spiking (see also Section 10.8). Some clients may require different spiking levels and/or target compounds, these specific needs are documented on the request for analysis forms.

12.7 Internal Standards

The internal standards used for this method are added to all samples, standards, and blanks. Refer to section 10.5 for preparation and concentration instructions.

13.0 CALIBRATION AND STANDARDIZATION

13.1 Mass Spectrometer Tuning Verification

Mass Spec is software-tuned with the BFB tuning macro using PFTBA. Each GC/MS system must be hardware-tuned to meet the criteria in Table 6 for a 50 ng injection of BFB. Analyses must not begin until all these criteria are met. Using a 10 µL syringe, inject 2 µL of BFB tuning standard solution directly on to the column. Analyze the solution using the following BFB method conditions:

BFB method operating conditions	
EMV	1300-2500
Mass Range	35-300
Scan Sampling Rate	2^2
Initial Column Temp.	70°C
Initial Temp Holding Time	2 minutes
Ramp 1 Temp Program	20°C/minute
Ramp 1 Final Column Temp.	230°C
Ramp 1 Holding Time	3 minutes
Injector Temp.	220°C
Source Temp.	250°C
Transfer Line Temp.	250°C
Split Ratio	50:1
Carrier Gas	UHP Helium

Background subtraction must be straightforward and designed only to eliminate column bleed or instrument background ions. Obtain a mass spectral analysis, using the method listed above, of BFB and confirm that all the key m/z criteria in Table 6 are achieved. The mass spectra of BFB are acquired using the following methods: three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged, the peak apex only is evaluated, or the entire BFB peak is averaged. If background subtraction is required, this must accomplished using a single scan no more than 20 scans prior to the elution of BFB. Do not background subtract part of the BFB peak. Note: the instrument-tuning file used to acquire the BFB criteria must be also used to acquire QC and sample data. If the criteria are not passed, the analyst must perform needed maintenance, retune the mass spectrometer and repeat the test until all criteria are achieved.

Note: the 12-hour tune period begins at the start of the BFB analysis, which is recorded as the data acquisition start time on the data file. The last valid calibration standard in the ICAL must have a data acquisition start time less than 12 hours from the start of the tune period.

Table 6 Acceptance Criteria for BFB

Target Mass	Relative to Mass	Lower Limit%	Upper Limit%
50	95	8	40
75	95	30	66
95	95	100	100
96	95	5	9
173	174	0	< 2
174	95	50	120
175	174	4	9
176	174	93	101
177	176	5	9

13.2 **Initial Calibration (ICAL)**

13.2.1 Analyze each calibration standard according to the procedure listed in Section 14 (standards are analyzed under the same conditions as samples) and tabulate the target ion area of the compound against concentration for each compound relative to the appropriate relative internal standard. See Attachment 5 for the list of internal standard assigned to each compound. Calculate response factors (RFs) for each compound in each calibration standard as follows:

$$RF = \frac{A_x * C_{is}}{A_{is} * C_x}$$

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} = Concentration of the specific internal standard (50 μg/L for this method)
C_x = Concentration of the compound being measured (μg/L).

13.2.2 Calculate the average response factor ($\overline{RF}$) for each compound as follows:

$$\overline{RF} = (\Sigma RF_1 \text{ to } RF_n)/n$$

where:

RF = RF for each of the calibration levels (i.e., 5)
n = Number of RF values (i.e., 5)

13.2.3 A system performance check must be performed to ensure that minimum average RFs are met before the calibration curve is used. If it is determined that one calibration level has an unacceptable response, that level may be reanalyzed once. If the minimum average RF is still not met, corrective action must be taken and the calibration sequence repeated. If any major changes are made to the system (e.g. column changed or detector cleaned), recalibration of the system must take place. For Volatiles, the System Performance Check Compounds (SPCCs) and the the minimum average RFs are as follows:

Chloromethane	0.100
1,1-Dichloroethane	0.100
Bromoform	0.100
Chlorobenzene	0.300
1,1,2,2-Tetrachloroethane	0.300

13.2.4 Calibration Check Compound (CCC) responses are monitored to check the integrity of the system. The CCCs are as follows:

Vinyl chloride	1,2-Dichloropropane
1,1-Dichloroethene	Toluene
Chloroform	Ethylbenzene

Using the RFs from the initial calibration, calculate the percent relative standard deviation (%RSD) for the Calibration Check Compounds (CCC).

To calculate %RSD: $\%RSD = 100\% \times SD/\overline{RF}$

where:

%RSD = % Relative Standard Deviation

$\overline{RF}$ = average of initial RFs for a compound
SD = standard deviation (n-1) of average RFs for a compound

To calculate Standard Deviation (n-1 degrees of freedom)

$$SD = \sqrt{\sum_{i=1}^{N} \frac{(RF_i - \overline{RF})^2}{N-1}}$$

where: RF_i = RF for each of the 5 calibration levels
N = Number of RF values (i.e., 5)

13.2.5 If the %RSD of any CCC compound is > 30%, then the chromatographic system is too reactive for analysis to begin. Check stability of the trap, replace if necessary. Perform the initial calibration procedure beginning with section 13.2.1.

13.2.6 Linearity : If the %RSD of any compound is 15% or less, then the relative response factor is assumed to be constant over the calibration range, and the average relative response factor is used for quantitation. If the %RSD is greater than 15%, first order linear regression is used. The calibration curve must meet the requirements for curve fitting listed in SW-846 8000B and the correlation coefficient is ≥0.99. The equation is not forced through the origin.

13.2.7 Retention Times: The Relative Retention Times (RRT) of each compound in each calibration standard should be within ± 0.06 RT units.

13.2.8 Before sample analysis can begin, a Initial Calibration Verification (ICV) (see Sec. 10.7) must be performed. The ICV results must be within the acceptance criteria as established for the CCV compounds (Section 13.3). Other components should be be recovered within 85 to 115% of the true value.

13.2.9

1. All calibration curves must have a unique identifier. The calibration date is incorporated into the method identifier for easy reference.
2. All initial calibration standards must be analyzed within the 12-hour BFB tune verification window.
3. Calibration must be completed (all standard levels analyzed) within 36 hours or the entire calibration sequence must be repeated. If the calibration was not completed in the first tune window it may continue into a second tune window. Standard calibration levels from either tune window can be used. An exception follows: If BFB criteria does not pass criteria for the second tune window and major maintenance was done to the instrument or the Mass Spec tuning parameters were adjusted in order to obtain an acceptable tune for BFB, the entire calibration sequence must be repeated.
4. All initial calibration standards must be analyzed and verified prior to field sample analyses.
5. Do not add calibration standards and update the curve after the original calibration date.
6. Multiple analyses of the same calibration level are not allowed to be included in the calibration curve.
7. Compound responses cannot be selected from different analyses of the same calibration level (i.e. all compound responses for level 1 must come from the same data file), except for bromomethane and/or chloroethane, see Section 10.4.4.
8. If more than five calibration levels are analyzed, it is permissible to either drop the low compound concentration (poor response) or the high compound concentration (detector saturation). Do not drop a point in the middle of the curve.
9. If more than five calibration levels are analyzed, it is permissible to drop an entire level if the analyst can document a specific reason or reasons why that level should be excluded. Mechanical failures, significant loss of all compound responses possibly due to poor technique in standard preparation, or software malfunction during data acquisition (system did not acquire all compound data) are plausible reasons. The reason must be justified and documented. The supervisor should review this situation and approve the analyst's decision.
10. The need to analyze more than two analyses of the same calibration level indicates a potential problem with the Working Standard solution. Prepare a fresh Working Standard solution and repeat all five-calibration levels. All calibration standard levels must come from the same Working Standard solution.
11. Manual integration must only be used if the software fails to properly integrate the peak (See SOP 1255 Manual Integration). If manual integration is used for a particular compound, all levels of that compound do not have to be manually integrated. Example: the computer generated integration of a compound in the low level standard is not technically sound. A manual integration of the compound is performed (due to baseline noise, etc) in order to achieve a technically sound integration. Other levels of the compound are integrated correctly by the computer. The manual integration of the low level must match, as best as possible, the computer generated integrations for all other levels.
12. If any compound in the mid-point level is manually integrated, the integration of this compound must be reviewed for every continuing calibration standard and QC check solution (i.e. LCS, and Matrix Spike) to ensure that the integration is the same as the manual integration performed in the initial calibration (ICAL) mid-point. A consistent manner of integration must be achieved.
13. All manual integrations must be reviewed and approved according to SOP 1255 Manual Integration.

13.3 Continuing Calibration Verification (CCV)

13.3.1 The mass spec must pass tune criteria (see Section 13.1) every 12 hours during analysis of samples.

13.3.2 A continuing calibration verification (CCV) sample is analyzed every 12 hours during analysis of samples. Different standards are analyzed for the CCV such that a wider range of the calibration curve is verified. For example: on successive days analyze the 50 µg/L and the next day the 100 µg/L standard solution. Compare the response factors, of the SPCCs and the CCCs, and the internal standards from the CCV with the following criteria.

13.3.3 The SPCC compounds must meet the minimum criteria as stated in Section 13.2.3.

13.3.4 Control limits for the CCC compounds are ± 20% difference from the ICAL Response Factor (RF) if the average RF is used for quantitation, or ± 20% drift from the true concentration of the CCV compound if linear regression is used.

13.3.5 The areas of the internal standards in the CCV must be between -50% and +100% of the respective areas of the internal standards in the ICAL mid-point calibration standard.

13.3.6 The retention times of the internal standards in the CCV must be within ± 30 seconds of the respective retention times of the internal standards in the ICAL mid-point calibration standard.

13.3.7 If the CCV results obtained are outside the acceptance criteria, corrective actions must be performed. If routine corrective actions fail to produce an acceptable *second consecutive (immediate)* CCV, then either the lab has to demonstrate performance after corrective action with two consecutive successful CCVs, or a new ICAL must be performed. If the instrument has not demonstrated acceptable performance, sample analyses cannot continue until a new ICAL is established and verified with an ICV. However, sample data associated with an unacceptable CCV may be reported as qualified data under the following special conditions:

13.3.7.1 When the acceptance criteria for CCV are exceeded high, i.e., high bias, and there are associated samples that are non-detects, then those non-detects may be reported. Otherwise the samples affected by the unacceptable calibration verification must be reanalyzed after a new ICAL has been established, evaluated and accepted.

13.3.7.2 When the acceptance criteria for the CCV are exceeded low, i.e., low bias, those sample results may be reported if they exceed a maximum regulatory limit/decision level. Otherwise the samples affected by the unacceptable verification must be reanalyzed after a new ICAL is established and verified with an ICV.

13.3.7.3 When the acceptance criteria for the CCV are exceeded and it is not possible to reanalyze the sample due to limited sample quantity AND a new sample cannot be obtained by the laboratory, the data may be reported with the appropriate data qualifiers if the client has been contacted and agrees, in writing, to accept the qualified data.

13.4 Records: Initial and Continuing Calibration Records will contain, at a minimum, the following:

1) Calibration date
2) Test method
3) Instrument
4) Analysis date
5) Each compound name
6) Analyst's initials or signature
7) Standard Concentration (appropriate units) and number of standards
8) Response (appropriate units)
9) Calibration curve or response factor
10) Evaluation of and Statistics for ICAL curve fit in order to judge calibration curve acceptance
11) Evaluation of and Acceptance Limits for ICV analysis in order to judge calibration curve acceptance
12) Evaluation of and Acceptance Limits for CCV analysis in order to judge continuing calibration acceptance

13.5 Thermometers - The thermometers in the sample refrigerators and the standards freezer must be checked daily. They must meet performance criteria. Check the thermometer to ensure the calibration is not expired (see SOP 1040 General Laboratory Practices).

13.6 Balances - Be sure the balance is checked prior to use and performance criteria are met (see SOP 1040 General Laboratory Practices).

14. PROCEDURE

14.1 Sample Preparation

14.1.1 Samples are removed from the refrigerator and placed in the Archon autosampler. The samples are allowed to warm to ambient temperature prior to analysis. All standards, method blanks, and QC solutions (made from the same reagent water) are prepared in 40 mL VOA vials and put in the Archon.

14.1.2 Samples are prepared for analysis by using a Purge and Trap. If the trap is new, condition it by purging it with Helium at 40ml/min for 30 minutes at room temperature followed by a bake at 270°C in the bake mode with Helium flow of 40 mL/min.

14.1.3 Purge and Trap Conditions

Purge and Trap operating conditions	
Purge Ready Temp	30°C
Sample Size	5 mL
Purge Time	11 minutes
Purge Flow	40 mL/min
Dry Purge Time	5 minutes
Pre-heat Temp	245°C
Desorb Temp	250°C
Desorb Time	2 minutes
Bake Temp	260°C
Bake Time	7 minutes
Transfer Line Temp.	250°C
Purge Gas	UHP Helium

14.1.4 Check the Internal Standards/Surrogate Solution reservoir to ensure that enough solution is present. One (1) microliter of this solution is added automatically to the 5 mL (or 25mL) water sample aliquot as it transfers to the 5 ml (or 25 ml) purging vessel. Soils samples are treated similarly except they are purged directly in the 40 ml VOA vial without opening. Five (5) ml of reagent water is added to transfer the one (1) microliter of internal standard/surrogate solution to the sample vial.

14.2 GC/MS Analysis

14.2.1 GC/MS Conditions:

GC/MS operating conditions	
EMV	1300-2500
Mass Range	35-300
Scan Sampling Rate	2^2
Initial Column Temp.	40°C
Initial Temp Holding Time	4 minutes
Ramp 1 Temp Program	10°C/minute
Ramp 1 Final Column Temp.	230°C
Ramp 1 Holding Time	5 minutes
Injector Temp.	220°C
Source Temp.	250°C
Transfer Line Temp.	250°C
Split Ratio	50:1
Carrier Gas	UHP Helium

14.2.2 Access the computer and create a batch sequence file by following Section 14.3.

14.2.3 Using a 10µL syringe, inject 2 µL of BFB tuning standard solution directly on to the column (50 ng on column). Analyze using the BFB method. Evaluate using the tune acceptance criteria (See Section 13.1).

14.2.4 Analyze the Continuing Calibration Verification Standard (CCV) and evaluate using CCV acceptance criteria (See Section 13.3).

14.2.5 Analyze the Method Blank The method blank must contain less than the reporting level for all target compounds. If target parameters achieve these limits, recovery and retention times of the surrogate compounds are within acceptance limits, and the chromatography (baseline noise and compound tailing) is acceptable, continue the analysis. If any one of these criteria is not met, take appropriate corrective action to identify and correct the problem.

14.2.6 Analyze the Laboratory Control Sample (in duplicate if a Matrix Spike/Matrix Spike Duplicate is not analyzed). Recovery (and RPD) must meet criteria specified in section 18.2.

14.2.7 If all criteria are met, continue with sample analysis as outlined below.

14.2.8 Water samples – a 5 mL (or 25mL) water sample aliquot is transferred to the 5 ml (or 25ml) purging vessel. One (1) microliter of Internal Standards/Surrogate Solution is added automatically to the 5 mL (or 25ml) water sample aliquot as it transfers to the 5 ml (or 25ml) purging vessel.

14.2.9 Soil samples: - VOA soil samples are prepared for analysis in the field with pre-preserved and pre-weighed 40 ml VOA Vial (5035 Kit). These vials are post-weighed and the sample amount is determined by the difference between post-weight and pre-weight. The weight is recorded in the VOA Soil Sample Prep Logbook and in the Prep Batch in LIMS (sees SOP 1400 LIMS). Each VOC sub-sample is assigned its

own unique Prep Batch. Three (3) EnCore samples (or equivalent) are usually collected for each sampling point and are placed in a tared 40 ml Vial with stir bar. The entire EnCore (or equivalent) soil sample is placed in the 40 ml VOA vial with the use of the extrusion tool (in cases where the sample collector has provided one 5 gm EnCore and one 25 gm Encore, the initial analysis is performed using the 5 gm EnCore and re-analysis and/or dilutions are performed using the 25 gm EnCore). The vial is weighed and recorded in the VOA Soil Sample Prep Logbook and the Prep Batch in LIMS (see SOP 1400 LIMS). Soil samples received in jars are also prepared into tared 40 ml VOA vials in a similar manner with care taken to minimize exposure of the sample to the environment (these samples are always reported without mention of Method 5035). The type of VOC collection device is recorded with the sample weights (5035 Kit, EnCore, or Jars). The sample of known weight is placed in the Archon autosampler and five (5) ml of reagent water is added to transfer the one (1) microliter of internal standard/surrogate solution to the sample vial. Medium level analysis is performed upon samples preserved in 5 ml or 10 ml (P&T) methanol. The volume of P&T methanol is noted. Aliquots of methanol are removed as appropriate; a 100 µL aliquot of methanol extract is the largest aliquot that can be analyzed as methanol may affect the system chemistry.

14.2.10 If the response for any quantitation ion exceeds the initial calibration curve range of the GC/MS system, sample dilution and reanalysis is an option. If sample dilution is required for water samples, the sample is diluted using the following procedure: A 50 mL volumetric flask is filled with reagent water close to the mark. A 5 mL syringe is filled with sample from a second (intact) 40 mL VOA vial. An appropriate amount of sample (minimum 1 mL) is injected into the flask, the solution is brought to volume with water and capped. The flask is gently inverted three times to mix the diluted sample. The contents of the neck portion of the flask are discarded prior to taking an aliquot. The diluted solution from the volumetric flask is gently decanted into an individual 40 mL VOA vial until the vial is filled to almost overflowing. The screw cap with Teflon faced septum is carefully placed on the vial; no air bubbles are trapped in solution. The VOA vial is placed in the Archon for analysis. If sample dilution is required for soil samples, the sample is diluted using the following procedure: Using microliter syringes, an appropriate amount of methanol extract (minimum 5.0 uL) is removed from sample preserved with methanol, and is injected into a 40ml VOA vial containing a stir bar and 5ml of reagent water. The VOA vial is placed in the Archon autosampler for analysis. Note: Some soil samples will be reported with an "E" (exceeded the calibration range on the undiluted analysis and reported with a "J" value on the diluted analysis. The "E" value is reported and a Quality Control Exception Report is generated and delivered to the project manager.

14.2.11 Perform all qualitative and quantitative measurements as described in Sections 14.4 and 14.5. After water (5030) analysis, check the sample pH using the pH strips and record the result. Used vials are kept for 14 days in VOC room and then disposed according to SOP 1330 Waste Disposal.

14.3 Analytical Sequence

START CHEMSTATION SOFTWARE:

From NT Desktop: Start/Programs/MSD ChemStation/Instrument #1/Instrument #1

The software will locate the instrument and all peripheral equipment. Once the software is fully loaded there will be two windows visible. Window one is the instrument control window. Instrument parameters are readily viewed from this window. The second window is the sequence control window. No instrument parameters are viewable from this window.

SEQUENCE SETUP

From menu: Sequence/Load

1. Load the method you want to use for analysis (soil/water)
2. OK (to save changes)

From menu: Sequence/Run

3. Set current date in Data File Directory space (ie., C:\MSDCHEM\1\DATA\060702\)
4. OK (to save changes)

From menu: Sequence/Edit Sample Log Table

1. Set data file name using current date using the following format MMDDYY## (ie., 06070201)
2. Set up sequence order using the following format: (**NOTE:** Tune and CCV must always run first)

LINE	TYPE	VIAL	DATA FILE	METHOD	SAMPLE NAME-INSTRUMENT
1	Sample	100	11240201	BFBS	TUNE VBFB112402-1
2	Sample	1	11240202	S1121002	CCV VSTD050
3	Sample	2	11240203	S1121002	MBLK VBLK112402-1
4	Sample	3	11240204	S1121002	LCS VLCS112402-1
5	Sample	4	11240205	S1121002	SAMP ###########
6	Sample	5	11240206	S1121002	SAMP ###########
7	Sample	6	11240207	S1121002	SAMP ###########

NOTE: The number of samples, including tune and CCV that can be analyzed within the 12 hour window varies with each analysis. Use this list as a guide but always check that the samples were analyzed within 12 hours of the BFB injection.

3. OK (to save changes)

From menu: Method/Set New Default Paths

1. Update the method and data file paths using the current date (ie., C:\MSDCHEM\1\DATA\060702\)
2. OK (to save changes)

Using Windows Explorer copy all of the method files from the previous day's folder into the current day's folder. Note: After each ICAL, the water/soil method is saved using the following format: matrixinstrumentMMDDYYof last ICAL (ie., S1121002).

TO START SEQUENCE:

From menu: Sequence/Run/Run Sequence

Start of the 12 hour sequence (as documented as the date/time stamp on the data file for the Tune Standard):

The analytical sequence for Initial Calibration is:

BFB (Tune Standard)
Calibration standard (S1)
Calibration standard (S2)
Calibration standard (S3)
Calibration standard (S4)
Calibration standard (S5)
Calibration standard (S6) optional
Calibration standard (S7) optional
Initial Calibration Verification Standard (ICV)
Method Blank (MBLK)

The analytical sequence for Sample Analysis is:

BFB
Continuing Calibration Verification Standard (CCV)
Method Blank (MBLK)
LCS
(LCS Duplicate optional)
Sample #1
Sample #1 Matrix Spike (MS)
Sample #1 Matrix Spike Duplicate (MSD)
Sample #1 Laboratory Duplicate (optional)
Samples #2, #3, etc. until the end of 12 hour tune period

14.4 Data Interpretation - Qualitative Analysis

14.4.1 An compound is identified based upon Relative Retention Time (RRT) and by comparison of the sample mass ions with the mass ions of a standard of the suspected compound (standard reference ions). The reference mass ion ratio must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass ion are defined to be the two or three ions of greatest relative intensity. See Attachment 2 for the ions to be monitored. Two criteria must be satisfied to verify identification: (1) elution of sample component at the same GC relative retention time (RRT) as those of the standard component; and (2) correspondence of the sample component and the standard component mass ions. Intensities of the characteristic ions must maximize in the same scan or within one scan of each other.

14.4.2 The RRT of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

14.4.3 The relative intensities of the characteristic ions must agree within 20% of the relative intensities of these ions in the reference spectrum. (example: For an ion abundance of 50% in the reference, the corresponding abundance in a sample spectrum can range between 30% and 70%.)

14.4.4 Structural isomers that produce very similar mass spectra must be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs. The Manual Integration SOP 1255 is used for guidance in the integration of these two peaks and for other situations that may require analyst efforts to correct computer generated integrations that are not technically sound.

14.4.5 Identification is hampered when sample components are not resolved chromatographically or co-elute and produce mass spectra containing ions contributed by more than one compound. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of compound spectra and background spectra is important. Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification of compounds, but each compound spectrum will contain extraneous ions contributed by the coeluting compound.

14.4.6 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose of the analyses being conducted. Computer generated library search routines must not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification. Guidelines for making tentative identification are:

14.4.6.1 Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) must be present in the sample spectrum.

14.4.6.2 The relative intensities of the major ions must agree within ± 20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).

14.4.6.3 Molecular ions present in the reference spectrum must be present in the sample spectrum.

14.4.6.4 Ions present in the sample spectrum but not in the reference spectrum must be reviewed for possible background contamination or presence of coeluting compounds.

14.4.6.5 Ions present in the reference spectrum but not in the sample spectrum must be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

14.5 Data Interpretation - Quantitative Analysis

14.5.1 Once a compound has been identified, the quantitation of that compound must be based on the integrated abundance from the EICP of the primary characteristic ion. The internal standard used shall be the one nearest the retention time of that of a given compound.

14.5.2 If the RSD of a compound's response factors is 15% or less, then the concentration in the sample is determined using the average response factor (RF) from initial calibration data (13.2). See Method 8000, Sec. 7.0, for the equations describing internal standard calibration and either linear or non-linear calibrations.

14.5.3 Where applicable or required, the concentration of any non-target compounds (TICs) identified in the sample are estimated. The same formulae must be used with the following modifications: The areas A_x and A_{is} must be from the total ion chromatograms, and the RF for the compound must be assumed to be 1. The resulting concentration must be reported indicating: (1) that the value is an estimate, and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

14.6 Record the following information in the appropriate logbook or data file. Include any deviations from this procedure. Analyst initials, date of analysis, sample number or ID, initial sample volume or weight processed, calibration standard sample or solution identifier, QC sample or solution identifier, surrogate solution identifier, internal standard solution identifier, any dilution information, readings from support equipment, data file name, instrument method name, visual observations, and any other information as deemed necessary.

14.7 Troubleshooting - The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Each day that the analysis is performed, the daily calibration standard (CCV) must be evaluated to determine if the chromatographic system is operating properly. Questions that must be asked: Do the peaks look normal? Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still good, the injector is leaking, the injector septum needs replacing, etc. If any major changes are made to the system (e.g. column changed or detector cleaned), recalibration of the system must take place.

14.8 Routine Maintenance - Record all maintenance, including the problem encountered, steps taken to correct the problem, and verification that the problem has been corrected (i.e. tune passed).

14.8.1 Change the septum and or the injection port liner as needed according to sample throughput. Trim a short section from the analytical column as necessary.

14.8.2 Clean the source on an as needed basis (loss of sensitivity).

14.8.3 Inspect the Archon autosampler, perform routine maintenance as necessary. Refill the standard reservoir of the autosampler with Internal Standards/Surrogate solution as needed according to sample throughput. Check Helium purge flow, clean the vial gripper, clean soil purge needle, and recalibrate as necessary.

14.8.4 Check the carrier gas supply; replace as necessary, record carrier gas change in the maintenance log book.

15. DATA REDUCTIONS, CALCULATIONS, AND LOADING

15.1 The data system performs the calculations.

15.1.1 If the %RSD of a compound's relative response factor is 15% or less, then the concentration in the sample may be determined using the average response factor (RF) from the initial calibration data (13.2) and the following equation. The equation is based upon all sample sizes equivalent to either 5 ml or 5 gram.

$$\text{Concentration } (\mu g/L \text{ or } \mu g/Kg) = \frac{A_x * C_{is} * D}{A_{is} * RF}$$

where:

A_x = Area of the characteristic ion for the compound being measured
C_{is} = Concentration of the specific internal standard (50 μg/L for this method)
A_{is}= Area of the characteristic ion for the specific internal standard
RF= average response factor for compound being measured
D = Dilution factor if dilutions are made

If another sample weight is analyzed, adjust the concentration using the factor: 5g / initial weight g

15.1.2 Alternatively, linear regression (Sec. 13.2) is used for determination of the sample concentration.

15.2 If appropriate, recalculate the concentration of the compound in the sample using the equations in Secs. 15.2.1, 15.2.2, and 15.2.3.

15.2.1 The concentration of the compound in the sample is reported as μg/L or μg/Kg. If conversion to mg/L or mg/Kg is required, calculate as follows:

$$\text{Concentration (mg/L or mg/Kg)} = \frac{\text{Conc } (\mu g/L \text{ or } \mu g/Kg) * D}{1000}$$

15.2.2 For soil samples reported on dry weight basis, divide the concentration by the decimal equivalent of the Percent Solids. For example: a sample contains 90% solids, thus

$$\text{Concentration } (\mu g/Kg \text{ or mg/Kg}) \text{ dry weight} = \frac{\text{Conc } (\mu g/Kg \text{ or mg/Kg})}{0.90}$$

15.2.3 If an aliquot of a methanol extract was analyzed, calculate as follows:

$$\text{Concentration in sample (mg/Kg)} = \frac{\text{Conc } (\mu g/L \text{ readout}) * 5 * V_{ex}}{W_i * V_a}$$

V_a = amount of methanol extract analyzed in μL
V_{ex} = total extract volume of methanol in mL
W_i = initial sample weight in g

15.3 The procedure for uploading data into the LIMS system is detailed in SOP 1400 LIMS.

16. METHOD PERFORMANCE

16.1 Demonstration of Capability (DOC)

All parameters of interest must meet the method acceptance criteria before actual sample analysis begins. See SOP 1230 Training for the procedure to perform and document the DOC. The DOCs for the analysts performing this method are located in the analysts' training form folders located in the QA office files.

A quality control (QC) reference concentrate in methanol is required containing each compound at a concentration of 10 µg/L to 200 µg/L. The QC reference sample used is the LCS solution (see Section 10.7). The QC reference sample is made using stock standards prepared independently from those used for calibration. This analysis is performed in quadruplicate. For each analyte calculate the mean recovery (X), standard deviation (s) and average % Recovery (%R). Water and soil recovery must be between 70 to 130%.

Continuing Demonstration of Capability will be documented with the use of PT sample results and four consecutive Laboratory Control Samples (LCS). This must be documented annually.

16.2 Comparison to Reference Method Data

EPA Method 8000B provides guidance for the establishment of control limits for the LCS and MS QC samples. Recovery limits of 70% to 130% are provided as initial benchmarks for performance (8000B Section 8.5.4). These limits are designed for a wide variety of organic test methods. Individual compound performance may vary.

16.3 In-House Control Limits

Method performance data is on file in the laboratory QC department. Comparison of method performance data for the laboratory to the reference method criteria occurs when laboratory in-house acceptance limits are generated. In-house generated data is compared to the specifications of the reference method. If the in-house limits are within the specifications of the reference method, the control limits are updated in LIMS. If the in-house limits are not within specifications, an investigation is performed to determine the cause(s) of the problem and a corrective action is completed. The analysis may continue until enough data points are collected to regenerate new control limits. Any QC data generated outside of reference method limits during that time frame is flagged.

The laboratory maintains performance records to document the quality of data that is generated. Method accuracy for samples is assessed and records maintained. After the analysis of at least 20 laboratory control samples and surrogates, calculate the average percent recovery (R) and the standard deviation of the percent recovery (S).

Control limits for method parameters are generated by the QC staff generates the method parameters and distributed to the analysts via updates to the LIMS control charts. The control limits are calculated based on in-house performance data. At a minimum, these limits are reviewed annually.

17. POLLUTION PREVENTION

The preparation of excessive volumes of laboratory reagents and standards shall be avoided so that waste and potential for pollution are minimized. Samples, reagents and standards shall be disposed in compliance with the lab waste disposal program, SOP 1130. With the consent of the client, the samples may be returned to their origin for treatment.

Uncontaminated paper waste, glass and cans should be separated for recycling. Laboratory staff are required to protect the laboratory's and our clients' business information when disposing of recycled paper or waste from the facility.

18. DATA ASSESSMENT AND CRITERIA FOR QUALITY CONTROL MEASURES

Data assessment includes review of: proper sample condition, preservation, and storage; analysis within holding time limitations; deviations from the SOP, evaluation of performance based or in-house control limits, reference method limits or project specific limits.

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a calibration verification standard is used to confirm the measurements were performed in an in-control mode of operation. The data review is conducted according to SOP 1250 Data Review.

18.1 Blanks

The method blank must contain less than reporting level for all target compounds. If the blank exceeds these limits, the source of contamination must be investigated and corrective actions taken. Re-analyze the method blank. If after re-analysis, the blank criteria is still exceeded, stop the analysis prior to sample analyses and correct the problem. Consult with the department manager for guidance. Refer to a client specific QAPP for additional guidance, if applicable.

If samples were analyzed with a contaminated method blank during unattended automated analysis, affected samples must be reanalyzed or data must be appropriately qualified if:

1) The concentration of a targeted compound in the blank is at or above the reporting limit as established by the SOP or by regulation, AND is greater than 1/10 of the amount measured in any sample.

2) The blank contamination otherwise affects the sample results as per the test method requirements or the individual project data quality objectives.

18.2 Laboratory Control Samples (LCS)

The results of the individual batch LCS are calculated in percent recovery (%R) and compared to established acceptance criteria. Current acceptance criteria used are 70 - 130% (SW-846 8000B Section 8.5.4) and 50-150% for water soluble compounds, until in-house LCS limits for both soils and waters are developed. If LCS Duplicate (LCSD) is performed, recovery limits must be met and the Relative Percent Difference (RPD) see the STAT QAM, Section 5.4 for the calculation for RPD, must be less than 20%. If the LCS is outside the acceptance criteria the analytical system is "out of control". Any affected samples associated with an out of control LCS must be reprocessed and reanalyzed or the results reported with appropriate data qualifiers. If after re-analysis the control criteria has not been met, the entire analysis batch must be re-analyzed. Always refer to a client specific QAPP for additional guidance.

18.3 Surrogates

18.3.1 The results of the individual Surrogate compounds are calculated in percent recovery (%R) and are compared to established acceptance criteria derived from in house generated control limits, see Attachment 3. Water Surrogate Recovery Limits are per Method 8260B. Soil Surrogate Recovery Limits are based on in house control limits due to the high clay content of Northeastern Illinois soils. Surrogates outside the acceptance criteria must be re-analyzed to determine matrix effect. Separate Soil Surrogate Recovery Limits are generated for samples preserved with sodium bisulfate as this acid has a destructive matrix effect (excessive CO_2 generation, reduction of metals to the elemental state, carbon dilsulfide and sulfur dioxide generation) using this preservative.

If surrogate recoveries are not within the established acceptance criteria, proceed as follows (SW-846 8000B):

1) Check to be sure that there are no errors in the calculations, surrogate solutions or internal standards. If errors are found, recalculate the data accordingly. Examine chromatograms for interfering peaks and integrated peak areas.

2) Check instrument performance. If an instrument performance problem is identified, correct the problem and re-analyze the sample.

3) Some samples may require dilution in order to bring one or more target compounds within the calibration range or to overcome significant interferences with some compounds. This may result in the dilution of the surrogate responses to the point that the recoveries cannot be measured. If the surrogate recoveries are available from a less diluted or undiluted aliquot of the sample, those recoveries may be used to demonstrate that the surrogates were within the QC limits, and no further action is required. However, the results of both the diluted and undiluted (or less-diluted) analyses should be provided to the data user.

4) If no instrument problem is found and if sufficient sample is available, the sample should be re-analyzed.

18.3.2 If, upon re-analysis (in either 2 or 4 above), the recovery is again not within limits, generate a Quality Exception Report (QER) as referenced in SOP 230 Corrective Action. If the recovery is within the limits in the re-analysis, provide the re-analysis data to the data user. If the holding time for the method has expired prior to the re-analysis, provide both the original and reanalysis results to the data user, and note the holding time problem.

18.4 Duplicates

The results from laboratory Duplicates are designed to assess the precision of analytical results in a given matrix and are expressed as relative percent difference (RPD). See the STAT QAM, Section 5.4 for the

calculation for RPD. Results are compared to established acceptance criteria as listed in the MS/MSD Attachment 4. For duplicates results outside established criteria corrective action must be documented or the data reported with appropriate data qualifying codes.

For this test method, the analysis of the MS/MSD pair is used for determination of method precision. Duplicate LCS samples will be analyzed for all matrices where it would be impractical to perform a MS/MSD, such as wipe samples. Precision data from 18.2 will be used for RPD acceptance criteria for LCS/LCSD.

18.5 Matrix Spikes

18.5.1 The results from MS/MSD are primarily designed to assess the precision and accuracy of analytical results in a given matrix and are expressed as percent recovery (%R) and relative percent difference (RPD). See the STAT QAM, Section 5.4 for the calculation for RPD. Sixteen compounds are listed in Attachment 4 for in house generated recovery and RPD control limits. Results are compared to established acceptance criteria derived from in house generated control limits. Note: SW846 Method 8000B mandates that RPD's be calculated based on concentration rather than % recovery. VOC soils have widely varied samples weights due to EnCore/5035 preservations. This will lead to very broad RPD control limits. For matrix spike results outside established criteria corrective action must be documented or the data reported with appropriate data qualifying codes.

18.6 Internal Standards

The results of the individual Internal Standard compounds on all samples, blanks, and spikes are calculated in percent recovery (%R) and are compared to established acceptance criteria. If the Internal Standard recovery is outside the acceptance criteria, see Table 7, corrective action may be taken. Note: the recovery of internal standards in these samples within the stated limits is not mandatory per the reference method, 8260B. It can be a useful diagnostic tool. Client specific project criteria may require the adherence to these limits. If so, then corrective action must be documented or the data reported with appropriate data qualifying codes.

Table 7 Internal Standards

INTERNAL STD COMPOUND	CRITERIA (%)
Chlorobenzene-d_5	-50 to +200
Pentafluorobenzene	-50 to +200
1,4-Dichlorobenzene-d_4	-50 to +200
1,4-Difluorobenzene	-50 to +200

18.6 Other

The laboratory will analyze standard reference materials and/or participate in relevant performance evaluation studies quarterly.

19 CORRECTIVE ACTIONS FOR OUT-OF-CONTROL DATA

The process for handling unacceptable and out of control data is found in SOP 230 Corrective Action.

If the CCV, MB, LCS/LCSD, MS/MSD, lab duplicate, surrogate, or internal standard recovery of any parameter falls outside the designated acceptance range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the samples is suspect and is only reported for regulatory compliance purposes with the appropriate corrective action form. Immediate corrective action includes reanalyzing all affected samples by using any retained sample before the expiration of the

holding time. Final data results must be qualified in the client report for reported results not meeting the laboratory defined criteria.

1) Review standards preparation logbocks. Check all calculations and ensure dilution factors are properly recorded.
2) Re-prepare the suspected standard or QC sample to identify possible preparation errors of the standard or QC sample.
3) Re-Analyze the samples when the CCV or LCS are not within acceptable limits.
4) Perform routine preventative maintenance following manufacturer's specification. Record all maintenance in the instrument logbook.

20 CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

Every effort is made to prevent problems from occurring. When out of control or unacceptable data occurs the first option is to identify the problem and reanalyze the samples within the holding times. When this is not possible, the QA Manager and/or the Laboratory Director reviews data and discusses options with the client. Reanalysis or reporting the data with qualification are alternatives. Out of control or unacceptable data reported to the client must include the data qualifier, flag and discussion on the rationale for reporting.

Holding time exceedence, improper preservation and improper sample condition or storage are noted on the corrective action form and included on the final report.

Review the CCV standard response, LCS result, surrogate recovery, and internal standard recovery for acceptable performance for each batch of samples. Record any trends or unusual performance on a corrective action form. Final data results must be qualified in the client report for results not meeting the laboratory defined criteria.

Manual integration must be minimized for standards, reagent blanks and surrogates. Routine manual integration of the same parameters indicates a system performance problem. Correct this problem or note in the instrument analysis logbook the suspected causes for routine manual integration. Sign and date all manually integrated chromatograms.

20.1 The process for handling unacceptable and out of control data is found in the Laboratory QAM Section 11. The reporting of data that is out of control must be approved and documented by Quality Assurance Manager and either the Technical Manager or the Laboratory Director.

20.2 Client Requested Modifications:

20.2.1 Clients must request modifications from the laboratory SOP in writing to the lab.

20.2.2 The lab director, technical manager and quality assurance manager will evaluate the requested client deviations, determine the feasibly of the deviation and the potential effects on the data.

20.2.3 If it is determined that the lab will perform the requested deviations, lab director, technical manager and quality assurance manager will decide if a method validation study is required.

20.2.4 The designated project manager will retain all documentation concerning the requested deviation, including all correspondence with the client, in the client folder.

20.2.5 The final analytical report must include the statement "*This report has analyses performed using client requested modifications*".

21 WASTE MANAGEMENT

The STAT Analysis Corporation Waste Disposal SOP 1130 identifies proper waste management practices for the chemicals and biological materials used in this procedure. Samples are stored and discarded accordance with SOP 1130 Waste Disposal.

22 REFERENCES

22.1 Method 8260B, Revision 2; Method 5030B, Revision 2; Method 5035 Revision 0, U.S. EPA SW-846 "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods" Update III, December 1996

22.2 STAT SOPs: 1210 [support equipment, recordkeeping, MDLs, etc]

22.3 SOP 230 Corrective Actions

22.4 SOP 1010 Standard and Reagent Preparation

22.5 SOP 1400 LIMS

22.6 SOP 1130 Waste Disposal

22.7 SOP 003 Chemical Hygiene Plan

22.8 SOP 1250 Data Review

22.9 Manufacturers' Equipment Instruction Manuals

22.10 SOP 1255 Manual Integration

22.11 SW-846 8000B Determinative Chromatographic Separations

22.12 SOP 1230 Training

22.13 "USEPA Contract Laboratory Program Statement of Work for Organic Analysis" Revision OLM04.2 May 1999, U. S. Environmental Protection Agency. Office of Solid Waste, Washington DC 20460.

22.14 NIST Library of Reference Spectra, 1998

23 FORMS, FIGURES, TABLES, DIAGRAMS, FLOWCHARTS, ATTACHMENTS OR VALIDATION DATA

Attachment 1
MDLs and REPORTING LIMITS FOR VOLATILE COMPOUNDS

CASN	Compound name	MDL (µg/L)	RL (µg/L)	RL (mg/L)	MDL (µg/Kg)	RL (µg/Kg)	RL (mg/Kg)
75-71-8	Dichlorodifluoromethane	0.2	10	0.01	0.1	10	0.01
75-01-4	Vinyl Chloride	0.2	5	0.005	0.1	5	0.005
74-87-3	Chloromethane	0.3	10	0.01	0.1	10	0.01
106-99-0	1,3-Butadiene	0.3	10	0.01	0.2	10	0.01
74-83-9	Bromomethane	0.6	10	0.01	0.3	10	0.01
75-00-3	Chloroethane	0.4	10	0.01	0.2	10	0.01
75-69-4	Trichlorofluoromethane	0.3	5	0.01	0.1	5	0.005
67-63-0	Isopropyl alcohol	39	400	0.4	55	400	0.4
67-64-1	Acetone	4.3	10	0.01	5.7	25	0.025
60297	Ethyl ether	0.4	50	0.05	0.2	50	0.05
76-13-1	Freon-TF	0.2	5	0.005	0.1	5	0.005
107925	Acrolein	1.6	50	0.05	2.9	50	0.05
75-35-4	1,1-Dichloroethene	0.2	5	0.005	0.1	5	0.005
75-15-0	Carbon Disulfide	0.3	5	0.005	0.1	5	0.005
75-09-2	Methylene Chloride	0.3	5	0.005	0.1	10	0.01
107131	Acrylonitrile	1.7	5	0.005	2.0	5	0.005
1634-04-4	MTBE	0.4	5	0.005	0.1	5	0.005
110-54-3	Hexane	0.3	5	0.005	0.1	5	0.005
156-60-5	trans-1,2-Dichloroethene	0.3	5	0.005	0.1	5	0.005
108-05-4	Vinyl acetate	0.4	10	0.01	1.5	10	0.01
75-34-3	1,1-Dichloroethane	0.2	5	0.005	0.1	5	0.005
78-93-3	2-Butanone	3.0	10	0.01	3.0	10	0.01
78-87-5	2,2-Dichloropropane	0.2	5	0.005	0.2	5	0.005
156-59-2	cis-1,2-Dichloroethene	0.3	5	0.005	0.1	5	0.005
67-66-3	Chloroform	0.3	5	0.005	0.1	5	0.005
78-83-1	Isobutyl alcohol	87	400	0.4	59	400	0.4
74-97-5	Bromochloromethane	0.2	5	0.005	0.2	5	0.005
141-78-6	Ethyl acetate	1.9	50	0.05	4.1	50	0.05
71-55-6	1,1,1-Trichloroethane	0.2	5	0.005	0.1	5	0.005
71-36-3	1-Butanol	55	400	0.400	69	400	0.4
563-58-6	1,1-Dichloropropene	0.3	5	0.005	0.1	5	0.005
56-23-5	Carbon Tetrachloride	0.3	5	0.005	0.1	5	0.005
107-06-2	1,2-Dichloroethane	0.2	5	0.005	0.1	5	0.005
71-43-2	Benzene	0.2	5	0.005	0.1	5	0.005
79-46-9	2-Nitropropane	1.6	50	0.05	2.9	50	0.05
74-95-3	Dibromomethane	0.1	5	0.005	0.3	5	0.005
79-01-6	Trichloroethene	0.2	5	0.005	0.1	5	0.005
78-87-5	1,2-Dichloropropane	0.3	5	0.005	0.1	5	0.005
107-06-2	1,4-Dioxane	50	200	0.2	33	200	0.2
75-27-4	Bromodichloromethane	0.3	5	0.005	0.2	5	0.005
110-75-8	2-Chloroethyl vinyl ether	4.8	50	0.05	1.2	50	0.05

Attachment 1
MDLs and REPORTING LIMITS FOR VOLATILE COMPOUNDS

CASN	Compound name	MDL (µg/L)	RL (µg/L)	RL (mg/L)	MDL (µg/Kg)	RL (µg/Kg)	RL (mg/Kg)
108-10-1	4-Methyl-2-Pentanone	0.4	10	0.01	0.2	10	0.01
10061-01-5	cis-1,3-Dichloropropene	0.3	5	0.005	0.1	5	0.005
108-88-3	Toluene	0.3	5	0.005	0.1	5	0.005
10061-02-6	trans-1,3-Dichloropropene	0.3	5	0.005	0.2	5	0.005
79-00-5	1,1,2-Trichloroethane	0.3	5	0.005	0.2	5	0.005
106-93-4	1,2-Dibromoethane	0.2	5	0.005	0.2	5	0.005
591-78-6	2-Hexanone	0.3	10	0.01	2.1	10	0.01
142-28-9	1,3-Dichloropropane	0.2	5	0.005	0.2	5	0.005
630-20-6	1,1,1,2-Tetrachloroethane	0.2	5	0.005	0.1	5	0.005
127-18-4	Tetrachloroethene	0.3	5	0.005	0.2	5	0.005
124-48-1	Dibromochloromethane	0.2	5	0.005	0.2	5	0.005
108-90-7	Chlorobenzene	0.2	5	0.005	0.2	5	0.005
100-41-4	Ethylbenzene	0.2	5	0.005	0.1	5	0.005
108-38-3	m&p-Xylene	0.5	10	0.01	0.3	10	0.01
95-47-6	o-Xylene	0.3	5	0.005	0.2	5	0.005
100-42-5	Styrene	0.2	5	0.005	0.2	5	0.005
75-25-2	Bromoform	0.2	5	0.005	0.9	5	0.005
108-94-1	Cyclohexanone	420	500	0.5	120	500	0.5
98-82-8	Isopropylbenzene	0.3	5	0.005	0.2	5	0.005
79-34-5	1,1,2,2-Tetrachloroethane	0.2	5	0.005	0.2	5	0.005
96-18-4	1,2,3-Trichloropropane	0.7	5	0.005	1.8	5	0.005
103-65-1	n-Propylbenzene	0.2	5	0.005	0.2	5	0.005
108-86-1	Bromobenzene	0.2	5	0.005	0.3	5	0.005
108-67-8	1,3,5-Trimethylbenzene	0.3	5	0.005	0.1	5	0.005
95-49-8	2-Chlorotoluene	0.2	5	0.005	0.7	5	0.005
106-43-4	4-Chlorotoluene	0.3	5	0.005	0.6	5	0.005
611-14-3	1-Ethyl-2-methylbenzene	0.3	5	0.005	0.2	5	0.005
98-06-6	tert-Butylbenzene	0.3	5	0.005	0.2	5	0.005
95-63-6	1,2,4-Trimethylbenzene	0.2	5	0.005	0.2	5	0.005
135-98-8	sec-Butylbenzene	0.3	5	0.005	0.2	5	0.005
98-82-8	p-Isopropyltoluene	0.3	5	0.005	0.2	5	0.005
541-73-1	1,3-Dichlorobenzene	0.3	5	0.005	0.4	5	0.005
106-46-7	1,4-Dichlorobenzene	0.2	5	0.005	0.4	5	0.005
104-51-8	n-Butylbenzene	0.3	5	0.005	0.3	5	0.005
95-50-1	1,2-Dichlorobenzene	0.3	5	0.005	0.3	5	0.005
96-12-8	1,2-Dibromo-3-chloropropane	1.4	10	0.010	2.1	10	0.010
87-61-6	1,2,3-Trichlorobenzene	0.5	5	0.005	0.9	5	0.005
120-82-1	1,2,4-Trichlorobenzene	0.4	5	0.005	0.9	5	0.005
87-68-3	Hexachlorobutadiene	0.8	5	0.005	0.6	5	0.005
91-20-3	Naphthalene	0.3	15	0.015	0.9	15	0.015

Attachment 2
CHARACTERISTIC IONS FOR VOLATILE COMPOUNDS

#	Compounds	Retention Time (min.)	Primary Ion	Secondary Ion(s)
1	Dichlorodifluoromethane	1.22	85	87
2	Vinyl Chloride	1.43	62	64
3	Chloromethane	1.35	50	52
4	1,3-Butadiene	1.45	39	54
5	Bromomethane	1.65	94	96
6	Chloroethane	1.73	64	66
7	Trichlorofluoromethane	1.93	101	103
8	Ethyl ether	2.17	59	45,74
9	Isopropyl Alcohol	2.54	45	43,59
10	Acrolein	2.27	56	55
11	Acetone	2.4	43	58
12	Freon-TF	2.36	151	101,152
13	1,1-Dichloroethene	2.36	96	61, 63
14	Carbon Disulfide	2.54	76	78
15	Methylene Chloride	2.77	84	49, 86
16	Acrylonitrile	2.99	53	52, 51
17	MTBE	3.02	73	57
18	Hexane	3.27	57	56, 41
19	trans-1,2-Dichloroethene	3.02	96	61, 98
20	Vinyl acetate	3.46	43	86
21	1,1-Dichloroethane	3.4	63	65, 83
22	2-Butanone	3.97	72	43, 57
23	Ethyl Acetate	4.04	45	43, 61
24	2,2-Dichloropropane	3.95	77	41,97
25	cis-1,2-Dichloroethene	3.95	96	61, 98
26	Chloroform	4.27	83	85, 47
27	Isobutyl Alcohol	4.79	43	74,41,42
28	Bromochloromethane	4.18	128	130, 49
29	1,1,1-Trichloroethane	4.44	97	61, 99
30	1-Butanol	5.5	56	41, 43
31	1,1-Dichloropropene	4.61	75	110, 77
32	Carbon Tetrachloride	4.61	117	119, 82
33	1,2-Dichloroethane	4.84	62	49, 98
34	Benzene	4.82	78	51
35	Dibromomethane	5.88	93	95, 174
36	Trichloroethene	5.51	95	97, 130, 132
37	1,2-Dichloropropane	5.75	63	112
38	2-Nitropropane	6.33	41	39, 43
39	1,4-Dioxane	5.92	88	58
40	Bromodichloromethane	6.07	83	85, 127
41	2-Chloroethylvinyl ether	6.44	63	65, 106
42	4-Methyl-2-Pentanone	6.78	43	58,85
43	cis-1,3-Dichloropropene	6.59	75	77, 39
44	Toluene	6.97	92	91
45	trans-1,3-Dichloropropene	7.26	75	77, 39
46	1,1,2-Trichloroethane	7.48	83	85, 97

Attachment 2
CHARACTERISTIC IONS FOR VOLATILE COMPOUNDS

#	Compounds	Retention Time (min.)	Primary Ion	Secondary Ion(s)
47	1,2-Dibromoethane	8.08	107	109, 188
48	2-Hexanone	7.81	43	58, 100
49	1,3-Dichloropropane	7.68	76	78
50	1,1,1,2-Tetrachloroethane	8.84	131	133, 119
51	Tetrachloroethene	7.63	164	129, 131, 166
52	Dibromochloromethane	7.95	129	127
53	Ethylbenzene	8.88	91	106
54	m&p-Xylene	9.04	106	91
55	o-Xylene	9.56	106	91
56	Styrene	9.59	104	78
57	Bromoform	9.81	173	175, 254
58	Chlorobenzene	8.72	112	77, 114
59	Isopropyl benzene	10.07	105	120
60	1,1,2,2-Tetrachloroethane	10.5	83	131, 85
61	Cyclohexanone	10.17	55	42, 69
62	1,2,3-Trichloropropane	10.90	75	77
63	n-Propyl benzene	10.64	91	120
64	Bromobenzene	10.44	156	77, 158
65	1,3,5-Trimethylbenzene	10.9	105	120
66	2-Chlorotoluene	10.73	91	126
67	4-Chlorotoluene	10.83	91	126
68	1-Ethyl-2-methylbenzene	11.17	105	120
69	tert-Butylbenzene	11.34	119	91, 134
70	1,2,4-Trimethylbenzene	11.41	105	120, 77
71	sec-Butylbenzene	11.65	105	134
72	p-Isopropyl Toluene	11.87	119	91, 134
73	1,3-Dichlorobenzene	11.77	146	111, 148
74	1,4-Dichlorobenzene	11.9	146	111, 148
75	n-Butylbenzene	12.46	91	92, 134
76	1,2-Dichlorobenzene	12.41	146	111, 148
77	1,2-Dibromo-3-chloropropane	13.54	75	155, 157
78	1,2,3-Trichlorobenzene	15.43	180	182, 145
79	1,2,4-Trichlorobenzene	14.74	180	182, 145
80	Hexachlorobutadiene	15.02	225	223, 227
81	Naphthalene	15.07	128	102
	Internal Standards:			
82	Pentafluorobenzene	4.49	168	99
83	1,4-Difluorobenzene	5.24	114	88
84	Chlorobenzene-d5	8.68	82	117, 119
85	1,4–Dichlorobenzene-d4	11.87	152	115, 150
	Surrogates:			
86	Dibromofluoromethane	4.43	113	111,192
87	1,2-Dichloroethane-d4	4.76	102	65
88	Toluene-d8	6.89	98	100
89	Bromoflurobenzene	10.27	174	95, 176

Attachment 3
SURROGATES RECOVERY LIMITS FOR VOC COMPOUNDS

Surrogate Compound	Soil % Recovery	Water% Recovery
1,2-Dichloroethane-d_4	84 - 129	80 - 120
Toluene-d_8	85 - 110	88 - 110
4-Bromofluorobenzene	63 - 110	86 - 115
Dibromofluoromethane	83 - 119	86 - 118
$NaHSO_4$ Preserved		
1,2-Dichloroethane-d_4	78 – 160	
Toluene-d_8	62 - 122	
4-Bromofluorobenzene	44 - 114	
Dibromofluoromethane	74 - 150	

Attachment 4
MS/MSD RECOVERY LIMITS FOR VOC COMPOUNDS

MATRIX SPIKE –WATER			
Compound	Amount added µg/L	RPD Limit	% Recovery
1,1-Dichloroethene	50	15	64 - 140
Methylene Chloride	50	11	71 - 134
trans-1,2-Dichloroethene	50	12	76 - 130
1,1-Dichloroethane	50	10	71 - 123
cis-1,2-Dichloroethene	50	8	71 - 133
Chloroform	50	9	74 - 127
1,1,1-Trichloroethane	50	9	87 - 118
Carbon tetrachloride	50	9	78 - 121
Benzene	50	8	78 - 123
Trichloroethene	50	11	74 - 124
cis-1,3-Dichloropropene	50	10	77 - 129
Toluene	50	10	80 - 123
trans-1,3-Dichloropropene	50	9	73 - 149
Tetrachloroethene	50	8	80 - 120
Chlorobenzene	50	8	88 - 115
Ethylbenzene	50	10	83 - 119
MATRIX SPIKE –SOIL			
Compound	Amount added µg/Kg	RPD Limit	% Recovery
1,1-Dichloroethene	50	54	61 - 137
Methylene Chloride	50	53	63 - 131
trans-1,2-Dichloroethene	50	53	61 - 134
1,1-Dichloroethane	50	54	60 - 123
cis-1,2-Dichloroethene	50	55	55 - 129
Chloroform	50	56	56 - 129
1,1,1-Trichloroethane	50	51	62 - 137
Carbon tetrachloride	50	55	59 - 131
Benzene	50	53	56. - 129
Trichloroethene	50	58	31 - 135
cis-1,3-Dichloropropene	50	58	45 - 120
Toluene	50	58	39 - 131
trans-1,3-Dichloropropene	50	65	45 - 133
Tetrachloroethene	50	62	39 - 132
Chlorobenzene	50	64	35 - 121
Ethylbenzene	50	59	41 - 130

Attachment 5
Volatile Internal Standards with Corresponding Compounds Assigned for Quantitation

Pentafluorobenzene (I)	1,4-Difluorobenzene (I)	Chlorobenzene-d5 (I)	1,4-Dichlorobenzene-d4 (I)
Dichlorodifluoromethane	1,2-Dichloroethane-d4 (S)	trans-1,3-Dichloropropene	1,2,3-Trichloropropane
Chloromethane (SPCC)	Isobutyl Alcohol	2-Hexanone	n-Propylbenzene
Vinyl Chloride (CCC)	Carbon Tetrachloride	1,1,2-Trichloroethane	Bromobenzene
1,3-Butadiene	1,2-Dichloroethane	1,3-Dichloropropane	1,3,5-Trimethylbenzene
Bromomethane	1,1,1-Trichloroethane	Tetrachloroethene	2-Chlorotoluene
Chloroethane	1,1-Dichloropropene	Dibromochloromethane	4-Chlorotoluene
Trichlorofluoromethane	1-Butanol	1,2-Dibromoethane	1-Ethyl-2-methylbenzene
Ethyl ether	Benzene	Chlorobenzene (SPCC)	tert-Butylbenzene
Isopropyl Alcohol	Trichloroethene	Ethylbenzene (CCC)	1,2,4-Trimethylbenzene
Acrolein	1,2-Dichloropropane (CCC)	1,1,1,2-Tetrachloroethane	sec-Butylbenzene
Acetone	1,4-Dioxane	m&p-Xylene	p-Isopropyl Toluene
Freon-TF	2-Nitropropane	o-Xylene	1,3-Dichlorobenzene
1,1-Dichloroethene (CCC)	Bromodichloromethane	Styrene	1,4-Dichlorobenzene
Methylene Chloride	Dibromomethane	Isopropyl benzene	n-Butylbenzene
Carbon Disulfide	2-Chloroethylvinyl ether	Cyclohexanone	1,2-Dichlorobenzene
Acrylonitrile	4-Methyl-2-Pentanone	Bromoform (SPCC)	1,2-Dibromo-3-hloropropane
MTBE	cis-1,3-Dichloropropene	1,1,2,2-Tetrachloroethane (SPCC)	1,2,4-Trichlorobenzene
Hexane	Toluene-d8 (S)	Bromofluorobenzene (S)	Hexachlorobutadiene
trans-1,2-Dichloroethene	Toluene (CCC)		Naphthalene
Vinyl acetate			1,2,3-Trichlorobenzene
1,1-Dichloroethane (SPCC)			
2-Butanone			
Ethyl Acetate			
2,2-Dichloropropane			
cis-1,2-Dichloroethene			
Chloroform (CCC)			
Bromochloromethane			
Dibromofluoromethane (S)			

(I) = Internal Standard
(S) = Surrogate
(CCC) = Calibration Check Compounds
(SPCC) = System Performance Check Compounds

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VOC SOIL PREP LOG

Date/Time	Analyst	Work Order	Sample Number	Sampling Type	Weight (gm)					
					Samp	Batch #	RA	Batch #	MeOH *	Batch #

Comments: _____

* MeOH 5 mls final volume (unless otherwise indicated) MeOH Reagent ID: _____

Reviewed By: _____ Date: _____

STA Analysis Corporation:

STANDARD OPERATING PROCEDURE 4020

SEMIVOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS) (EPA Method 8270C)

Revision 03
Effective Date: October 31, 2003

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1.0 IDENTIFICATION OF TEST METHOD

SOP Title: SemiVolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS) is abbreviated as SVOC in laboratory records.

2.0 APPLICABLE MATRICES

Methylene chloride and organic solvent extracts from soil, sediment, ground and surface water, and mobility extracts are analyzed using this method.

3.0 DETECTION LIMITS

The lab follows the procedure found in 40CFR Part 136B to determine the MDL for each matrix type on an annual basis. See the STAT Analysis SOP 1210 for the MDL procedure, frequency and acceptance criteria. The MDLs measured by the lab and all supporting documentation are in the laboratory QA files for review.

The laboratory determined MDL must always be less than the reporting limit (RL), which is determined by the lowest calibration standard. The RLs will usually range from three to ten times the laboratory measured MDLs but this relationship may vary dependent on dilution of sample aliquots, matrix interferences, moisture adjustments (in solid samples), or method-specified requirements. Attachment 1 contains the current MDLs and reporting limits (RLs) for this SOP.

4.0 SCOPE AND APPLICATION

4.1 This standard operating procedure describes in detail the precise methods used at STAT Analysis Corporation for the analysis of environmental samples for SemiVolatile Organic Compounds (SVOCs) by GC-MS. This SOP as written is to be applied when SW-846 Method 8270C is requested. This SOP is used to determine the concentration of (SVOC's) in extracts prepared from all types of solid waste matrices, soils, and ground water.

4.2 SOP 4020 can be used to quantitate SVOCs that are soluble in methylene chloride and other organic solvents and are capable of being eluted without derivatization as sharp peaks from a gas chromatographic fused-silica capillary column coated with a slightly polar silicone. See Attachment 2 for a list of compounds and their characteristic ions that have been evaluated on the specified GC/MS system.

4.3 The reporting limits (RLs) for this SOP are shown in Attachment 1 for soils and water. RLs will be proportionately higher for sample extracts and samples that require dilution or reduced sample size to avoid saturation of the detector.

4.4 This method is restricted to use by or under the supervision of analysts experienced in the use of a Gas Chromatograph/Mass Spectrometer (GC/MS) and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

5.0 SUMMARY OF TEST METHOD

5.1 Prior to using this method, the samples must be prepared for the GC/MS using the appropriate sample preparation and cleanup SOPs (Section 14.1). Samples are extracted at neutral pH with methylene chloride. This method describes chromatographic conditions that will allow for the separation of the compounds in the extract and for their qualitative and quantitative analysis by gas chromatography/mass spectrometry. Identification of target analytes is accomplished by comparing component retention times to those of authentic standards and by comparing their mass spectra with the electron impact (or electron impact-like) spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using a five-point calibration curve.

5.2 **Method Modifications from Reference** – This SOP is based on EPA Method 8270C except that no polychlorinated biphenyls (PCBs), pesticides, organophosphate esters or quinolines are reported. PCBs and Pesticides are reported using STAT Analysis SOP 4050. Organophosphate esters and quinolines are not reported by the lab. The Mass Spectrometer Tuning criteria used in this SOP is referenced from the CLP Statement of Work (SOW) for Organic Analyses Revision OLM04.2 May 1999. This is an option in Method SW-846 8270C.

6.0 DEFINITIONS

The STAT Analysis Quality Manual Section 19.0 contains all the definitions of standard terms used in SOPs.

7.0 INTERFERENCES

7.1 Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation and/or cleanup of the samples and take corrective action to eliminate the problem.

7.2 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed out between samples with solvent. Whenever an unusually concentrated sample is encountered, the sample after it must be reanalyzed to check for cross contamination.

8.0 SAFETY

Methylene chloride is a suspected carcinogen as are numerous compounds analyzed by this method. Proper personal protective equipment including safety glasses, nitrile gloves and a lab coat are required during different parts of this method. Other safety precautions must be conducted in accordance with the Chemical Hygiene Plan (STAT QA SOP 003). Other actions can also be applied if deemed necessary. A reference file of Material Safety Data Sheets (MSDS) is available to all personnel involved in this method.

9.0 EQUIPMENT AND SUPPLIES

The following apparatus is recommended for performing this procedure. Equivalent items can be used, if with their use, the analytical and QA/QC requirements in this SOP can be met. All catalog numbers in this SOP are current as of the effective date and thereafter subject to change.

9.1 Gas Chromatograph/Mass Spectrometer system (GC/MS)

9.1.1 Gas chromatograph(GC) – Agilent 6890 with electronic flow control gas chromatograph with the column directly coupled to the source. Equipped with an Agilent Autosampler Model 7683

9.1.2 Column - 30 m x 0.25 mm ID (or 0.33mm ID) 0.5µm film thickness silicone-coated fused-silica capillary column (J&W Scientific HP-5MS).

9.1.3 Mass spectrometer(MS) - Agilent 5973N.

9.1.4 Data system - An Agilent Kayak computer system using 3365 Chemstation Version C.00.01 to interpret data is attached to the GC.

9.1.5 NIST Library of Reference Spectra, Edition Number NIST98

9.2 Micro syringes - 10 µL, 25 µL, 100 µL, 250 µL, 500 µL and 1,000 µL.

9.3 Volumetric flasks, Class A - 10 mL, 25 mL, 50 mL with ground glass stoppers.

9.4 Glass vials - 2-mL, for GC auto sampler with Teflon-lined screw caps or crimp tops.

9.5 Amber glass vials - 10 mL with Teflon-lined screw caps

10.0 REAGENTS AND STANDARDS

The following reagents and standards are required to perform this procedure. When instructions are given on how to prepare a specific volume of a reagent or standard, larger or smaller volumes can be prepared as needed so long as the final concentrations remain the same. Any other deviations from the reagents or

standards listed in this SOP could be detrimental to the quality of the data produced. Such deviations would have to be approved and documented (see SOP QA 230 Corrective Action). Equivalent items can be used, if with their use, the analytical and QA/QC requirements in this SOP can be met.

Instructions for labeling and record keeping of reagents and standards are contained in SOP 1010 Analytical Standards and Reagents Receipt and Preparation.

10.1 Analytical reagent grade chemicals shall be used in all tests. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.

10.2 Organic-free reagent water - All references to water in this SOP refers to Type II reagent water (in-house system).

10.3 Stock Standard solutions - Standard solutions can be prepared from pure standard materials or purchased as certified solutions (e.g. SV standards). The routine laboratory practice is to purchase these standards from approved vendors. The standards used are: 8270 MegaMix (Restek Catalog # 31686), 605-Benzidines Standard (Restek Catalog # 31030), Custom 8270 Addition (Restek Catalog # 555680), Base/Neutral Surrogate Spike Mix (Restek Catalog # 31072) and Acids Surrogate Spike Mix (Restek Catalog # 31003). Stock standard solutions and QC solutions are stored at < -10°C and must be replaced after six months, or sooner if comparison with quality control check samples indicates a problem. Different storage conditions and expiration dates of other solutions are noted as warranted.

10.3.1 Secondary Stock Standard Solution – This solution is made using the individual Stock Standard solutions. Using microliter syringes, the following amounts of each Stock Standard solution is injected into a 10 mL volumetric flask. The solution is brought to volume with methylene chloride. The final concentration of each component is listed in Table 1. Note: this Secondary Stock Standard solution is also used as the high-level calibration standard. It is also the source solution to prepare the calibration standards in Section 10.4. This standard is stored at < -10°C in a 10 mL amber screw cap vial equipped with a Teflon lined cap. It is freshly prepared every six months, or sooner if check standards indicate a problem.

Table 1 Secondary Stock Standard Solution

Stock Solution	Conc. Stock (µg/ml)	Vol. Stock (µL)	Final Conc. (µg/ml)
8270 Mega-mix	500-1000	1600	160
605 Benzidines	2000	800	160
Custom 8270 Addition	2000	800	160
B/N Surr.	5000	320	160
Acid Surr.	1500	1067	160

10.4 Calibration standards - A minimum of five calibration standards are prepared. The low standard is the RL and above the MDL. The others define the working range of the GC/MS system. Calibration standards in current use: 5, 10, 20, 50, 80, 120 and 160 µg/ml. (Table 2). Using microliter syringes, the following amount of the Secondary Stock solution is injected into a 1 ml syringe. The solution is brought to volume with Methylene chloride. The final concentration of each component is listed in Table 2. Each solution is transferred to an autosampler vial. Each 1 mL aliquot of calibration standard must be spiked with 10 µL of the internal standard solution (4000 µg/ml) prior to analysis. Storage is as indicated in 10.1.4. The continuing calibration verification standards (CCV) are prepared weekly and stored at 4°C. Levels 2, 3 and 4 (20, 50, 80 µg/mL) are used for the CCVs.

Table 2 Calibration Standards

Level	Volume (µL) Secondary Stock	Volume (µL) $MeCl_2$	Final Concentration (µg/ml)
1	31.25	968.75	5
2	62.5	937.5	10
3	125	875	20
4	312.5	687.5	50
5	500	500	80
6	750	250	120
7	1000	0	160

10.5 Surrogate standards - The surrogate standards phenol-d_6, 2-fluorophenol, 2,4,6-tribromophenol, nitrobenzene-d_5, 2-fluorobiphenyl and p-terphenyl-d_{14} (1,2-dichlorobenzene-d_4, 2-chlorophenol-d_4 are optional surrogate compounds). Surrogate stock solutions are purchased from Supelco (Cat. No. 4-7261 and 4-7262, store at room temp until dilution is prepared). The spike solution is prepared by injecting 1000 µL of the stock standard solution, concentration of 5000 µg/mL for Base/Neutrals and 10000 µg/mL for Acids, into a 100mL volumetric flask. The flask is diluted to the mark with methanol for a final concentration of 50 µg/mL for Base/Neutral surrogates and 100 µg/mL for Acid surrogates. All samples, blanks, LCSs, and MS/MSDs are spiked with 1.0 mL of the surrogate spike solution prior to extraction. This standard is stored at < -10°C in an amber glass vial with a Teflon lined screw cap.

10.6 Internal standard solutions - The internal standards used are 1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}. The SV internal standards containing the recommended compounds at 4000 µg/mL are purchased from Supelco (cat. no. 4-7906). Just prior to analysis 10 µL of the solution (4000 µg/ml) is injected into each sample vial. Store at room temperature per manufacturer's instructions when not being used. The internal standards permit most of the compounds of interest in a chromatogram to have retention times of 0.80-1.20 relative to one of the internal standards. Use the base peak ion from the specific internal standard as the primary ion for quantitation (see Attachment 2, i.e. for 1,4-dichlorobenzene-d_4, use 152 m/z for quantitation). If interferences are noted, use the next most intense ion as the quantitation ion.

10.7 GC/MS tuning standard - A methylene chloride solution containing 50 ng/µL each of decafluorotriphenylphosphine (DFTPP), 4,4'-DDT, pentachlorophenol, and benzidine is used to tune the mass spectrometer, and to verify injection port inertness and GC column performance. The SV tuning standard is purchased from Supelco (Cat. No. 4-7387). Store at < -10°C when not being used. Inject 1 µL of this standard at the start of every 12 hours of operation.

10.8 Laboratory Control Sample/Matrix Spike standards - The LCS/matrix spike compounds are phenol, 2-chlorophenol, 1,4-dichlorobenzene, N-nitrosodi-n-propylamine, 1,2,4-trichlorobenzene, 4-chloro-3-methylphenol, acenaphthene, 4nitrophenol, 2,4-dinitrotoluene, pentachlorophenol and pyrene. Samples will be spiked with acid compounds at 100 mg/sample, 3330 mg/kg for soil and 100 mg/L for water and base/neutral compounds at 50 mg/sample, 1670 mg/kg for soil and 50 mg/L for water (see SOP 3500 for LCS/Matrix Spike Solution preparation). This standard is stored at < -10°C in an amber glass vial with a Teflon lined screw cap.

10.9 Initial Calibration Verification Standard – A standard prepared from a different source at the midpoint of the calibration to verify the initial calibration. This solution concentration is 50 µg/mL The solution is made using the individual ICV Stock Standard solutions purchased from Supelco. Using microliter syringes, the following amounts of each Stock Standard solution is injected into a 10 mL volumetric flask. The solution is brought to volume with methylene chloride. The final concentration of each component is listed in Table 1a. This standard is stored at < -10°C.

Table 1a ICV Secondary Stock Standard Solution

Stock Solution	Conc. Stock (µg/ml)	Vol. Stock (µL)	Final Conc. (µg/ml)
TCL Base/Neutrals Mix 1	2000	250	50
TCL Base/Neutrals Mix 2	2000	250	50
TCL PNA Mix	2000	250	50
TCL Phenols Mix	2000	250	50
TCL Benzidine Mix	2000	250	50
TCL Hazardous Mix 1	2000	250	50
TCL Hazardous Mix 2	2000	250	50
3-Methyl Phenol Standard	5000	100	50
1-Chloronaphthalene Standard	2000	250	50
B/N Surrogate	5000	100	50
Acids Surrogate	10000	50	50

10.8 Acetone, hexane, methylene chloride, isooctane, carbon disulfide, toluene and other appropriate solvents, pesticide quality or equivalent.

10.9 Helium – UHP grade

11.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

11.1 Containers used to collect samples for the determination of semivolatile organic compounds are glass: 1 Liter bottles for water samples and various size jars for soil samples. They are equipped with screw caps with Teflon liners. Water samples containing residual chlorine should be field treated to remove the chlorine prior to collection. Plastic containers or lids may NOT be used for the storage of samples due to the possibility of sample contamination from the phthalate esters and other hydrocarbons within the plastic.

11.2 Samples must be stored under refrigeration at between 0.1 and 6.0°C. Extraction must be within 7 days from sampling date for water and 14 days for solids. Sample extracts are stored in the dark at between 0.1 and 6.0°C and must be analyzed within 40 days of extraction.

11.3 No chemical preservation is required for this method.

11.4 All samples are stored away from all standards, reagents, food, and other potentially contaminating sources in order to prevent cross contamination.

12.0 QUALITY CONTROL

The following details the QC requirements that apply to this analysis. Each Quality Control Indicator (QCI) provides information pertaining to either method or individual sample performance. Our goal is to produce defensible data of known and documented quality. The results of these Quality Control Indicator (QCI) samples are used to assess the acceptability of data.

12.1 Blanks

Method Blank analysis is performed to determine if any contamination is present in the analytical process and is used to evaluate acceptance of the batch of samples. A method blank shall be prepared once per preparation batch of 20 or less samples per matrix type. If more than 20 samples are prepared a second blank shall be prepared after the twentieth sample. The method blank shall be processed through all preparatory steps used for the samples, including cleanup procedures. The blank shall be analyzed using the same instrument and conditions as the samples.

The Solvent Blank, clean solvent injected into the GC/MS, is used to monitor the GC/MS system for potential cross-contamination from one sample to another or for residual contamination in the system.

12.2 Calibration Verification

An Initial Calibration Verification (ICV) standard containing all of the target analytes reported in this method (refer to section 10.9) shall be analyzed immediately after the completion of the initial calibration. The ICV shall be purchased from a second source to verify analyte concentrations.

12.3 Laboratory Control Sample (LCS)

The LCS is used to evaluate the performance of the total analytical system, including all preparation and analysis steps. The LCS shall be prepared once per preparation batch of 20 or less samples per matrix type. If more than 20 samples are prepared a second LCS shall be prepared after the twentieth sample.

The LCS shall be processed through all preparatory steps used for the samples, including cleanup procedures. The LCS shall be analyzed using the same instrument and conditions as the samples. Refer to section 10.8 for LCS analytes and concentrations.

12.4 Surrogates

The surrogates used for this method are added to all samples, standards, and blanks. Refer to section 10.5 for preparation and concentration instructions.

12.5 Duplicates

Duplicates of field samples or of the LCS must be prepared in compliance with the method requirements and client directives. Duplicate LCS's are prepared for sample wipes. It would be impractical to prepare a matrix spike and matrix spike duplicate. Reproducibility performance would be the same as for a matrix spike/matrix spike duplicate.

12.6 Matrix Spike and Matrix Spike Duplicate (MS/MSD)

MS/MSDs indicate the effect of the sample matrix on the precision and accuracy of the results generated using the selected method. This information does not determine the validity of the entire batch. MS/MSDs must be analyzed at a minimum of 1 per 20 samples per matrix per preparation procedure, or one per preparation batch, or as specified by the required test method. For cases where the sample cannot be divided (e.g., wipes, air samples, not enough sample provided by customer) and thus a MS/MSD pair is cannot be prepared in the preparation batch, an LCS/LCSD pair is prepared and analyzed to measure precision. Samples chosen for matrix spiking are rotated among different clients and/or different client projects. This is accomplished through communication between the Department Manager and the analyst. In addition, designated samples, as indicated by client request or contract requirement, are matrix spiked. The MS/MSD pair shall be processed through all preparatory steps used for the samples. They shall be analyzed using the same instrument and conditions as the samples. Refer to section 10.8 for MS analytes and concentrations. Some clients may require different spiking levels and/or target analytes, these specific needs are documented on the request for analysis forms.

12.7 Internal Standards

The internal standards used for this method are added to all samples, standards, and blanks. Refer to section 10.6 for preparation and concentration instructions.

13.0 CALIBRATION AND STANDARDIZATION

13.1 Mass Spectrometer Tuning

Each GC/MS system must be software-tuned to meet the criteria in Table 3 for a 50 ng injection of DFTPP. Analyses must not begin until all these criteria are met. Tuning criteria used in this SOP is referenced from the CLP Statement of Work (SOW) for Organic Analyses Revision OLM04.2 May 1999.

Using the ChemStation software to tune the GC/MS perform the following steps:

Set oven temperature to 250 °C (the elution temperature for DFTPP)

On the Instrument Control Panel click on View/Manual Tune…
On the Manual Tune Panel click on File/Load Tune Values/ and select DFTPP.u
On the Manual Tune Panel click on Tune/DFTPP Tune
The software automatically adjusts the tune parameters using PFTBA to meet the criteria in Table 3. After the software has completed the tune click on File/Save Tune Values/ and select DFTPP.u and save the new parameters.
Click on View/Instrument Control to start analyzing standards and samples.

Table 3 Acceptance Criteria for DFTPP

Target Mass	Relative to Mass	Lower Limit%	Upper Limit%
51	198	30	80
68	69	0	2
69	198	0	100
70	69	0	2
127	198	25	75
197	198	0	1
198	198	100	100
199	198	5	9
275	198	10	30
365	198	1	100
441	443	0.01	100
442	198	40	110
443	442	15	24

Using the autosampler, inject 1 µL of DFTPP tuning standard solution on to the column. Analyze the solution using the DFTPP method which accelerates the elution of the compounds of interest.

Background subtraction must be straightforward and designed only to eliminate column bleed or instrument background ions. Obtain a background-corrected mass spectrum of DFTPP and confirm that all the key m/z criteria in Table 3 are achieved. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan no more than 20 scans prior to the elution of DFTPP. Do not background subtract part of the DFTPP peak. Option: a single scan with background subtraction can also be used to evaluate the DFTPP spectrum. Note: the tuning file used to obtain and evaluate the DFTPP criteria must also be used to obtain and evaluate the sample data. If the criteria are not passed, the analyst must perform needed maintenance, retune the mass spectrometer and repeat the test until all criteria are achieved.

The GC/MS tuning standard must also be used to assess GC column performance and injection port inertness. Degradation of DDT to DDE and DDD must not exceed 20%. The following formula is used to calculate the percent breakdown:

$$\% \text{ breakdown of DDT} = \frac{\text{sum of degradation peak areas (DDE + DDD)} * 100\ \%}{\text{sum of all peak areas (DDT + DDE + DDD)}}$$

Benzidine and pentachlorophenol must be present at their normal responses, and no peak tailing must be visible. If degradation is excessive and/or poor chromatography is noted, the injection port may require cleaning. It may also be necessary to cut off an additional 10 to 20 cm of the capillary column.

To generate a custom report that calculates the % breakdown of DDT perform the following steps. Within the Data Review software click on Quant/QEdit Quant Result. Verify that all of the target peaks are correctly identified. Exit QEdit and click on CustRpt/Print Report. To review the report before printing click on CustRpt/Custom Reports.../ Select Edit Template DFTPP.CRT/OK. The report can be printed by clicking on the printer button or clicking on File/Print/OK.

Note: the 12 hour tune period begins at the start of the DFTPP analysis which is recorded as the data acquisition start time on the data file. The last valid calibration standard in the ICAL must have a data acquisition start time less than 12 hours from the start of the tune period.

13.2 **Initial Calibration (ICAL)**

13.2.1 Analyze 1 µL of each calibration standard and tabulate the area of the analyte against concentration for each compound. Calculate response factors (RFs) for each compound in each calibration standard as follows:

13.2.2

$$RF = \frac{A_x * C_{is}}{A_{is} * C_x}$$

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} = Concentration of the specific internal standard (40 ng/µL for this method)
C_x = Concentration of the compound being measured (ng/µL = µg/mL = mg/L).

13.2.3 Calculate the average response factor ($\overline{RF}$) for each compound as follows:

$$\overline{RF} = (S\ RF_1 \text{ to } RF_n)/n$$

where: RF = RF for each of the calibration levels (i.e., 5)
n = Number of RF values (i.e., 5)

13.2.3 A system performance check must be performed to ensure that minimum average RFs are met before the calibration curve is used. For semivolatiles the System Performance Check Compounds (SPCCs) are: N-Nitroso-di-n-propylamine, Hexachlorocyclopentadiene, 2,4-

Dinitrophenol, and 4-Nitrophenol. The minimum acceptable average RF for these compounds is 0.050. If it is determined that one calibration level has an unacceptable response, that level may be reanalyzed once. If the minimum average RF is still not met, corrective action must be taken and the calibration sequence repeated. If any major changes are made to the system (e.g. column changed or detector cleaned), recalibration of the system must take place.

13.2.4 Calibration Check Compound (CCC) responses are monitored to check the integrity of the system. The CCCs are as follows:

Base/Neutral Fraction	Acid Fraction
1,4-Dichlorobenzene	Phenol
Hexachlorobutadiene	2-Nitrophenol
Acenaphthene	2,4-Dichlorophenol
N-Nitrosodiphenylamine	4-Chloro-3-methylphenol
Fluoranthene	2,4,6-Trichlorophenol
Di-n-octyl phthalate	Pentachlorophenol
Benzo(a)pyrene	

Using the RFs from the initial calibration, calculate the percent relative standard deviation (%RSD) for the Calibration Check Compounds (CCC).

To calculate %RSD: $\%RSD = 100\% \times SD/\overline{RF}$

where:

%RSD = % Relative Standard Deviation

$\overline{RF}$ = average of initial RFs for a compound
SD = standard deviation (n-1) of average RFs for a compound

To calculate Standard Deviation (n-1 degrees of freedom)

$$SD = \sqrt{\frac{\sum_{i=1}^{N} (RF_i - \overline{RF})^2}{n-1}}$$

where: RF_i = RF for each of the 5 calibration levels
n = Number of RF values (i.e., 5)

13.2.5 If the %RSD of any CCC compound is > 30%, then the chromatographic system is too reactive for analysis to begin. Clean or replace the injector and/or capillary column, then repeat the calibration procedure beginning with section 13.2.1.

13.2.6 Linearity - If the %RSD of any compound is 15% or less, then the relative response factor is assumed to be constant over the calibration range, and the average relative response factor is used for quantitation. If the %RSD is greater than 15%, first order linear regression is used. The calibration curve must meet the requirements for curve fitting listed in SW-846 8000B and the correlation coefficient is = 0.99. The equation is not forced through the origin.

13.2.7 Retention Times: The Relative Retention Times (RRT) of each compound in each calibration standard should be within ± 0.06 RT units.

13.2.8 Before sample analysis can begin, a Initial Calibration Verification (ICV) (see Sec. 10.9) must be performed. The ICV results must be within the acceptance criteria as established for the CCV compounds (Section 13.3). Other components should be recovered within 70 to 130% of the true value. Note: Benzidine is one exception: Recovery of > 50% is acceptable for this compound.

NOTE:

1. All calibration curves must have a unique identifier. It is recommended that the calibration date be incorporated into the identifier for easy reference.
2. All initial calibration standards must be analyzed within the 12 hour DFTPP tune window.
3. Calibration must be completed (all standard levels analyzed) within 24 hours or the entire calibration sequence must be repeated. If the calibration was not completed in the first tune window it may continue into a second tune window. Standard calibration levels from either tune window can be used. An exception follows: If DFTPP criteria does not pass criteria for the second tune window and major maintenance was done to the instrument or the Mass Spectrometer tuning parameters were adjusted in order to obtain an acceptable tune for DFTPP, the entire calibration sequence must be repeated.
4. All initial calibration standards must be analyzed as a group. No field sample analyses are allowed during the calibration sequence.
5. Do not add calibration standards and update the curve after the original calibration date.
6. Multiple analyses of the same calibration level are not allowed to be included in the calibration curve.
7. Compound responses cannot be selected from different analyses of the same calibration level (i.e. all compound responses for level 1 must come from the same data file).
8. If more than five calibration levels are analyzed, it is permissible to either drop the low compound concentration (poor response) or the high compound concentration (detector saturation). It is not allowed to drop a point in the middle of the curve.
9. If more than five calibration levels are analyzed, it is permissible to drop an entire level if the analyst can document a specific reason or reasons why that level should be excluded. Mechanical failure, significant loss of all analyte responses possibly due to poor technique in standard preparation, or software malfunction during data acquisition (system did not acquire all compound data) are plausible reasons. The reason must be justified and documented. The supervisor should review this situation and approve the analyst's decision.
10. The need to analyze more than two analyses of the same calibration level indicates a potential problem with the secondary stock solution. Prepare a fresh secondary stock solution and

repeat all seven calibration levels. It is recommended that all calibration standard levels come from the same secondary stock solution.

11. Manual integration must only be used if the software fails to properly integrate the peak. If manual integration is used for a particular compound, all levels of that compound do not have to be manually integrated, but all levels must be integrated in a similar manner. Example: the computer generated integration of a compound in the low level standard is not technically sound. A manual integration of the compound is performed (due to baseline noise, etc) in order to achieve a technically sound integration. Other levels of the compound are integrated correctly by the computer. The manual integration of the low level must match, as best as possible, the computer generated integrations for all other levels.
12. If any compound in the mid-point level is manually integrated, the integration of this compound must be reviewed for every continuing calibration standard and QC check solution (i.e. LCS, and Matrix Spike) to ensure that the integration is the same as the manual integration performed in the initial calibration (ICAL) mid-point. A consistent manner of integration must be achieved.
13. All manual integrations must be reviewed and approved at the supervisory level.

13.3 Continuing Calibration Verification (CCV)

13.3.1 The mass spectrometer must pass tune criteria (see Section 13.1) every 12 hours during analysis of samples.

13.3.2 A continuing calibration verification (CCV) sample is analyzed every 12 hours during analysis of samples. Different standards are analyzed for the CCV such that a wider range of the calibration curve is verified. For example: on successive days analyze the 20 µg/mL, then the 50 µg/mL and on the third day, the 80 µg/mL standard solution. Compare the response factors, of the SPCC's and the CCC's, and the internal standards from the CCV with the following criteria.

13.3.3 The SPCC compounds must have an RF = 0.05.

13.3.4 Control limits for the CCC compounds are ± 20% difference from the ICAL Response Factor (RF) if the average RF is used for quantitation, or ± 20% drift from the true concentration of the CCV compound if linear regression is used.

13.3.5 The areas of the internal standards in the CCV must be between −50% and +100% of the respective areas of the internal standards in the ICAL mid-point calibration standard.

13.3.6 The retention times of the internal standards in the CCV must be within ± 30 seconds of the respective retention times of the internal standards in the ICAL mid-point calibration standard.

13.3.7 If the CCV results obtained are outside the acceptance criteria, corrective actions must be performed. If routine corrective actions fail to produce an acceptable second consecutive (immediate) CCV, then either the lab has to demonstrate performance after corrective action with two consecutive successful CCVs, or a new ICAL must be performed. If the instrument has not

demonstrated acceptable performance, sample analyses cannot continue until a new ICAL is established and verified with an ICV. However, sample data associated with an unacceptable CCV may be reported as qualified data under the following special conditions:

13.3.7.1 When the acceptance criteria for CCV are exceeded high, i.e., high bias, and there are associated samples that are non-detects, then those non-detects may be reported. Otherwise the samples affected by the unacceptable calibration verification must be reanalyzed after a new ICAL has been established, evaluated and accepted.

13.3.7.2 When the acceptance criteria for the CCV are exceeded low, i.e., low bias, those sample results may be reported if they exceed a maximum regulatory limit/decision level. Otherwise the samples affected by the unacceptable verification must be reanalyzed after a new ICAL is established and verified with an ICV.

13.3.7.3 When the acceptance criteria for the CCV are exceeded and it is not possible to reanalyze the sample due to limited sample quantity AND a new sample cannot be obtained by the laboratory, the data may be reported with the appropriate data qualifiers if the client has been contacted and agrees, in writing, to accept the qualified data.

13.4 Records: Initial and Continuing Calibration Records will contain, at a minimum, the following:

1) Calibration date
2) Test method
3) Instrument
4) Analysis date
5) Each analyte name
6) Analyst's initials or signature
7) Standard Concentration (appropriate units) and number of standards
8) Response (appropriate units)
9) Calibration curve or response factor
10) Evaluation of and Statistics for ICAL curve fit in order to judge calibration curve acceptance
11) Evaluation of and Acceptance Limits for ICV analysis in order to judge calibration curve acceptance
12) Evaluation of and Acceptance Limits for CCV analysis in order to judge continuing calibration acceptance

13.5 Thermometers - The thermometers in the sample refrigerators and the standards freezer must be checked daily. They must meet performance criteria.

14. PROCEDURE

14.1 Sample Preparation

14.1.1 Water, soil, sediment and waste samples must be prepared by SOP 3500 Extractions of Samples for Semi-Volatile Organic Analyses (EPA Methods 3510C, 3520C, 3550B, 3580A) prior to GC/MS analysis.

14.1.2 Extract Cleanup: Extracts may be cleaned up by any of the following methods prior to GC/MS analysis.

Compounds	SOPs
Semivolatile hydrocarbons	3330 Silicia Gel Clean-up for Semivolatile Organic Analyses
PCB Pesticides	3060 Florisil Clean-up for PCB's and Pesticides

14.1.3 Direct Injection: In very limited applications direct injection of the sample into the GC/MS system with a 10 µL syringe may be appropriate (see SOP 3500 for preparation). The reporting limit is very high (approximately 100 to 1000 mg/L); therefore, it is only applicable where concentrations in excess of 100 mg/L are expected.

14.1.4 Extract Preparation: Sample extracts and the Internal Standard solution should be at ambient temperature prior to use. Using a 10 µL microliter syringe, inject 10 µL of the Internal Standard solution into the 1 mL sample extract just prior to the start of the analytical batch. Ensure that there is no precipitation in the internal standard mixture. If there is precipitation then gently warm the standard until all is dissolved.

14.2 GC/MS Analysis

14.2.1 Instrument Conditions: The recommended GC/MS operating conditions:

EMV	1600 to 2500 (nominal)
Mass range:	35 to 500 amu (see Attachment 2 for ions monitored)
Scan time:	3.15 scans/sec
Initial temperature:	40°C hold for 1 minutes
Ramp 1 temperature program	15.0 °C/min
Final temperature 1:	100 °C hold for 0.0 minutes
Ramp 2 temperature program	15 °C/min
Final temperature 2:	240 °C hold for 0.0 minutes
Ramp 3 temperature program	10 °C/min
Final temperature 3:	310°C hold for 9.0 minutes
Injector temperature:	250°C
Source temperature:	310 °C
Sample volume:	1 µL
Carrier gas:	Helium at 44 cm/sec
Split flow:	Splitless
Flow Ramp	
Initial Flow	1.2 mL/min hold for 0.0 minutes
Ramp 1 Fow program	99 ml/min^2

Final Flow 1:	2.0 mL/min hold for 3.5 minutes
Ramp 2 Flow program	10 ml/min^2
Final Flow 2:	1.2 ml/min hold for 0.0 minutes

14.2.2 Access the computer and create a batch sequence file. Refer to section 14.3 for instructions.

14.2.3 Using the autosampler, inject 1 µL of the Tuning Standard (DFTPP) and evaluate using tune acceptance criteria. See Section 13.1

14.2.4 Inject 1 µL of the Continuing Calibration Verification Standard (CCV) and evaluate using CCV acceptance criteria. See Section 13.3.

14.2.5 If all criteria are met, continue with sample analysis, injecting 1 µL of each extract, as outlined below.

14.2.6 If the response for any quantitation ion exceeds the initial calibration curve range of the GC/MS system, extract dilution is an option. If extract dilution is required, additional internal standard must be added to the diluted extract to maintain the required 40 ng/µL of each internal standard in the extracted volume. Then the diluted extract is analyzed.

DILUTION PROCEDURE

1. Clean a 1ml syringe equipped with a luer lock needle with rinse and clean solvent. (dichloromethane or hexane) Fill syringe with clean solvent such that there is sufficient volume remaining for the dilution volume (see Table 4) and remove the needle. Place the needle on the counter top such that the tip of the syringe is elevated.

2. Clean an appropriate syringe (see Table 4) with rinse and clean solvent. Expel excess solvent by pumping plunger several times. Puncture the sample vial with the syringe needle and withdraw the sample into the syringe.

3. Remove the syringe from the sample vial and insert the needle into the barrel of the 1ml syringe. Inject the sample into the clean solvent. Hold the 1ml syringe so that the tip is up and gently push up on the plunger to remove excess air from the barrel.

4. Replace the needle on the 1ml syringe and add sufficient clean solvent to a final volume of 1ml. Transfer the entire contents of the syringe into a labeled sample vial. Add an appropriate amount of internal standard (see Table 4) if necessary. Cap vial.

Table 4 STANDARD DILUTIONS

Dilution	Sample Volume µL	Total Volume µL	Amount of Internal Standard

			added µL
1:5	200	1000	8.0
1:10	100	1000	9.0
1:20	50	1000	9.5
1:50	20	1000	9.8
1:100	10	1000	9.9

14.2.7 Perform all qualitative and quantitative measurements as described in Sections 14.4 and 14.5. After analysis, store the extracts in the dark at 0.1- 6°C.

14.3 Analytical Sequence

START CHEMSTATION SOFTWARE:

From NT Desktop: Start/Programs/MSD ChemStation/Instrument #1/Instrument #1

The software will locate the instrument and all peripheral equipment. Once the software is fully loaded there will be two windows visible. Window one is the instrument control window. Instrument parameters are readily viewed from this window. The second window is the sequence control window. No instrument parameters are viewable from this window.

SEQUENCE SETUP

From menu: Sequence/Run

1. Set current date in Data File Directory space (ie., C:\MSDCHEM\1\DATA\060702\)
2. OK (to save changes)

From menu: Sequence/Edit Sample Log Table

1. Set data file name using current date using the following format MMDDYY## (ie., 06070201)
2. Set up sequence order using the following format: (**NOTE:** Tune and CCV must always run first)

VIAL	METHOD	SAMPLE NAME
1	DFTPP	TUNE STUNE001
2	SVOC0610	CCV SSTD050-1
3	SVOC0610	MBLK MB-1234-SVOC
4	SVOC0610	LCS LCS-1234-SVOC
5	SVOC0610	SAMP 0206001-001A
...	...	...
18	SVOC0610	SAMP 0206001-010A
1	DFTPP	TUNE STUNE002
2	SVOC0610	CCV SSTD050-2

19	SVOC0610	SAMP 0206001-011A

NOTE: The number of samples, including tune and CCV that can be analyzed within the 12 hour window varies with each analysis. Use this list as a guide but always check that the samples were analyzed within 12 hours of the DFTPP injection.

SVOC = 18 total samples
PNA(SIM) = 21 total samples
PCB/PEST = 20 total samples

3. OK (to save changes)

From menu: Method/Set New Default Paths

1. Update the method and data file paths using the current date (ie., C:\MSDCHEM\1\DATA\060702\)
2. OK (to save changes)

Use Windows Explorer to copy all of the method files from the previous day's folder into the current day's folder.

TO START SEQUENCE:

From menu: Sequence/Run/Run Sequence

Start of the 12 hour sequence (as documented as the date/time stamp on the data file for the Tune Standard):

The analytical sequence for Initial Calibration is:

DFTPP (Tune Standard)
Calibration standard (S1)
Calibration standard (S2)
Calibration standard (S3)
Calibration standard (S4)
Calibration standard (S5)
Calibration standard (S6) optional
Calibration standard (S7) optional
Initial Calibration Verification Standard (ICV)

The analytical sequence for Sample Analysis is:

DFTPP

Continuing Calibration Verification Standard (CCV)
Method Blank (MB)
LCS
LCS Duplicate (if applicable)
Sample #1
Sample #1 Matrix Spike (MS)
Sample #1 Matrix Spike Duplicate (MSD)
Sample #1 Laboratory Duplicate (if applicable)
Samples #2, #3, etc. until the end of 12 hour tune period

DFTPP
CCV
Samples up to #20
Method Blank (MB) #2
LCS #2
LCSD #2 (if applicable)
Sample #21
Sample #21 Matrix Spike (MS)
Sample #21 Matrix Spike Duplicate (MSD)
Sample #21 Laboratory Duplicate (if applicable)
Samples #22, #23, etc. until the end of 12 hour tune period

14.4 Data Interpretation - Qualitative Analysis

14.4.1 An analyte is identified based upon Relative Retention Time (RRT) and by comparison of the sample mass ions with the mass ions of a standard of the suspected compound (standard reference ions). The reference mass ion ratio must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass ion are defined to be the two or three ions of greatest relative intensity. See Attachment 2 for the ions to be monitored. Two criteria must be satisfied to verify identification:
(1) elution of sample component at the same GC relative retention time (RRT) as those of the standard component; and (2) correspondence of the sample component and the standard component mass ions. Intensities of the characteristic ions must maximize in the same scan or within one scan of each other.

14.4.2 The RRT of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

14.4.3 The relative intensities of the characteristic ions must agree within 30% of the relative intensities of these ions in the reference spectrum. (example: For an ion abundance of 50% in the reference, the corresponding abundance in a sample spectrum can range between 20% and 80%.)

14.4.4 Structural isomers that produce very similar mass spectra must be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs. An exception to this guidance occurs for the compounds Benzo(b)fluoranthene and Benzo(k)fluoranthene. Although the GC resolution may be minimal between the two, they are routinely reported as individual compounds. The Manual Integration SOP 1255 is used for guidance in the integration of these two peaks and for other situations that may require analyst efforts to correct computer generated integrations that are not technically sound.

14.4.5 Identification is hampered when sample components are not resolved chromatographically or coelute and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important. Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification of compounds, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

14.4.6 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose of the analyses being conducted. Computer generated library search routines must not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. For example, the RCRA permit or waste delisting requirements may require the reporting of nontarget analytes. Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification. Guidelines for making tentative identification are:

14.4.6.1 Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) must be present in the sample spectrum.

14.4.6.2 The relative intensities of the major ions must agree within ± 20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).

14.4.6.3 Molecular ions present in the reference spectrum must be present in the sample spectrum.

14.4.6.4 Ions present in the sample spectrum but not in the reference spectrum must be reviewed for possible background contamination or presence of coeluting compounds.

14.4.6.5 Ions present in the reference spectrum but not in the sample spectrum must be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

14.5 Data Interpretation - Quantitative Analysis

14.5.1 Once a compound has been identified, the quantitation of that compound must be based on the integrated abundance from the EICP of the primary characteristic ion. The internal standard used shall be the one nearest the retention time of that of a given analyte.

14.5.2 If the RSD of a compound's response factor is 15% or less, then the concentration in the extract is determined using the average response factor (RF) from initial calibration data (13.2). See Method 8000, Sec. 7.0, for the equations describing internal standard calibration and either linear or non-linear calibrations.

14.5.3 Where applicable or required, the concentration of any non-target analytes (TICs) identified in the sample are estimated. The same formulae must be used with the following modifications: The areas A_x and A_{is} must be from the total ion chromatograms, and the RF for the compound must be assumed to be 1. The resulting concentration must be reported indicating: (1) that the value is an estimate, and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

14.6 Record the following information in the appropriate logbook or data file. Include any deviations from this procedure. Analyst initials, date of analysis, sample number or ID, initial sample volume or weight processed, final extract volume, calibration standard sample or solution identifier, QC sample or solution identifier, surrogate solution identifier, internal standard solution identifier, any dilution information, readings from support equipment, data file name, instrument method name, visual observations, and any other information as deemed necessary.

14.7 Troubleshooting

The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Each day that the analysis is performed, the daily calibration standard (CCV) must be evaluated to determine if the chromatographic system is operating properly. Questions that must be asked: Do the peaks look normal? Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still good the injector is leaking, the injector septum needs replacing, etc. If any major changes are made to the system (e.g. column changed or detector cleaned), recalibration of the system must take place.

14.8 Routine Maintenance - Record all maintenance

14.8.1 Daily, or as needed according to sample throughput, change the septum and or the injection port liner. Trim a short section from the analytical column as necessary. Alternatively, the use of a guard column helps to protect the analytical column from residue buildup. A short section, 10 to 20 cm, of the guard column may be trimmed as to improve column performance.

14.8.2 Clean the source on an as needed basis (loss of sensitivity).

14.8.3 Inspect the autosampler syringe for wear; replace as necessary.

14.8.4 Check the carrier gas supply; replace as necessary.

15. DATA REDUCTIONS, CALCULATIONS, AND LOADING

15.1 The data system performs the calculations.

15.1.1 If the %RSD of a compound's relative response factor is 15% or less, then the concentration in the extract may be determined using the average response factor (RF) from the initial calibration data (13.2) and the following equation:

$$C_{ex}(mg/L) = \frac{A_x \times C_{is}}{A_{is} \times RF}$$

where C_{ex} is the concentration of the compound in the extract, and the other terms are defined in Sec. 13.2.

15.1.2 Alternatively, linear regression (Sec. 13.2) may be used for determination of the extract concentration.

15.2 Compute the concentration of the analyte in the sample using the equations in Secs. 15.2.1 and 15.2.2.

15.2.1 The concentration of the analyte in the liquid samples is calculated using the concentration of the analyte in the extract and the volume of liquid extracted, as follows:

$$\text{Concentration in liquid (mg/L)} = \frac{C_{ex} * V_f}{V_i}$$

or

$$\text{Concentration in liquid (µg/L)} = \frac{C_{ex} * V_f * 1000}{V_i}$$

where:

V_f = final extract volume in mL (includes any dilution volumes)
V_i = initial volume of liquid extracted, in mL.

15.2.2 The concentration of the analyte in the solid sample is calculated using the concentration of the analyte in the extract and the weight of the solid extracted, as follows:

$$\text{Concentration in solid (mg/Kg)} = C_{ex} * V_f$$

W_i

or

$$\text{Concentration in solid } (\mu g/Kg) = \frac{C_{ex} * V_f * 1000}{W_i}$$

where:

V_f = final extract volume in mL (includes any dilution volumes)
W_i = initial sample weight, in g.

For soil samples reported on dry weight basis, divide the Concentration by the decimal equivalent of the Percent Solids. For example: a sample contains 90% solids, thus

$$\text{Concentration in solid (mg/Kg) dry weight} = \frac{C_{ex} * V_f}{W_i * 0.90}$$

16. METHOD PERFORMANCE

Demonstration of Capability (DOC)

All parameters of interest must meet the method acceptance criteria before actual sample analysis begins. See SOP 1230 Training for the procedure to perform and document the DOC. The DOCs for the analysts performing this method are located in the analysts' training form folders located in the QA office files.

A quality control (QC) reference concentrate is required containing each analyte at a concentration of 50 µg/mL in acetone. The QC reference sample used is the Semivolatiles ICV (refer to Section 10.9 for composition). The QC reference sample is made using stock standards prepared independently from those used for calibration.

For each analyte calculate the mean recovery (x) and standard deviation (s) and the average % Recovery (%R). Compare X and s and %R with the corresponding acceptance criteria for accuracy and precision, respectively. Note: x must be within 15 and 75 µg/mL and s must be less than 25 µg/L and %R must be within 30 TO 150%. If x and s and %R for all analytes meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual x or %R falls outside the range for accuracy or any individual s exceeds the precision limit, then the system performance is unacceptable for that analyte and corrective action must be taken.

Locate and correct the source of the problem and repeat the test only for those analytes that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest.

Comparison to Reference Method Data

EPA Method 8000B provides guidance for the establishment of control limits for the LCS and MS QC samples. Recovery limits of 70% to 130% are provided as initial benchmarks for performance (8000B Section 8.5.4). These limits are designed for a wide variety of organic test methods. Individual analyte performance may vary. The control limits stated in Section 18 of this SOP are referenced from the CLP Statement of Work (SOW) for Organic Analyses Revision OLM04.2 May 1999 and in-house recovery data.

In-House Control Limits

Method performance data is on file in the laboratory QC department. Comparison of method performance data for the laboratory to the reference method criteria occurs when laboratory in-house acceptance limits are generated. In-house generated data is compared to the specifications of the reference method. If the in-house limits are within the specifications of the reference method, the control limits are updated in LIMS. If the in-house limits are not within specifications, an investigation is performed to determine the cause(s) of the problem and a corrective action is completed. The analysis may continue until enough data points are collected to regenerate new control limits. Any QC data generated outside of reference method limits during that time frame is flagged.

The laboratory maintains performance records to document the quality of data that is generated. Method accuracy for samples is assessed and records maintained. After the analysis of 20 laboratory control samples and surrogates, calculate the average percent recovery (R) and the standard deviation of the percent recovery (S).

Control limits for the method parameters are generated by the QC staff and distributed to the analysts via updates to the LIMS control charts. The control limits are calculated based on in-house performance data. At a minimum, these limits are updated annually.

17. POLLUTION PREVENTION

The preparation of excessive volumes of laboratory reagents and standards shall be avoided so that waste and potential for pollution are minimized. Samples, reagents and standards shall be disposed in compliance with the lab waste disposal program, SOP 1130 Waste Disposal. With the consent of the client, the samples may be returned to their origin for treatment.

Uncontaminated paper waste, glass and cans should be separated for recycling. Laboratory staff are required to protect the laboratory's and our clients' business information when disposing recycled paper or waste from the facility.

18. DATA ASSESSMENT AND CRITERIA FOR QUALITY CONTROL MEASURES

Data assessment includes review of: proper sample condition, preservation, and storage; analysis within holding time limitations; deviations from the SOP, evaluation of performance based or in-house control limits, reference method limits or project specific limits.

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a calibration verification standard is used to confirm the measurements were performed in an in-control mode of operation. The data review is conducted according to SOP 1250 Data Review.

18.1 Blanks

If the blank exceeds the RL (usually the lowest calibration standard or specifically defined in this test method SOP), the source of contamination must be investigated and corrective actions taken. The compound concentrations in the method blank of an extraction batch must be less than the RL's listed in Attachment 1, except for common laboratory contaminants, i.e. bis-2-ethylhexyl phthalate which must be less than 5 times the RL listed in Attachment 1. If this criteria is exceeded, re-analyze the method blank. If after re-analysis, the blank criteria is still exceeded, then the entire extraction batch must be re-extracted. Always refer to a client specific QAPP for additional guidance.

If the surrogate recovery is outside the QA limits as defined in this test method the source of the nonconformance must be investigated and corrective actions taken. If this criteria is exceeded, re-analyze the method blank. If after re-analysis, the blank criteria is still exceeded, then the entire extraction batch must be re-extracted. Always refer to a client specific QAPP for additional guidance.

Affected samples must be reprocessed and reanalyzed or Data must be appropriately qualified if:

1) The concentration of a targeted analyte in the blank is at or above the reporting limit as established by the SOP or by regulation, AND is greater than 1/10 of the amount measured in any sample.

2) The blank contamination otherwise affects the sample results as per the test method requirements or the individual project data quality objectives.

18.2 Laboratory Control Samples (LCS)

The results of the individual batch LCS are calculated in percent recovery (%R) and compared to established acceptance criteria from in house analyses. If the LCS is outside the acceptance criteria, see Table 5 for current acceptance criteria, the analytical system is "out of control." Any affected samples associated with an out of control LCS must be reprocessed and reanalyzed or the results reported with appropriate data qualifiers. If after re-analysis the control criteria has not been met, the entire extraction batch must be re-extracted. Always refer to a client specific QAPP for additional guidance.

Table 5 LCS

Compound	Soil % Recovery	Water % Recovery
Phenol	46 – 78	12 – 101
2-Chlorophenol	51 – 82	30 – 97
1,4-Dichlorobenzene	49 – 81	27 – 99
N-Nitrosodi-n-propylamine	46 – 106	36 – 104
1,2,4-Trichlorobenzene	51 – 85	31 – 101
4-Chloro-3-methylphenol	54 – 101	43 – 113
Acenaphthene	58 – 106	43 – 122
4-Nitrophenol	52 – 114	10 – 129
2,4-Dinitrotoluene	52 – 116	10 – 123
Pentachlorophenol	50 – 111	50 – 113
Pyrene	42 – 136	54 – 131

18.3 Surrogates

18.3.1 The results of the individual Surrogate compounds are calculated in percent recovery (%R) and are compared to established acceptance criteria from the CLP Statement of Work (SOW) for Organic Analyses Revision OLM04.2 May 1999. Surrogates outside the acceptance criteria, see Table 6 for current acceptance criteria, must be evaluated for the effect indicated for the individual sample results.

Table 6 Surrogates

Surrogate Compound	Soil % Recovery	Water % Recovery
Nitrobenzene-d_5	51-104	35-114
2-Fluorobiphenyl	54-105	43-116
Terphenyl-d_{14}	62-110	33-141
Phenol-d_5	48-115	10-110
2-Fluorphenol	54-109	21-110
2,4,6-Tribromophenol	55-115	10-123
1,2-Dichlorobenzene-d_4	31-121	16-110
2-Chlorophenol-d_4	34-123	33-110

If surrogate recoveries are not within the established acceptance criteria, proceed as follows (SW-846 8000B):

1) Check to be sure that there are no errors in the calculations, surrogate solutions or internal standards. If errors are found, recalculate the data accordingly. Examine chromatograms for interfering peaks and integrated peak areas.

2) Check instrument performance. If an instrument performance problem is identified, correct the problem and re-analyze the extract (or re-analyze the sample for volatiles).

3) Some samples may require dilution in order to bring one or more target analytes within the calibration range or to overcome significant interferences with some analytes. This may result in the dilution of the surrogate responses to the point that the recoveries cannot be measured. If the surrogate recoveries are available from a less diluted or undiluted aliquot of the sample or sample extract, those recoveries may be used to demonstrate that the surrogates were within the QC limits, and no further action is required. However, the results of both the diluted and undiluted (or less-diluted) analyses should be provided to the data user.

4) If no instrument problem is found and if sufficient sample is available, the sample should be re-extracted and re-analyzed.

18.3.2 If, upon re-analysis (in either 2 or 4 above), the recovery is again not within limits, report the data as an "estimated concentration." If the recovery is within the limits in the re-analysis, provide the re-analysis data to the data user. If the holding time for the method has expired prior to the re-analysis, provide both the original and reanalysis results to the data user, and note the holding time problem.

18.4 Duplicates

The results from laboratory duplicates are designed to assess the precision of analytical results in a given matrix and are expressed as relative percent difference (RPD). See the STAT Quality Assurance

Manual, Section 5.4 for the calculation for RPD. Results are compared to established acceptance criteria as listed in the MS/MSD Tables 7 and 8. For duplicates results outside established criteria, corrective action must be documented or the data reported with appropriate data qualifying codes.

For this test method, the analysis of the MS/MSD pair is used for determination of method precision. For cases where the sample cannot be divided (e.g., wipes, air samples, not enough sample provided by customer) and thus a MS/MSD pair is cannot be prepared in the preparation batch, an LCS/LCSD pair is prepared and analyzed to measure precision. Precision data from Tables 7 and 8 will be used for RPD acceptance criteria for LCS/LCSD.

18.5 Matrix Spikes

18.5.1 The results from MS/MSD are primarily designed to assess the precision and accuracy of analytical results in a given matrix and are expressed as percent recovery (%R) and relative percent difference (RPD). See the STAT Quality Assurance Manual, Section 5.4 for the calculation for RPD. Results are compared to established acceptance criteria from the CLP Statement of Work (SOW) for Organic Analyses Revision OLM04.2 May 1999. For matrix spike results outside established criteria corrective action must be documented or the data reported with appropriate data qualifying codes.

18.5.2 Tables 7 and 8 show the compounds spiked, the levels and the current QC criteria for soils and water samples.

Table 7 Matrix Spike - Soil

Compound	Amount added µg/Kg	RPD Limit	% Recovery
Phenol	3330	35	46 – 78
2-Chlorophenol	3330	50	51 – 82
1,4-Dichlorobenzene	1670	27	49 – 81
N-Nitrosodi-n-propylamine	1670	38	46 – 106
1,2,4-Trichlorobenzene	1670	23	51 – 85
4-Chloro-3-methylphenol	3330	33	54 – 101
Acenaphthene	1670	19	58 – 106
4-Nitrophenol	3330	50	52 – 114
2,4-Dinitrotoluene	1670	47	52 – 116
Pentachlorophenol	3330	47	50 – 111
Pyrene	1670	36	42 – 136

Table 8 Matrix Spike - Water

Compound	Amount added µg/L	RPD Limit	% Recovery
Phenol	200	42	12 – 101
2-Chlorophenol	200	40	30 – 97
1,4-Dichlorobenzene	100	28	27 – 99
N-Nitrosodi-n-propylamine	100	38	36 – 104
1,2,4-Trichlorobenzene	100	28	31 – 101
4-Chloro-3-methylphenol	200	42	43 – 113
Acenaphthene	100	31	43 – 122
4-Nitrophenol	200	50	10 – 129
2,4-Dinitrotoluene	100	38	10 – 123
Pentachlorophenol	200	50	50 – 113
Pyrene	100	31	54 – 131

18.6 Internal Standards

The results of the individual Internal Standard compounds on all samples, blanks, and spikes are calculated in percent recovery (%R) and are compared to established acceptance criteria. If the Internal Standard recovery is outside the acceptance criteria, see Table 9, corrective action should be taken. Note: the recovery of internal standards in these samples within the stated limits is not mandatory per the reference method, 8270C. It can be a useful diagnostic tool. Client specific project criteria may require the adherence to these limits. If so, then corrective action must be documented or the data reported with appropriate data qualifying codes.

Table 9 Internal Standards

INTERNAL STD COMPOUND	CRITERIA (%)
Acenaphthene-d_{10}	-50 to +100
Chrysene-d_{12}	-50 to +100
1,4-Dichlorobenzene-d_4	-50 to +100
Naphthalene-d_8	-50 to +100
Perylene-d_{12}	-50 to +100
Phenathrene-d_{10}	-50 to +100

18.7 Other

The laboratory will analyze standard reference materials and participate in relevant performance evaluation studies quarterly.

19 CORRECTIVE ACTIONS FOR OUT-OF-CONTROL DATA

The process for handling unacceptable and out of control data is found in SOP 230 Corrective Action.

If the CCV, MB, LCS/LCSD, MS/MSD, lab duplicate, surrogate, internal standard, or recovery of any parameter falls outside the designated acceptance range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the samples is suspect and is only reported for regulatory compliance purposes with the appropriate corrective action form. Immediate corrective action includes reanalyzing all affected samples by using any retained sample before the expiration of the holding time. Final data results must be qualified in the client report for reported results not meeting the laboratory defined criteria.

1) Review standards preparation logbooks. Check all calculations and ensure dilution factors are properly recorded.
2) Re-prepare the suspected standard or QC sample to identify possible preparation errors of the standard or QC sample.
3) Re-Analyze the samples when the CCV or LCS is not within acceptable limits.
4) Perform routine preventative maintenance following manufacturer's specification. Record all maintenance in the instrument logbook.

20 CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

Every effort is made to prevent problems from occurring. When out of control or unacceptable data occurs the first option is to identify the problem and reanalyze the samples within the holding times. When this is not possible, the QA Manager and/or the Laboratory Director reviews data and discusses options with the client. Reanalysis or reporting the data with qualification are alternatives. Out of control or unacceptable data reported to the client must include the data qualifier, flag and discussion on the rationale for reporting.

Holding time exceedence, improper preservation and improper sample condition or storage are noted on the corrective action form and included on the final report.

Review the CCV standard response, LCS result, the surrogate recovery, and internal standard recovery for acceptable performance for each batch of samples. Record any trends or unusual performance on a corrective action form. Final data results must be qualified in the client report for results not meeting the laboratory defined criteria.

Manual integration must be minimized for standards, reagent blanks and surrogates. Routine manual integration of the same parameters indicates a system performance problem. Correct this problem or note in the instrument analysis logbook the suspected causes for routine manual integration. Sign and date all manually integrated chromatograms.

20.1 The process for handling unacceptable and out of control data is found in the Laboratory QAM Section 11. The reporting of data that is out of control must be approved and documented by Quality Assurance Manager and either the Technical Manager or the Laboratory Director.

20.2 Client Requested Modifications:

20.2.1 Clients must request modifications from the laboratory SOP in writing to the lab.

20.2.2 The lab director, technical manager and quality assurance manager will evaluate the requested client deviations, determine the feasibly of the deviation and the potential effects on the data.

20.2.3 If it is determined that the lab will perform the requested deviations, lab director, technical manager and quality assurance manager will decide if a method validation study is required.

20.2.4 The designated project manager will retain all documentation concerning the requested deviation, including all correspondence with the client, in the client folder.

20.2.5 The final analytical report must include the statement "This report has analyses performed using client requested modifications ".

21 WASTE MANAGEMENT

The STAT Analysis Corporation Waste Disposal SOP 1130 identifies proper waste management practices for the chemicals and biological materials used in this procedure. Samples are stored and discarded accordance with SOP 1130 Waste Disposal.

22 REFERENCES

22.1 Method 8270C, Revision 3, December 1996; U.S. EPA SW-846 "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods" Update III, December 1996.
22.2 STAT SOP for sample prep: 3500
22.3 STAT Extract Cleanup SOPs: 3060, 3330
22.4 STAT SOPs: 1210 Method Detection Limits
22.5 SOP 230 Corrective Actions
22.6 SOP 1010 Standard and Reagent Preparation
22.7 SOP 1400 LIMSa
22.8 SOP 1130 Waste Disposal
22.9 SOP 003 Chemical Hygiene Plan
22.10 SOP 1250 Data Review
22.11 Manufacturers' Equipment Instruction Manuals
22.12 SOP 1255 Manual Integration
22.13 SW-846 8000B Determinative Chromatographic Separations
22.14 SOP 1230 Training

22.15 "USEPA Contract Laboratory Program Statement of Work for Organic Analysis" Revision OLM04.2 May 1999, U. S. Environmental Protection Agency. Office of Solid Waste, Washington DC 20460.

22.16 NIST Library of Reference Spectra, Edition Number NIST98

23 FORMS, FIGURES, TABLES, DIAGRAMS, FLOWCHARTS, ATTACHMENTS OR VALIDATION DATA

MDLs and REPORTING LIMITS FOR SEMIVOLATILE COMPOUNDS (Attachment 1)

CASN	Compounds	MDL (µg/L)	RL (µg/L)	RL (mg/L)	MDL (µg/Kg)	RL (µg/Kg)	RL (mg/Kg)
83-32-9	Acenaphthene	2.8	10	0.010	124	330	0.33
208-96-8	Acenaphthylene	2.7	10	0.010	123	330	0.33
62-53-3	Aniline	2.0	10	0.010	134	330	0.33
120-12-7	Anthracene	4.0	10	0.010	113	330	0.33
65-85-0	Benzoic acid	12.4	50	0.050	169	1700	1.7
56-55-3	Benzo(a)anthracene	3.9	10	0.010	110	330	0.33
205-99-2	Benzo(b)fluoranthene	3.3	10	0.010	159	330	0.33
207-08-9	Benzo(k)fluoranthene	3.8	10	0.010	102	330	0.33
191-24-2	Benzo(g,h,i)perylene	3.3	10	0.010	137	330	0.33
50-32-8	Benzo(a)pyrene	4.1	10	0.010	120	330	0.33
100-51-6	Benzyl alcohol	1.8	10	0.010	152	330	0.33
111-91-1	Bis(2-chloroethoxy)methane	2.0	10	0.010	116	330	0.33
111-44-4	Bis(2-chloroethyl) ether	1.6	10	0.010	147	330	0.33
108-60-1	2,2'-oxybis(1-Chloropropane)	1.9	10	0.010	119	330	0.33
117-81-7	Bis(2-ethylhexyl)phthalate	3.2	10	0.010	112	330	0.33
101-55-3	4-Bromophenyl phenyl ether	3.8	10	0.010	140	330	0.33
85-68-7	Butyl benzyl phthalate	3.8	10	0.010	106	330	0.33
106-47-8	4-Chloroaniline	2.5	10	0.010	118	330	0.33
59-50-7	4-Chloro-3-methylphenol	3.5	10	0.010	123	330	0.33
91-58-7	2-Chloronaphthalene	2.5	10	0.010	125	330	0.33
95-57-8	2-Chlorophenol	2.0	10	0.010	98	330	0.33
7005-72-3	4-Chlorophenyl phenyl ether	3.2	10	0.010	124	330	0.33
218-01-9	Chrysene	3.9	10	0.010	117	330	0.33
53-70-3	Dibenz(a,h)anthracene	3.2	10	0.010	281	330	0.33
132-64-9	Dibenzofuran	2.9	10	0.010	115	330	0.33
84-74-2	Di-n-butyl phthalate	5.4	10	0.010	116	330	0.33
95-50-1	1,2-Dichlorobenzene	1.8	10	0.010	98	330	0.33
541-73-1	1,3-Dichlorobenzene	1.8	10	0.010	127	330	0.33
106-46-7	1,4-Dichlorobenzene	1.8	10	0.010	107	330	0.33
91-94-1	3,3'-Dichlorobenzidine	4.6	20	0.020	231	660	0.66
120-83-2	2,4-Dichlorophenol	2.1	10	0.010	124	330	0.33
84-66-2	Diethyl phthalate	3.7	10	0.010	119	330	0.33
131-11-3	Dimethyl phthalate	3.7	10	0.010	154	330	0.33
534-52-1	4,6-Dinitro-2-methylphenol	3.5	50	0.050	121	1700	1.7
51-28-5	2,4-Dinitrophenol	10.5	50	0.050	86	1700	1.7

121-14-2	2,4-Dinitrotoluene	3.2	10	0.010	133	330	0.33
606-20-2	2,6-Dinitrotoluene	3.4	10	0.010	127	330	0.33
117-84-0	Di-n-octyl phthalate	3.1	10	0.010	100	330	0.33
206-44-0	Fluoranthene	4.1	10	0.010	114	330	0.33
86-73-7	Fluorene	3.0	10	0.010	129	330	0.33
118-74-1	Hexachlorobenzene	3.8	10	0.010	102	330	0.33
87-68-3	Hexachlorobutadiene	2.3	10	0.010	121	330	0.33
77-47-4	Hexachlorocyclopentadiene	1.8	10	0.010	90	330	0.33
CASN	**Compounds**	**MDL (µg/L)**	**RL (µg/L)**	**RL (mg/L)**	**MDL (µg/Kg)**	**RL (µg/Kg)**	**RL (mg/Kg)**
67-72-1	Hexachloroethane	1.7	10	0.010	88	330	0.33
193-39-5	Indeno(1,2,3-cd)pyrene	3.1	10	0.010	270	330	0.33
95-48-7	2-Methylphenol	2.0	10	0.010	115	330	0.33
108-39-4	3-Methylphenol	1.9	10	0.010	107	330	0.33
106-44-5	4-Methylphenol	1.9	10	0.010	107	330	0.33
91-20-3	Naphthalene	2.2	10	0.010	110	330	0.33
88-74-4	2-Nitroaniline	3.4	10	0.010	117	330	0.33
99-09-2	3-Nitroaniline	3.6	10	0.010	152	330	0.33
100-01-6	4-Nitroaniline	3.7	10	0.010	134	330	0.33
98-95-3	Nitrobenzene	1.7	10	0.010	111	330	0.33
88-75-5	2-Nitrophenol	2.2	10	0.010	85	330	0.33
100-02-7	4-Nitrophenol	10.9	50	0.050	117	1700	1.7
62-75-9	N-Nitrosodimethylamine	1.2	10	0.010	151	330	0.33
86-30-6	N-Nitrosodiphenylamine	3.5	10	0.010	117	330	0.33
621-64-7	N-Nitrsosdi-n-propylamine	2.2	10	0.010	125	330	0.33
87-86-5	Pentachlorophenol	4.1	50	0.050	110	1700	1.7
85-01-8	Phenanthrene	3.9	10	0.010	125	330	0.33
108-95-2	Phenol	1.0	10	0.010	131	330	0.33
129-00-0	Pyrene	4.1	10	0.010	114	330	0.33
110-86-1	Pyridine	1.5	10	0.010	151	330	0.33
120-82-1	1,2,4-Trichlorobenzene	2.0	10	0.010	121	330	0.33
95-95-4	2,4,5-Trichlorophenol	3.2	10	0.010	118	330	0.33
88-06-2	2,4,6-Trichlorophenol	3.2	10	0.010	120	330	0.33

Attachment 2: CHARACTERISTIC IONS FOR SEMIVOLATILE COMPOUNDS

#	Compounds	Retention Time (min.)	Primary Ion	Secondary Ion(s)
1	1,4-Dichlorobenzene-d4 (ISTD)	8.63	152	150, 154
2	N-Nitrosodimethylamine	2.69	74	79, 42
3	Pyridine	2.58	79	51, 52
4	2-Fluorophenol (SURR)	5.29	112	64, 92
5	Phenol-d5 (SURR)	8.35	99	71, 42
6	Phenol (MS)	8.40	94	65, 66
7	Aniline	7.84	66	65, 39
8	bis-(2-Chloroethyl)ether	8.17	63	65
9	2-Chlorophenol (MS)	8.22	128	64, 130, 132
10	1,3-Dichlorobenzene	8.48	146	148, 75, 111
11	1,4-Dichlorobenzene (MS)	8.69	146	148, 111
12	Benzyl Alcohol	9.60	108	107, 79
13	1,2-Dichlorobenzene-d4 (SURR)	9.28	152	154, 115
14	2-Chlorophenol-d4 (SURR)	8.13	132	134
15	1,2-Dichlorobenzene	9.33	146	148, 111
16	2-Methylphenol	10.37	107	108, 79
17	2,2'-oxybis(1-Chloropropane)	10.10	45	41, 121
18	3- & 4-Methylphenol	11.06	107	108, 77
19	N-Nitrosodi-n-propylamine (MS)	10.74	70	43, 42
20	Hexachloroethane	10.38	117	119, 121
21	Nitrobenzene-d5 (SURR)	10.90	82	128, 54
22	Nitrobenzene	10.97	77	123, 51
23	Isophorone	12.01	82	138, 95
24	2-Nitrophenol	12.24	139	109, 65
25	2,4-Dimethylphenol	13.03	122	107, 121
26	Benzoic acid	14.49	122	105, 77
27	bis(2-Chloroethoxy)methane	13.23	93	63, 95
28	2,4-Dichlorophenol	13.44	162	98, 164, 166
29	1,2,4-Trichlorobenzene (MS)	13.47	180	182, 184
30	Naphthalene-d8 (ISTD)	13.58	136	68
31	Naphthalene	13.67	128	129, 127
32	4-Chloroaniline	14.40	127	129, 65
33	Hexachlorobutadiene	14.61	225	223, 227
34	4-Chloro-3-methylphenol (MS)	17.04	107	142, 144
35	2-Methylnaphthalene	16.69	142	115, 141
36	Hexachlorocylopentadiene	17.76	237	235, 239
37	2,4,6-Trichlorophenol	18.36	196	198, 200
38	2,4,5-Trichlorophenol	18.55	196	132, 97, 198
39	2-Fluorobiphenyl (SURR)	18.60	172	171, 170
40	2-Chloronaphthalene	18.70	162	127, 164
41	1-Chloronaphthalene	18.80	162	127, 164
42	2-Nitroaniline	19.36	138	92, 65
43	Dimethyl phthalate	19.98	163	194, 77
44	Acenaphthylene	19.80	152	151, 76

45	2,6-Dinitrotoluene	20.08	165	89, 63
#	Compounds	Retention Time (min.)	Primary Ion	Secondary Ion(s)
46	3-Nitroaniline	20.35	138	92, 65
47	Acenaphthene-d10 (ISTD)	20.16	164	162, 160
48	Acenaphthene (MS)	20.23	153	154, 152
49	2,4-Dinitrophenol	20.50	184	154, 63
50	Dibenzofuran	20.56	168	139
51	4-Nitrophenol (MS)	20.93	109	65, 39
52	2,4-Dinitrotoluene (MS)	20.79	165	89, 63
53	Diethyl phthalate	21.29	149	177, 150
54	4-Chlorophenyl phenyl ether	21.25	204	206, 141
55	Fluorene	21.16	166	165, 167
56	4-Nitroaniline	21.43	138	108, 92
57	N-Nitrosodiphenylamine	21.49	169	168, 167
58	4,6-Dinitro-2-methylphenol	21.46	198	51, 105
59	Azobenzene	21.49	77	51, 182
60	2,4,6-Tribromophenol (SURR)	21.61	330	332, 328
61	4-Bromophenyl phenyl ether	21.97	248	250, 141
62	Hexachlorobenzene	22.13	284	286, 282
63	Pentachlorophenol (MS)	22.44	266	264, 268
64	Phenanthrene-d10 (ISTD)	22.54	188	94, 80
65	Phenanthrene	22.58	178	176, 152
66	Anthracene	22.64	178	176, 179
67	Carbazole	22.91	167	166, 168
68	Di-n-butyl phthalate	23.51	149	104, 150
69	Fluoranthene	24.11	202	200, 203
70	Benzidine	24.35	184	185, 183
71	Pyrene (MS)	24.38	202	200, 203
72	p-Terphenyl-d14 (SURR)	24.65	244	240, 243
73	Butyl benzyl phthalate	25.33	149	206, 91
74	3,3'-Dichlorobenzidine	25.90	252	254, 256
75	Chrysene-d12 (ISTD)	25.90	240	236, 120
76	Benzo(a)anthracene	25.87	228	226, 229
77	Chrysene	25.94	228	226, 229
78	bis-(2-Ethylhexyl)phthalate	26.08	149	167, 279
79	Di-n-octyl phthalate	26.80	149	279, 43
80	Benzo(b)fluoranthene	27.12	252	250, 126
81	Benzo(k)fluoranthene	27.15	252	250, 126
82	Benzo(a)pyrene	27.46	252	126, 113
83	Perylene-d12 (ISTD)	27.51	264	260, 265
84	Indeno(1,2,3-cd)pyrene	28.75	276	138, 277
85	Dibenz(a,h)anthracene	28.77	278	139, 279
86	Benzo(g,h,i)perylene	29.08	276	138, 277

ISTD = Internal Standard
SURR = Surrogate

MS = Matrix Spike

STAT Analysis Corporation:

STANDARD OPERATING PROCEDURE 4050

ORGANOCHLORINE PESTICIDES & POLYCHLORINATED BIPHENYLS by GAS CHROMATOGRAPHY/ ELECTRON CAPTURE DETECTOR (EPA Methods 8081A and 8082)

Revision 02
Effective Date: November 27, 2002

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1.0 IDENTIFICATION OF TEST METHOD

SOP Title: Organochlorine Pesticides & Polychlorinated Biphenyls by Gas Chromatography/Electron Capture Detector is abbreviated as Pest-PCBs in laboratory records.

2.0 APPLICABLE MATRICES

Methylene chloride and organic solvent extracts from soil, sediment, ground and surface water, and mobility extracts are analyzed using this method.

3.0 DETECTION LIMITS

The lab follows the procedure found in 40CFR Part 136B to determine the MDL for each matrix type on an annual basis. See the STAT Analysis SOP 1210 for the MDL procedure, frequency and acceptance criteria. The MDLs measured by the lab and all supporting documentation are in the laboratory QA files for review.

The laboratory determined MDL must always be less than the reporting limit (RL), which is determined by the lowest calibration standard. The RLs will usually range from three to ten times the laboratory measured MDLs but this relationship may vary dependent on dilution of sample aliquots, matrix interferences, moisture adjustments (in solid samples), or method-specified requirements. Attachment 1 contains the current MDLs and reporting limits (RLs) for this SOP.

4.0 SCOPE AND APPLICATION

4.1 This standard operating procedure describes in detail the precise methods used at STAT Analysis Corporation for the analysis of environmental samples for Organochlorine Pesticides & PCBs by GC/ECD. This SOP as written is to be applied when SW-846 Methods 8081A or 8082 are requested. This SOP is used to determine the concentration of Pest-PCBs in extracts prepared from all types of solid waste matrices, soils, and ground water.

4.2 SOP 4020 can be used to quantitate Pest-PCBs that are soluble in hexane and other organic solvents and are capable of being eluted without derivatization as sharp peaks from gas chromatographic fused-silica capillary columns coated with a slightly polar silicone.

4.3 The reporting limits (RLs) for this SOP are shown in Attachment 1 for soils and water. RLs will be proportionately higher for sample extracts and samples that require dilution or reduced sample size to avoid saturation of the detector. PCBs are reported as Aroclors.

4.4 This method is restricted to use by or under the supervision of analysts experienced in the use of a Gas Chromatograph/Electron Capture Detector (GC/ECD) and skilled in the interpretation of complex chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

5.0 SUMMARY OF TEST METHOD

5.1 Prior to using this method, the samples must be prepared for the GC/ECD using the appropriate sample preparation and cleanup SOPs (Section 14.1). Samples are extracted at neutral pH with methylene chloride or other mixed organic solvents, and then solvent exchanged with hexane. This method describes chromatographic conditions that will allow for the separation of the compounds in the extract and for their qualitative and quantitative analysis by gas chromatography using an Electron Capture Detectors. Electron Capture Detectors are selective to electronegative compounds, especially chlorinated, fluorinated or brominated molecules. The ECD utilizes a radioactive ^{63}Ni source that ionizes the makeup gas (argon/methane 5%, P5) to form a stable cloud of free electrons in the ECD cell. When an electronegative compound enters the cell it immediately combines with some of the free electrons. This reduction of free electrons is proportional to the concentration of the compound. Identification of target analytes is accomplished by comparing component retention times to those of authentic standards. Quantitation is accomplished by comparing the response of a compound relative to an external standard using a five-point calibration curve.

5.2 **Method Modifications from Reference** – This SOP is based on EPA Methods 8081A and 8082 except that all samples are cleaned for sulfur by the addition into the autosampler vial of a small amount of granulated copper metal prior to analysis.

6.0 DEFINITIONS

The STAT Analysis Quality Manual Section 19.0 contains all the definitions of standard terms used in SOPs.

7.0 INTERFERENCES

7.1 GC/ECD data from all blanks, samples, and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation and/or cleanup of the samples and take corrective action to eliminate the problem. Specific interferences are sulfur, polynuclear aromatics, chlorophenols, and phthalates.

7.2 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed out between samples with solvent. Whenever an unusually concentrated sample is encountered, the sample after it must be reanalyzed to check for cross contamination.

7.3 Extract Cleanup SOPs (Section 14.1) are employed to remove interferences.

8.0 SAFETY

Numerous compounds analyzed by this method are suspected carcinogens. Proper personal protective equipment including safety glasses, nitrile gloves and a lab coat are required during different parts of this method. Other safety precautions must be conducted in accordance with the Chemical Hygiene Plan. Other actions can also be applied if deemed necessary. A reference file of Material Safety Data Sheets (MSDS) is available to all personnel involved in this method. The Electron Capture Detector (ECD) uses a radioactive source (Ni^{63}) as a source of electrons for analyte detection. The detector is wipe tested every six months for radioactive leakage. The wipes are analyzed by the National Leak Test Center in North Tonawanda, NY or at another Nuclear Regulatory Committee certified laboratory. Records of the leak tests are kept with the instrument.

9.0 EQUIPMENT AND SUPPLIES

The following apparatus is recommended for performing this procedure. Equivalent items can be used, if with their use, the analytical and QA/QC requirements in this SOP can be met. All catalog numbers in this SOP are current as of the effective date and thereafter subject to change.

9.1 Gas Chromatograph/Electron Capture Detector (GC/ECD)

9.1.1 Gas chromatograph(GC) – Agilent 6890 with electronic flow control Gas Chromatograph with Dual Agilent Microelectron Capture Detectors (Agilent G2397A) capable of utilizing dual capillary columns coupled to the detectors. The columns are coupled together and joined to a single injection port. Equipped with an Agilent Autosampler Model 7683

9.1.2 Primary column: 30 m x 0.25 mm ID x 0.25µm film thickness silicone-coated fused-silica capillary column (Restek Rtx-CLPesticides or equivalent)

9.1.3 Confirmatory column: 30 m x 0.25 mm ID x 0.25µm film thickness silicone-coated fused-silica capillary column (Restek Rtx-CLPesticides2 or equivalent)

9.1.4 Data system - An Agilent Kayak computer system using 3365 Chemstation Version C.00.01 to interpret data is attached to the GC

9.2 Micro syringes - 10 µL, 25 µL, 100 µL, 250 µL, 500 µL and 1,000 µL

9.3 Volumetric flasks, Class A - 10 mL, 25 mL, 50 mL with ground glass stoppers

9.4 Glass vials - 2-mL, for GC auto sampler with Teflon-lined screw caps or crimp tops

9.5 Amber glass vials - 10 mL with Teflon-lined screw caps

10.0 REAGENTS AND STANDARDS

The following reagents and standards are required to perform this procedure. When instructions are given on how to prepare a specific volume of a reagent or standard, larger or smaller volumes can be prepared as needed so long as the final concentrations remain the same. Any other deviations from the reagents or standards listed in this SOP could be detrimental to the quality of the data produced. Such deviations would have to be approved and documented (see 230 Corrective Action SOP).

Instructions for labeling and record keeping of reagents and standards are contained in SOP 1010 Standard and Reagent Preparation.

10.1 Analytical reagent grade chemicals shall be used in all tests. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.

10.2 Organic-free reagent water - All references to water in this SOP refers to Type II reagent water (in-house system).

10.3 Stock Standard solutions - Standard solutions can be prepared from pure standard materials or purchased as certified solutions. The routine laboratory practice is to purchase these standards from approved vendors. The standards used are: Organochlorine Pesticide Mix AB #2 (Restek catalog # 32292) and Pesticides Surrogate Mix (Restek catalog #32000). The standards used for the PCB stock solution are Aroclor 1016/1260 (Restek catalog #32039 or equivalent) and Pesticides Surrogate Mix (Restek catalog # 32000). Stock standard solutions and QC solutions are stored at < -10°C and must be replaced after six months, or sooner if comparison with quality control check samples indicates a problem. Different Storage conditions and expiration dates of other solutions are noted as warranted. The Aroclors are prepared using the following purchased standards: Aroclor 1221 (Supelco Catalog #4-8098), Aroclor 1232 (Supelco Catalog # 4-4805), Aroclor 1242 (Supelco Catalog #), Aroclor 1248 (Supelco Catalog #), Aroclor 1254 (Supelco Catalog #), Aroclor 1262 (Supelco Catalog # 4-4810) and Aroclor 1268 (Supelco Catalog # 502146). The Toxaphene stock standard is prepared using Supelco Catalog # 4-8243) and the technical Chlordane stock standard is prepared using Supelco Catalog # 4-8699.

10.3.1 Secondary Stock Standard Solutions – These two solutions are made using the individual Stock Standard solutions. Using microliter syringes, the following amounts of each Pesticide/Surrogate Stock solution are injected into a 10 mL volumetric flask containing 8 to 9 mL of hexane. The solution is brought to volume with hexane. The same procedure is used to make the PCB/Surrogate solution. The final concentration of each component is listed in Table 1. Note: these Secondary Stock solutions are the source solutions to prepare the calibration standards in Section 10.4. These standards are stored at < -10°C in 10 mL amber screw cap vials equipped with a Teflon lined caps. They are freshly prepared every six months, or sooner if check standards indicate a problem.

Table 1 Secondary Stock Standard Solutions

Stock Solution	Conc. Stock (µg/ml)	Vol. Stock (µL)	Final Conc. (µg/ml)
			Pesticide Secondary Stock Solution
Pesticide Mix AB #2 *	8 (16) (80)	125	0.10 (0.20) (1.0) *
Pesticide Surrogate	200	10	0.20
			PCB Secondary Stock Solution
Aroclor 1016	1000	100	10
Aroclor 1260	1000	100	10
Pesticide Surrogate	200	50	1.0

* Some analytes, that exhibit less sensitive responses, are at double the concentration , Methoxychlor is at 10 times the concentration

10.4 Calibration standards - A minimum of five calibration standards are prepared. The low standard is the RL and above the MDL. The others define the working range of the GC/ECD system. Calibration standards in current use for Pesticides: 0.005, 0.010, 0.025, 0.050, and 0.100µg/ml. Some analytes are at double the stated concentrations. (Table 2). Note: The Secondary Stock Solution standard is also used as the high level calibration standard. Calibration standards in current use for PCBs: 0.1, 0.5, 1.0, 1.5, and 2.0 µg/ml (Table 3). Using microliter syringes, the following amount of the Secondary Stock solution is injected into a 1 ml syringe. The solution is brought to volume with hexane. The final concentration of each component is listed in Table 2 and Table 3. Each solution is transferred to an autosampler vial. Storage is as indicated in 10.1.4. The continuing calibration verification standards (CCVs) are prepared weekly and stored at 4°C. Levels 2, 3 and 4 are used for the CCVs.

Table 2 Pesticide Calibration Standards

Level	Volume (µL) Secondary Stock	Volume (µL) hexane	Final Concentration (µg/ml) * +
1	50	950	0.005 (0.010)
2	100	900	0.010 (0.020)
3	250	750	0.025 (0.050)
4	500	500	0.050 (0.10)
5	1000	0	0.10 (0.20)

* Some analytes, that exhibit less sensitive responses, are at double the concentration,
\+ The surrogate concentration is equal to the concentration in ( )

For the multipeak response organochlorine pesticides, initially inject the midpoint calibration level for the target analyte to assist in qualitative identification. Initial calibration is performed if qualitative identification of a multipeak response pesticide is made in a sample. To perform the initial calibration, inject at least 3 concentration levels of separate standards for Technical Chlordane and Toxaphene into the gas chromatographic system. The following table provides guidance for concentration levels of the commonly performed target analytes. At least one of the levels for the calibration standards corresponds to a sample concentration at or below the reporting limit. The remaining standards correspond to the range of concentrations found in actual samples but do not exceed the working range of the GC system.

Components (units in ug/mL)	**Level 1**	**Level 2**	**Level 3**	**Level 4**	**Level 5**
Technical Chlordane	0.1	0.5	1.0	1.5	2.0
Toxaphene	0.1	0.5	1.0	1.5	2.0

Table 3: PCB Calibration Standards 1016 and 1260

Level	Volume (µL) Secondary Stock	Volume (µL) hexane	Final Concentration (µg/ml) #
1	10	990	0.10 (0.01)
2	50	950	0.50 (0.05)
3	100	900	1.0 (0.10)
4	150	850	1.5 (0.15)
5	200	800	2.0 (0.20)

\# The surrogate concentration is equal to the concentration in ( )

In addition, these calibration standards can be used qualitatively to demonstrate that a sample does <u>not</u> contain peaks that represent any one of the seven reported Aroclors.

A single midpoint standard of each of the other five Aroclors are required to aid the analyst in pattern recognition. The Aroclor 1016/1260 standards have been used to demonstrate the linearity of the detector, the midpoint standard of the remaining five Aroclors is used to determine the calibration factor for each Aroclor when qualitative identification of an

Aroclor is found in a sample. Preparation of the secondary stock standards is provided in the following table. The working standard is prepared by diluting 100 uL of the secondary stock standard solution to a final volume of 1000 uL in Hexane.

Aroclor Secondary Stock Standard Solutions

Stock Solution	Conc. Stock (µg/ml)	Vol. Stock (µL)	Final Conc. (µg/ml)
Aroclor 1221	1000	100	10.0
Pesticide Surrogate	200	50	1.0
Aroclor 1232	1000	100	10.0
Pesticide Surrogate	200	50	1.0
Aroclor 1242	1000	100	10.0
Pesticide Surrogate	200	50	1.0
Aroclor 1248	1000	100	10.0
Pesticide Surrogate	200	50	1.0
Aroclor 1254	1000	100	10.0
Pesticide Surrogate	200	50	1.0
Aroclor 1262	1000	100	10.0
Pesticide Surrogate	200	50	1.0
Aroclor 1268	1000	100	10.0
Pesticide Surrogate	200	50	1.0

10.5 Surrogate standards – Tetrachloro-meta-xylene (TCMX) and Decachlorobiphenyl (DCB) are the surrogates used for this method. Surrogate spike solutions are prepared using a stock standard solution purchased from Supelco (Cat. No. 4-8460 or equivalent). The spike solution is prepared by injecting 500 µL of the stock standard solution, concentration of 200 µg/mL, into a 100 ml volumetric flask. The flask is diluted to the mark with acetone for a final concentration of 1.0 µg/mL. All samples, blanks, LCSs, and MS/MSDs are spiked with 1.0 mL of the surrogate spike solution prior to extraction. This standard is stored at < -10°C in a glass vial with a Teflon lined screw cap.

10.6 Pesticide Performance Check (PPC) (Pesticide Breakdown Check Solution)- A hexane solution containing 4,4'-DDT and Endrin is used to verify injection port inertness and GC column performance. The breakdown standard used is Pesticide Performance Evaluation Mix w/ Surrogates (Restek Catalog #32074) Store at < -10°C when not being used. Inject 1 µL of this standard at the start of every 12 hours of operation.

10.7 Laboratory Control Sample/Matrix Spike standards - The LCS/matrix spike compounds for Pesticides are aldrin, alpha-BHC, beta-BHC, delta-BHC , gamma-BHC, p,p'-DDD, p,p'-DDE, p,p'-DDT, dieldrin, endosulfan I, endosulfan II, endosulfan sulfate, endrin, endrin aldehyde, endrin ketone, heptachlor, heptachlor epoxide and methoxychlor. Pesticide samples will be spiked at 0.25 µg/sample, 8.33 µg/kg for soil, 0.25 ug/kg for waste dilutions and 0.25 µg/L for water. The LCS/matrix spike compounds for PCBs are Aroclor 1016 and Aroclor 1260 unless otherwise client specified. PCB samples will be spiked at 1.0 µg/sample, 33.3 µg/kg for soil, 1.0 ug/mL for waste dilutions and 1.0 µg/L for water. See SOP 3500 for soils and SOPs 3030 and 3040 for water for LCS/Matrix Spike Solutions preparation. These standards are stored at < -10°C in a glass vial with Teflon lined screw cap.

10.8 Initial Calibration Verification Standards – Standards prepared from a different source at the midpoint of the calibration to verify the initial calibration. These two solutions are made using the following individual Stock Standard solutions: TCL Pesticides Mix (Supelco Cat. # 4-8913) and Pesticide Surrogate Spike Mix (Supelco Cat. # 4-8460 or equivalent; Aroclor 1016 (Supelco Cat. # 4-8097 or equivalent) and Aroclor 1260 (Supelco Cat. # 4-4809 or equivalent. Using microliter syringes, the following amounts of each Pesticide/Surrogate Stock solution are injected into a 10 mL volumetric flask containing 8 to 9 mL of hexane. The solution is brought to volume with hexane. The same procedure is used to make the PCB/Surrogate solution. The final concentration of each component is listed in Table 4. Note: these solutions are the Secondary ICV Stock source solutions to prepare the ICV Check Standards in Table 5. The Secondary Stock Standards are stored at < -10°C. in 10 mL amber screw cap vials equipped with Teflon lined caps. They are freshly prepared every six months, or sooner if check standards indicate a problem.

Table 4 Pesticide and PCBs ICV Secondary Stock Standards

Stock Solution	Conc. Stock (µg/ml)	Vol. Stock (µL)	Final Conc. (µg/ml)
			Pesticide Secondary ICV Stock Solution
TCL Pesticides Mix	2000	125	0.10
Pesticide Surrogate Mix	200	50	1.0
			PCB Secondary ICV Stock Solution
Aroclor 1016	1000	100	10
Aroclor 1260	1000	100	10
Pesticide Surrogate Mix	200	50	1.0

To prepare the ICV Check Standards: Using microliter syringes, the following amounts of the ICV Secondary Stock solution is injected into a 1 ml syringe. The solution is brought to volume with hexane. The final concentration of each component is listed in Table 5. Each solution is transferred to an autosampler vial. Storage is as indicated in 10.1.4.

Table 5 Pesticide and PCBs ICV Calibration Check Standards

Level	Volume (µL) ICV Secondary Stock	Volume (µL) hexane	Final Concentration (µg/ml)
PEST	250	750	0.025 (0.050) +
PCB	100	900	1.0 (0.10) #

+ The surrogate concentration is equal to the concentration in ( )
# The surrogate concentration is equal to the concentration in ( )

10.9 Acetone, hexane, isooctane, toluene and other appropriate solvents, pesticide quality or equivalent.

10.10 Helium – UHP grade

10.11 Copper – Granular, J.T. Baker Catalog #1720-01 or equivalent.

11.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

11.1 Containers used to collect samples for the determination of semivolatile organic compounds are glass: 1 Liter bottles for water samples and various size jars for soil samples. They are equipped with screw caps with Teflon liners. Water samples containing residual chlorine should be field treated to remove the chlorine prior to collection. Plastic containers or lids may NOT be used for the storage of samples due to the possibility of sample contamination from the phthalate esters and other hydrocarbons within the plastic.

11.2 Samples must be stored under refrigeration at between 0.1 and 6.0°C. Extraction must be within 7 days from sampling date for water and 14 days for solids. Sample extracts are stored in the dark at between 0.1 and 6.0°C and must be analyzed within 40 days of extraction.

11.3 No chemical preservation is required for this method.

11.4 All samples are stored away from all standards, reagents, food, and other potentially contaminating sources in order to prevent cross contamination.

12.0 QUALITY CONTROL

The following details the QC requirements that apply to this analysis. Each Quality Control Indicator (QCI) provides information pertaining to either method or individual sample performance. Our goal is to produce defensible data of known and documented quality. The results of these Quality Control Indicator (QCI) samples are used to assess the acceptability of data.

12.1 Blanks

Method Blank analysis is performed to determine if any contamination is present in the analytical process and is used to evaluate acceptance of the batch of samples. A method blank shall be prepared once per preparation batch of 20 or less samples per matrix type. If more than 20 samples are prepared a second blank shall be prepared after the twentieth sample. The method blank shall be processed through all preparatory steps used for the samples, including cleanup procedures. The blank shall be analyzed using the same instrument and conditions as the samples.

The Solvent Blank, clean solvent injected into the GC/ECD, is used to monitor the GC/ECD system for potential cross-contamination from one sample to another or for residual contamination in the system.

12.2 Calibration Verification

An Initial Calibration Verification (ICV) standard containing all of the target analytes reported in this method (refer to section 10.9) shall be analyzed immediately after the completion of the initial calibration. The ICV shall be purchased from a second source to verify analyte concentrations.

12.3 Laboratory Control Sample (LCS)

The LCS is used to evaluate the performance of the total analytical system, including all preparation and analysis steps. The LCS shall be prepared once per preparation batch of 20 or less samples per matrix type. If more than 20 samples are prepared a second LCS shall be prepared after the twentieth sample. The LCS shall be processed through all preparatory steps used for the samples, including cleanup procedures. The LCS shall be analyzed using the same instrument and conditions as the samples. Refer to section 10.8 for LCS analytes and concentrations.

12.4 Surrogates

The surrogates used for this method are added to all samples, standards, and blanks. Refer to section 10.5 for preparation and concentration instructions.

12.5 Duplicates

Duplicates of field samples or of the LCS must be prepared in compliance with the method requirements and client directives. Duplicate LCS's are prepared for sample wipes. It would be impractical to prepare a matrix spike and matrix spike duplicate. Reproducibility performance would be the same as for a matrix spike/matrix spike duplicate.

12.6 Matrix Spike and Matrix Spike Duplicate (MS/MSD)

MS/MSDs indicate the effect of the sample matrix on the precision and accuracy of the results generated using the selected method. This information does not determine the validity of the entire batch. MS/MSDs must be analyzed at a minimum of 1 per 20 samples per matrix per preparation procedure, or as specified by the required test method. If an MS/MSD pair is not analyzed in the preparation batch, an LCS/LCSD pair is analyzed. Samples chosen for matrix spiking are rotated among different clients and/or different client projects. This is accomplished through communication between the Department Manager and the analyst. In addition, designated samples, as indicated by client request or contract requirement, are matrix spiked. The MS/MSD pair shall be processed through all preparatory steps used for the samples. They shall be analyzed using the same instrument and conditions as the samples. Refer to section 10.8 for MS analytes and concentrations. Some clients may require different spiking levels and/or target analytes, these specific needs are documented on the request for analysis forms.

13.0 CALIBRATION AND STANDARDIZATION

13.1 GC Performance

Because of the sensitivity of the electron capture detector, the injection port and column should always be cleaned prior to performing the initial calibration. If the instrument has been idle for a few days, it may have to be primed by injecting a high level standard followed by a solvent blank. This may help to coat active sites on the column and determine if any residue elutes from the column.

Each GC/ECD system must be evaluated to meet the criteria of ≤15% breakdown of 4,4'-DDT and ≤15% breakdown of Endrin using the PPC solution in 10.6. Using the autosampler, inject 1 µL of the solution on to the column. Analyze the solution using the same instrument operational procedure as the samples. A custom report was written using the ChemStation software to automatically calculate pesticide breakdown. It is invoked by clicking on CustRpt/Print Report after reviewing the pesticide breakdown injection.
The following formulae are used to calculate the percent breakdown:

$$\% \text{ breakdown of DDT} = \frac{\text{sum of degradation peak areas (DDE + DDD)} * 100\ \%}{\text{sum of all peak areas (DDT + DDE + DDD)}}$$

$$\% \text{ breakdown of Endrin} = \frac{\text{sum of degradation peak areas (aldehyde + ketone)} * 100\ \%}{\text{sum of all peak areas (Endrin + aldehyde + ketone)}}$$

Analyses must not begin until these criteria are met. If degradation exceeds criteria for either compound and/or poor chromatography is noted, the injection port may require cleaning. It may also be necessary to cut off an additional 10 to 20 cm of the capillary column.

Note: the 12 hour analytical batch period begins at the start of the PPC analysis (DDT/Endrin breakdown check) that is recorded as the data acquisition start time on the data file. The last valid calibration standard in the ICAL must have a data acquisition start time less than 12 hours from the start of the batch period.

13.2 **Initial Calibration (ICAL)**

13.2.1 Analyze 1 µL of each calibration standard and tabulate the area of the analyte against concentration for each compound. Calculate Calibration Factors (CFs) for each compound in each calibration standard as follows:

$$CF = A_x / C_x$$

where:

A_x = Area of the peak for the compound being measured.

C_x = Concentration of the compound being measured (ng/µL = µg/mL = mg/L).

13.2.2 Calculate the average calibration factor ($\overline{CF}$) for each compound as follows:

$$\overline{CF} = (\Sigma CF_1 \text{ to } CF_n)/n$$

where: CF = CF for each of the calibration levels (i.e., 5)

n = Number of CF values (i.e., 5)

13.2.3 The initial calibration information for the single peak response organochlorine pesticides, the multipeak response organochlorine pesticides and the Aroclors are stored in separate quantitation files for processing. The quantitation of multipeak organochlorine pesticides and aroclors are performed by pattern recognition and fingerprinting techniques using 5 peaks corresponding to major (>25% height of largest peak) components unique to the 1016/1260 mixture; 3 to 5 peaks for all other aroclors; and 4 to 6 peaks for multipeak response organochlorine pesticides. If it is determined that one calibration level has an unacceptable response, that level may be reanalyzed once. If any major changes are made to the system (e.g. column changed or detector cleaned), recalibration of the system must take place.

13.2.4 Using the CFs from the initial calibration, calculate the percent relative standard deviation (%RSD) for the compounds as follows:

To calculate %RSD: $\%RSD = 100\% \times SD/\overline{CF}$

where:

%RSD = % Relative Standard Deviation

$\overline{CF}$ = average of initial CFs for a compound

SD = standard deviation (n-1) of average CFs for a compound

To calculate Standard Deviation (n-1 degrees of freedom)

$$SD = \sum_{i=1}^{N} \frac{(CF_i - CF)^2}{n-1}$$

where: CF_i = CF for each of the 5 calibration levels
n = Number of CF values (i.e., 5)

13.2.5 Guidance: If the %RSD of any compound is > 30%, then the chromatographic system may be too reactive for analysis to begin. Check the linearity test in Section 13.2.6 to determine if the calibration curve is acceptable (it will probably fail criteria of r ≥0.99). Clean or replace the injector and/or capillary column, then repeat the calibration procedure beginning with section 13.1.

13.2.6 Linearity - If the %RSD of any compound is 20% or less, then the calibration factor is assumed to be constant over the calibration range, and the average calibration factor is used for quantitation. If the %RSD is greater than 20%, first order linear regression is used. The calibration curve must meet the requirements for curve fitting listed in SW-846 8000B and the correlation coefficient is ≥0.99. The equation is not forced through the origin.

The regression will produce the slope and intercept terms for a linear equation in the form:

$y = (a * x) + b$

where:

y = Instrument response (peak area or height)
a = Slope of the line (also called the coefficient of x)
x = Concentration of the calibration standard
b = The intercept

13.2.7 Retention Time Windows: See Attachment 3 for the procedure to establish Retention Time Windows. If, in the professional judgment of the Department Manager or the Technical Manager, the calculated window is artificially too narrow and the potential for reporting a false negative exists, the retention time window is expanded.

13.2.8 PCB analysis: A minimum of 3 peaks must be chosen for each Aroclor, and preferably 5 peaks. The peaks must be characteristic of the Aroclor in question. Choose peaks in the Aroclor standards that are at least 25% of the height of the largest Aroclor peak. For each Aroclor, the set of 3 to 5 peaks should include at least one peak that is unique to that Aroclor. Use at least five peaks for the Aroclor 1016/1260 mixture, none of which should be found in both of these Aroclors. Late-eluting Aroclor peaks are generally the most stable in the environment. NOTE: this same approach is used for the multi-component pesticide Technical Chlordane. Toxaphene is quantitated using a total peak area summary. The individual concentrations for each peak are transferred to the LIMS software. The LIMS software is set up to add all the individual peaks and calculate the average of all the multi-component peaks. The calculated average is used to determine, based on sample preparation values, the final concentration of the Aroclor or multi-component pesticide.

13.2.9 Before sample analysis can begin, a Initial Calibration Verification (ICV) (see Sec. 10.9) must be performed. The ICV results must be within the acceptance criteria as established for the CCV compounds (Section 13.3).

NOTE:

1. All calibration curves must have a unique identifier. It is recommended that the calibration date be incorporated into the identifier for easy reference.
2. All initial calibration standards (Pesticide or PCBs) should be analyzed within 12 hours after the start time of the PPC check analysis. See also point #3.
3. Calibration must be completed (all standard levels analyzed) within 24 hours or the entire calibration sequence must be repeated. If the calibration was not completed in the first 12 hour period, it may continue into a second 12 hour period. Standard calibration levels from either 12 hour period can be used. An exception follows: If the PPC check analysis does not pass criteria for the second 12 hour period and major maintenance was done to the instrument or the instrument parameters were adjusted in order to obtain an acceptable PPC check analysis, the entire calibration sequence must be repeated.
4. All initial calibration standards must be analyzed as a group. No field sample analyses are allowed during the calibration sequence.
5. Do not add calibration standards and update the curve after the original calibration date.
6. Multiple analyses of the same calibration level are not allowed to be included in the calibration curve.
7. Compound responses cannot be selected from different analyses of the same calibration level (i.e. all compound responses for level 1 must come from the same data file).
8. If more than five calibration levels are analyzed, it is permissible to either drop the low compound concentration (poor response) or the high compound concentration (detector saturation). It is not allowed to drop a point in the middle of the curve.
9. If more than five calibration levels are analyzed, it is permissible to drop an entire level if the analyst can document a specific reason or reasons why that level should be excluded. Mechanical failure, significant loss of all analyte responses possibly due to poor technique in standard preparation, or software malfunction during data acquisition (system did not acquire all compound data) are plausible reasons. The reason must be justified and documented. The supervisor should review this situation and approve the analyst's decision.
10. The need to analyze more than two analyses of the same calibration level indicates a potential problem with the secondary stock solution. Prepare a fresh secondary stock solution and repeat all five calibration levels. It is recommended that all calibration standard levels come from the same secondary stock solution.
11. Manual integration must only be used if the software fails to properly integrate the peak. If manual integration is used for a particular compound, all levels of that compound do not have to be manually integrated, but all levels must be integrated in a similar manner. Example: the computer generated integration of a compound in the low level standard is not technically sound. A manual integration of the compound is performed (due to baseline noise, etc) in order to achieve a technically sound integration. Other levels of the compound are integrated correctly by the computer. The manual integration of the low level must match, as best as possible, the computer generated integrations for all other levels.
12. If any compound in the mid-point level is manually integrated, the integration of this compound must be reviewed for every continuing calibration standard and QC check solution (i.e. LCS, and Matrix Spike) to ensure that the integration is the same as the manual integration performed in the initial calibration (ICAL) mid-point. A consistent manner of integration must be achieved.
13. All manual integrations must be reviewed and approved at the supervisory level.

13.3 Continuing Calibration Verification (CCV)

13.3.1 The GC/ECD system must meet performance criteria every 12 hours during analysis of samples (see Section 13.1).

13.3.2 A continuing calibration verification (CCV) standard is analyzed every 12 hours during analysis of samples. Different standards are analyzed for the CCV such that a wider range of the calibration curve is verified. For example: on successive days analyze the Level 2, then the Level 3 and on the third day, the Level 4

standard solution. Compare the calibration factors and retention times from the CCV with the following criteria.

13.3.3 Control limits for the CCV compounds are ± 15% difference from the ICAL Calibration Factor (CF) if the average CF is used for quantitation, or ± 15% drift from the true concentration of the CCV compound if linear regression is used.

EXCEPTION: If this criterion is exceeded for any compound, use the approach described in Sec. 7 of EPA Method 8000B to calculate the average percent difference across all compounds. If the average of the responses for all compounds is within ±15%, then the calibration has been verified. However, the conditions in Sec. 7 of EPA Method 8000B also apply, e.g., the average must include all compounds in the calibration, regardless of whether they are target compounds for a specific project, and the data user must be provided with the calibration verification data or a list of those compounds that exceeded the ±15% limit.

13.3.4 Compare the retention time of each compound in the calibration standard with the absolute retention time windows. The center of the absolute retention time window for each compound is its retention time in the mid-concentration standard analyzed during the initial calibration. Each compound in each standard must fall within its respective retention time window. If not, the gas chromatographic system must either be adjusted so that a second analysis of the standard does result in all compounds falling within their retention time windows, or a new initial calibration must be performed and new retention time windows established.

13.3.5 If the CCV results obtained are outside the acceptance criteria, corrective actions must be performed. If routine corrective actions fail to produce an acceptable *second consecutive (immediate)* CCV, then either the lab has to demonstrate performance after corrective action with two consecutive successful CCVs, or a new ICAL must be performed. If the instrument has not demonstrated acceptable performance, sample analyses cannot continue until a new ICAL is established and verified with an ICV. However, sample data associated with an unacceptable CCV may be reported as qualified data under the following special conditions:

13.3.5.1 When the acceptance criteria for CCV are exceeded high, i.e., high bias, and there are associated samples that are non-detects, then those non-detects may be reported. Otherwise the samples affected by the unacceptable calibration verification must be reanalyzed after a new ICAL has been established, evaluated and accepted.

13.3.5.2 When the acceptance criteria for the CCV are exceeded low, i.e., low bias, those sample results may be reported if they exceed a maximum regulatory limit/decision level. Otherwise the samples affected by the unacceptable verification must be reanalyzed after a new ICAL is established and verified with an ICV.

13.3.5.3 When the acceptance criteria for the CCV are exceeded and it is not possible to reanalyze the sample due to limited sample quantity AND a new sample cannot be obtained by the laboratory, the data may be reported with the appropriate data qualifiers if the client has been contacted and agrees, in writing, to accept the qualified data.

13.4 Records: Initial and Continuing Calibration Records will contain, at a minimum, the following:

1) Calibration date
2) Test method
3) Instrument
4) Analysis date
5) Each analyte name
6) Analyst's initials or signature

7) Standard Concentration (appropriate units) and number of standards
8) Response (appropriate units)
9) Calibration curve or calibration factor
10) Evaluation of and Statistics for ICAL curve fit in order to judge calibration curve acceptance
11) Evaluation of and Acceptance Limits for ICV analysis in order to judge calibration curve acceptance
12) Evaluation of and Acceptance Limits for CCV analysis in order to judge continuing calibration acceptance

13.5 Thermometers - The thermometers in the sample refrigerators and the standards freezer must be checked daily. They must meet performance criteria.

14. PROCEDURE

14.1 Sample Preparation

14.1.1 Samples must be prepared in accordance with SOP 3500.

14.1.2 Extract Cleanup: Extracts may be cleaned up by any of the following methods prior to GC/ECD analysis. Fine powdered copper is added to all blank, LCS, MS, MSD and sample vials immediately prior to analysis. This is a preliminary step in sulfur cleanup.

Compounds	SOPs
Polychlorinated Biphenyls	3060, 3070, 3080, 3330
Pesticides	3060, 3070, 3330

If crystals of sulfur are present in the extract, then SOP 3070 (EPA Method 3660B) should be employed prior to Florisil cleanup.

14.1.3 Direct Injection: In very limited applications direct injection of the sample into the GC/ECD system with a 10 µL syringe may be appropriate (see SOP 3050 for preparation). The reporting limit is very high (approximately 1 to 10 mg/L); therefore, it is only applicable where concentrations in excess of 1 mg/L are expected.

14.1.4 Extract Preparation: Sample extracts should be at ambient temperature prior to use. If there is precipitation in any sample autosampler vial, notify the Department Manager prior to analysis to determine what approach to take.

14.2 GC/ECD Analysis

14.2.1 Instrument Conditions: The recommended GC/ECD operating conditions:

Initial temperature:	140°C hold for 2 minutes
Ramp 1 temperature program	10.0°C/min
Final temperature 1:	200°C hold for 0.0 minutes
Ramp 2 temperature program	20 °C/min
Final temperature 2:	310 °C hold for 6.50 minutes
Injector temperature:	250°C
Source temperature:	300 °C
Sample volume:	1 µL
Carrier gas:	Helium at 1.2 mL/min
Split flow:	Splitless
Makeup (Ar/Me) Flow:	60 ml/minute (constant)

14.2.2 Access the computer and create a batch sequence file. See Section 14.3

14.2.3 Using the autosampler, inject 1 µL of the PPC and inject 1 µL of the column performance check solution. Evaluate using acceptance criteria. See Section 13.1

14.2.4 Inject 1 µL of the Continuing Calibration Verification Standard (CCV) and evaluate using CCV acceptance criteria. See Section 13.3.

14.2.5 If all criteria are met, continue with sample analysis, injecting 1 µL of each extract, as outlined below.

14.2.6 If the extract result exceeds the initial calibration curve range of the GC/ECD system, extract dilution is an option. If extract dilution is required, perform the appropriate dilution. Then the diluted extract is analyzed.

14.2.7 Perform all qualitative and quantitative measurements as described in Sections 14.4 and 14.5. After analysis, store the extracts in the dark at 0.1- 6°C.

14.3 Analytical Sequence

START CHEMSTATION SOFTWARE:

From NT Desktop: Start/Programs/MSD ChemStation/Instrument #1/Instrument #1

The software will locate the instrument and all peripheral equipment. Once the software is fully loaded there will be two windows visible. Window one is the instrument control window. Instrument parameters are readily viewed from this window. The second window is the sequence control window. No instrument parameters are viewable from this window.

SEQUENCE SETUP

From menu: Sequence/Run

1. Set current date in Data File Directory space (ie., C:\MSDCHEM\1\DATA\060702\)
2. OK (to save changes)

From menu: Sequence/Edit Sample Log Table

1. Set data file name using current date using the following format MMDDYY## (ie., 06070201)
2. Set up sequence order using the following format: (**NOTE:** Tune and CCV must always run first)

Vial	METHOD	SAMPLE NAME
1	BAKEOUT	BLANK001
2	PCB0610	PE PESTEVAL
3	PCB0610	CCV PESTSTD0.025
4	PCB0610	CCV PCBSTD1.0
5	PCB0610	CCV PCB1242STD1.0
6	PCB0610	CCV PCB1254STD1.0
7	PCB0610	MBLK MB-4426-PP
8	PCB0610	LCS LCS-4426-PCB
9	PCB0610	LCS LCS-4426-PEST
10	PCB0610	SAMP 0211034-001B

...	...	...
33	PCB0610	SAMP 0211045-010A
1	BAKEOUT	BLANK002
2	PCB0610	PE PESTEVAL
3	PCB0610	CCV PESTSTD0.025-2
4	PCB0610	CCV PCBSTD1.0-2
5	PCB0610	CCV PCB1242STD1.0-2
6	PCB0610	CCV PCB1254STD1.0-2
34	PCB0610	SAMP 0211045-011A

NOTE: The number of samples, including tune and CCV that can be analyzed within the 12 hour window varies with each analysis. Use this list as a guide but always check that the samples were analyzed within 12 hours of the PPC injection.

PCB/PEST = 32 total samples

3. OK (to save changes)

From menu: Method/Set New Default Paths

1. Update the method and data file paths using the current date (ie., C:\MSDCHEM\1\DATA\060702\)
2. OK (to save changes)

Using Windows Explorer copy all of the method files from the previous day's folder into the current day's folder.

TO START SEQUENCE:

From menu: Sequence/Run/Run Sequence

Start of the 12 hour sequence (as documented as the date/time stamp on the data file for the PPC Standard):

The analytical sequence for Initial Calibration is: * Solvent Blanks are optional if carryover is not an issue.

Solvent Blank
PPC Standard (breakdown check)
Calibration standard (S1) Pesticides
Calibration standard (S2) Pesticides
Calibration standard (S3) Pesticides
Calibration standard (S4) Pesticides
Calibration standard (S5) Pesticides
Toxaphene mid-point concentration standard (optional)
Technical Chlordane mid-point concentration standard (optional)
Initial Calibration Verification Standard (ICV) Pesticides

Solvent Blank
PPC Standard (breakdown check if also analyzing for Pesticides)
Calibration standard (S1) PCBs 1016 / 1260
Calibration standard (S2) PCBs 1016 / 1260
Calibration standard (S3) PCBs 1016 / 1260
Calibration standard (S4) PCBs 1016 / 1260
Calibration standard (S5) PCBs 1016 / 1260
PCB 1221 mid-point concentration standard (optional)
PCB 1232 mid-point concentration standard (optional)

PCB 1242 mid-point concentration standard
PCB 1248 mid-point concentration standard
PCB 1254 mid-point concentration standard
Initial Calibration Verification Standard (ICV) PCBs 1016 / 1260

The analytical sequence for Sample Analysis is:

Start of first 12 hour period

Solvent Blank*
PPC Standard (breakdown check) (if analyzing for pesticides)
Continuing Calibration Verification Standard (CCV) Pesticides (as per sample batch requirement)
Continuing Calibration Verification Standard (CCV) PCBs (as per sample batch requirement)
Method Blank (MB)
LCS
(LCS Duplicate optional)
Sample #1
Sample #1 Matrix Spike (MS)
Sample #1 Matrix Spike Duplicate (MSD)
Sample #1 Laboratory Duplicate (optional)
Samples #2, #3, etc.
End of 12 hour period

Start of second 12 hour period

Solvent Blank*
PPC Standard (breakdown check) (if analyzing for pesticides)
(CCV) Pesticides (as per sample batch requirement)
(CCV) PCBs (as per sample batch requirement)
Samples up to #20
Method Blank (MB) #2
LCS #2
(LCS #2 Duplicate optional)
Sample #21
Sample #21 Matrix Spike (MS)
Sample #21 Matrix Spike Duplicate (MSD)
Sample #21 Laboratory Duplicate (optional)
Samples #22, #23, etc.
End of 12 hour period

14.4 Data Interpretation - Qualitative Analysis

14.4.1 An analyte is tentatively identified based upon Retention Time (RT). See Attachment 2 for approximate analyte retention times for both GC columns. Two criteria must be satisfied to verify identification: (1) elution of sample component at the same GC retention time (RT) as those of the standard component on the first column; and (2) elution of sample component at the same GC retention time (RT) as those of the standard component on the second (confirmational) column. Note: both columns must exhibit acceptable performance for the tentatively identified component (13.3).

14.4.2 PCB analysis: A minimum of 3 peaks must be chosen for each Aroclor, and preferably 5 peaks. The peaks must be characteristic of the Aroclor in question. Choose peaks in the Aroclor standards that are at least 25% of the height of the largest Aroclor peak. For each Aroclor, the set of 3 to 5 peaks should include at least one peak that is unique to that Aroclor. Use at least five peaks for the Aroclor 1016/1260 mixture, none of which should be found in both of these Aroclors. Late-eluting Aroclor peaks are generally the most stable in the environment. NOTE: this same approach is used for the multi-component pesticide Technical Chlordane. Toxaphene is quantitated using a total peak area summary. The analyst must use his professional judgment to determine if chromatographic patterns are discernable and if they match those of known multi-component Aroclors or pesticides. The Department Manager must also agree with the conclusions of the analyst.

14.4.3 Comparison between results from different columns. When sample results are confirmed using the two dissimilar columns, the agreement between the quantitative results should be evaluated after the identification has been confirmed. Calculate the relative percent difference (RPD) between the two results. If one result is significantly higher (e.g., >40%), check the chromatograms to see if an obviously overlapping peak is causing an erroneously high result. If no overlapping peaks are noted, examine the baseline parameters established by the instrument data system (or operator) during peak integration. If no anomalies are noted, review the chromatographic conditions. If there is no evidence of chromatographic problems, report the higher result. This approach is conservative relative to protection of the environment. The data user should be advised of the disparity between the results on the two columns.

14.4.4 Closely eluting compounds: Sufficient GC resolution is achieved if the height of the valley between two peaks is less than 25% of the sum of the two peak heights. An exception to this guidance occurs for the compounds Endosulfan I and p,p'-DDE (4,4'-DDE). Although the GC resolution may be minimal between the two, they are routinely reported as individual compounds. The Manual Integration SOP 1255 is used for guidance in the integration of these two peaks and for other situations that may require analyst efforts to correct computer generated integrations that are not technically sound.

14.4.5 Identification is hampered when sample components are not resolved chromatographically or coelute. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more peaks), the analyst must use his professional judgment to determine the presence/absence of the target compound and its concentration. Or the elevation of the reporting limit that would indicate a level at which the compound concentration could not exceed. The Department Manager must also agree with the conclusions of the analyst.

14.4.6 Confirmational analysis: Note: Confirmational analysis is required for GC analysis methods of organic compounds unless stipulated in writing by the client. For this GC method, dual dissimilar column analyses are employed to verify the compound identification and quantitation when results greater than the reporting limit are detected on a sample from a location that has not been previously tested by the laboratory. Note that confirmations are documented and included with the initial analysis.

14.4.6.1 The routine laboratory approach: Identify the analyte and calculate its concentration from one column and confirm the analyte identification and concentration using data from the second (confirmational) column. The following may also be employed:

14.4.6.2 GC/MS confirmation may be used if the concentration is sufficient for detection by GC/MS using a SIM mode for qualitative screening purposes. GC/MS confirmation should be accomplished by analyzing the same extract that is used for GC/ECD analysis and the extract of the associated method blank. The base/neutral/acid extract and the associated blank may be used for GC/MS confirmation if the surrogates and internal standards do not interfere and if it is demonstrated that the analyte is stable during acid/base partitioning. However, if the compounds are *not* detected in the base/neutral/acid extract, then GC/MS analysis of the pesticide extract must be performed. A QC reference sample containing the compound must also be analyzed by GC/MS. The concentration of the QC reference sample must demonstrate that those pesticides identified by GC/ECD can be confirmed by GC/MS.

14.4.6.3 Confirmation is by using GC/MS SIM mode: A solution containing the compound in question at a known concentration is injected into the GC/MS and analyzed. The retention time and a major ion are determined. The sample extract is then injected and analyzed to confirm the presence of the compound. If present, the GC analysis concentration is reported unless, in the professional judgment of the GC/MS analyst, the GC concentration is > twice the estimated GC/MS value. Further analysis can be performed to clarify the data or all data can be reported to the client.

14.4.6.4 As noted in Section 14.4.6.1, the laboratory confirms positive findings for the single peak response analytes from the second (confirmational) column. GC/MS quantitation is not performed unless specifically required by the pertinent regulatory authority or per client project requirements.

14.5 Data Interpretation - Quantitative Analysis

14.5.1 Once a compound has been identified, the quantitation of that compound is based on its response (peak area).

14.5.2 If the RSD of an analyte's average calibration factor is ≤15%, then the concentration in the extract is determined using the average calibration factor (CF) from initial calibration data. If the RSD of an analyte's average calibration factor is > 15%, linear regression is used to determine the concentration (13.2).

14.5.3 PCB analysis: The following information is taken directly from EPA Method 8082 Sections 7.7.3 and 7.9:

7.7.3 When samples are analyzed from a source known to contain specific Aroclors, the results from a single-column analysis may be confirmed on the basis of a clearly recognizable Aroclor pattern. This approach should not be attempted for samples from unknown or unfamiliar sources or for samples that appear to contain mixtures of Aroclors. In order to employ this approach, the analyst must document:

• The peaks that were evaluated when comparing the sample chromatogram and the Aroclor standard.

• The absence of major peaks representing any other Aroclor.

• The source-specific information indicating that Aroclors are anticipated in the sample (e.g., historical data, generator knowledge, etc.). This information should either be provided to the data user or maintained by the laboratory.

7.9 Quantitation of PCBs as Aroclors

The quantitation of PCB residues as Aroclors is accomplished by comparison of the sample chromatogram to that of the most similar Aroclor standard. A choice must be made as to which Aroclor is most similar to that of the residue and whether that standard is truly representative of the PCBs in the sample.

7.9.1 Use the individual Aroclor standards (not the 1016/1260 mixtures) to determine the pattern of peaks on Aroclors 1221, 1232, 1242, 1248, 1254, 1262 and 1268. The patterns for Aroclors 1016 and 1260 will be evident in the mixed calibration standards.

7.9.2 Once the Aroclor pattern has been identified, compare the responses of 3 to 5 major peaks in the single-point calibration standard for that Aroclor with the peaks observed in the sample extract. The amount of Aroclor is calculated using the individual calibration factor for each of the 3 to 5 characteristic peaks chosen in (this SOP Section 14.4.2) and the calibration model (linear or non-linear) established from the multi-point calibration of the 1016/1260 mixture. A concentration is determined using each of the characteristic peaks and then those 3 to 5 concentrations are averaged to determine the concentration of that Aroclor.

7.9.3 Weathering of PCBs in the environment and changes resulting from waste treatment processes may alter the PCBs to the point that the pattern of a specific Aroclor is no longer recognizable. Samples containing more than one Aroclor present similar problems. If the purpose of the analysis is not regulatory compliance monitoring on the basis of Aroclor concentrations, then it may be more appropriate to perform the analyses using the PCB congener approach described in this method (EPA Method 8082). If results in terms of Aroclors are required, then the quantitation as Aroclors may be performed by measuring the total area of the PCB pattern and quantitating on the basis of the Aroclor standard that is most similar to the sample. Any peaks that are not identifiable as PCBs on the basis of retention times should be subtracted from the total area. When quantitation is performed in this manner, the problems should be fully described for the data user and the specific procedures employed by the analyst should be thoroughly documented.

14.6 Record the following information in the appropriate logbook or data file. Include any deviations from this procedure. Analyst initials, date of analysis, sample number or ID, initial sample volume or weight processed, final extract volume, calibration standard sample or solution identifier, QC sample or solution identifier, surrogate solution identifier, any dilution information, readings from support equipment, data file name, instrument method name, visual observations, and any other information as deemed necessary.

14.7 Troubleshooting

The experience of the analyst performing GC/ECD analyses is invaluable to the success of the methods. Each day that the analysis is performed, the daily calibration standard (CCV) must be evaluated to determine if the chromatographic system is operating properly. Questions that must be asked: Do the peaks look normal? Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still good, the injector is leaking, the injector septum needs replacing, etc. If any major changes are made to the system (e.g. column changed or detector cleaned), recalibration of the system must take place.

14.8 Routine Maintenance - Record all maintenance

14.8.1 Daily, or as needed according to sample throughput, change the septum and or the injection port liner. Trim a short section from the analytical column as necessary. Alternatively, the use of a guard column helps to protect the analytical column from residue buildup. A short section, 10 to 20 cm, of the guard column may be trimmed as to improve column performance.

14.8.2 Clean the detector on an as needed basis (loss of sensitivity). Follow the manufacturer's instructions.

14.8.3 Inspect the autosampler syringe for wear; replace as necessary.

14.8.4 Check the carrier gas supply; replace as necessary.

15. DATA REDUCTIONS, CALCULATIONS, AND LOADING

15.1 The data system performs the calculations.

15.1.1 If the %RSD of an analyte's calibration factor is 15% or less, then the concentration in the extract may be determined using the average calibration factor (CF) from the initial calibration data (13.2) and the following equation:

$C_{ex}(mg/L) = A_x / CF$

where:

A_x = Area of the peak for the compound being measured.
C_{ex} = Concentration of the compound being measured in the extract (ng/µL = µg/mL = mg/L).

15.1.2 Alternatively, linear regression (Sec. 13.2) may be used for determination of the extract concentration.

15.2 Compute the concentration of the analyte in the sample using the equations in Secs. 15.2.1 and 15.2.2.

15.2.1 The concentration of the analyte in the liquid samples is calculated using the concentration of the analyte in the extract and the volume of liquid extracted, as follows:

$$\text{Concentration in liquid (mg/L)} = \frac{C_{ex} * V_f}{V_i}$$

or

$$\text{Concentration in liquid (µg/L)} = \frac{C_{ex} * V_f * 1000}{V_i}$$

where:

V_f = final extract volume in mL (includes any dilution volumes)
V_i = initial volume of liquid extracted, in mL.

15.2.2 The concentration of the analyte in the solid sample is calculated using the concentration of the analyte in the extract and the weight of the solid extracted, as follows:

$$\text{Concentration in solid (mg/Kg)} = \frac{C_{ex} * V_f}{W_i}$$

or

$$\text{Concentration in solid (µg/Kg)} = \frac{C_{ex} * V_f * 1000}{W_i}$$

where:

V_f = final extract volume in mL (includes any dilution volumes)
W_i = initial sample weight, in g.

For soil samples reported on dry weight basis, divide the Concentration by the decimal equivalent of the Percent Solids. For example: a sample contains 90% solids, thus

$$\text{Concentration in solid (mg/Kg) dry weight} = \frac{C_{ex} * V_f}{W_i * 0.90}$$

15.3 The procedure for uploading data into the LIMS system is detailed in SOP 1400 LIMS.

16. METHOD PERFORMANCE

Demonstration of Capability (DOC)

All parameters of interest must meet the method acceptance criteria before actual sample analysis begins. See SOP 1230 Training for the procedure to perform and document the DOC. The DOCs for the analysts performing this method are located in the analysts' training form folders located in the QA office files.

A quality control (QC) reference concentrate is required. For the single component Pesticides, the concentration is 0.25 µg/mL in acetone. For the PCBs 1016/1260, the concentration is 10 µg/mL in acetone. The sources of the QC reference samples are the ICV Stock Solutions listed in Section 10.9. The QC reference samples are made using stock standards prepared independently from those used for calibration.

For each analyte calculate the mean recovery (X) and standard deviation (s) and the average % Recovery (%R). Compare X and s and %R with the corresponding acceptance criteria for accuracy and precision, respectively. Note: For the single component Pesticides, X must be within 0.075 and 0.375 µg/L and s must be less than 0.0625 µg/L and %R must be within 30 and 150%. For the PCBs 1016/1260, X must be within 3.0 and 15 µg/L and s must be less than 2.5 µg/L and %R must be within 30 and 150%. These limits are taken from the EPA CLP Statement of Work (SOW) for Organic Analyses Revision OLM04.2 May 1999. If X and s and %R for all analytes meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual X or %R falls outside the range for accuracy or any individual s exceeds the precision limit, then the system performance is unacceptable for that analyte and corrective action must be taken.

Comparison to Reference Method Data

EPA Method 8000B provides guidance for the establishment of control limits for the LCS and MS QC samples. Recovery limits of 70% to 130% are provided as initial benchmarks for performance (8000B Section 8.5.4). These limits are designed for a wide variety of organic test methods. Individual analyte performance may vary. The control limits stated in Section 18 of this SOP are referenced from the CLP Statement of Work (SOW) for Organic Analyses Revision OLM04.2 May 1999.

In-House Control Limits

Method performance data is on file in the laboratory QC department. Comparison of method performance data for the laboratory to the reference method criteria occurs when laboratory in-house acceptance limits are generated. In-house generated data is compared to the specifications of the reference method. If the in-house limits are within the specifications of the reference method, the control limits are updated in LIMS. If the in-house limits are not within specifications, an investigation is performed to determine the cause(s) of the problem and a corrective action is completed. The analysis may continue until enough data points are collected to regenerate new control limits. Any QC data generated outside of reference method limits during that time frame, is flagged.

The laboratory maintains performance records to document the quality of data that is generated. Method accuracy for samples is assessed and records maintained. After the analysis of 20 laboratory control samples and surrogates, calculate the average percent recovery (R) and the standard deviation of the percent recovery (S).

Control limits for the method parameters are generated by the QC staff and distributed to the analysts via updates to the LIMS control charts. The control limits are calculated based on in-house performance data. At a minimum, these limits are updated annually.

17. POLLUTION PREVENTION

The preparation of excessive volumes of laboratory reagents and standards shall be avoided so that waste and potential for pollution are minimized. Samples, reagents and standards shall be disposed in compliance with the lab waste disposal program, SOP 1130. With the consent of the client, the samples may be returned to their origin for treatment.

Uncontaminated paper waste, glass and cans should be separated for recycling. Laboratory staff are required to protect the laboratory's and our clients' business information when disposing recycled paper or waste from the facility.

18. DATA ASSESSMENT AND CRITERIA FOR QUALITY CONTROL MEASURES

Data assessment includes review of: proper sample condition, preservation, and storage; analysis within holding time limitations; deviations from the SOP, evaluation of performance based or in-house control limits, reference method limits or project specific limits.

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a calibration verification standard is used to confirm the measurements were performed in an in-control mode of operation. The data review is conducted according to SOP 1250 Data Review.

18.1 Blanks

If the blank exceeds the RL (usually the lowest calibration standard or specifically defined in this test method SOP), the source of contamination must be investigated and corrective actions taken. The analyte concentrations in the method blank of an extraction batch must be less than the RL's listed in Attachment 1. If this criteria is exceeded, re-analyze the method blank. If after re-analysis, the blank criteria is still exceeded, then the entire extraction batch must be re-extracted. Always refer to a client specific QAPP for additional guidance.

Affected samples must be reprocessed and reanalyzed **or** Data must be appropriately qualified if:

1) The concentration of a targeted analyte in the blank is at or above the reporting limit as established by the SOP or by regulation, AND is greater than 1/10 of the amount measured in any sample.

2) The blank contamination otherwise affects the sample results as per the test method requirements or the individual project data quality objectives.

18.2 Laboratory Control Samples (LCS)

The results of the individual batch LCS are calculated in percent recovery (%R) and compared to established acceptance criteria from the EPA CLP Statement of Work (SOW) for Organic Analyses Revision OLM04.2 May 1999. If the LCS is outside the acceptance criteria, see Table 4 for current acceptance criteria, the analytical system is "out of control". Any affected samples associated with an out of control LCS must be reprocessed and reanalyzed or the results reported with appropriate data qualifiers. If after re-analysis the control criteria has not been met, the entire extraction batch must be re-extracted. Always refer to a client specific QAPP for additional guidance.

Table 4: LCS

Compound	Water % Recovery	Soil % Recovery
Alpha-BHC	30 – 150	30 – 150
Beta-BHC	30 – 150	30 – 150
Gamma-BHC	30 – 150	30 – 150
Delta-BHC	30 – 150	30 – 150
Heptachlor	30 – 150	30 – 150
Aldrin	30 – 150	30 – 150
Heptachlor Epoxide	30 – 150	30 – 150
Endosulfan I	30 – 150	30 – 150
Dieldrin	30 – 150	30 – 150
P,P'-DDE	30 – 150	30 – 150
Endrin	30 – 150	30 – 150
Endosulfan II	30 – 150	30 – 150
P,P'-DDD	30 – 150	30 – 150
Endrin Aldehyde	30 – 150	30 – 150
Endosulfan Sulfate	30 – 150	30 – 150
P,P'-DDT	30 – 150	30 – 150
Endrin Ketone	30 – 150	30 – 150
Methoxychlor	30 – 150	30 – 150
Alpha-Chlordane	30 – 150	30 – 150
Gamma-Chlordane	30 – 150	30 – 150
Chlordane, Technical	30 – 150	30 – 150
Toxaphene	30 – 150	30 – 150
Aroclor 1016	30 – 150	30 – 150
Aroclor 1260	30 – 150	30 – 150
Aroclors 1221, 1232, 1242, 1248, 1254	30 – 150	30 – 150

18.3 Surrogates

18.3.1 The results of the individual Surrogate compounds are calculated in percent recovery (%R) and are compared to established acceptance criteria from the CLP Statement of Work (SOW) for Organic Analyses Revision OLM04.2 May 1999. Surrogates outside the acceptance criteria, see Table 5 for current acceptance criteria, must be evaluated for the effect indicated for the individual sample results.

Table 5: Surrogates

Surrogate Compound	Water % Recovery	Soil % Recovery
Tetrachloro-m-xylene (TCMX)	30-150	30-150
Decachlorobiphenyl (DCB)	30-150	30-150

If surrogate recoveries are not within the established acceptance criteria, proceed as follows (SW-846 8000B):

1) Check to be sure that there are no errors in the calculations, surrogate solutions or internal standards. If errors are found, recalculate the data accordingly. Examine chromatograms for interfering peaks and integrated peak areas.

2) Check instrument performance. If an instrument performance problem is identified, correct the problem and re-analyze the extract (or re-analyze the sample for volatiles).

3) Some samples may require dilution in order to bring one or more target analytes within the calibration range or to overcome significant interferences with some analytes. This may result in the dilution of the surrogate responses to the point that the recoveries cannot be measured. If the surrogate recoveries are available from a less diluted or undiluted aliquot of the sample or sample extract, those recoveries may be used to demonstrate that the surrogates were within the QC limits, and no further action is required. However, the results of both the diluted and undiluted (or less-diluted) analyses should be provided to the data user.

4) If no instrument problem is found and if sufficient sample is available, the sample should be re-extracted and re-analyzed.

18.3.2 If, upon re-analysis (in either 2 or 4 above), the recovery is again not within limits, report the data as an "estimated concentration." If the recovery is within the limits in the re-analysis, provide the re-analysis data to the data user. If the holding time for the method has expired prior to the re-analysis, provide both the original and reanalysis results to the data user, and note the holding time problem.

18.4 Duplicates

The results from laboratory Duplicates are designed to assess the precision of analytical results in a given matrix and are expressed as relative percent difference (RPD). See the STAT QAM, Section 5.4 for the calculation for RPD. Results are compared to established acceptance criteria as listed in the MS/MSD tables 6 and 7. For duplicates results outside established criteria corrective action must be documented or the data reported with appropriate data qualifying codes.

For this test method, the analysis of the MS/MSD pair is used for determination of method precision. Duplicate LCS samples will be analyzed for all matrices where it would be impractical to perform a MS/MSD, such as wipe samples. Precision data from Tables 6 and 7 will be used for RPD acceptance criteria for LCS/LCSD.

18.5 Matrix Spikes

18.5.1 The results from MS/MSD are primarily designed to assess the precision and accuracy of analytical results in a given matrix and are expressed as percent recovery (%R) and relative percent difference (RPD). See the STAT QAM, Section 5.4 for the calculation for RPD. Results are compared to established acceptance criteria from the CLP Statement of Work (SOW) for Organic Analyses Revision OLM04.2 May 1999. For matrix spike results outside established criteria corrective action must be documented or the data reported with appropriate data qualifying codes.

18.5.2 Tables 6 and 7 show the compounds spiked, the levels and the current QC criteria for soils and water samples.

Table 6: Matrix Spikes - Soil

Compound	Amount added µg/Kg	RPD Limit	% Recovery
Alpha-BHC	8.0	25	30-150
Beta-BHC	8.0	25	30-150
Gamma-BHC	8.0	25	30-150
Delta-BHC	8.0	25	30-150
Heptachlor	8.0	25	30-150
Aldrin	8.0	25	30-150
Heptachlor Epoxide	8.0	25	30-150
Endosulfan I	8.0	25	30-150
Dieldrin	8.0	25	30-150
P,P'-DDE	8.0	25	30-150
Endrin	8.0	25	30-150
Endosulfan II	8.0	25	30-150
P,P'-DDD	8.0	25	30-150
Endrin Aldehyde	8.0	25	30-150
Endosulfan Sulfate	8.0	25	30-150
P,P'-DDT	8.0	25	30-150
Endrin Ketone	8.0	25	30-150
Methoxychlor	8.0	25	30-150
Alpha-Chlordane			
Gamma-Chlordane			
Chlordane, Technical			
Toxaphene			
Aroclor 1016	330	25	30-150
Aroclor 1260	330	25	30-150
Aroclors 1221, 1232, 1242, 1248, 1254			

Table 7: Matrix Spikes - Water

Compound	Amount added µg/L	RPD Limit	% Recovery
Alpha-BHC	0.50	25	30-150
Beta-BHC	0.50	25	30-150
Gamma-BHC	0.50	25	30-150
Delta-BHC	0.50	25	30-150
Heptachlor	0.50	25	30-150
Aldrin	0.50	25	30-150
Heptachlor Epoxide	0.50	25	30-150
Endosulfan I	0.50	25	30-150
Dieldrin	0.50	25	30-150
P,P'-DDE	0.50	25	30-150
Endrin	0.50	25	30-150
Endosulfan II	0.50	25	30-150

P,P'-DDD	0.50	25	30-150
Endrin Aldehyde	0.50	25	30-150
Endosulfan Sulfate	0.50	25	30-150
P,P'-DDT	0.50	25	30-150
Endrin Ketone	0.50	25	30-150
Methoxychlor	0.50	25	30-150
Alpha-Chlordane			
Gamma-Chlordane			
Chlordane, Technical			
Toxaphene			
Aroclor 1016	20	25	30-150
Aroclor 1260	20	25	30-150
Aroclors 1221, 1232, 1242, 1248, 1254			

18.6 Other

The laboratory will analyze standard reference materials and participate in relevant performance evaluation studies quarterly.

19 CORRECTIVE ACTIONS FOR OUT-OF-CONTROL DATA

The process for handling unacceptable and out of control data is found in SOP 230 Corrective Action.

If the CCV, MB,LCS/LCSD, MS/MSD, lab duplicate, surrogate, or [some other QC sample] recovery of any parameter falls outside the designated acceptance range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the samples is suspect and is only reported for regulatory compliance purposes with the appropriate corrective action form. Immediate corrective action includes reanalyzing all affected samples by using any retained sample before the expiration of the holding time. Final data results must be qualified in the client report for reported results not meeting the laboratory defined criteria.

1) Review standards preparation logbooks. Check all calculations and ensure dilution factors are properly recorded.
2) Re-prepare the suspected standard or QC sample to identify possible preparation errors of the standard or QC sample.
3) Re-Analyze the samples when the CCV or LCS are not within acceptable limits.
4) Perform routine preventative maintenance following manufacturer's specification. Record all maintenance in the instrument logbook.

20 CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

Every effort is made to prevent problems from occurring. When out of control or unacceptable data occurs the first option is to identify the problem and reanalyze the samples within the holding times. When this is not possible, the QA Manager and/or the Laboratory Director reviews data and discusses options with the client. Reanalysis or reporting the data with qualification are alternatives. Out of control or unacceptable data reported to the client must include the data qualifier, flag and discussion on the rationale for reporting.

Holding time exceedence, improper preservation and improper sample condition or storage are noted on the corrective action form and included on the final report.

Review the CCV standard response, LCS result, and surrogate recovery for acceptable performance for each batch of samples. Record any trends or unusual performance on a corrective action form. Final data results must be qualified in the client report for results not meeting the laboratory defined criteria.

Manual integration must be minimized for standards, reagent blanks and surrogates. Routine manual integration of the same parameters indicates a system performance problem. Correct this problem or note in the instrument analysis logbook the suspected causes for routine manual integration. Sign and date all manually integrated chromatograms.

20.1 The process for handling unacceptable and out of control data is found in the Laboratory QAM Section 11. The reporting of data that is out of control must be approved and documented by Quality Assurance Manager and either the Technical Manager or the Laboratory Director.

20.2 Client Requested Modifications:

20.2.1 Clients must request modifications from the laboratory SOP in writing to the lab.

20.2.2 The lab director, technical manager and quality assurance manager will evaluate the requested client deviations, determine the feasibly of the deviation and the potential effects on the data.

20.2.3 If it is determined that the lab will perform the requested deviations, lab director, technical manager and quality assurance manager will decide if a method validation study is required.

20.2.4 The designated project manager will retain all documentation concerning the requested deviation, including all correspondence with the client, in the client folder.

20.2.5 The final analytical report must include the statement "*This report has analyses performed using client requested modifications*".

21 WASTE MANAGEMENT

The STAT Analysis Corporation Waste Disposal SOP 1130 identifies proper waste management practices for the chemicals and biological materials used in this procedure. Samples are stored and discarded accordance with SOP 1130 Waste Disposal.

22 REFERENCES

22.1 Method 8081A and 8082, Revision 3, December 1996; U.S. EPA SW-846 "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods" Update III, December 1996
22.2 STAT SOPs for sample prep: 3030, 3040, 3210, 3050
22.3 STAT Extract Cleanup SOPs: 3060, 3330
22.4 STAT SOPs: 4050, 1210 [support equipment, recordkeeping, MDLs, etc]
22.5 SOP 230 Corrective Actions
22.6 SOP 1010 Standard and Reagent Preparation
22.7 SOP 1400 LIMS
22.8 SOP 1130 Waste Disposal
22.9 SOP 003 Chemical Hygiene Plan
22.10 SOP 1250 Data Review

22.11 Manufacturers' Equipment Instruction Manuals
22.12 SOP 1255 Manual Integration
22.13 SW-846 8000B Determinative Chromatographic Separations
22.14 SOP 1230 Training
22.15 "USEPA Contract Laboratory Program Statement of Work for Organic Analysis" Revision OLM04.2 May 1999, U. S. Environmental Protection Agency. Office of Solid Waste, Washington DC 20460.

23 FORMS, FIGURES, TABLES, DIAGRAMS, FLOWCHARTS, ATTACHMENTS OR VALIDATION DATA

Attachment 1: MDLs and Reporting Limits
Attachment 2: Retention Times
Attachment 3: Procedure for Establishing Retention Time Windows

ATTACHMENT 1: MDLs and Reporting Limits

MDLs and REPORTING LIMITS for SEMIVOLATILE COMPOUNDS (Attachment 1)

CASN	Compounds	MDL (µg/L)	RL (µg/L)	RL (mg/L)	MDL (µg/Kg)	RL (µg/Kg)	RL (mg/Kg)
309-00-2	Aldrin	0.020	0.050	0.00005	0.002	0.008	0.000008
319-84-6	Alpha-BHC	0.020	0.050	0.00005	0.002	0.008	0.000008
319-85-7	Beta-BHC	0.020	0.050	0.00005	0.002	0.008	0.000008
319-86-8	Delta-BHC	0.020	0.050	0.00005	0.002	0.008	0.000008

58-89-9	Gamma-BHC (Lindane)	0.020	0.050	0.00005	0.002	0.008	0.000008
72-55-9	P,P'-DDE	0.020	0.100	0.0001	0.002	0.008	0.000008
72-54-8	P,P'-DDD	0.040	0.100	0.0001	0.002	0.008	0.000008
50-29-3	P,P'-DDT	0.020	0.100	0.0001	0.002	0.008	0.000008
60-57-1	Dieldrin	0.010	0.100	0.0001	0.002	0.016	0.000016
959-98-8	Endosulfan I	0.010	0.050	0.00005	0.002	0.008	0.000008
33212-65-9	Endosulfan II	0.010	0.100	0.0001	0.002	0.016	0.000016
1031-07-8	Endosulfan Sulfate	0.100	0.100	0.0001	0.002	0.016	0.000016
72-20-8	Endrin	0.010	0.100	0.0001	0.002	0.016	0.000016
7421-93-4	Endrin Aldehyde	0.050	0.100	0.0001	0.002	0.016	0.000016
53494-70-5	Endrin Ketone	0.030	0.100	0.0001	0.002	0.016	0.000016
76-44-8	Heptachlor	0.030	0.050	0.00005	0.002	0.008	0.000008
1024-57-3	Heptachlor Epoxide	0.010	0.050	0.00005	0.002	0.008	0.000008
72-43-5	Methoxychlor	0.020	0.500	0.0005	0.002	0.080	0.00008
5103-71-9	Alpha-Chlordane	0.025	0.500	0.0005	0.002	0.008	0.000008
5103-74-2	Gamma-Chlordane	0.025	0.500	0.0005	0.002	0.008	0.000008
57-74-9	Chlordane, Technical	0.025	0.500	0.0005	0.002	0.080	0.00008
8001-35-2	Toxaphene	1.000	1.000	0.001	0.002	0.160	0.00016
12674-11-2	Aroclor 1016	0.100	0.500	0.0005	0.010	0.080	0.00008
11104-28-2	Aroclor 1221	0.100	1.0	0.0005	0.010	0.160	0.00008
11141-16-5	Aroclor 1232	0.100	0.500	0.0005	0.010	0.080	0.00008
53469-21-9	Aroclor 1242	0.100	0.500	0.0005	0.010	0.080	0.00008
12672-29-6	Aroclor 1248	0.100	0.500	0.0005	0.010	0.080	0.000008
11097-69-1	Aroclor 1254	0.100	0.500	0.001	0.010	0.080	0.00016
11096-82-5	Aroclor 1260	0.100	0.500	0.001	0.010	0.080	0.00016

ATTACHMENT 2: Retention Times

RETENTION TIMES for SINGLE RESPONSE COMPOUNDS

#	Compounds	Retention Time (min.) Column 1	Retention Time (min.) Column 2
1	TCMX (surrogate)	7.89	6.37
2	Alpha-BHC	9.26	7.68
3	Gamma-BHC (Lindane)	9.89	8.37
4	Beta-BHC	10.02	8.56
5	Delta-BHC	10.47	8.88
6	Heptachlor	10.56	9.22
7	Aldrin	11.01	9.69
8	Heptachlor Epoxide	11.71	10.55
9	Gamma-Chlordane	11.93	10.71
10	Alpha-Chlordane	12.09	10.87
11	Endosulfan I	12.16	11.03
12	P,P'-DDE	12.25	10.99
13	Dieldrin	12.46	11.31
14	Endrin	12.78	11.57
15	P,P'-DDD	12.84	11.65
16	Endosulfan II	12.99	11.82
17	P,P'-DDT	13.15	11.94
18	Endrin Aldehyde	13.31	12.26
19	Methoxychlor	13.78	12.43
20	Endosulfan Sulfate	13.58	12.69
21	Endrin Ketone	14.15	12.96
22	DCB (surrogate)	15.62	13.87

ATTACHMENT 3:

PROCEDURE for ESTABLISHING RETENTION TIME WINDOWS
EPA METHOD 8000B SECTION 7.6 (Attachment 3)

7.6 Retention time windows are crucial to the identification of target compounds. Retention time windows are established to compensate for minor shifts in absolute retention times as a result of sample loadings and normal chromatographic variability. The width of the retention time window should be carefully established to minimize the occurrence of both false positive and false negative results. Tight retention time windows may result in false negatives and/or may cause unnecessary reanalysis of samples when surrogates or spiked compounds are erroneously not identified. Overly wide retention time windows may result in false positive results that cannot be confirmed upon further analysis.

7.6.1 Before establishing retention time windows, make sure that the chromatographic system is operating reliably and that the system conditions have been optimized for the target analytes and surrogates in the sample matrix to be analyzed. Make three injections of all single component standard mixtures and multi-component analytes (such as PCBs) over the course of a 72-hour period. Serial injections or injections over a period of less than 72 hours may result in retention time windows that are too tight.

7.6.2 Record the retention time for each single component analyte and surrogate to three decimal places (e.g., 0.007). Calculate the mean and standard deviation of the three absolute retention times for each single component analyte and surrogate. For multi-component analytes, choose three to five major peaks (see the determinative methods for more details) and calculate the mean and standard deviation of those peaks.

7.6.3 If the standard deviation of the retention times for a target compound is 0.000 (i.e., no difference between the absolute retention times), then the laboratory may either collect data from additional injections of standards or use a default standard deviation of 0.01 minutes. (Recording retention times to three decimal places rather than only two should minimize the instances in which the standard deviation is calculated as 0.000).

7.6.4 The width of the retention time window for each analyte, surrogate, and major constituent in multi-component analytes is defined as ± 3 times the standard deviation of the mean absolute retention time established during the 72-hour period. If the default standard deviation in Sec. 7.6.3 is employed, the width of the window will be 0.03 minutes.

7.6.5 Establish the center of the retention time window for each analyte and surrogate by using the absolute retention time for each analyte and surrogate from the calibration verification standard at the beginning of the analytical shift. For samples run during the same shift as an initial calibration, use the retention time of the mid-point standard of the initial calibration.

7.6.6 The laboratory must calculate absolute retention time windows for each analyte and surrogate on each chromatographic column and instrument. New retention time windows must be established when a new GC column is installed. The retention time windows should be reported with the analysis results in support of the identifications made.

7.6.7 If the instrument data system is not capable of employing compound-specific retention time windows, then the analyst may choose the widest window and apply it to all compounds. As noted above, other approaches may also be employed, but must be documented by the analyst.

7.6.8 The surrogates are added to each sample, blank, and QC sample and are also contained in each calibration standard. Although the surrogates may be diluted out of certain sample extracts, their retention times in the calibration standards may be useful in tracking retention time shifts. Whenever the observed retention time of a surrogate is outside of the established retention time window, the analyst is advised to determine the cause and correct the problem before continuing analyses.

STAT Analysis Corporation:

STANDARD OPERATING PROCEDURE 4080

CHLOROPHENOXY HERBICIDES BY HPLC (EPA Method 8321A)

Revision 00
Effective Date: August 16, 2004

Author: Jeremiah Favero

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This Standard Operating Procedure has been prepared for the sole use of STAT Analysis Corporation.

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1.0 IDENTIFICATION OF TEST METHOD

SOP Title: Chlorophenoxy Herbicides by HPLC (EPA Method 8321A).

2.0 APPLICABLE MATRICES

Methylene chloride, ether and organic solvent extracts from soil, sediment, ground and surface water, and mobility extracts are analyzed using this method.

3.0 DETECTION LIMITS

The lab follows the procedure found in 40CFR Part 136B to determine the MDL for each matrix type on an annual basis. See the STAT Analysis SOP 1210 Method Detection Limits for the MDL procedure, frequency and acceptance criteria. The MDL's measured by the lab and all supporting documentation are in the laboratory QA files for review.

The laboratory determined MDL must always be less than the reporting limit (RL), which may be determined by the lowest calibration standard. The RL's will usually range from three to ten times the laboratory measured MDL's but this relationship may vary depending upon dilution of sample aliquots, matrix interferences, moisture adjustments (in solid samples), or method-specified requirements. Attachment 1 contains the current MDLs and reporting limits (RL's) for this SOP.

4.0 SCOPE AND APPLICATION

4.1 This standard operating procedure describes in detail the precise methods used at STAT Analysis Corporation for the analysis of environmental samples for Chlorophenoxy Herbicides by HPLC. This SOP as written is to be applied when SW-846 Method 8321A is requested. This SOP is used to determine the concentration of herbicides in extracts prepared from all types of solid waste matrices, soils, and ground water.

4.2 This SOP can be used to quantitate herbicides that are soluble in methylene chloride, ether and other organic solvents and are capable of being eluted without derivatization as sharp peaks from a liquid chromatographic column. See Attachment 1 for a list of compounds that have been evaluated on the specified HPLC system.

4.3 The reporting limits (RL's) for this SOP are shown in Attachment 1 for soils and water. RL's will be proportionately higher for sample extracts and samples that require dilution or reduced sample size to avoid saturation of the detector.

4.4 This method is restricted to use by or under the supervision of analysts experienced in the use of a High Performance Liquid Chromatograph (HPLC) and skilled in the interpretation of chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

5.0 SUMMARY OF TEST METHOD

5.1 Prior to using this method, the samples must be prepared for the HPLC using the appropriate sample preparation and cleanup SOPs (Section 14.1). Solid samples are extracted at acidic pH with methylene chloride. Aqueous samples are extracted at acidic pH with ether. This method describes chromatographic conditions that will allow for the separation of the compounds in the extract and for their qualitative and quantitative analysis by high performance liquid chromatography. Identification of target analytes is accomplished by comparing component retention times to those of authentic standards. Quantitation is accomplished by comparing the response of the peak area using a five-point calibration curve.

5.2 **Method Modifications from Reference** – A daily Continuing Calibration Verification (CCV) must be analyzed on the same day as analysis of samples. EPA Method 8321A requires that a calibration curve be generated on the same day as analysis. This SOP is based on EPA Method 8321A except that only the chlorinated phenoxyacid compounds are reported. This lab does not report the other compounds.

6.0 DEFINITIONS

The STAT Analysis Quality Manual Section 19.0 contains all the definitions of standard terms used in SOPs.

7.0 INTERFERENCES

7.1 Raw HPLC data from all blanks, samples, and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation and/or cleanup of the samples and take corrective action to eliminate the problem.

7.2 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed out between samples with solvent. Whenever an unusually concentrated sample is encountered, the sample after it must be reanalyzed to check for cross contamination.

8.0 SAFETY

Methylene chloride is a suspected carcinogen as are numerous compounds analyzed by this method. Ether is extremely flammable and an anesthetic. Only use ether in a properly functioning fume hood. Proper personal protective equipment including safety glasses, nitrile gloves and a lab coat are required during different parts of this method. Other safety precautions must be conducted in accordance with the SOP 003 Chemical Hygiene Plan. Other actions can also be applied if deemed necessary. A reference file of Material Safety Data Sheets (MSDS) is available to all personnel involved in this method.

9.0 EQUIPMENT AND SUPPLIES

The following apparatus is recommended for performing this procedure. Equivalent items can be used, if with their use, the analytical and QA/QC requirements in this SOP can be met. All catalog numbers in this SOP are current as of the effective date and thereafter subject to change.

9.1 High Performance Liquid Chromatography System

9.1.1 Liquid Chromatograph(LC) – Agilent 1100 with a Vacuum Degasser (G1322A), Quarternary Pump (G1311A), Autosampler (G1313A), Fluorescence Detector (G1321A), Variable Wavelength Detector (G1314A) and a Column Heater (G1316A)

9.1.2 Column – 50m x 4.6mm, 3 µm particle size, (Restek Ultra Aqueous C18, Cat# 9178355)

9.1.3 Data system - An Agilent Kayak computer system using Chemstation for LC Version A.09.03 [1417] to collect data is attached to the LC. An Agilent Kayak computer system using ChemStation version C.00.00 is used to quantitate the data.

9.2 Micro syringes - 10 µL, 25 µL, 100 µL, 250 µL, 500 µL and 1,000 µL.

9.3 Volumetric flasks, Class A - 10 mL, 25 mL, 50 mL with ground glass stoppers.

9.4 Glass vials - 2-mL, for GC auto sampler with Teflon-lined screw caps or crimp tops.

9.5 Amber glass vials - 10 mL with Teflon-lined screw caps

10.0 REAGENTS AND STANDARDS

The following reagents and standards are required to perform this procedure. When instructions are given on how to prepare a specific volume of a reagent or standard, larger or smaller volumes can be prepared as needed so long as the final concentrations remain the same. Any other deviations from the reagents or standards listed in this SOP could be detrimental to the quality of the data produced. Such deviations would have to be approved and documented (see SOP QA 230 Corrective Action). Equivalent items can be used, if with their use, the analytical and QA/QC requirements in this SOP can be met.

Instructions for labeling and record keeping of reagents and standards are contained in SOP 1010 Analytical Standards and Reagents Receipt and Preparation.

10.1 Analytical reagent grade chemicals shall be used in all tests. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.

10.2 Standards

10.2.1 At least one of the standards must be traceable to a NIST traceable source when available. The manufacturer should include a certificate of analysis for each standard. If one is not provided, contact the manufacturer. Retain all certificates in the designated binder (see SOP 1010 Analytical Standards and Reagents Receipt and Preparation).

10.2.2 Standards must be prepared volumetrically using class-A volumetric glassware, calibrated micropipettes, or gas tight syringes. Do not use disposable pipettes to prepare standards.

10.2.3 The use of alternative standards will be allowed as long as the analytical and quality objectives of this SOP can be met.

10.3 Organic-free reagent water - All references to water in this SOP refers to Type II reagent water (in-house system).

10.4 Mobile Phase – Phosphoric Acid solution 0.05%. Prepare by adding 50 mL of 10% Phosphoric Acid (VWR Catalog # VW-3346-1) to a 1000 ml volumetric flask. Dilute to volume with reagent water. Store at room temperature.

10.5 Stock Standard solutions - Standard solutions can be prepared from pure standard materials or purchased as certified solutions (e.g. SV standards). The routine laboratory practice is to purchase these standards from approved vendors. The standards used are: Chlorinated Acids by HPLC, Mix A (Restek Catalog # 32431), Chlorinated Acids by HPLC, Mix B (Restek Catalog # 32430), Herbicide Mix #2 (Restek Catalog # 32056) and Herbicide Surrogate Mix (Restek Catalog # 32049). Stock standard solutions and QC solutions are stored at < -10°C and must be replaced after six months, or sooner if comparison with quality control check samples indicates a problem. Different storage conditions and expiration dates of other solutions are noted as warranted.

10.5.1 Secondary Stock Standard Solution – This solution is made using the individual Stock Standard solutions. Using microliter syringes, the following amounts of each Stock Standard solution is injected into a 10 mL volumetric flask. The solution is brought to volume with acetonitrile. The final concentration of each component is listed in Table 1.
Note: this Secondary Stock Standard solution is also used as the high-level calibration standard. It is also the source solution to prepare the calibration standards in Section 10.6. This standard is stored at < -10°C in a 10 mL amber screw cap vial equipped with a Teflon lined cap. It is freshly prepared every six months, or sooner if check standards indicate a problem.

Table 1 Secondary Stock Standard Solution

Stock Solution	Conc. Stock (µg/ml)	Vol. Stock (µL)	Final Conc. (µg/ml)
Chlorinated Acids, Mix A	1000	100	10
Chlorinated Acids, Mix B	1000	100	10
Herbicide Mix #2, Dalapon	2000	500	100
Herbicide Surrogate Mix	200	500	10

10.6 Calibration standards - A minimum of five calibration standards are prepared. The low standard is the RL and above the MDL. The others define the working range of the LC system. Calibration standards in current use: 0.1, 0.5, 1.0, 5.0, 7.5 and 10.0 µg/ml. (Table 2). Using microliter syringes, the following amount of the Secondary Stock solution is injected into a 1 ml syringe. The solution is brought to volume with methanol. The final concentration of each component is listed in Table 2. Each solution is transferred to an autosampler vial. Storage is as indicated in 10.5.1. The continuing calibration verification standards (CCV) are prepared weekly and stored at 4°C. Levels 2, 3 and 4 (0.5, 1.0, 5.0 µg/mL) are used for the CCVs.

Table 2 Calibration Standards

Level	Volume (µL) Secondary Stock	Volume (µL) Acetonitrile	Final Concentration (µg/ml)
1	10	990	0.1 (1.0)
2	50	950	0.5 (5.0)
3	100	900	1.0 (10.0)
4	500	500	5.0 (50.0)
5	750	250	7.5 (75.0)
6	1000	----	10.0 (100.0)

( ) Concentration of Dalapon

10.7 Laboratory Control Sample/Matrix Spike standards - The LCS/matrix spike compounds listed in Table 3. Samples will be spiked at 1.0 ug/sample, 0.033 mg/Kg for soil and 0.001 mg/L for water (see SOP 3500 for LCS/Matrix Spike Solution preparation). This standard is stored at < -10°C in an amber glass vial with a Teflon lined screw cap.

Table 3. ICV Secondary Stock (LCS/MS/MSD)Standard Solution

Compound	Conc. Stock (µg/ml)	Vol. Stock (µL)	Final Conc. (µg/ml)
2,4-D	100	100	1.0
2,4-DB acid	100	100	1.0
Dalapon	1000	100	10.0
Dicamba	100	100	1.0
Dichlorprop	100	100	1.0
Dinoseb	100	100	1.0
MCPA	100	100	1.0
MCPP	100	100	1.0
Pentachlorophenol	100	100	1.0
Picloram	100	100	1.0
2,4,5-T	100	100	1.0
2,4,5-TP (Silvex)	100	100	1.0

10.8 Surrogate Standard – The surrogate standard is 2,4-dichlorophenyl acetic acid. Surrogate stock solution is purchased from AccuStandard (Cat. No. 5-ACES-8150B-SS, store at room temp until dilution is prepared). The spike solution is prepared by diluting 1000 µL of the stock standard into a 100mL volumetric flask. The flask is diluted to the mark with acetone for a final concentration of 1.0 µg/mL. All samples, blanks, LCS's, and MS/MSDs are spiked with 1.0 mL of the surrogate spike solution prior to extraction. This standard is stored at < -10°C in an amber glass vial with a Teflon lined screw cap.

10.9 Initial Calibration Verification Standard – A standard prepared from a different source at the midpoint of the calibration to verify the initial calibration. The solution is made using the custom ICV Stock Standard solution (Supelco Catalog # 20481237). Using microliter syringes, 100 µl of Stock Standard solution is injected into a 10 mL volumetric flask. The solution is brought to volume with acetonitrile. The final concentration of each component is listed in Table 3. This standard is stored at < -10°C.

10.10 Acetone, hexane, acetonitrile, methanol, diethyl ether and other appropriate solvents, pesticide quality or equivalent.

11.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

11.1 Containers used to collect samples for the determination of herbicides are glass: 1 Liter bottles for water samples and various sizes of jars for soil samples. They are equipped with screw caps with Teflon liners. Water samples containing residual chlorine should be field treated to remove the chlorine prior to collection. Plastic containers or lids may NOT be used for the storage of samples due to the possibility of sample contamination from the phthalate esters and other hydrocarbons within the plastic.

11.2 Samples must be stored under refrigeration at between 0.1 and 6.0°C. Extraction must be within 7 days from sampling date for water and 14 days for solids. Sample extracts are stored in the dark at between 0.1 and 6.0°C and must be analyzed within 40 days of extraction.

11.3 No chemical preservation is required for this method.

11.4 All samples are stored away from all standards, reagents, food, and other potentially contaminating sources in order to prevent cross contamination.

12.0 QUALITY CONTROL

The following details the QC requirements that apply to this analysis. Each Quality Control Indicator (QCI) provides information pertaining to either method or individual sample performance. Our goal is to produce defensible data of known and documented quality. The results of these Quality Control Indicator samples are used to assess the acceptability of data.

12.1 Blanks

Method Blank analysis is performed to determine if any contamination is present in the analytical process and is used to evaluate acceptance of the batch of samples. A method blank shall be prepared once per preparation batch of 20 or less samples per matrix type. If more than 20 samples are prepared a second blank shall be prepared after the twentieth sample. The method blank shall be processed through all preparatory steps used for the samples, including cleanup procedures. The blank shall be analyzed using the same instrument and conditions as the samples.

The Solvent Blank, clean acetonitrile injected into the HPLC, is used to monitor the HPLC system for potential cross-contamination from one sample to another or for residual contamination in the system.

12.2 Calibration Verification

An Initial Calibration Verification (ICV) standard containing all of the target analytes reported in this method (Attachment 1) shall be analyzed immediately after the completion of the initial calibration. The ICV shall be purchased from a second source to verify analyte concentrations.

12.3 Laboratory Control Sample (LCS)

The LCS is used to evaluate the performance of the total analytical system, including all preparation and analysis steps. The LCS shall be prepared once per preparation batch of 20 or less samples per matrix type. If more than 20 samples are prepared a second LCS shall be prepared after the twentieth sample. The LCS shall be processed through all preparatory steps used for the samples, including cleanup procedures. The LCS shall be analyzed using the same instrument and conditions as the samples. Refer to section 10.7 for LCS analytes and concentrations.

12.4 Surrogate

The surrogate used for this method is added to all samples, standards, and blanks. Refer to section 10.8 for preparation and concentration instructions.

12.5 Duplicates

Duplicates of field samples or of the LCS must be prepared in compliance with the method requirements and client directives. Duplicate LCS's are prepared for sample wipes. It would be impractical to prepare a matrix spike and matrix spike duplicate. Reproducibility performance would be the same as for a matrix spike/matrix spike duplicate.

12.6 Matrix Spike and Matrix Spike Duplicate (MS/MSD)

MS/MSD's indicate the effect of the sample matrix on the precision and accuracy of the results generated using the selected method. This information does not determine the validity of the entire batch. MS/MSDs must be analyzed at a minimum of 1 per 20 samples per matrix per preparation procedure, or one per preparation batch, or as specified by the required test method. For cases where the sample cannot be divided (e.g., wipes, air samples, not enough sample provided by customer) and thus a MS/MSD pair cannot be prepared in the preparation batch, an LCS/LCSD pair is prepared and analyzed to measure precision.

Samples chosen for matrix spiking are rotated among different clients and/or different client projects. This is accomplished through communication between the Department Manager and the analyst. In addition, designated samples, as indicated by client request or contract requirement, are matrix spiked. The MS/MSD pair shall be processed through all preparatory steps used for the samples. They shall be analyzed using the same instrument and conditions as the samples. Refer to section 10.7 for MS analytes and concentrations. Some clients may require different spiking levels and/or target analytes; these specific needs are documented on the request for analysis forms.

13.0 CALIBRATION AND STANDARDIZATION

13.1 Initial Calibration (ICAL)

13.1.1 Analyze 10 µL of each calibration standard and tabulate the area of the analyte against concentration for each compound. Calculate calibration factors (CF's) for each compound in each calibration standard as follows:

$$CF = \frac{A_x}{C_x}$$

where:

A_x = Area of the compound being measured.

C_x = Concentration of the compound being measured (ng/µL = µg/mL = mg/L).

13.1.2 Calculate the average response factor ($\overline{CF}$) for each compound as follows:

$$\overline{CF} = (\Sigma\ CF_1 \text{ to } CF_n)/n$$

where: CF = CF for each of the calibration levels (i.e., 6)

n = Number of RF values (i.e., 6)

13.1.3 Calibration Check Compound (CCC) responses are monitored to check the integrity of the system. The CCCs are all compounds reported by this method. Refer to Attachment 1 for a complete compound list.

Using the CF's from the initial calibration, calculate the percent relative standard deviation (%RSD) for the Calibration Check Compounds (CCC).

To calculate %RSD: $\%RSD = 100\% \times SD/\overline{CF}$

where:

%RSD = % Relative Standard Deviation

$\overline{CF}$ = average of initial CFs for a compound

SD = standard deviation (n-1) of average CFs for a compound

To calculate Standard Deviation (n-1 degrees of freedom)

$$SD = \sum_{i=1}^{N} \sqrt{\frac{(CF_i - \overline{CF})^2}{n-1}}$$

where: CF_i =CF for each of the 6 calibration levels

n = Number of RF values (i.e., 6)

13.1.4 Linearity - If the %RSD of any compound is 20% or less, then the relative response factor is assumed to be constant over the calibration range, and the average relative response factor is used for quantitation. If the %RSD is greater than 20%, use first order linear regression. The calibration curve must meet the requirements for curve fitting listed in SW-846 8000B and the correlation coefficient is ≥0.99. The equation is not forced through the origin.

13.1.5 Retention Times: The Retention Times (RT) of each compound in each calibration standard should be within ± 0.03 RT units.

13.1.6 Before sample analysis can begin, a Initial Calibration Verification (ICV) (see Sec. 10.9) must be performed. The ICV results must be within the acceptance criteria as established for the CCV compounds (Section 13.2).

NOTES:

1. All calibration curves must have a unique identifier. It is recommended that the calibration date be incorporated into the identifier for easy reference.
2. Calibration must be completed (all standard levels analyzed) within 24 hours or the entire calibration sequence must be repeated.
3. All initial calibration standards must be analyzed as a group. No field sample analyses are allowed during the calibration sequence.
4. Do not add calibration standards and update the curve after the original calibration date.
5. Multiple analyses of the same calibration level are not allowed to be included in the calibration curve.
6. Compound responses cannot be selected from different analyses of the same calibration level (i.e. all compound responses for level 1 must come from the same data file).
7. If more than five calibration levels are analyzed, it is permissible to either drop the low compound concentration (poor response) or the high compound concentration (detector saturation). It is not allowed to drop a point in the middle of the curve.
8. If more than five calibration levels are analyzed, it is permissible to drop an entire level if the analyst can document a specific reason or reasons why that level should be excluded. Mechanical failures, significant loss of all analyte responses possibly due to poor technique in standard preparation, or software malfunction during data acquisition (system did not acquire all compound data) are plausible reasons. The reason must be justified and documented. The supervisor should review this situation and approve the analyst's decision.
9. The need to analyze more than two analyses of the same calibration level indicates a potential problem with the secondary stock solution. Prepare a fresh secondary stock solution and repeat all calibration levels. It is recommended that all calibration standard levels come from the same secondary stock solution.
10. Manual integration must only be used if the software fails to properly integrate the peak. If manual integration is used for a particular compound, all levels of that compound do not have to be manually integrated, but all levels must be integrated in a similar manner. Example: the computer generated integration of a compound in the low level standard is not technically sound. A manual integration of the compound is performed (due to baseline noise, etc) in order to achieve a technically sound integration. Other levels of the compound are integrated correctly by the computer. The manual integration of the low level must match, as best as possible, the computer generated integrations for all other levels.

11. If any compound in the mid-point level is manually integrated, the integration of this compound must be reviewed for every continuing calibration standard and QC check solution (i.e. LCS, and Matrix Spike) to ensure that the integration is the same as the manual integration performed in the initial calibration (ICAL) mid-point. A consistent manner of integration must be achieved.
12. All manual integrations must be reviewed and approved at the supervisory level.

13.2 Continuing Calibration Verification (CCV)

13.2.1 A continuing calibration verification (CCV) sample is analyzed before samples and after every 20 samples during analysis. Different standards are analyzed for the CCV such that a wider range of the calibration curve is verified. For example: on successive days analyze the 1 µg/mL, then the 5 µg/mL and on the third day, the 7.5 µg/mL standard solution. Compare the response factors of the with the following criteria:

13.2.1.1 Control limits for the CCC compounds are ± 20% difference from the ICAL Response Factor (RF) if the average RF is used for quantitation, or ± 20% drift from the true concentration of the CCV compound if linear regression is used.

13.2.1.2 If the CCV results obtained are outside the acceptance criteria, corrective actions must be performed. If routine corrective actions fail to produce an acceptable *second consecutive (immediate)* CCV, then either the lab has to demonstrate performance after corrective action with two consecutive successful CCVs, or a new ICAL must be performed. If the instrument has not demonstrated acceptable performance, sample analyses cannot continue until a new ICAL is established and verified with an ICV. However, sample data associated with an unacceptable CCV may be reported as qualified data under the following special conditions:

13.2.1.2.1 When the acceptance criteria for CCV are exceeded high, i.e., high bias, and there are associated samples that are non-detects, then those non-detects may be reported. Otherwise the samples affected by the unacceptable calibration verification must be reanalyzed after a new ICAL has been established, evaluated and accepted.

13.2.1.2.2 When the acceptance criteria for the CCV are exceeded low, i.e., low bias, those sample results may be reported if they exceed a maximum regulatory limit/decision level. Otherwise the samples affected by the unacceptable verification must be reanalyzed after a new ICAL is established and verified with an ICV.

13.2.1.2.3 When the acceptance criteria for the CCV are exceeded and it is not possible to reanalyze the sample due to limited sample quantity AND the laboratory cannot obtain a new sample, the data may be reported with the appropriate data qualifiers if the client has been contacted and agrees, in writing, to accept the qualified data.

13.3 Records:

Initial and Continuing Calibration Records will contain, at a minimum, the following:

1) Calibration date.
2) Test method.
3) Instrument.
4) Analysis date.
5) Each analyte name.
6) Analyst's initials or signature.
7) Standard Concentration (appropriate units) and number of standards.
8) Response (appropriate units).
9) Calibration curve or response factor.
10) Evaluation of and Statistics for ICAL curve fit in order to judge calibration curve acceptance.
11) Evaluation of and Acceptance Limits for ICV analysis in order to judge calibration curve acceptance.
12) Evaluation of and Acceptance Limits for CCV analysis in order to judge continuing calibration acceptance.

13.4 Thermometers

The thermometers in the sample refrigerators and the standards freezer must be checked daily. They must meet performance criteria.

14.0 PROCEDURE

14.1 Sample Preparation

14.1.1 Water, soil, sediment and waste samples must be prepared by SOP 3500 Extractions of Samples for Organic Analyses (EPA Methods 3510C, 3520C, 3550B, 3580A, 8151A) prior to HPLC analysis.

14.1.2 Direct Injection: In very limited applications direct injection of the sample into the HPLC system with a 10 µL syringe may be appropriate (see SOP 3500 for preparation). The reporting limit is very high (approximately 100 to 1000 mg/L); therefore, it is only applicable where concentrations in excess of 100 mg/L are expected.

14.1.3 Extract Preparation: Sample extracts should be at ambient temperature prior to use.

14.2 HPLC Analysis

14.2.1 Instrument Conditions: The recommended HPLC with Variable Wavelength Detector operating conditions:

Detector Wavelength:	225 nm
Sample volume:	10 µL
Column:	Ultra Aqueous C18, 150 x 4.0mm, 5 µm (Restek Catalog #
Guard Column:	Pelliguard LC-18 (Supelco Catalog # 59654)
Column Flow:	1.0 ml/minute
Column Temperature:	40 °C
Stop Time:	26.0 minutes

Solvents:

Solvent A:	Water
Solvent B:	Acetonitrile
Solvent C:	0.05% Phosphoric Acid
Solvent D:	Isopropanol

Gradient Program:

Time	% B (Acetonitrile)	% C (0.05% Phosphoric)
0	20	80
15	80	20
20	80	20
21	20	80

14.2.2 Access the computer and create a batch sequence file. Refer to section 14.3 for instructions.

14.2.3 Inject 10 µL of the Continuing Calibration Verification Standards (CCV) and evaluate using CCV acceptance criteria. See Section 13.2.

14.2.4 If all criteria are met, continue with sample analysis, injecting 10 µL of each extract, as outlined below.

DILUTION PROCEDURE

1. Clean a 1ml syringe equipped with a luer lock needle with rinse and clean solvent. (Acetonitrile) Fill syringe with clean solvent such that there is sufficient volume remaining for the dilution volume (see Table 4) and remove the needle. Place the needle on the counter top such that the tip of the syringe is elevated.

2. Clean an appropriate syringe (see Table 4) with rinse and clean solvent. Expel excess solvent by pumping plunger several times. Puncture the sample vial with the syringe needle and withdraw the sample into the syringe.

3. Remove the syringe from the sample vial and insert the needle into the barrel of the 1ml syringe. Inject the sample into the clean solvent. Hold the 1-ml syringe so that the tip is up and gently push up on the plunger to remove excess air from the barrel.

4. Replace the needle on the 1-ml syringe and add sufficient clean solvent to a final volume of 1 ml. Transfer the entire contents of the syringe into a labeled sample vial. Cap vial.

Table 4 STANDARD DILUTIONS

Dilution	Sample Volume mL	Total Volume µL
1:5	200	1000
1:10	100	1000
1:20	50	1000
1:50	20	1000
1:100	10	1000

14.2.5 Perform all qualitative and quantitative measurements as described in Sections 14.4 and 14.5. After analysis, store the extracts in the dark at 0.1- 6°C.

14.3 Analytical Sequence

START CHEMSTATION SOFTWARE:
From NT Desktop: Start/Programs/MSD ChemStation/Instrument #1/Instrument #1

The software will locate the instrument and all peripheral equipment. Once the software is fully loaded there will be one window visible. All instrument and sequence controls are accessed through this one window.

Check the solvent bottles on top of the instrument to ensure that there is sufficient solvent to last for the entire sequence. If necessary, fill bottles with appropriate solvent and adjust the bottle level in the software. In the Method and Run Control panel select Instrument/More Pump/Bottle Filling... and adjust the fill levels to the appropriate amount.

From Method and Run Control panel select Instrument/System On to start the pump and the detectors.

SEQUENCE SETUP
From menu: Sequence/Sequence Parameters
1. Set current date in Prefix and Subdirectory space (i.e., 060704)
2. OK (to save changes)

From menu: Sequence/Sequence Table
1. Set up sequence order using the following format: (**NOTE:** CCVs must always run first)

LOCATION	SAMPLE NAME	METHOD NAME	Inj./ Location	SAMPLE TYPE
Vial 1	BLANK ACN	HERB0330	1	SAMPLE
Vial 2	CCV HERB-A-1.0	HERB0330	1	SAMPLE
Vial 3	CCV HERB-B-1.0	HERB0330	1	SAMPLE
Vial 4	MB-9513-HERB	HERB0330	1	SAMPLE

Vial 5	LCS-9513-HERB	HERB0330	1	SAMPLE
Vial 6	0405123-001A	HERB0330	1	SAMPLE
...	...	...	...	...
Vial 18	0405123-012A	HERB0330	1	SAMPLE
Vial 1	BLANK ACN	HERB0330	1	SAMPLE
Vial 2	CCV HERB-A-1.0	HERB0330	1	SAMPLE
Vial 3	CCV HERB-B-1.0	HERB0330	1	SAMPLE

NOTE: The number of samples, including CCV's that can be analyzed within the 12-hour window varies with each analysis. Use this list as a guide but always check that the samples were analyzed within 12-hours of the first CCV injection.

2. OK (to save changes)
3. Save the sequence to the current subdirectory by selecting Sequence/Save Sequence As.../ and renaming the sequence to match the current subdirectory name (i.e., 060704.s).
4. Save the method to the current subdirectory by selecting Sequence/Save Method As.../ and saving the method to the current subdirectory.

TO START SEQUENCE:
From Method and Run Control panel click on the "START →" button.

Start of the 12 hour sequence (as documented as the date/time stamp on the data file for the CCV Standard):

The analytical sequence for Initial Calibration is:

Blank (Solvent Blank)
Calibration standard-A (S1)
Calibration standard-A (S2)
Calibration standard-A (S3)
Calibration standard-A (S4)
Calibration standard-A (S5)
Calibration standard-A (S6) optional
Calibration standard-A (S7) optional
Calibration standard-B (S1)
Calibration standard-B (S2)
Calibration standard-B (S3)
Calibration standard-B (S4)
Calibration standard-B (S5)
Calibration standard-B (S6) optional
Calibration standard-B (S7) optional
Initial Calibration Verification Standard (ICV)

The analytical sequence for Sample Analysis is:

Blank (Solvent Blank)
Continuing Calibration Verification Standard-A (CCV-A)
Continuing Calibration Verification Standard-B (CCV-B)
Method Blank (MB)
LCS
LCS Duplicate (if applicable)
Sample #1
Sample #1 Matrix Spike (MS)
Sample #1 Matrix Spike Duplicate (MSD)
Sample #1 Laboratory Duplicate (if applicable)
Samples #2, #3, etc. until the end of 12-hour period
Blank (Solvent Blank)
Continuing Calibration Verification Standard-A (CCV-A)
Continuing Calibration Verification Standard-B (CCV-B)
Samples up to #20
Method Blank (MB) #2
LCS #2
LCSD #2 (if applicable)
Sample #21
Sample #21 Matrix Spike (MS)
Sample #21 Matrix Spike Duplicate (MSD)
Sample #21 Laboratory Duplicate (if applicable)
Samples #22, #23, etc. until the end of 12-hour period

14.4 Interpretation - Qualitative Analysis

14.4.1 An analyte is identified based upon the Retention Time (RT) of a standard of the suspected compound.

14.4.2 The RT of the sample component is within ± 0.06 RT units of the RT of the standard component.

14.4.3 Identification is hampered when sample components are not resolved chromatographically or coelute. When chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), use SOP 1255 Manual Integration for guidance in the integration of these two peaks. Use SOP 1255 Manual Integration for other situations that may require analyst efforts to correct computer generated integrations that are not technically sound.

14.4.4 Several sets of compounds coelute on this analytical column. The following pairs of compounds coelute:

Bentazon and 2,4-Dichlorophenylacetic acid (surrogate)
2,4-D and MCPA
Dichlorprop and MCPP

Perform the following steps to help identify the correct peak during analysis:

14.4.4.1 The surrogate is present in every sample analyzed. The peak is assumed to be 2,4-Dichlorophenylacetic acid unless there is an enhanced response as in the case of the analysis of an LCS/LCSD or MS/MSD when Bentazon has been spiked in the sample.

14.4.4.1 If there is a peak for 2,4-D and MCPA assume that the peak is 2,4-D and not MCPA. In an LCS/LCSD and an MS/MSD both peaks are present.

14.4.4.1 If there is a peak for Dichloroprop and MCPP the analyst will use best judgement to determine the identification of the peak. Confer with the Project Manager to determine which compounds are suspected. In an LCS/LCSD and an MS/MSD both peaks are present.

14.5 Data Interpretation - Quantitative Analysis

14.5.1 Once a compound has been identified, the quantitation of that compound must be based on the integrated abundance.

14.5.2 If the RSD of a compound's response factor is 20% or less, then the concentration in the extract is determined using the average calibration factor (CF) from initial calibration data (13.2). See Method 8000, Sec. 7.0, for the equations describing internal standard calibration and either linear or non-linear calibrations. If the RSD is greater than 20%, refer to section 15.1.2.

14.6 Logbook Records

Record the following information in the appropriate logbook or data file. Include any deviations from this procedure. Analyst initials, date of analysis, sample number or ID, initial sample volume or weight processed, final extract volume, calibration standard sample or solution identifier, QC sample or solution identifier, surrogate solution identifier, any dilution information, readings from support equipment, data file name, instrument method name, visual observations, and any other information as deemed necessary.

14.7 Troubleshooting

The experience of the analyst performing HPLC analyses is invaluable to the success of the methods. Each day that the analysis is performed, the daily calibration standards (CCV-A and CCV-B) must be evaluated to determine if the chromatographic system is operating properly. Questions that must be asked: Do the peaks look normal? Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still good, if there is a leak, the inline filter needs replacing, etc. If any major changes are made to the system (e.g. column changed or detector cleaned), recalibration of the system must take place.

14.8 Routine Maintenance - Record all maintenance

14.8.1 Daily, or as needed according to sample throughput, change the inline filters and/or rinse the column. Alternatively, the use of a guard column helps to protect the analytical column from residue buildup. Replacing the guard column may be done to improve column performance.

14.8.2 Clean the detector windows on an as needed basis (loss of sensitivity).

14.8.3 Inspect the autosampler syringe for wear; replace as necessary.

14.8.4 Check the solvent supply; replace as necessary.

15.0 DATA REDUCTIONS, CALCULATIONS, AND LOADING

15.1 The data system performs the calculations.

15.1.1 If the %RSD of a compound's relative response factor is 15% or less, then the concentration in the extract may be determined using the average response factor (RF) from the initial calibration data (13.2) and the following equation:

$$C_{ex}(mg/L) = \frac{A_x \times C_{is}}{A_{is} \times CF}$$

where C_{ex} is the concentration of the compound in the extract, and the other terms are defined in Sec. 13.2.

15.1.2 Alternatively, linear regression (Sec. 13.2) may be used for determination of the extract concentration.

15.2 Compute the concentration of the analyte in the sample using the equations in Secs. 15.2.1 and 15.2.2.

15.2.1 The concentration of the analyte in the liquid samples is calculated using the concentration of the analyte in the extract and the volume of liquid extracted, as follows:

$$\text{Concentration in liquid (mg/L)} = \frac{C_{ex} * V_f}{V_i}$$

or

$$\text{Concentration in liquid } (\mu g/L) = \frac{C_{ex} * V_f * 1000}{V_i}$$

where:
V_f = final extract volume in mL (includes any dilution volumes)
V_i = initial volume of liquid extracted, in mL.

15.2.2 The concentration of the analyte in the solid sample is calculated using the concentration of the analyte in the extract and the weight of the solid extracted, as follows:

$$\text{Concentration in solid (mg/Kg)} = \frac{C_{ex} * V_f}{W_i}$$

or

$$\text{Concentration in solid } (\mu g/Kg) = \frac{C_{ex} * V_f * 1000}{W_i}$$

where:
V_f = final extract volume in mL (includes any dilution volumes)
W_i = initial sample weight, in g.

For soil samples reported on dry weight basis, divide the Concentration by the decimal equivalent of the Percent Solids. For example: a sample contains 90% solids, thus

$$\text{Concentration in solid (mg/Kg) dry weight} = \frac{C_{ex} * V_f}{W_i * 0.90}$$

15.3 See Section 14.10 of STAT SOP 1040 General Laboratory Practices for calculations.

16.0 METHOD PERFORMANCE

Demonstration of Capability (DOC)
All parameters of interest must meet the method acceptance criteria before actual sample analysis begins. See SOP 1230 Training for the procedure to perform and document the DOC. The DOCs for the analysts performing this method are located in the analysts' training form folders located in the QA office files.

A quality control (QC) reference concentrate is required containing each analyte at a concentration of 1 µg/mL in acetone. The QC reference sample used is the Herbicides ICV (refer to Section 10.9 for composition). The QC reference sample is made using stock standards prepared independently from those used for calibration.

For each analyte calculate the mean recovery (x) and standard deviation (s) and the average % Recovery (%R). Compare X and s and %R with the corresponding acceptance criteria for accuracy and precision, respectively. Note: x must be within 0.5 and 1.5 µg/mL and s must be less than 0.25 µg/L and %R must be within 50 to 150%. If x and s and %R for all analytes meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual x or %R falls outside the range for accuracy or any individual s exceeds the precision limit, then the system performance is unacceptable for that analyte and corrective action must be taken.

Locate and correct the source of the problem and repeat the test only for those analytes that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest.

Comparison to Reference Method Data
EPA Method 8000B provides guidance for the establishment of control limits for the LCS and MS QC samples. Recovery limits of 70% to 130% are provided as initial benchmarks for performance (8000B Section 8.5.4). These limits are designed for a wide variety of organic test methods. Individual analyte performance may vary.

In-House Control Limits
Method performance data is on file in the laboratory QC department. Comparison of method performance data for the laboratory to the reference method criteria occurs when laboratory in-house acceptance limits are generated. In-house generated data is compared to the specifications of the reference method. If the in-house limits are within the specifications of the reference method, the control limits are updated in LIMS. If the in-house limits are not within specifications, an investigation is performed to determine the cause(s) of the problem and a corrective action is completed. The analysis may continue until enough data points are collected to regenerate new control limits. Any QC data generated outside of reference method limits during that time frame is flagged.

The laboratory maintains performance records to document the quality of data that is generated. Method accuracy for samples is assessed and records maintained. After the analysis of 20 laboratory control samples and surrogates, calculate the average percent recovery (R) and the standard deviation of the percent recovery (S).

Control limits for the method parameters are generated by the QC staff and distributed to the analysts via updates to the LIMS control charts. The control limits are calculated based on in-house performance data. At a minimum, these limits are reviewed annually.

17.0 POLLUTION PREVENTION

The preparation of excessive volumes of laboratory reagents and standards shall be avoided so that waste and potential for pollution are minimized. Samples, reagents and standards shall be disposed in compliance with the lab waste disposal program, SOP 1130 Waste Disposal. With the consent of the client, the samples may be returned to their origin for treatment.

Uncontaminated paper waste, glass and cans should be separated for recycling. Laboratory staff are required to protect the laboratory's and our clients' business information when disposing recycled paper or waste from the facility.

18.0 DATA ASSESSMENT AND CRITERIA FOR QUALITY CONTROL MEASURES

Data assessment includes review of: proper sample condition, preservation, and storage; analysis within holding time limitations; deviations from the SOP, evaluation of performance based or in-house control limits, reference method limits or project specific limits.

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a calibration verification standard is used to confirm the measurements were performed in an in-control mode of operation. The data review is conducted according to SOP 1250 Data Review.

18.1 Blanks

If the blank exceeds the RL (usually the lowest calibration standard or specifically defined in this test method SOP), the source of contamination must be investigated and corrective actions taken. The compound concentrations in the method blank of an extraction batch must be less than the RL's listed in Attachment 1. If this criteria is exceeded, re-analyze the method blank. If after re-analysis, the blank criteria is still exceeded, then the entire extraction batch must be re-extracted. Always refer to a client specific QAPP for additional guidance.

If the surrogate recovery is outside the QA limits as defined in this test method the source of the nonconformance must be investigated and corrective actions taken. If this criteria is exceeded, re-analyze the method blank. If after re-analysis, the blank criteria is still exceeded, then the entire extraction batch must be re-extracted. Always refer to a client specific QAPP for additional guidance.

Affected samples must be reprocessed and reanalyzed **or** Data must be appropriately qualified if:

1) The concentration of a targeted analyte in the blank is at or above the reporting limit as established by the SOP or by regulation, <u>AND</u> is greater than 1/10 of the amount measured in any sample.

2) The blank contamination otherwise affects the sample results as per the test method requirements or the individual project data quality objectives.

18.2 Laboratory Control Samples (LCS)

The results of the individual batch LCS are calculated in percent recovery (%R) and compared to established acceptance criteria from in house analyses. If the LCS is outside the acceptance criteria, see Table 5 for current acceptance criteria, the analytical system is "out-of-control." Any affected samples associated with an out-of-control LCS must be reprocessed and reanalyzed or the results reported with appropriate data qualifiers. If after re-analysis the control criteria has not been met, the entire extraction batch must be re-extracted. Always refer to a client specific QAPP for additional guidance.

Table 5 LCS

Compound	Soil Recovery %	Water Recovery %
2,4-D	50-150	50-150
2,4-DB acid	50-150	50-150
Dalapon	50-150	50-150
Dicamba	50-150	50-150
Dichlorprop	50-150	50-150
Dinoseb	50-150	50-150
MCPA	50-150	50-150
MCPP	50-150	50-150
Pentachlorophenol	50-150	50-150
Picloram	50-150	50-150
2,4,5-T	50-150	50-150
2,4,5-TP (Silvex)	50-150	50-150
Acifluorfen	50-150	50-150
Bentazon	50-150	50-150
Chloramben	50-150	50-150
3,5-Dichlorobenzoic Acid	50-150	50-150
4-Nitrophenol	50-150	50-150

18.3 Surrogates

18.3.1 The results of the individual Surrogate compounds are calculated in percent recovery (%R). Surrogates outside the acceptance criteria, see Table 6 for current acceptance criteria, must be evaluated for the effect indicated for the individual sample results.

Table 6 Surrogate

Surrogate Compound	Soil % Recovery	Water % Recovery
2,4-Dichlorophenylacetic acid	50-150	50-150

If surrogate recoveries are not within the established acceptance criteria, proceed as follows (SW-846 8000B):

1) Check to be sure that there are no errors in the calculations, surrogate solutions or internal standards. If errors are found, recalculate the data accordingly. Examine chromatograms for interfering peaks and integrated peak areas.

2) Check instrument performance. If an instrument performance problem is identified, correct the problem and re-analyze the extract (or re-analyze the sample for volatiles).

3) Some samples may require dilution in order to bring one or more target analytes within the calibration range or to overcome significant interferences with some analytes. This may result in the dilution of the surrogate responses to the point that the recoveries cannot be measured. If the surrogate recoveries are available from a less diluted or undiluted aliquot of the sample or sample extract, those recoveries may be used to demonstrate that the surrogates were within the QC limits, and no further action is required. However, the results of both the diluted and undiluted (or less-diluted) analyses should be provided to the data user.

4) If no instrument problem is found and if sufficient sample is available, the sample should be re-extracted and re-analyzed.

18.3.2 If, upon re-analysis (in either 2 or 4 above), the recovery is again not within limits, report the data as an "estimated concentration." If the recovery is within the limits in the re-analysis, provide the re-analysis data to the data user. If the holding time for the method has expired prior to the re-analysis, provide both the original and reanalysis results to the data user, and note the holding time problem.

18.4 Duplicates

The results from laboratory duplicates are designed to assess the precision of analytical results in a given matrix and are expressed as relative percent difference (RPD). See the STAT Quality Assurance Manual, Section 5.4 for the calculation for RPD. Results are compared to established acceptance criteria as listed in the MS/MSD Tables 7. For duplicates results outside established criteria, corrective action must be documented or the data reported with appropriate data qualifying codes.

For this test method, the analysis of the MS/MSD pair is used for determination of method precision. For cases where the sample cannot be divided (e.g., wipes, air samples, not enough sample provided by customer) and thus a MS/MSD pair cannot be prepared in the preparation batch, an LCS/LCSD pair is prepared and analyzed to measure precision. Precision data from Tables 7 will be used for RPD acceptance criteria for LCS/LCSD.

18.5 Matrix Spikes

18.5.1 The results from MS/MSD are primarily designed to assess the precision and accuracy of analytical results in a given matrix and are expressed as percent recovery (%R) and relative

percent difference (RPD). See the STAT Quality Assurance Manual, Section 5.4 for the calculation for RPD.

18.5.2 Tables 7 show the compounds spiked, the levels and the current QC criteria for soils and water samples.

Table 7 Matrix Spike – Soil and Aqueous

Compound	Amount added µg/Kg	Amount added µg/L	RPD Limit	% Recovery
2,4-D	33.3	1.0	25	50-150
2,4-DB acid	33.3	1.0	25	50-150
Dalapon	33.3	1.0	25	50-150
Dicamba	33.3	1.0	25	50-150
Dichlorprop	33.3	1.0	25	50-150
Dinoseb	33.3	1.0	25	50-150
MCPA	33.3	1.0	25	50-150
MCPP	33.3	1.0	25	50-150
Pentachlorophenol	33.3	1.0	25	50-150
Picloram	33.3	1.0	25	50-150
2,4,5-T	33.3	1.0	25	50-150
2,4,5-TP (Silvex)	33.3	1.0	25	50-150
Acifluorfen	33.3	1.0	25	50-150
Bentazon	33.3	1.0	25	50-150
Chloramben	33.3	1.0	25	50-150
3,5-Dichlorobenzoic Acid	33.3	1.0	25	50-150
4-Nitrophenol	33.3	1.0	25	50-150

18.6 Other

The laboratory will analyze standard reference materials and participate in relevant performance evaluation studies quarterly.

19.0 CORRECTIVE ACTIONS FOR OUT-OF-CONTROL DATA

The process for handling unacceptable and out-of-control data is found in SOP 230 Corrective Action.

If the CCV, MB, LCS/LCSD, MS/MSD, lab duplicate, surrogate, or recovery of any parameter falls outside the designated acceptance range, the laboratory performance for that parameter is judged to be out-of-control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the samples is suspect and is only reported for regulatory compliance purposes with the appropriate corrective action form. Immediate corrective action includes reanalyzing all affected samples by using any retained sample before the expiration of the holding time. Final data results must be qualified in the client report for reported results not meeting the laboratory-defined criteria.

1) Review standards preparation logbooks. Check all calculations and ensure dilution factors are properly recorded.
2) Re-prepare the suspected standard or QC sample to identify possible preparation errors of the standard or QC sample.
3) Re-Analyze the samples when the CCV or LCS is not within acceptable limits.
4) Perform routine preventative maintenance following manufacturer's specification. Record all maintenance in the instrument logbook.

20.0 CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

Every effort is made to prevent problems from occurring. When out-of-control or unacceptable data occurs the first option is to identify the problem and reanalyze the samples within the holding times. When this is not possible, the QA Manager and/or the Laboratory Director reviews data and discusses options with the client. Reanalysis or reporting the data with qualification are alternatives. Out-of-control or unacceptable data reported to the client must include the data qualifier, flag and discussion on the rationale for reporting.

Holding time exceedence, improper preservation and improper sample condition or storage are noted on the corrective action form and included on the final report.

Review the CCV standard response, LCS result, the surrogate recovery, and internal standard recovery for acceptable performance for each batch of samples. Record any trends or unusual performance on a corrective action form. Final data results must be qualified in the client report for results not meeting the laboratory-defined criteria.

Manual integration must be minimized for standards, reagent blanks and surrogates. Routine manual integration of the same parameters indicates a system performance problem. Correct this problem or note in the instrument analysis logbook the suspected causes for routine manual integration. Sign and date all manually integrated chromatograms.

20.1 The process for handling unacceptable and out-of-control data is found in the Laboratory QAM Section 10. The reporting of data that is out-of-control must be approved and documented by Quality Assurance Manager and either the Technical Manager or the Laboratory Director.

20.2 Client Requested Modifications:

20.2.1 Clients must request modifications from the laboratory SOP in writing to the lab.

20.2.2 The lab director, technical manager and quality assurance manager will evaluate the requested client deviations, determine the feasibly of the deviation and the potential effects on the data.

20.2.3 If it is determined that the lab will perform the requested deviations, lab director, technical manager and quality assurance manager will decide if a method validation study is required.

20.2.4 The designated project manager will retain all documentation concerning the requested deviation, including all correspondence with the client, in the client folder.

20.2.5 The final analytical report must include the statement "*This report has analyses performed using client requested modifications* ".

21.0 WASTE MANAGEMENT

The STAT Analysis Corporation Waste Disposal SOP 1130 identifies proper waste management practices for the chemicals and biological materials used in this procedure. Samples are stored and discarded accordance with SOP 1130 Waste Disposal.

22.0 REFERENCES

22.1 Method 8321A, Revision 1, December 1996; U.S. EPA SW-846 "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods" Update III, December 1996.
22.2 SW-846 8000B Determinative Chromatographic Separations
22.3 "USEPA Contract Laboratory Program Statement of Work for Organic Analysis" Revision OLM04.2 May 1999, U. S. Environmental Protection Agency. Office of Solid Waste, Washington DC 20460.
22.4 SOP for sample prep: 3500
22.5 SAP 003 Chemical Hygiene Plan
22.6 SOP 230 Corrective Actions
22.7 SOP 1010 Analytical Standards and Reagents Receipt and Preparation
22.8 SOP 1130 Waste Disposal
22.9 SOP 1210 Method Detection Limits
22.10 SOP 1230 Training
22.11 SOP 1250 Data Review
22.12 SOP 1255 Manual Integration
22.13 SOP 1400 LIMS
22.14 Manufacturers' Equipment Instruction Manuals

23.0 FORMS, FIGURES, TABLES, DIAGRAMS, FLOWCHARTS, ATTACHMENTS OR VALIDATION DATA

Attachment 1. MDL's And Reporting Limits for Herbicide Compounds

ATTACHMENT 1. MDL's and REPORTING LIMITS FOR HERBICIDE COMPOUNDS

CASN	Compounds	MDL (µg/L)	RL (µg/L)	RL (mg/L)	MDL (µg/Kg)	RL (µg/Kg)	RL (mg/Kg)
94-75-7	2,4-D	0.115	0.3	0.0003	2.86	8.6	0.0086
94-82-6	2,4-DB acid	0.077	0.2	0.0002	5.85	17.6	0.0176
75-99-0	Dalapon	8.120	24.4	0.0244	1.83	5.5	0.0055
1918-00-9	Dicamba	0.074	0.2	0.0002	51.14	153.4	0.1534
120-36-5	Dichlorprop	0.084	0.3	0.0003	4.93	14.8	0.0148
88-85-7	Dinoseb	0.204	0.6	0.0006	5.77	17.3	0.0173
94-74-6	MCPA	0.094	0.3	0.0003	2.17	6.5	0.0065
7085-19-0	MCPP	0.063	0.2	0.0002	4.97	14.9	0.0149
87-86-5	Pentachlorophenol	0.155	0.5	0.0005	8.32	25.0	0.0250
1918-02-1	Picloram	0.079	0.2	0.0002	4.32	13.0	0.0130
93-76-5	2,4,5-T	0.046	0.1	0.0001	1.05	3.2	0.0032
93-72-1	2,4,5-TP (Silvex)	0.063	0.2	0.0002	1.34	4.0	0.0040
133-90-4	Chloramben	0.141	0.4	0.0004	2.30	6.9	0.0069
51-36-5	3,5-Dichlorobenzoic Acid	0.125	0.4	0.0004	0.87	2.6	0.0026
100-02-7	4-Nitrophenol	0.043	0.4	0.0004	25.30	75.9	0.0759

STAT Analysis Corporation:

STANDARD OPERATING PROCEDURE 4090

TOTAL PETROLEUM HYDROCARBONS (TPH) BY GC-FID

(EPA Method 8015B)

Revision 00
Effective Date: October 20, 2004

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1.0 IDENTIFICATION OF TEST METHOD

SOP Title: Total Petroleum Hydrocarbons (TPH) by GC-FID SW-846 8015B.

2.0 APPLICABLE MATRICES

Methylene chloride and organic solvent extracts from soil, sediment, ground and surface water, and mobility extracts are analyzed using this method.

3.0 DETECTION LIMITS

The lab follows the procedure found in 40CFR Part 136B to determine the MDL for each matrix type on an annual basis. See the STAT Analysis SOP 1210 for the MDL procedure, frequency and acceptance criteria. The MDL's measured by the lab and all supporting documentation are in the laboratory QA files for review.

The laboratory determined MDL must always be less than the reporting limit (RL), which is determined by the lowest calibration standard. The RLs will usually range from three to ten times the laboratory measured MDLs but this relationship may vary dependent on dilution of sample aliquots, matrix interferences, moisture adjustments (in solid samples), or method-specified requirements. Attachment 1 contains the current MDLs and reporting limits (RLs) for this SOP.

4.0 SCOPE AND APPLICATION

4.1 This standard operating procedure describes in detail the precise methods used at STAT Analysis Corporation for the analysis of environmental samples for Total Petroleum Hydrocarbons (TPH) by GC-FID. This SOP as written is to be applied when SW-846 Method 8015B is requested. This SOP is used to determine the concentration of TPH in extracts prepared from all types of solid waste matrices, soils, and ground water.

4.2 SOP 4090 can be used to quantitate petroleum hydrocarbons that are soluble in methylene chloride and other organic solvents and are capable of being eluted without derivatization as sharp peaks from a gas chromatographic column. See Attachment 1 for a list of ranges that have been evaluated on the specified GC-FID system.

Gasoline Range: $C_6 - C_{10}$ (boiling range 60 °C – 220 °C)
Diesel Range: $C_{10} - C_{18}$ (boiling range 170 °C – 430 °C)
Oil Range: $C_{18} - C_{28}$

4.3 The reporting limits (RLs) for this SOP are shown in Attachment 1 for soils and water. RLs will be proportionately higher for sample extracts and samples that require dilution or reduced sample size to avoid saturation of the detector.

4.4 This method is restricted to use by or under the supervision of analysts experienced in the use of a Gas Chromatograph (GC) and skilled in the interpretation of chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

5.0 SUMMARY OF TEST METHOD

5.1 Prior to using this method, the samples must be prepared for the GC using the appropriate sample preparation SOP (Section 14.1). Solid samples are extracted as received with methylene chloride. Aqueous samples are extracted as received with methylene chloride. This method describes chromatographic conditions that will allow for the separation of the compound ranges in the extract and for their qualitative and quantitative analysis by Gas Chromatography- Flame Ionization Detection. Identification of target analytes is accomplished by comparing component retention time ranges to those of authentic standards. Quantitation is accomplished by comparing the response of the peak area using a five-point calibration curve.

5.2 **Method Modifications from Reference**

5.2.1 This SOP is based on EPA SW-846 Method 8015B except that the TPH are reported as a range of compounds (i.e., gasoline range, diesel range and oil range) and not as individual peaks.

5.2.2 Samples are extracted for all ranges including GRO. Internal Blind samples have shown acceptable quality control using this technique.

5.2.3 No surrogate or internal standards are used in this method, because they would interfere with analyses of the ranges.

6.0 DEFINITIONS

The STAT Analysis Quality Manual Section 19.0 contains all the definitions of standard terms used in SOPs.

7.0 INTERFERENCES

7.1 Raw GC data from all blanks, samples, and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation and/or cleanup of the samples and take corrective action to eliminate the problem.

7.2 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed out between samples with solvent. Whenever an unusually concentrated sample is encountered, the sample after it should be reanalyzed to check for cross contamination.

8.0 SAFETY

Methylene chloride is a suspected carcinogen as are numerous compounds analyzed by this method. Proper personal protective equipment including safety glasses, nitrile gloves and a lab coat are required during different parts of this method. Other safety precautions must be conducted in accordance with the Chemical Hygiene Plan (STAT QA SAP 003). Other actions can also be applied if deemed necessary. A reference file of Material Safety Data Sheets (MSDS) is available to all personnel involved in this method.

9.0 EQUIPMENT AND SUPPLIES

The following apparatus is recommended for performing this procedure. Equivalent items can be used, if with their use, the analytical and QA/QC requirements in this SOP can be met. All catalog numbers in this SOP are current as of the effective date and thereafter subject to change.

9.1 Gas Chromatography System

9.1.1 Gas Chromatograph (GC) – Hewlett Packard 5890 Series II equipped with a Flame Ionization Detector (FID) and an Agilent Technologies 18593B autosampler.

9.1.2 Column – 30m x 0.250mm, 0.25 um film, (Agilent HP-5MS, Catalog # 19091S-433)

9.1.4 Data system – A Hewlett Packard Vectra VL computer system using EnviroQuant Chemstation G1701AA Version A.03.00 to collect and process the data is attached to the GC.

9.2 Micro syringes - 10 µL, 25 µL, 100 µL, 250 µL, 500 µL and 1,000 µL.

9.3 Volumetric flasks, Class A - 10 mL, 25 mL, 50 mL with ground glass stoppers.

9.4 Glass vials - 2-mL, for GC auto sampler with Teflon-lined screw caps or crimp tops.

9.5 Amber glass vials - 10 mL with Teflon-lined screw caps

10.0 REAGENTS AND STANDARDS

The following reagents and standards are required to perform this procedure. When instructions are given on how to prepare a specific volume of a reagent or standard, larger or smaller volumes can be prepared as needed so long as the final concentrations remain the same. Any other deviations from the reagents or standards listed in this SOP could be detrimental to the quality of the data produced. Such deviations would have to be approved and documented (see SOP QA 230 Corrective Action). Equivalent items can be used, if with their use, the analytical and QA/QC requirements in this SOP can be met.

Instructions for labeling and record keeping of reagents and standards are contained in SOP 1010 Analytical Standards and Reagents Receipt and Preparation.

10.1 Analytical reagent grade chemicals shall be used in all tests. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.

10.2 Organic-free reagent water - All references to water in this SOP refers to Type II reagent water (in-house system).

10.3 Stock Standard solutions - Standard solutions can be prepared from pure standard materials or purchased as certified solutions (e.g. SV standards). The routine laboratory practice is to purchase these standards from approved vendors. The standards used are: XHc Unleaded Gasoline Composite (Restek Catalog 30205), Diesel Fuel #2 Composite (Restek Catalog 31258) and Motor Oil Composite (Restek Catalog 31464). Stock standard solutions and QC solutions are stored at < -10°C and must be replaced after six months, or sooner if comparison with quality control check samples indicates a problem. Different storage conditions and expiration dates of other solutions are noted as warranted.

10.3.1 Secondary Stock Standard Solution – This solution is made using the individual Stock Standard solutions. Using microliter syringes, the following amounts of each Stock Standard solution is injected into three separate 10 mL volumetric flasks. The solution is brought to volume with methylene chloride. The final concentration of each component is listed in Table 1. Note: this Secondary Stock Standard solution is also used as the high-level calibration standard. It is also the source solution to prepare the calibration standards in Section 10.4. This standard is stored at < -10°C in a 10 mL amber screw cap vial equipped with a Teflon lined cap. It is freshly prepared every six months, or sooner if check standards indicate a problem.

Table 1 Secondary Stock Standard Solution

Stock Solution	Conc. Stock (µg/ml)	Vol. Stock (µL)	Final Conc. (µg/ml)
Gasoline Composite	50000	1000	5000
Diesel Fuel #2 Composite	50000	1000	5000
Motor Oil Composite	50000	1000	5000

10.4 Calibration standards - A minimum of five calibration standards are prepared. The low standard is the RL and above the MDL. The others define the working range of the GC system. Calibration standards in current use: 20, 100, 500, 1000, 2500 and 5000 µg/ml. (Table 2). Using microliter syringes, the following amount of the Secondary Stock solution is injected into a 1 ml syringe. The solution is brought to volume with methylene chloride. The final concentration of each component is listed in Table 2. Each solution is transferred to an autosampler vial. Storage is as indicated in 10.3. The continuing calibration verification standards (CCV) are prepared weekly and stored at 0.1-6 °C. Levels 3, 4 and 5 (500, 1000, 2500 µg/mL) are used for the CCVs.

Table 2 Calibration Standards

Level	Volume (µL) Secondary Stock	Volume (µL) Methylene Chloride	Final Concentration (µg/ml)

1	20 µL of 100 µg/ml	980	20
2	20	980	100
3	100	900	500
4	200	800	1000
5	500	500	2500
6	1000	----	5000

10.5 Laboratory Control Sample/Matrix Spike standards - The LCS/matrix spike compound range is composed of all these ranges. Samples will be spiked at 1000 ug/sample, 200 mg/Kg for soil and 1.0 mg/L for water (see SOP 3500 for LCS/Matrix Spike Solution preparation). This standard is stored at < -10°C in an amber glass vial with a Teflon lined screw cap.

10.6 Initial Calibration Verification Standard – A standard prepared from a different source at the midpoint of the calibration to verify the initial calibration. The solution is made using the following stock standards from AccuStandard. Gasoline-Regular Unleaded (Catalog GA-001-D-40X), #2 Diesel Fuel (Catalog FU-009-D-40X) and SAE 30W Motor Oil (Catalog FU-018-D-40X). Using microliter syringes, 500 µl of each Stock Standard solution is injected into a separate 10 mL volumetric flask. The solution is brought to volume with methylene chloride. The final concentration of each component is listed in Table 3 . This standard is stored at < -10°C.

Table 3 ICV Secondary Stock Standard Solutions

Compound Range	Conc. Stock (µg/ml)	Vol. Stock (µL)	Final Conc. (µg/ml)
Gasoline – Regular Unleaded	20000	500	1000
#2 Diesel Fuel	20000	500	1000
SAE 30W Motor Oil	20000	500	1000

10.7 Acetone, hexane, methanol, and other appropriate solvents, pesticide quality or equivalent.

11.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

11.1 Containers used to collect samples for the determination of Total Petroleum Hydrocarbons are glass: 1 Liter bottles for water samples and various size jars for soil samples. They are equipped with screw caps with Teflon liners. Water samples containing residual chlorine should be field treated to remove the chlorine prior to collection. Plastic containers or lids may NOT be used for the storage of samples due to the possibility of sample contamination from the phthalate esters and other hydrocarbons within the plastic.

11.2 Samples must be stored under refrigeration at between 0.1 and 6.0°C. Extraction must be within 7 days from sampling date for water and 14 days for solids. Sample extracts are stored in the dark at between 0.1 and 6.0°C and must be analyzed within 40 days of extraction.

11.3 No chemical preservation is required for this method.

11.4 All samples are stored away from all standards, reagents, food, and other potentially contaminating sources in order to prevent cross contamination.

12.0 QUALITY CONTROL

The following details the QC requirements that apply to this analysis. Each Quality Control Indicator (QCI) provides information pertaining to either method or individual sample performance. Our goal is to produce defensible data of known and documented quality. The results of these Quality Control Indicator (QCI) samples are used to assess the acceptability of data.

12.1 Blanks

Method Blank analysis is performed to determine if any contamination is present in the analytical process and is used to evaluate acceptance of the batch of samples. A method blank shall be prepared once per preparation batch of 20 or less samples per matrix type. If more than 20 samples are prepared a second blank shall be prepared after the twentieth sample. The method blank shall be processed through all preparatory steps used for the samples, including cleanup procedures. The blank shall be analyzed using the same instrument and conditions as the samples.

The Solvent Blank, clean methylene chloride injected into the GC, is used to monitor the GC system for potential cross-contamination from one sample to another or for residual contamination in the system.

12.2 Calibration Verification

An Initial Calibration Verification (ICV) standard containing all of the target analytes reported in this method (refer to 10.6) shall be analyzed immediately after the completion of the initial calibration. The ICV shall be purchased from a second source to verify analyte concentrations.

12.3 Laboratory Control Sample (LCS)

The LCS is used to evaluate the performance of the total analytical system, including all preparation and analysis steps. The LCS shall be prepared once per preparation batch of 20 or less samples per matrix type. If more than 20 samples are prepared a second LCS shall be prepared after the twentieth sample. The LCS shall be processed through all preparatory steps used for the samples, including cleanup procedures. The LCS shall be analyzed using the same instrument and conditions as the samples. Refer to section 10.5 for LCS analytes and concentrations.

12.4 Duplicates

Duplicates of field samples or of the LCS must be prepared in compliance with the method requirements and client directives. Duplicate LCS's are prepared for sample wipes. It would be impractical to prepare a matrix spike and matrix spike duplicate. Reproducibility performance would be the same as for a matrix spike/matrix spike duplicate.

12.5 Matrix Spike and Matrix Spike Duplicate (MS/MSD)

MS/MSDs indicate the effect of the sample matrix on the precision and accuracy of the results generated using the selected method. This information does not determine the validity of the entire batch. MS/MSDs must be analyzed at a minimum of 1 per 20 samples per matrix per preparation procedure, or one per preparation batch, or as specified by the required test method. For cases where

the sample cannot be divided (e.g., wipes, air samples, not enough sample provided by customer) and thus a MS/MSD pair is cannot be prepared in the preparation batch, an LCS/LCSD pair is prepared and analyzed to measure precision. Samples chosen for matrix spiking are rotated among different clients and/or different client projects. This is accomplished through communication between the Department Manager and the analyst. In addition, designated samples, as indicated by client request or contract requirement, are matrix spiked. The MS/MSD pair shall be processed through all preparatory steps used for the samples. They shall be analyzed using the same instrument and conditions as the samples. Refer to section 10.5 for MS analytes and concentrations. Some clients may require different spiking levels and/or target analytes, these specific needs are documented on the request for analysis forms.

13.0 CALIBRATION AND STANDARDIZATION

13.1 Initial Calibration (ICAL)

13.1.1 Analyze 1 µL of each calibration standard and tabulate the area sum of the analyte against concentration for each compound range. All compounds are reported as boiling point ranges. All peak areas within defined retention times are summed and reported as one peak. Calculate calibration factors (CFs) for each range in each calibration standard as follows:

$$CF = \frac{A_x}{C_x}$$

where:
A_x = Area of the compound range being measured.
C_x = Concentration of the compound range being measured (ng/µL = µg/mL = mg/L).

13.1.2 Calculate the average calibration factor ($\overline{CF}$) for each compound range as follows:

$$\overline{CF} = (\Sigma\, CF_1 \text{ to } CF_n)/n$$

where: CF = CF for each of the calibration levels (i.e., 5)
n = Number of CF values (i.e., 5)

13.1.3 Calibration Check Compound Range (CCC) responses are monitored to check the integrity of the system.

Using the CFs from the initial calibration, calculate the percent relative standard deviation (%RSD) for the Calibration Check Compound Ranges (CCC).

To calculate %RSD: $\%RSD = 100\% \times SD/\overline{CF}$

where:
%RSD = % Relative Standard Deviation

$\overline{CF}$ = average of initial CFs for a compound range
SD = standard deviation (n-1) of average CFs for a compound range

To calculate Standard Deviation (n-1 degrees of freedom)

$$SD = \sum_{i=1}^{N} \sqrt{\frac{(CF_i - \overline{CF})^2}{n-1}}$$

where: CF_i =CF for each of the 5 calibration levels
n = Number of CF values (i.e., 5)

13.1.4 Linearity - If the %RSD of any range is 20% or less, then the relative calibration factor is assumed to be constant over the calibration range, and the average relative calibration factor is used for quantitation. If the %RSD is greater than 20%, first order linear regression is used. The calibration curve must meet the requirements for curve fitting listed in SW-846 8000B and the correlation coefficient is ≥0.99. The equation is not forced through the origin.

13.1.5 Before sample analysis can begin, a Initial Calibration Verification (ICV) (see Sec. 10.9) must be performed. The ICV results must be within the acceptance criteria as established for the CCV ranges (Section 13.2).

NOTES:

1. All calibration curves must have a unique identifier. It is recommended that the calibration date be incorporated into the identifier for easy reference.
2. Calibration must be completed (all standard levels analyzed) within 24 hours or the entire calibration sequence must be repeated.
3. All initial calibration standards must be analyzed as a group. No field sample analyses are allowed during the calibration sequence.
4. Do not add calibration standards and update the curve after the original calibration date.
5. Multiple analyses of the same calibration level are not allowed to be included in the calibration curve.
6. If more than five calibration levels are analyzed, it is permissible to either drop the low compound range concentration (poor response) or the high compound range concentration (detector saturation). It is not allowed to drop a point in the middle of the curve.
7. If more than five calibration levels are analyzed, it is permissible to drop an entire level if the analyst can document a specific reason or reasons why that level should be excluded. Mechanical failures, significant loss of all analyte responses possibly due to poor technique in standard preparation, or software malfunction during data acquisition (system did not acquire all compound range data) are plausible reasons. The reason must be justified and documented. The supervisor should review this situation and approve the analyst's decision.
8. The need to analyze more than two analyses of the same calibration level indicates a potential problem with the secondary stock solution. Prepare a fresh secondary stock solution and repeat all calibration levels. It is recommended that all calibration standard levels come from the same secondary stock solution.
9. Manual integration must only be used if the software fails to properly integrate the peak. If manual integration is used for a particular compound range, all levels of that compound range do not have to be manually integrated, but all levels must be integrated in a similar manner. Example: the computer generated integration of a compound range in the low level standard is not technically sound. A manual integration of the compound range is performed

(due to baseline noise, etc) in order to achieve a technically sound integration. The computer integrates other levels of the compound range correctly. The manual integration of the low level must match, as best as possible, the computer generated integrations for all other levels.

10. If any compound range in the mid-point level is manually integrated, the integration of this compound range must be reviewed for every continuing calibration standard and QC check solution (i.e. LCS, and Matrix Spike) to ensure that the integration is the same as the manual integration performed in the initial calibration (ICAL) mid-point. A consistent manner of integration must be achieved.
11. All manual integrations must be reviewed and approved at the supervisory level.

13.2 Continuing Calibration Verification (CCV)

13.2.1 All three continuing calibration verification (CCV) samples are analyzed every 20 samples during analysis of samples. Different standards are analyzed for the CCV such that a wider range of the calibration curve is verified. For example: on successive days analyze the 500 µg/mL, then the 1000 µg/mL and on the third day, the 2500 µg/mL standard solution. Compare the calibration factors of the CCC's from the CCV with the following criteria.

13.2.2 Control limits for the CCC ranges are ± 15% difference from the ICAL Calibration Factor (CF) if the average CF is used for quantitation, or ± 15% drift from the true concentration of the CCV range if linear regression is used.

13.2.3 If the CCV results obtained are outside the acceptance criteria, corrective actions must be performed. If routine corrective actions fail to produce an acceptable *second consecutive (immediate)* CCV, then either the lab has to demonstrate performance after corrective action with two consecutive successful CCVs, or a new ICAL must be performed. If the instrument has not demonstrated acceptable performance, sample analyses cannot continue until a new ICAL is established and verified with an ICV. However, sample data associated with an unacceptable CCV may be reported as qualified data under the following special conditions:

13.2.3.1 When the acceptance criteria for CCV are exceeded high, i.e., high bias, and there are associated samples that are non-detects, then those non-detects may be reported. Otherwise the samples affected by the unacceptable calibration verification must be reanalyzed after a new ICAL has been established, evaluated and accepted.

13.2.3.2 When the acceptance criteria for the CCV are exceeded low, i.e., low bias, those sample results may be reported if they exceed a maximum regulatory limit/decision level. Otherwise the samples affected by the unacceptable verification must be reanalyzed after a new ICAL is established and verified with an ICV.

13.2.3.3 When the acceptance criteria for the CCV are exceeded and it is not possible to reanalyze the sample due to limited sample quantity AND a new sample cannot be obtained by the laboratory, the data may be reported with the appropriate data qualifiers if the client has been contacted and agrees, in writing, to accept the qualified data.

13.3 Records: Initial and Continuing Calibration Records will contain, at a minimum, the following:

1) Calibration date
2) Test method
3) Instrument
4) Analysis date
5) Each analyte name

6) Analyst's initials or signature
7) Standard Concentration (appropriate units) and number of standards
8) Response (appropriate units)
9) Calibration curve or calibration factor
10) Evaluation of and Statistics for ICAL curve fit in order to judge calibration curve acceptance
11) Evaluation of and Acceptance Limits for ICV analysis in order to judge calibration curve acceptance
12) Evaluation of and Acceptance Limits for CCV analysis in order to judge continuing calibration acceptance

13.4 Thermometers - The thermometers in the sample refrigerators and the standards freezer must be checked daily. They must meet performance criteria.

14.0 PROCEDURE

14.1 Sample Preparation

14.1.1 Water, soil, sediment and waste samples must be prepared by SOP 3500 Extractions of Samples for Semi-Volatile Organic Analyses (EPA Methods 3510C, 3520C, 3550B, 3580A) prior to GC/FID analysis.

14.1.2 Extract Preparation: Sample extracts should be at ambient temperature prior to use.

14.2 GC Analysis

14.2.1 Instrument Conditions: The recommended GC with Flame Ionization Detector (FID) operating conditions:

Sample volume:	1 µL
Column Head Pressure:	10 psig Helium
Oven Temperature Program:	
Initial Temperature	40 °C
Initial Time	4 minutes
Temperature Ramp	20 °C/minute
Final Temperature	300 °C
Final Time	13 minutes
Injection Port (B)	250 °C
Detector (B)	300 °C
Flame Ionization Detector Fuel Flowrates:	
Hydrogen	30 ml/minute
Zero Air	300 ml/minute
Makeup (Helium)	30 ml/minute

14.2.2 Access the computer and create a batch sequence file. Refer to section 14.3 for instructions.

14.2.3 Inject 1 µL of the Continuing Calibration Verification Standards (CCV) and evaluate using CCV acceptance criteria. See Section 13.2.

14.2.4 If all criteria are met, continue with sample analysis, injecting 1 µL of each extract, as outlined below.

Dilution Procedure

1. Clean a 1ml syringe equipped with a luer lock needle with rinse and clean solvent (methylene chloride). Fill syringe w th clean solvent such that there is sufficient volume remaining for the dilution volume (see Table 4) and remove the needle. Place the needle on the counter top such that the tip of the syringe is elevated.

2. Clean an appropriate syr nge (see Table 4) with rinse and clean solvent. Expel excess solvent by pumping plunger several times. Puncture the sample vial with the syringe needle and withdraw the sample into the syringe.

3. Remove the syringe from the sample vial and insert the needle into the barrel of the 1ml syringe. Inject the sample into the clean solvent. Hold the 1ml syringe so that the tip is up and gently push up on the plunger to remove excess air from the barrel.

4. Replace the needle on the 1ml syringe and add sufficient clean solvent to a final volume of 1ml. Transfer the entire contents of the syringe into a labeled sample vial. Consult Table 4 for the appropriate volumes for standard dilutions. Cap vial.

Table 4 STANDARD DILUTIONS

Dilution	Sample Volume mL	Total Volume µL
1 5	200	1000
1:10	100	1000
1:20	50	1000
1:50	20	1000
1:100	10	1000

14.2.5 Perform all qualitative and quantitative measurements as described in Sections 14.4 and 14.5. After analysis, store the extracts in the dark at 0.1- 6°C.

14.3 **Analytical Sequence**

START CHEMSTATION SOFTWARE:

From Win95 Desktop: Start/Programs/GC_MS Instrument #1/GC_MS Instrument #1

The software will locate the instrument and all peripheral equipment. Once the software is fully loaded there will be two windows visible. Window one is the instrument control window. Instrument parameters are readily viewed from this window. The second window is the sequence control window. No instrument parameters are viewable from this window.

SEQUENCE SETUP

From menu: Sequence/Run

1. Set current date in Data File Directory space (i.e., C:\HPCHEM\1\DATA\060702\)
2. OK (to save changes)

From menu: Sequence/Edit Sample Log Table

1. Set data file name using current date using the following format MMDDYY## (e.g., 06070201)
2. Set up sequence order using the following format: (**NOTE:** CCV must always run first)

VIAL	METHOD	SAMPLE NAME
1	TPH_0219	BLANK
2	TPH_0219	CCV_TPHDIESEL-500
3	TPH_0219	CCV_TPHGAS-500
4	TPH_0219	CCV_TPHOIL-500
5	TPH_0219	MBLK MB-1234-TPH
6	TPH_0219	LCS_LCS-1234-TPH
7	TPH_0219	SAMP 0206001-001A
...	...	...
24	TPH_0219	SAMP 0206001-010A
1	TPH_0219	BLANK002
2	TPH_0219	CCV_TPHDIESEL-500-2
3	TPH_0219	CCV_TPHGAS-500
4	TPH_0219	CCV_TPHOIL-500
25	TPH_0219	SAMP 0206001-011A

NOTE: The CCV must be run after every 20 samples.

3. OK (to save changes)

From menu: Method/Set New Default Paths

1. Update the method and data file paths using the current date (i.e., C:\MSDCHEM\1\DATA\060702\)
2. OK (to save changes)

Use Windows Explorer to copy all of the method files from the previous day's folder into the current day's folder.

TO START SEQUENCE:
From menu: Sequence/Run/Run Sequence

The analytical sequence for Initial Calibration is:

Solvent Blank
Calibration standard (S1) (Gasoline)
Calibration standard (S2) (Gasoline)
Calibration standard (S3) (Gasoline)
Calibration standard (S4) (Gasoline)
Calibration standard (S5) (Gasoline)

Calibration standard (S6) (Gasoline)
Calibration standard (S7) optional
Initial Calibration Verification Standard (ICV) (Gasoline)
Calibration standard (S1) (Diesel)
Calibration standard (S2) (Diesel)
Calibration standard (S3) (Diesel)
Calibration standard (S4) (Diesel)
Calibration standard (S5) (Diesel)
Calibration standard (S6) (Diesel)
Calibration standard (S7) optional
Initial Calibration Verification Standard (ICV) (Diesel)
Calibration standard (S1) (Motor Oil)
Calibration standard (S2) (Motor Oil)
Calibration standard (S3) (Motor Oil)
Calibration standard (S4) (Motor Oil)
Calibration standard (S5) (Motor Oil)
Calibration standard (S6) (Motor Oil)
Calibration standard (S7) optional
Initial Calibration Verification Standard (ICV) (Motor Oil)

The analytical sequence for Sample Analysis is:

Solvent Blank
Continuing Calibration Verification Standard (CCV (oil, gas, diesel))
Method Blank (MB)
LCS
LCS Duplicate (if applicable)
Sample #1
Sample #1 Matrix Spike (MS)
Sample #1 Matrix Spike Duplicate (MSD)
Sample #1 Laboratory Duplicate (if applicable)
Samples #2, #3, etc. until the 20th injection from the last CCV

Solvent Blank
CCV (oil, gas, diesel)
Samples #21
Method Blank (MB) #2
LCS #2
LCSD #2 (if applicable)
Sample #21
Sample #21 Matrix Spike (MS)
Sample #21 Matrix Spike Duplicate (MSD)
Sample #21 Laboratory Duplicate (if applicable)
Samples #22, #23, etc. until the 20th injection from the last CCV

14.4 Data Interpretation - Qualitative Analysis

14.4.1 An analyte is identified based upon the Retention Time (RT) range of a standard of the suspected compounds, unless requested otherwise by the client.

14.4.2 Identification is determined by retention time of the area summed peaks. Use SOP 1255 Manual Integration for other situations that may require analyst efforts to correct computer generated integrations that are not technically sound.

14.4.3 The following area sum start and stop times are to be used as a guide. Determine the appropriate stop and start times by overlaying the chromatograms of the three different standards at the 5000 ppm level.

Gasoline Range	3.6 – 10.0 minutes (gasoline start time – after $MeCl_2$ peak)
Diesel Range	10.0 – 16.5 minutes (gas/diesel stop/start – at lowest intersection)
Oil Range	16.5 – 30 minutes (diesel/oil) stop/start – at lowest intersection)

14.5 Data Interpretation - Quantitative Analysis

14.5.1 Once a compound range has been identified, the quantitation of that compound range must be based on the integrated abundance.

14.5.2 If the RSD of a range's response factor is 20 % or less, then the concentration in the extract is determined using the average calibration factor (CF) from initial calibration data (13.2). See Method 8000, Sec. 7.0, for the equations describing internal standard calibration and either linear or non-linear calibrations.

14.6 Records

Record the following information in the appropriate logbook or data file. Include any deviations from this procedure. Analyst initials, date of analysis, sample number or ID, initial sample volume or weight processed, final extract volume, calibration standard sample or solution identifier, QC sample or solution identifier, surrogate solution identifier, any dilution information, readings from support equipment, data file name, instrument method name, visual observations, and any other information as deemed necessary.

14.7 Troubleshooting

The experience of the analyst performing GC analyses is invaluable to the success of the methods. Each day that the analysis is performed, the daily calibration standards must be evaluated to determine if the chromatographic system is operating properly. Questions that must be asked: Do the peaks look normal? Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still good, if the injector is leaking, the injector septum needs replacing, etc. If any major changes are made to the system (e.g. column changed or detector cleaned), recalibration of the system must take place.

14.8 Routine Maintenance - Record all maintenance

14.8.1 Daily, or as needed according to sample throughput, change the septum and or the injection port liner. Trim a short section from the analytical column as necessary. Alternatively, the use of a guard column helps to protect the analytical column from residue buildup. A short section, 10 to 20 cm, of the guard column may be trimmed as to improve column performance. Replace the column on an as needed basis (loss of resolution).

14.8.2 Clean the detector on an as needed basis (loss of sensitivity).

14.8.3 Inspect the autosampler syringe for wear; replace as necessary.
14.8.4 Check the carrier gas supply; replace as necessary.

15.0 DATA REDUCTIONS, CALCULATIONS, AND LOADING

15.1 The data system performs the calculations.

15.1.1 If the %RSD of a range's relative calibration factor is 20% or less, then the concentration in the extract may be determined using the average calibration factor (CF) from the initial calibration data (13.2) and the following equation:

$$C_{ex}(mg/L) = \frac{A_x \times C_{is}}{A_{is} \times CF}$$

where C_{ex} is the concentration of the compound range in the extract, and the other terms are defined in Sec. 13.2.

15.1.2 Alternatively, linear regression (Sec. 13.2) may be used for determination of the extract concentration.

15.2 Compute the concentration of the analyte in the sample using the equations in Secs. 15.2.1 and 15.2.2.

15.2.1 The concentration of the analyte in the liquid samples is calculated using the concentration of the analyte in the extract and the volume of liquid extracted, as follows:

$$\text{Concentration in liquid (mg/L)} = \frac{C_{ex} * V_f}{V_i}$$

or

$$\text{Concentration in liquid (}\mu\text{g/L)} = \frac{C_{ex} * V_f * 1000}{V_i}$$

where:
V_f = final extract volume in mL (includes any dilution volumes)
V_i = initial volume of liquid extracted, in mL.

15.2.2 The concentration of the analyte in the solid sample is calculated using the concentration of the analyte in the extract and the weight of the solid extracted, as follows:

$$\text{Concentration in solid (mg/Kg)} = \frac{C_{ex} * V_f}{W_i}$$

or

$$\text{Concentration in solid (}\mu\text{g/Kg)} = \frac{C_{ex} * V_f * 1000}{W_i}$$

where:
V_f = final extract volume in mL (includes any dilution volumes)

W_i = initial sample weight, in g.

For soil samples reported on dry weight basis, divide the Concentration by the decimal equivalent of the Percent Solids. For example: a sample contains 90% solids, thus

$$\text{Concentration in solid (mg/Kg) dry weight} = \frac{C_{ex} * V_f}{W_i * 0.90}$$

15.3 See SOP 1040 General Laboratory Practices for additional calculations.

16.0 METHOD PERFORMANCE

Demonstration of Capability (DOC)

All parameters of interest must meet the method acceptance criteria before actual sample analysis begins. See SOP 1230 Training for the procedure to perform and document the DOC. The DOCs for the analysts performing this method are located in the analysts' training form folders located in the QA office files.

A quality control (QC) reference concentrate is required containing each analyte at a concentration of 1000 µg/mL in acetone. The QC reference sample used is the ICV Spike solutions (refer to Section 10.6 for composition). The QC reference sample is made using stock standards prepared independently from those used for calibration.

For each analyte calculate the mean recovery (x) and standard deviation (s) and the average % Recovery (%R). Compare X and s and %R with the corresponding acceptance criteria for accuracy and precision, respectively. Note: x must be within 25% (750 and 1250 µg/mL) and s must be less than 250 µg/L and %R must be within 50 to 150%. If x and s and %R for all analytes meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual x or %R falls outside the range for accuracy or any individual s exceeds the precision limit, then the system performance is unacceptable for that analyte and corrective action must be taken.

Locate and correct the source of the problem and repeat the test only for those analytes that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compound ranges of interest.

Comparison to Reference Method Data

EPA Method 8000B provides guidance for the establishment of control limits for the LCS and MS QC samples. Recovery limits of 70% to 130% are provided as initial benchmarks for performance (8000B Section 8.5.4). These limits are designed for a wide variety of organic test methods. Individual analyte performance may vary.

In-House Control Limits

Method performance data is on file in the laboratory QC department. Comparison of method performance data for the laboratory to the reference method criteria occurs when laboratory in-house acceptance limits are generated. In-house generated data is compared to the specifications of the reference method. If the in-house limits are within the specifications of the reference method, the control limits are updated in

LIMS. If the in-house limits are not within specifications, an investigation is performed to determine the cause(s) of the problem and a corrective action is completed. The analysis may continue until enough data points are collected to regenerate new control limits. Any QC data generated outside of reference method limits during that time frame is flagged.

The laboratory maintains performance records to document the quality of data that is generated. Method accuracy for samples is assessed and records maintained. After the analysis of 20 laboratory control samples, calculate the average percent recovery (R) and the standard deviation of the percent recovery (S).

Control limits for the method parameters are generated by the QC staff and distributed to the analysts via updates to the LIMS control charts. The control limits are calculated based on in-house performance data. At a minimum, these limits are reviewed annually.

17.0 POLLUTION PREVENTION

The preparation of excessive volumes of laboratory reagents and standards shall be avoided so that waste and potential for pollution are minimized. Samples, reagents and standards shall be disposed in compliance with the lab waste disposal program, SOP 1130 Waste Disposal. With the consent of the client, the samples may be returned to their origin for treatment.

Uncontaminated paper waste, glass and cans should be separated for recycling. Laboratory staff are required to protect the laboratory's and our clients' business information when disposing recycled paper or waste from the facility.

18.0 DATA ASSESSMENT AND CRITERIA FOR QUALITY CONTROL MEASURES

Data assessment includes review of: proper sample condition, preservation, and storage; analysis within holding time limitations; deviations from the SOP, evaluation of performance based or in-house control limits, reference method limits or project specific limits.

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a calibration verification standard is used to confirm the measurements were performed in an in-control mode of operation. The data review is conducted according to SOP 1250 Data Review.

18.1 Blanks

If the blank exceeds the RL, the lowest calibration standard, the source of contamination must be investigated and corrective actions taken. The range concentrations in the method blank of an extraction batch must be less than the RL's listed in Attachment 1. If this criteria is exceeded, re-analyze the method blank. If after re-analysis, the blank criteria is still exceeded, then the entire extraction batch must be re-extracted. Always refer to a client specific QAPP for additional guidance.

Affected samples must be reprocessed and reanalyzed **or** Data must be appropriately qualified if:

1) The concentration of a targeted analyte in the blank is at or above the reporting limit as established by the SOP or by regulation, AND is greater than 1/10 of the amount measured in any sample.

2) The blank contamination otherwise affects the sample results as per the test method requirements or the individual project data quality objectives.

18.2 Laboratory Control Samples (LCS)

The results of the individual batch LCS are calculated in percent recovery (%R) and compared to established acceptance criteria from in house analyses. If the LCS is outside the acceptance criteria, see Table 5 for current acceptance criteria, the analytical system is "out of control." Any affected samples associated with an out of control LCS must be reprocessed and reanalyzed or the results reported with appropriate data qualifiers. If after re-analysis the control criteria has not been met, the entire extraction batch must be re-extracted. Always refer to a client specific QAPP for additional guidance.

Table 5 LCS

Compound range	Soil Recovery %	Water Recovery %
Gas Range	30-150	30-150
Diesel Range	30-150	30-150
Oil range	30-150	30-150

18.3 Duplicates

The results from laboratory duplicates are designed to assess the precision of analytical results in a given matrix and are expressed as relative percent difference (RPD). See the STAT Quality Assurance Manual, Section 5.4 for the calculation for RPD. Results are compared to established acceptance criteria as listed in the MS/MSD Tables 7 and 8. For duplicates results outside established criteria, corrective action must be documented or the data reported with appropriate data qualifying codes.

For this test method, the analysis of the MS/MSD pair is used for determination of method precision. For cases where the sample cannot be divided (e.g., wipes, air samples, not enough sample provided by customer) and thus a MS/MSD pair is cannot be prepared in the preparation batch, an LCS/LCSD pair is prepared and analyzed to measure precision. Precision data from Tables 7 and 8 will be used for RPD acceptance criteria for LCS/LCSD.

18.4 Matrix Spikes

18.4.1 The results from MS/MSD are primarily designed to assess the precision and accuracy of analytical results in a given matrix and are expressed as percent recovery (%R) and relative percent difference (RPD). See the STAT Quality Assurance Manual, Section 5.4 for the calculation for RPD. For matrix spike results outside established criteria corrective action must be documented or the data reported with appropriate data qualifying codes.

18.4.2 Table 7 shows the compound ranges spiked, the levels and the current QC criteria for soils and water samples.

Table 7 Matrix Spike – Soil and Aqueous

Compound range	Amount added µg/Kg	Amount added µg/L	RPD Limit	% Recovery
Gas Range	200	1000	25	30-150
Diesel Range	200	1000	25	30-150
Oil Range	200	1000	25	30-150

18.5 Other

The laboratory will analyze standard reference materials and participate in relevant Internal Blind QC studies semi-annually.

19.0 CORRECTIVE ACTIONS FOR OUT-OF-CONTROL DATA

The process for handling unacceptable and out of control data is found in SOP 230 Corrective Action.

If the CCV, MB, LCS/LCSD, MS/MSD, lab duplicate, or recovery of any parameter falls outside the designated acceptance range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the samples is suspect and is only reported for regulatory compliance purposes with the appropriate corrective action form. Immediate corrective action includes reanalyzing all affected samples by using any retained sample before the expiration of the holding time. Final data results must be qualified in the client report for reported results not meeting the laboratory-defined criteria.

1) Review standards preparation logbooks. Check all calculations and ensure dilution factors are properly recorded.
2) Re-prepare the suspected standard or QC sample to identify possible preparation errors of the standard or QC sample.
3) Re-Analyze the samples when the CCV or LCS is not within acceptable limits.
4) Perform routine preventative maintenance following manufacturer's specification. Record all maintenance in the instrument logbook.

20.0 CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

Every effort is made to prevent problems from occurring. When out of control or unacceptable data occurs the first option is to identify the problem and reanalyze the samples within the holding times. When this is not possible, the QA Manager and/or the Laboratory Director reviews data and discusses options with the client. Reanalysis or reporting the data with qualification are alternatives. Out of control or unacceptable data reported to the client must include the data qualifier, flag and discussion on the rationale for reporting.

Holding time exceedence, improper preservation and improper sample condition or storage are noted on the corrective action form and included on the final report.

Review the CCV standard response and LCS result for acceptable performance for each batch of samples. Record any trends or unusual performance on a corrective action form. Final data results must be qualified in the client report for results not meeting the laboratory-defined criteria.

Manual integration must be minimized for standards and reagent blanks. Routine manual integration of the same parameters indicates a system performance problem. Correct this problem or note in the instrument analysis logbook the suspected causes for routine manual integration. Sign and date all manually integrated chromatograms.

20.1 The process for handling unacceptable and out of control data is found in the Laboratory QAM Section 11. The reporting of data that is out of control must be approved and documented by Quality Assurance Manager and either the Technical Manager or the Laboratory Director.

20.2 Client Requested Modifications:

20.2.1 Clients must request modifications from the laboratory SOP in writing to the lab.

20.2.2 The lab director, technical manager and quality assurance manager will evaluate the requested client deviations, determine the feasibly of the deviation and the potential effects on the data.

20.2.3 If it is determined that the lab will perform the requested deviations, lab director, technical manager and quality assurance manager will decide if a method validation study is required.

20.2.4 The designated project manager will retain all documentation concerning the requested deviation, including all correspondence with the client, in the client folder.

20.2.5 The final analytical report must include the statement "*This report has analyses performed using client requested modifications* ".

21.0 WASTE MANAGEMENT

The STAT Analysis Corporation Waste Disposal SOP 1130 identifies proper waste management practices for the chemicals and biological materials used in this procedure. Samples are stored and discarded accordance with SOP 1130 Waste Disposal.

22.0 REFERENCES

22.1 Method 8015B, Revision 1, December 1996; U.S. EPA SW-846 "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods" Update III, December 1996.
22.2 SW-846 8000B Determinative Chromatographic Separations
22.3 "USEPA Contract Laboratory Program Statement of Work for Organic Analysis" Revision OLM04.2 May 1999, U. S. Environmental Protection Agency. Office of Solid Waste, Washington DC 20460.
22.4 SAP 003 Chemical Hygiene Plan
22.5 SOP QA 230 Corrective Actions
22.6 SOP 1000 Control and Use of Laboratory Notebooks
22.7 SOP 1010 Analytical Standards and Reagents Receipt and Preparation
22.8 SOP 1040 General Laboratory Practices
22.9 SOP 1130 Waste Disposal
22.10 SOP 1210 Method Detection Limit
22.11 SOP 1230 Training
22.12 SOP 1250 Data Review
22.13 SOP 1255 Manual Integration
22.14 SOP 1400 LIMS
22.15 SOP 3500 Extractions of Samples for Semi-Volatile Organic Analysis
22.16 Manufacturers' Equipment Instruction Manuals

23.0 FORMS, FIGURES, TABLES, DIAGRAMS, FLOWCHARTS, ATTACHMENTS OR VALIDATION DATA

Attachment 1: MDL's and REPORTING LIMITS FOR TPH COMPOUND RANGES

Attachment 1: MDL's and REPORTING LIMITS FOR TPH COMPOUND RANGES

Compound ranges	Water MDL (µg/L)	Water RL (mg/L)	Soil MDL (mg/Kg)	Soil RL (mg/Kg)
Gasoline Range	0.03	0.1	3.0	20
Diesel Range	0.05	0.1	0.9	20
Oil Range	0.01	0.1	1.1	20

STAT Analysis Corporation

STANDARD OPERATING PROCEDURE 4210

pH of Aqueous, Soil, and Waste Samples by EPA 9040B, 9045C, 150.1

Revision 01

Effective Date: 07/15/05

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1.0 Identification of Test Method

SOP Title: pH of Aqueous, Soil, and Waste Samples by EPA 9040B, 9045C, 150.1 is also known as pH in the laboratory records.

2.0 Applicable Matrix or Matrices

The applicable matrices for this analysis are water, soils and non-aqueous wastes Multiphasic aqueous wastes must contain at least 20% aqueous content for this test to be effective. Soils and non-aqueous waste must contain less than 20% aqueous content for this test to be effective. The method is not applicable to organic liquids and concentrated acids and bases.

3.0 Detection Limits

There is no laboratory Reporting Limit (RL) for this method. This method measures a property of the tested sample and is based upon the instrument used to perform the analysis. The theoretical range for pH measurement is 0 to14 pH units. MDL is not applicable for this test. However, the laboratory uses a reporting range of 2 to 12.4 pH units.

4.0 Scope and Application

This method is used to measure the pH or hydrogen ion content of aqueous liquids and aqueous extracts of solid samples. pH is a measure of the acidic (increased hydrogen ion content), neutral, or basic (decreased hydrogen ion content) nature of the tested material. A reading of 7 indicates a neutral solution. pH readings less than 7 indicate an acidic nature. The lower the pH reading, the more acidic the solution. pH readings greater than 7 indicate a basic nature. The higher the pH reading, the more basic the solution.

Note: Each analyst/ work cell must demonstrate the ability to generate acceptable results with this method.

5.0 Summary of Method

5.1 The pH of the sample is determined electrometrically using either a glass electrode in combination with a reference potential or a combination electrode.

5.2 The pH of a sample is measured using a pH meter calibrated using a series of standard solutions of known pH.

5.3 Whenever possible, samples are analyzed @ 25°C. Unless a temperature correction routine is used by the instrument, samples of different temperatures must be equilibrated to and results reported @ 25°C.

5.4 The instrument used for this test has an automatic temperature compensation routine to correct pH readings at various temperatures. The reported result is stated as pH @ 25°C.

5.5 For solid samples and non-aqueous sludges, the sample is mixed with laboratory reagent water. The pH of the water extract is then measured.

Method Modifications from Reference

a) The method recommends that the sample pH measurement be determined as soon as possible. The laboratory endeavors to perform this test as soon as is reasonably possible after sample receipt.
b) The laboratory measures reagent water used in 9040 B and 9045C in grams instead of milliliters.

6.0 Definitions

The STAT Analysis Corporation Quality Assurance Manual (QAM) contains the definitions of standard terms used in this SOP.

7.0 Interferences

7.1 The glass electrode, in general, is not subject to solution interferences from color, turbidity, colloidal matter, oxidants, reductants, or moderate (<0.1 molar solution) salinity.

7.2 Sodium error at pH levels >10 can be reduced or eliminated by using a low-sodium-error electrode.

7.3 Coatings of oily material or particulate matter can impair electrode response. These coatings can usually be removed by gentle wiping or detergent washing followed by rinsing with reagent water. An additional treatment with hydrochloric acid (1:10) may be necessary to remove any remaining film.

7.4 Temperature effects on the electrometric determination of pH arise from two sources. The first is caused by the change in electrode output at various temperatures. This interference should be controlled with instruments having temperature compensation or by calibrating the electrode-instrument system at the temperature of the samples. The second source of temperature effects is the change of pH due to changes in the sample as the temperature changes. This error is sample-dependent and cannot be controlled.

8.0 Safety

8.1 All samples must be assumed as hazardous and appropriate precautions taken during handling.

8.2 Safety glasses, gloves, lab coats and closed toe shoes are to be worn.

8.3 Other safety precautions must be conducted in accordance with the Chemical Hygiene Plan. Other actions can also be applied if deemed necessary. A reference file of material safety data sheets (MSDS) is available in each room for personnel involved in an analysis using chemicals.

9.0 Equipment and Supplies

9.1 Model 340 pH meters with electrode (a combination electrode that incorporates both measuring and referenced functions with solid, gel-type filling materials that require minimal maintenance).

9.2 Top loading balance, capable of weighing to 0.01 g

9.3 Glass Beaker, 50 mL, 100 mL and 250 mL

9.4 Magnetic stirrer with stir bar

9.5 Disposable plastic beakers

9.6 Glass or plastic storage bottles with caps

9.7 Metal or wooden spatulas

10.0 Reagents and Standards

The following reagents and standards are required to perform this procedure. When instructions are given on how to prepare a specific volume of a reagent or standard, larger or smaller volumes can be prepared as needed so long as the final concentrations remain the same. Any other deviations from the reagents or standards listed in this SOP could be detrimental to the quality of the data produced. Such deviations would have to be approved and documented (see SOP 230 Corrective Action).

10.1 Instructions for labeling and record keeping of reagents and standards are contained in SOP 1010 Analytical Standards and Reagents Receipt and Preparation.

10.2 Reagents – In methods where the purity of reagents is not specified, analytical reagent grade shall be used. Reagents of lesser purity than those specified by the test method shall not be used.

10.3 Standards

10.3.1 At least one of the standards must be traceable to a NIST traceable source when available. The manufacturer should include a certificate of analysis for each standard. If one is not provided, contact the manufacturer. Retain all certificates in the designated binder (see SOP 1010 Analytical Standards and Reagents Receipt and Preparation).

10.3.2 pH buffer solutions: Commercially purchased used for the ICAL. Buffers at pH 4 and 10. The solutions can be stored in the original container at room temperature for 1 year or as indicated per the manufacturer's instructions.

10.3.3 pH buffer solutions: Commercially purchased used for the ICV/CCV. These must be from a second source or different lot number from the ICAL buffer solutions. Buffers are at pH 2, 4, 7, 10, and 12.45. The solutions can be stored in the original container at room temperature for 1 year or as indicated per the manufacturer's instructions.

10.3.4 pH buffers may be transferred from the original container and stored in small plastic or glass vials for up to one week. The electrode may be placed directly in the vial for pH determination. Cap the vial after each use. Label each vial accordingly.

11.0 Sample Collection, Shipment, Preservation and Storage

11.1 Sample Collection

Samples should be collected in plastic (preferable) or glass bottles. All bottles must be thoroughly cleaned and rinsed with reagent water. The volume collected (minimum 100 mL or 4 oz) should be sufficient to insure a representative sample, allow for replicate analysis (if required), and minimize waste disposal.

11.2 Sample Preservation
Aqueous samples must be analyzed as soon as possible upon receipt at the laboratory. Store samples at 0.1 to 6 °C. Non-aqueous samples must be analyzed as soon as is reasonably possible upon receipt at the laboratory or when requested by the client. Store samples at 0.1 to 6 °C.

11.3 Sample Shipment and Handling
Samples should be received by the laboratory on ice (preferably in a cooler).

11.4 Sample Storage
Samples are stored refrigerated at 0.1 - 6°C. Sample analysis cannot be performed within holding time (15 minutes). See Section 5, Method Modifications.

12.0 Quality Control

The following details the QC requirements that apply to this analysis. Each Quality Control Indicator (QCI) provides information pertaining to either method or individual sample performance.

The results of these QCI samples are used to assess the acceptability of data.

Duplicates
Duplicates are defined as replicate aliquots of the same sample taken through the entire analytical procedure. The results from this analysis indicate the precision of the results for the specific sample using the selected method. The duplicate provides a usable measure of precision only when target analytes are found in the sample chosen for duplication.

Duplicates are analyzed at one per batch of 20 samples or fewer. Duplicates are performed on replicate aliquots of actual samples.

Samples chosen for duplicate analyses are rotated among different clients and/or different client projects. This is accomplished through communication between the Department Manager and the analyst. In addition, designated samples, as indicated by client request or contract requirement, are analyzed as laboratory duplicates.

13.0 Calibration and Standardization

Initial Calibration (ICAL)
In addition to achieving the reference method requirements for the minimum number of calibration standards and the acceptance criteria (statistics) for calibration curve fit, the following ICAL criteria also apply:

13.1 The ICAL must be a minimum of 2 standards.

13.2 The ICAL must be verified with a second source standard (ICV) prior to the analysis of samples.

13.3 The theoretical range of measurement for the instrument is 0 to 14 pH units.

13.4 MDL is not applicable for this test.

Initial Calibration Verification (ICV):
The following ICV criteria also apply:

13.5 Must be a second source standard from the ICAL standards or from a different manufacturer lot number.

13.6 Must be traceable to NIST when available.

Continuing Calibration Verification (CCV)
In addition to the method requirements, the following CCV criteria also apply:

13.7 May be repeated at the beginning of each analytical batch.

13.8 Must be repeated every 10 samples and at the end of each analytical batch.

13.9 If the CCV results obtained are outside the acceptance criteria, routine corrective actions must be performed. If routine corrective actions fail to produce an acceptable *second consecutive (immediate)* CCV, then either the lab has to demonstrate performance after corrective action with two consecutive successful CCVs, or a new ICAL must be performed. If the instrument has not demonstrated acceptable performance, sample analyses cannot continue until a new ICAL is established and verified with an ICV.

13.10 Records: Initial and Continuing Calibration Records will contain, at a minimum, the following:

Calibration date
Test method
Instrument
Analysis date
Analyst's initials or signature
Standard pH and number of standards
Response (appropriate units)
Evaluation of and Acceptance Limits for ICV analysis in order to judge calibration curve acceptance
Evaluation of and Acceptance Limits for CCV analysis in order to judge continuing calibration acceptance
Calibration Standards Solutions IDs

Table 13.1 Quick reference of Instrument Calibration Requirements

QCI	Frequency	Standards	Control Limits	Corrective Action
ICAL	Daily, or as needed	pH 4 and 10 buffers	N/A	Correct problem then repeat initial calibration
ICV	After ICAL	pH 7 buffer,	± 0.05 pH unit	Correct problem then repeat initial calibration
CCV	Beginning (optional), every 10 sample and end of batch	pH 7 buffer, as applicable to the 4 to 10 test range	± 0.1 pH unit	Correct problem then repeat CCV or repeat initial calibration
CCV	Beginning (optional) and after samples < 4	pH 2 buffer, as applicable to the test range	± 0.1 pH unit	Correct problem then repeat CCV or repeat initial calibration
CCV	After any sample with pH > 10	pH 12.45 buffer, as applicable to the test range	± 0.1 pH units*	Correct problem then repeat CCV or repeat initial calibration

* The 12.45 buffers is temperature sensitive. Record the test conditions (i.e., temperature) for comparison purposes to the certified value.

Balances - Be sure the balance is checked prior to use and performance criteria are met (see SOP 1040 General Laboratory Practices for Calibration of Balances).

14.0 Procedure

14.1 Instrument Set-Up (General)

14.1.1 Connect the electrode to the meter

14.1.2 Plug the AC power connector into the back of the unit and plug the adaptor into the AC power source.

14.1.3 Turn on the pH meter – on/off button.

14.1.4 Place the electrode in the solution, stir electrode in solution or use magnetic stirrer, allow meter to stabilize and read answer on display.

14.1.5 Turn off pH meter – on/off button.

14.2 Calibration

14.2.1 Erase any existing calibration data.

14.2.1.1. Press the "cal" button, then the "clear" button to remove the existing calibration.

14.2.1.2. The message "clr" appears in the numeric display. To confirm the removal of the calibration, press "clear" again.

14.2.2 Pour the ICAL solution (first pH buffer) into a clean beaker with stir-bar and place on magnetic stirrer.

14.2.3 Insert the electrode completely into the ICAL solution.

14.2.4 Press "read" key. Wait until the Auto-eye stops flashing, indicative of a stable reading.

14.2.5 Repeat the above steps 14.2.2 through 14.2.4 for the additionalcalibration buffers.

14.2.6 Press "cal" to complete calibration.

14.2.7 The instrument is now calibrated.

14.2.8 Analyze the ICV/CCV buffer according to Table 13.1. Take corrective action if sample acceptance criteria are not met.

14.3 pH Measurement – Aqueous Samples

14.3.1 Allow samples to come to room temperature (23 to 27°C) if possible.

14.3.2 Place the electrode in the sample solution (15 to 50 mL of sample in a clean beaker or disposable plastic cup with stir-bar) and place on magnetic stirrer. Swirling the electrode, instead of using a magnetic stir bar, in the solution is permitted provided that the solution is well mixed and a steady reading is obtained.

14.3.3 Read the answer on the digital display while stirring the electrode in the solution. Record the pH value in the logbook. Ensure that the temperature compensation is in effect.

14.3.4 Set the ON/OFF toggle switch to the OFF position when finished.

NOTE: For samples containing multiple phases, where the aqueous content is greater than 20%, remove approximately 20 mL of the aqueous phase. From the subsampled portion, follow the above procedure (14.3)

14.4 pH Measurement – Soil Samples

14.4.1 Weigh 20 g of soil (to the nearest 0.5 g) in a 50-mL beaker, record weight in logbook, add 20 g of reagent water, add a stir bar, and continuously stir the suspension for 5 minutes on the magnetic stirrer. Be sure to break up solid material as much as possible in order to obtain a homogeneous sample while stirring. Additional dilutions are allowed if working with hygroscopic soils and salts or other problematic matrices.

14.4.1.1 NOTE: There is a pH test for soil samples that is called "10% pH". This is a specific request and has its own test code in LIMS. For this test, perform the following: Weigh 10 g of soil (to the nearest 0.1 g) in a 250-mL beaker, add 100 g of reagent water, add a stir bar, and continuously stir the suspension for 5 minutes on the magnetic stirrer. Record the weight of the sample in the logbook.

14.4.2 Let the soil suspension stand for about 30 minutes to allow most of the suspended clay to settle out from the suspension or filter or centrifuge off the aqueous phase for pH measurement.

14.4.3 Place the electrode in the sample solution, immerse just below the suspension to obtain good contact.

14.4.4 Read the answer on the digital display. Record the pH value in the logbook.

14.4.5 Set the ON/OFF toggle switch located on the back of the unit to the OFF position when finished.

14.5 pH Measurement – Non-Aqueous Waste Samples

14.5.1 Weigh 20 g of waste sample (to the nearest 0.5 g) in a 50-mL beaker, add 20g of reagent water, add a stir bar, and continuously stir the suspension for 5 minutes on the magnetic stirrer. Record the weight of the sample in the logbook. Additional dilutions are allowed if working with hygroscopic wastes and salts or other problematic matrices.

14.5.2 Let the waste suspension stand for about 15 minutes to allow most of the suspended waste to settle out from the suspension or filter or centrifuge off aqueous phase for pH measurement. NOTE: If the waste is hygroscopic and absorbs all the reagent water, begin the determination again using 20 g of waste and 40 g of reagent water. NOTE: If the supernatant is multiphasic, decant the oily phase and measure the pH of the aqueous phase. The electrode may need to be cleaned if it becomes coated with an oily material.

14.5.3 Place the electrode in the sample solution, immerse just below the suspension to obtain good contact.

14.5.4 Read the answer on the digital display. Record the pH value.

14.5.5 Set the ON/OFF toggle switch located on the back of the unit to the OFF position when finished.

14.6 General Operating Techniques

14.6.1 Use very clean beakers or disposable cups.

14.6.2 Avoid cross-contamination between measurements by rinsing the electrode in reagent water and by rinsing the electrode and the beaker in the solution to be tested.

14.6.3 For best results, the solution temperature should remain constant during the readings. The ideal temperature is 25.0°C (77.0°F).

14.6.4 Make certain to sustain flow through the electrode while making your readings. Stirring helps prevent polarization, ensures that the solution is well mixed, and helps to maintain a uniform temperature within the solution.

14.6.5 When finished using the electrode, always rinse it in reagent water and store dry or in reagent water. Solutions which are allowed to dry on the electrode will eventually block the membrane and the surface area will be reduced. A new electrode may be required.

14.7 Troubleshooting and cleaning procedures can be found in the instrument manual.

15.0 Data Reduction, Calculations and Loading

15.1 The procedure for uploading data into the LIMS system is detailed in SOP 1400 LIMS.

15.2 Temperature correction: All readings displayed are automatically temperature compensated and corrected to the internationally accepted standard of 25°C.

15.3 Report results as pH @ 25°C.

16.0 Method Performance

Demonstration of Capability (DOC)
All parameters of interest must meet the method acceptance criteria before actual sample analyses begin. See SOP 1230 Training for the procedure to perform and document the DOC. The DOCs for the analysts performing this method are located in the analysts' training form folders located in the QA office files.

The ICV/CCV solution, pH 7 @ 25°C, may be used for calculating the DOC.

For each determination, calculate the mean recovery (x) and standard deviation (s). Compare x and s with the corresponding acceptance criteria for accuracy and precision, respectively. Note: x must be within 0.1 pH units @ 25°C and s must be less than 0.1 pH units @ 25°C. These limits are based upon the reference method. If x and s for the determinations meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual x falls outside the range for accuracy, or s exceeds the precision limit, then the system performance is unacceptable for the determination and corrective action must be taken.

Comparison to Reference Method Data
There is no reference method data for laboratory duplicate analyses of environmental test sample matrices.

In-House Control Limits
Method performance data is on file in the laboratory QC department. Comparison of method performance data for the laboratory to the reference method criteria occurs when laboratory in-house acceptance limits are generated. In-house generated data is compared to the specifications of the reference method. If the in-house limits are within the specifications of the reference method, the control limits are updated in LIMS. If the in-house limits are not within specifications, an investigation is performed to determine the cause(s) of the problem and a corrective action is completed. The analysis may continue until enough data points are collected to regenerate new control limits. Any QC data generated outside of reference method limits during that time frame is flagged.

The laboratory maintains performance records to document the quality of data that is generated. Method accuracy for samples is assessed and records maintained.

17.0 Pollution Prevention

The preparation of excessive volumes of laboratory reagents and standards shall be avoided so that waste and potential for pollution are minimized. Samples, reagents and standards shall be disposed in compliance with the laboratory waste disposal program and applicable waste disposal regulations. With the consent of the client, the samples may be returned to their origin for treatment.

Uncontaminated paper waste, glass and cans should be separated for recycling. Laboratory staff are required to protect the laboratory's and our clients' business information when disposing of recycling or waste from the facility.

18.0 Data Assessment and Criteria for Quality Control Measures

The laboratory must maintain records to document the quality of data that is generated. Ongoing quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. The data review is conducted according to SOP 1250 Data Review.

Duplicates

The results from laboratory Duplicates are designed to assess the precision of analytical results in a given matrix and are expressed as relative percent difference (RPD). See the STAT QAM, Section 5.4 for the calculation for RPD.

Results are compared to established acceptance criteria (in-house limits); Duplicate RPD limits are 10% for water samples and 20% for solid or waste samples.

For duplicates results outside established criteria corrective action must be documented, or the data for the duplicate sample is reported with appropriate data qualifying codes.

19.0 Corrective Actions for Out-of-Control Data

The process for handling corrective actions is found in SOP 230 Corrective Action.

If the CCV or lab duplicate recovery falls outside the designated acceptance range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the samples is suspect and is only reported for regulatory compliance purposes with the appropriate corrective action form. Immediate corrective action includes reanalyzing all affected samples by using any retained sample before the expiration of the holding time. Final data results must be qualified in the client report for reported results not meeting the laboratory-defined criteria.

1) Review standards preparation logbooks. Check all calculations and ensure dilution factors are properly recorded.

2) Re-prepare the suspected standard or QC sample to identify possible preparation errors of the standard or QC sample.

3) Re-Analyze the samples when the CCV is not within acceptable limits.

4) Perform routine preventative maintenance following manufacturer's specification. Record all maintenance in the logbook.

20.0 Contingencies for Handling Out-of-Control Or Unacceptable Data

Every effort is made to prevent problems from occurring. When out of control or unacceptable data occurs the first option is to identify the problem and reanalyze the samples within the holding times. When this is not possible, the QA Manager and/or the Laboratory Director reviews data and discusses options with the client. Reanalysis or reporting the data with qualification are alternatives. Out of control or unacceptable data reported to the client must include the data qualifier, flag and discussion on the rationale for reporting.

20.1 The process for handling unacceptable and out of control data is found in the Laboratory QAM Section 11. The reporting of data that is out of control must be approved and documented by Quality Assurance Manager and either the Technical Manager or the Laboratory Director.

21.0 Waste Management

The STAT Analysis Corporation SOP 1130 Waste Disposal identifies proper waste management practices for the chemicals and biological materials used in this procedure. Samples are stored and discarded accordance with SOP 1130 Waste Disposal. Buffer solutions may be disposed of in the sink.

22.0 References

22.1 Methods 9040B and 9045C, U.S. EPA SW-846 "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods" Update III, December 1996
22.2 Method 150.1, EPA Manual 600/4-079-020, Revised March 1983
22.3 Instruction Manual for Bench pH Meter
22.4 STAT Analysis Corporation Quality Assurance Manual
22.5 STAT SOP 003 Chemical Hygiene Plan
22.6 STAT SOP 230 Corrective Actions
22.7 STAT SOP 1000 Control and Use of Laboratory Notebooks
22.8 STAT SOP 1010 Standard and Reagent Preparation
22.9 STAT SOP 1040 General Laboratory Procedures
22.10 STAT SOP 1130 Waste Disposal
22.11 STAT SOP 1230 Training
22.12 STAT SOP 1250 Data Review
22.13 STAT SOP 1400 LIMS

23.0 Forms, Figures, Tables, Diagrams, Flowcharts, Attachments or Validation Data

Not applicable to the SOP.

STAT Analysis Corporation:

STANDARD OPERATING PROCEDURE 4510

METALS ANALYSIS BY INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY (EPA METHOD 6020 AND EPA METHOD IO-3.5)

Revision 05

Effective Date: May 16, 2005

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1.0 IDENTIFICATION OF TEST METHOD

SOP Title: Metals Analysis by Inductively Coupled Plasma - Mass Spectrometry (EPA Method 6020 and EPA Method IO-3.5) is abbreviated as ICP-MS in the laboratory records.

2.0 APPLICABLE MATRICES

Inductively coupled plasma-mass spectrometry (ICP-MS) is applicable to the determination of µg/L and sub-µg/L concentrations of a large number of elements in water samples and in waste extracts or digests. When dissolved constituents are required, samples must be filtered and acid-preserved prior to analysis. No digestion is required prior to analysis for dissolved elements in water samples. Acid digestion prior to filtration and analysis is required for aqueous, solids, and air filters for which total (acid-leachable) elements are required.

3.0 DETECTION LIMITS

The lab follows the procedure found in 40CFR Part 136B to determine the MDL for each matrix type on an annual basis. See the STAT Analysis SOP 1210 Method Detection Limits for the MDL procedure, frequency, and acceptance criteria. The MDLs measured by the lab and all supporting documentation are in the laboratory QA files for review.

The laboratory determined method detection limit (MDL) must always be less than the reporting limit (RL). The RLs will usually range from three to ten times the laboratory measured MDLs but this relationship may vary dependent on dilution, reduced sample size to avoid saturation of the detector, matrix interferences, moisture adjustments (in solid samples), or method-specified requirements. Attachment 1 contains the current MDLs and reporting limits (RLs) for soils, waters and air filters.

4.0 SCOPE AND APPLICATION

4.1 Inductively coupled plasma-mass spectrometry (ICP-MS) is applicable to the determination of sub-µg/L concentrations of a large number of elements in water samples and in waste extracts or digests. When dissolved constituents are required, samples must be filtered and acid-preserved prior to analysis. No digestion is required prior to analysis for dissolved elements in water samples. Acid digestion prior to filtration and analysis is required for groundwater, aqueous samples, industrial wastes, soils, sludges, sediments, air filters, wipes, and other solid wastes for which total (acid-leachable) elements are required.

4.2 ICP-MS has been historically applied to the determination of over 60 elements in various matrices. Analytes determined at this laboratory for this method are listed in Attachment 1 (along with the masses used for determination). If Method 6020 is used to determine any analyte not listed in Attachment 1, it is the responsibility of the laboratory to demonstrate the accuracy and precision of this method in the material to be analyzed. The analyst is always

required to monitor potential sources of interferences and take appropriate action to ensure data of known quality (see Section 14.4 Qualitative Analysis).

4.3 This method is restricted to use by or under the supervision of analysts experienced in the use of ICP-MS and knowledgeable in the recognition and correction of spectral, chemical, and physical interferences in ICP-MS. Each analyst must demonstrate the ability to generate acceptable results with this method.

5.0 SUMMARY OF TEST METHOD

5.1 Samples that require total "acid-leachable" values must be digested using appropriate sample preparation methods prior to analysis.

5.2 EPA methods 6020 and IO-3.5 describes the multi-elemental determination of analytes by ICP-MS. The method measures ions produced by a radio frequency inductively coupled plasma. Analyte species originating in a liquid are nebulized and the resulting aerosol transported by argon gas into the plasma. The ions produced are entrained in the plasma gas and introduced, by means of an interface, into a mass spectrometer. The ions are sorted according to their mass-to-charge ratios and quantified with a channel electron multiplier. Interferences must be assessed and valid corrections applied or the data flagged to indicate problems. Interference correction must include compensation for background ions contributed by the plasma gas, reagents, and constituents of the sample matrix. An appropriate internal standard is required for each analyte determined by ICP-MS.

5.3 Method Modifications from Reference – This SOP is based on EPA Method 6020 and incorporates IO-3.5 for TSP/PM10 high-volume filters except that: 1) polypropylene volumetric flasks are used since analysis for boron is occasionally required, 2) the instrument resolution is set for 1 amu peak width at 10% peak height according to 6020 but is less stringent than IO-3.5, 3) samples which fail high or low for one or more internal standards are diluted as needed to bring within range for the internal standard, 4) A matrix spike and matrix spike duplicate are digested and analyzed, since a duplicate sample is not typically analyzed, 5) Dilution test may be performed on aqueous matrices. Non-aqueous matrices are already diluted before analysis 6) reagent water must be at least Type II (ASTM) for all standards, solutions, and sample preparation according to 6020 but is less stringent than IO-3.5, 7) internal standards and tuning solutions cover the entire mass range of analysis, but the elements used vary slightly from IO-3.5, 8) the MDLs are determined annually according to the requirements described in SOP 1210 Method Detection Limits 9) the ICB/CCB acceptance limit is the lower reporting limit and not the MDL per IO-3.5, since we do not report down to the MDL. 10) Germanium instead of yttrium is used as an internal standard, since yttrium is found in environmental samples.

6.0 DEFINITIONS

The STAT Analysis Quality Assurance Manual Section 19.0 contains all the definitions of standard terms used in SOPs.

7.0 INTERFERENCES

7.1 Isobaric elemental interferences in ICP-MS are caused by isotopes of different elements forming atomic ions with the same nominal mass-to-charge ratio (m/z). A data system must be used to correct for these interferences. This involves determining the signal for another isotope of the interfering element and subtracting the appropriate signal from the analyte isotope signal. Since commercial ICP-MS instruments nominally provide unit resolution at 10% of the peak height, very high ion currents at adjacent masses can also contribute to ion signals at the mass of interest. Although this type of interference is uncommon, it is not easily corrected, and samples exhibiting a significant problem of this type could require resolution improvement, matrix separation, or analysis using another verified and documented isotope, or use of another method.

7.2 Isobaric molecular and doubly charged ion interferences in ICP-MS are caused by ions consisting of more than one atom or charge, respectively. Most isobaric interferences that could affect ICP-MS determinations have been identified in the literature. Examples include $ArCl^+$ ions on the ^{75}As signal and MoO^+ ions on the cadmium isotopes. While the approach used to correct for molecular isobaric interferences is demonstrated below using the natural isotope abundances from the literature, the most precise coefficients for an instrument can be determined from the ratio of the net isotope signals observed for a standard solution at a concentration providing suitable (<1 percent) counting statistics. Because the ^{35}Cl natural abundance of 75.77 percent is 3.13 times the ^{37}Cl abundance of 24.23 percent, the chloride correction for arsenic can be calculated (approximately) as follows (where the $^{38}Ar\ ^{37}Cl$ contribution at m/z 75 is a negligible 0.06 percent of the $^{40}Ar\ ^{35}Cl$ signal): corrected arsenic signal (using natural isotopes abundances for coefficient approximations) = (m/z 75 signal) - (3.13) (m/z 77 signal) + (2.73) (m/z 82 signal), (where the final term adjusts for any selenium contribution at 77 m/z).

NOTE: Arsenic values can be biased high by this type of equation when the net signal at m/z 82 is caused by ions other than $^{82}Se^+$, (e.g., $^{81}BrH^+$ from bromine wastes. Similarly, corrected cadmium signal (using natural isotopes abundances for coefficient approximations) = (m/z 114 signal) - (0.027)(m/z 118 signal) - (1.63)(m/z 108 signal), (where last 2 terms adjust for any tin or MoO^+ contributions at m/z 114).

NOTE: Cadmium values will be biased low by this type of equation when $^{92}ZrO^+$ ions contribute at m/z 108, but use of m/z 111 for Cd is even subject to direct ($^{94}ZrOH^+$) and indirect ($^{90}ZrO^+$) additive interferences when Zr is present.

NOTE: As for the arsenic equation above, the coefficients in the Cd equation are **ONLY** illustrative. The most appropriate coefficients for an instrument can be determined from the ratio of the net isotope signals observed for a standard solution at a concentration providing suitable (<1 percent) counting precision. The accuracy of these types of equations is based upon the constancy of the OBSERVED isotopic ratios for the interfering species. Corrections that presume a constant fraction of a molecular ion relative to the "parent" ion have not been found to be reliable, e.g., oxide levels can vary. If a correction for an oxide ion is based upon the ratio of parent-to-oxide ion intensities, the correction must be adjusted for the degree of oxide formation by the use of an appropriate oxide internal standard previously demonstrated to form a similar level of oxide as the interferent. This

type of correction has been reported for oxide-ion corrections using ThO^+ /Th^+ for the determination of rare earth elements. The use of aerosol, desolvation, and/or mixed plasmas has been shown to greatly reduce molecular interferences. These techniques can be used provided that method detection limits, accuracy, and precision requirements for analysis of the samples can be met.

7.3 Physical interferences are associated with the sample nebulization and transport processes as well as with ion-transmission efficiencies. Nebulization and transport processes can be affected if a matrix component causes a change in surface tension or viscosity. Changes in matrix composition can cause significant signal suppression or enhancement. Dissolved solids can deposit on the nebulizer tip of a pneumatic nebulizer and on the interface skimmers (reducing the orifice size and the instrument performance). Total solid levels below 0.2% (2,000 mg/L) have been currently recommended to minimize solid deposition. An internal standard can be used to correct for physical interferences, if it is carefully matched to the analyte so that the two elements are similarly affected by matrix changes. When the intensity level of an internal standard is less than 30 percent or greater than 120 percent of the intensity of the first standard used during calibration, the sample must be reanalyzed after a fivefold (1+4) or greater dilution has been performed.

7.4 Memory interferences can occur when there are large concentration differences between samples or standards which are analyzed sequentially, deposition on the sampler and skimmer cones, spray chamber design, and the type of nebulizer affect the extent of the memory interferences which are observed. The rinse period between samples must be long enough to eliminate significant memory interference. Whenever an unusually concentrated sample is encountered, the sample after it may need to be reanalyzed to check for cross contamination.

8.0 SAFETY

Proper personal protective equipment including safety glasses, gloves and a lab coat are required during different parts of this method. Other safety precautions must be conducted in accordance with the Chemical Hygiene Plan. Other actions can also be applied if deemed necessary. A reference file of Material Safety Data Sheets (MSDS) for all reagents/chemical involved in this method is available to all personnel

Stock metal standards and acid solutions (strong oxidizers) may pose potential health risks. Extreme care should be utilized when handling these solutions.

9.0 EQUIPMENT AND SUPPLIES

The following apparatus is recommended for performing this procedure. Equivalent items can be used, if with their use, the analytical and QA/QC requirements in this SOP can be met.

9.1 Inductively coupled plasma-mass spectrometer: Aglient 7500i or equivalent.

9.1.1 A system capable of providing resolution, better than or equal to 1.0 amu at 10% peak height is required. The system must have a mass range from at least 6 to 240 amu and

a data system that allows corrections for isobaric interferences and the application of the internal standard technique. Use of a mass-flow controller for the nebulizer argon and a peristaltic pump for the sample solution are recommended.

9.1.2 Chiller - Neslab CT 100 or equivilent

9.1.3 Argon gas supply – high purity grade (99.99%).

9.1.4 Data system - An Agilent Kayak computer system using 3365 Chemstation Version C.00.01 to interpret spectral data is attached to the ICP-MS.

9.1.5 Autosampler – Cetac ASX-450 or equivalent.

9.2 Autopipettes – 0.01 to 0.10 mL, 0.1 to 1.0 mL, 1.0 to 5.0 mL.

9.3 Dispensing pipettes – 1 to 10 mL

9.4 Polypropylene Volumetric Flasks, - 50 mL, 100 mL, 250 mL, and 500 mL with screw caps. See section 14.8 for the procedure of checking the flask volume.

9.5 Plastic Tubes – 14 mL culture tubes and 50-mL graduated with screw caps.

9.6 Plastic bottles – 250 mL, 500 mL and one liter with Teflon screw caps

10.0 REAGENTS AND STANDARDS

The following reagents and standards are required to perform this procedure. When instructions are given on how to prepare a specific volume of a reagent or standard, larger or smaller volumes can be prepared as needed so long as the final concentrations remain the same. Any other deviations from the reagents or standards listed in this SOP could be detrimental to the quality of the data produced. Such deviations would have to be approved and documented (see SOP 230 Corrective Action).

Instructions for labeling and record keeping of reagents and standards are contained in SOP 1010 Analytical Standards and Reagents Receipt and Preparation. All standards solutions and QC solutions are stored at room temperature in plastic bottles.

10.1 Analytical reagent grade chemicals shall be used in all tests. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.

10.2 Reagent water - All references to water in this SOP refers to Type II reagent water (in-house system).

10.3 Calibration Stock Standard - Standard solutions can be prepared from pure standard materials or purchased as certified solutions. The routine laboratory practice is to purchase these standards from approved vendors. These stock standard solutions are purchased or prepared from ultra-high purity grade chemicals or metals (99.99 or greater purity) for most elements. The stock standards for individual elements are usually at concentrations of 1000 or 10,000 mg/L in solution. Custom blend stock standard solutions may also be purchased and used. Stock standard solutions and QC solutions are stored at room temperature in their original containers.

10.3.1 Secondary Calibration Stock Standard – These solutions are made using the individual Stock Standard solutions. Three secondary solutions are prepared by combining and diluting the individual stock standard solutions to levels in the linear range for the instrument in a matrix consisting of 2% (v/v) HNO_3 in reagent water. When preparing the secondary stock standards, each stock solution must be initially verified to determine correct preparation and/or the presence of impurities. Care must be taken when preparing the mixed standards that the elements are compatible and stable. The following amounts of each Stock Standard solution are pipetted into a 250 mL volumetric flask. The solution is brought to volume with 2% nitric acid (HNO_3). The final concentration of each component is listed in Table 1. These Secondary Stock Standard solutions are the source solutions to prepare the calibration standards in Section 10.4. Fresh mixed standards must be prepared as needed with the realization that concentrations can change on aging. Calibration standards must be initially verified using a quality control standard and monitored weekly for stability.

Table 1 Secondary Calibration Stock Standard Solutions

Secondary Stock Solution	Elements	Conc. Stock (mg/L)	Vol. Stock (mL)	Final Volume (mL)	Final Conc. (mg/L)
A	Al, As, B, Ba Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, Se, Tl, V, Zn	1000 each	2.5 mL each	250	10
	Sb, Mo, Sn, Ti		1.25 mL each		5
B	Ag	1000 each	2.5 mL each	250	10
C	Na, Ca, Mg, K, Fe	10,000 each	2.5 mL each	250	100

10.4 Calibration standards - Four calibration standards are prepared. Calibration standards in current use: 1, 10, 100, and 200 mg/L (for all elements except Ca, Fe, K, Mg, Mo, Na, Sb, Sn , and Ti (see Table 2). The following amounts of Secondary Stock Standard Solutions A, B, and C are pipetted into a 50 mL volumetric flask. Each calibration standard solution is brought to volume with 2% nitric acid (HNO_3). The final concentration of each component is listed in Table 2. Level 1 Calibration standard can be prepared by taking 5 mL of level 2 and diluting to 50 mL.

Table 2 Calibration Standards

Level	Volume (µL) Secondary Stock A and B	Volume (µL) Secondary Stock C	Final Volume (mL)	Final Conc. Trace Elements * (µg/L)	Final Conc. of Sb, Mo, Sn, & Ti (µg/L)	Final Conc. Major Elements (µg/L) Na, Ca, Mg, K, Fe
1	5mL of level 2 standard		50	1	0.5	10
2	50	50	50	10	5	100
3	500	500	50	100	50	1000
4	1000	5000	50	200	100	10000

* Except Sb, Mo, Sn, and Ti.

10.5 ICP-MS Internal Standard Stock Solutions: A solution containing 100 µg/mL ^{6}Li, ^{45}Sc, ^{159}Tb, ^{89}Y, ^{115}In and ^{209}Bi. Single element Germanium Standard 1000 mg/L. These solutions are purchased commercially.

10.5.1. Working Internal Standard Solution (1 mg/L): Pipette 1.0 mL of the mixed ICP-MS Internal Standard Stock Solution and 0.10 mL of the Germanium Standard into a 100 mL volumetric flask and bring to volume with 2% nitric acid (HNO_3). The working internal standard solution is added to a reservoir and will be added on-line to each standard, QC sample, and test sample at the time of analysis using a second channel of the peristaltic pump and an appropriate mixing manifold. This will deliver approximately 40 mg/L at the instrument for every sample/standard analyzed. Generally, an internal standard should be no more than 50 amu removed from the analyte.

10.6 ICP-MS Tuning Solution Stock 10 mg/L: Commercially purchased. This solution contains 10 mg/L each of Ce, Tl, Li and Y.

10.6.1. Working ICP-MS Tuning Solution 10 µg/L: Pipette 0.25 mL of the ICP-MS Tuning Stock Solution into a 250 mL volumetric flask and bring to volume with 2% nitric acid (HNO_3).

10.7 Stock 6020 Tune Check Solution: A solution containing elements representing all of the mass regions of interest (10 mg/L each of Li, Co, In, and Tl) must be prepared to verify that the resolution and mass calibration of the instrument are within the required specifications. This solution is also used to verify that the instrument has reached thermal stability. Purchased commercially.

10.7.1. Working 6020 Tune Check Solution 100 µg/L: Pipette 1.0 mL of the Stock 6020 Tune Check Solution into a 100 mL volumetric flask and bring to volume with 2% nitric acid (HNO_3).

10.8 Stock P/A Factor Tuning Solution (10 mg/L): Using multi-element Standards prepare a 10 mg/L Standard in 2% Nitric Acid.

10.8.1. Working P/A Factor Tuning solution 100 µg/L: Pipette 1.0 mL of the Stock 6020 Tune Check Solution into a 100 mL volumetric flask and bring to volume with 2% nitric acid (HNO_3).

NOTE: Working Calibration Standards 1, 2, 3, and 4 may also be used to determine P/A Factors.

10.9 ICP-MS Interference Check Solutions A and AB: Purchased commercially. See Attachment 2 for concentrations.

Working ICS Solutions:

10.9.1. ICS-A: Pipette 20.0 mL of ICP-MS Interference Check Solution A and 2 mL of concentrated Nitric Acid into a 100 mL volumetric flask and bring to volume with reagent water. ICS solution A must be prepared fresh weekly.

10.9.2. ICS-AB: Pipette 20.0 mL of ICP-MS Interference Check Solution AB and 2 mL of concentrated Nitric Acid into a 100 mL volumetric flask and bring to volume with reagent water. ICS solution AB must be prepared fresh weekly. The analyst should be aware that the solution might precipitate silver more quickly.

10.10 Laboratory Control Sample/Matrix Spike Stock - The LCS/matrix spike is prepared from individually purchased elements or custom blend stock standards. The Calibration Verification Stock Standards or Independent Stock Standards may be used to prepare the solution. The LCS/Matrix Spike Stock is prepared according to Table 3 below. Fill a 1000 mL volumetric flask with 400 mL of 2% v/v nitric acid. Pipette the appropriate volume of each analyte into the flask and bring to volume with 2% v/v nitric acid. This solution has a shelf life of six months.

Table 3 Laboratory Control Sample/Matrix Spike Stock

Elements	Conc. Stock (mg/L)	Vol. Stock (mL)	Final Volume (mg/L)	Final Conc. (mg/L)
Al, As, B, Ba Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, Se, Tl, V, Zn	1000 each	25 mL each	1000	25
Sb, Mo, Sn, Ti	1000 each	12.5 mL ea.		12.5
Ag	1000 each	10 mL each		10
Na, Ca, Mg, K, Fe	10,000 each	10 mL each		100

Spike with one milliliter of this stock solution per 50 ml digestate when preparing the LCS, LCSD, MS, MSD. For the Post Digestion Spike (PDS) samples, spike in the ratio of 1 mL per 50 mL digestate.

10.10.1 If ambient air filters are to be analyzed for Barium or Zinc, additional spike will need to be added. The additional spike should have a concentration of 24 mg/L of Barium and 0.5 mg/L of Zinc. Spike with 1 mL of the Barium and Zinc spike. To prepare this solution, add 100 mL of 2% HNO_3 to a 250 mL volumetric flask.

Pipette 6 mL of 1000 mg/L Ba standard and 0.125 mL of 1000 g/mL Zn standard. Dilute to volume.

10.11 Calibration Verification Stock Standard Solutions (ICV/CCV) – The Calibration Verification Stock Standard Solutions A and B are prepared from 1000mg/L single element standards. These solutions are prepared by combining and diluting individual stock standard to levels in the linear range for the instrument in a matrix consisting of 2 percent (v/v) HNO_3 in reagent water. Prior to preparing the calibration verification stock standards, each stock solution must be analyzed to determine correct preparation and/or the presence of impurities. Care must be taken when preparing the mixed standards that the elements are compatible and stable. The following amounts of each Stock Standard solution are pipetted into a 250 mL volumetric flask. The solution is brought to volume with 2 percent (v/v) HNO_3 in reagent water. The final concentration of each component is listed in Table 4. These Calibration Verification Stock Standard Solutions are the source solutions to prepare the Initial Calibration Verification (ICV), and Continuing Calibration Verification (CCV) standards. Fresh mixed standards must be prepared as needed with the realization that concentrations can change on aging. Calibration standards must be initially verified using a quality control standard and monitored for stability.

Table 4. Calibration Verification Stock Standard Solutions (ICV/CCV)

Secondary Stock Solution	Elements	Conc. Stock (mg/L)	Vol. Stock (mL)	Final Volume (mL)	Final Conc. (mg/L)
A	Al, As, B, Ba Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, Se, Tl, V, Zn	1000 each	2.5 mL each	250	10
	Sb, Mo, Sn, Ti	1000 each	1.25	250	5
	Na, Ca, Mg, K, Fe	10,000 each	2.5 mL each	250	100
B	Ag	1000 each	2.5 mL each	250	10

10.11.1 Initial Calibration Verification Standard (ICV) - To a 100-mL volumetric flask add about 80 mL of 2% Nitric Acid (HNO_3). Pipette 0.5 ml of secondary stock solutions A and B into this flask and dilute to the mark with 2 percent (v/v) HNO_3 .

10.11.2 Continuing Calibration Verification Standard (CCV) – To a 250-mL volumetric flask add about 200 mL of 2% Nitric Acid HNO_3). Pipette 2.5 ml of secondary stock solutions A and B into a 250-ml flask and dilute to the mark with 2 percent (v/v) HNO_3.

10.12 Blanks: Three types of blanks are required for the analysis. The calibration blank is used in establishing the calibration curve. The method blank is used to monitor for possible contamination resulting from the sample preparation procedure. The rinse blank is used to flush the system between all samples and standards.

10.12.1 The calibration blank consists of the same concentration(s) of the same acid(s) used to prepare the calibration standard solutions of the analytes (usually 2 % HNO_3in reagent water).

10.12.2 The method (or digestion) blank must be carried through the complete digestion procedure and contain the same volumes of reagents as the sample solutions.

10.12.3 The rinse blank consists of 2% HNO_3 in reagent water. Prepare a sufficient quantity to flush the system between standards and samples.

10.13 Nitric Acid: Acids used in the preparation of standards and for sample processing must be of high purity. Redistilled acids are recommended because of the high sensitivity of ICP-MS. Many more molecular-ion interferences are observed on the analytes when hydrochloric and sulfuric acids are used.

10.13.1 1:1 HNO_3: Cautiously and slowly add 100 mL concentrated HNO_3 to 100 mL of reagent water.

10.13.2 2% v/v HNO_3: Cautiously and slowly add 20 mL concentrated HNO_3 to a 1000 mL volumetric flask and bring to volume with reagent water and mix.

10.14 Argon gas supply: high-purity grade (99.99%).

11.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

11.1 The recommended containers used to collect samples for the determination of metals are polyethylene or fluorocarbon (TFE or PFA): 500 mL for water samples and 4 to 8 oz jars for soil samples.

11.2 Samples may be transported to the laboratory and stored at room temperature. Solid samples may be stored under refrigeration at between 0.1 and 6.0°C until time of digestion. Digestion and analysis must be within 180 days from sampling date. Sample digestates are stored at room temperature.

11.3 Aqueous samples must be preserved with 1:1 HNO_3 to a pH < 2.

11.4 For proper handling and storage of the PM10/SPM filters, see SOP 3115 Extraction of High Volume Filters.

12.0 QUALITY CONTROL

The following details the QC requirements that apply to this analysis. Each Quality Control Indicator (QCI) provides information pertaining to either method or individual sample performance. Our goal is to produce defensible data of known and documented quality. The results of these QCI samples are used to assess the acceptability of data.

12.1 **Blanks**

Method Blank analysis is performed to determine if any contamination is present in the analytical process and is used to evaluate acceptance of the batch of samples. A method blank shall be prepared once per preparation batch of 20 or less samples per matrix type. If more than 20 samples are prepared a second blank shall be prepared after the twentieth sample. The method blank shall be processed through all preparatory steps used for the

samples, including cleanup procedures. The blank shall be analyzed using the same instrument and conditions as the samples.

The Calibration Blank is used to monitor the initial level of contamination in the reagent solutions prior to initial calibration.

The Rinse Blank is used to monitor the ICP-MS system for potential cross-contamination from one sample to another or for residual contamination in the system.

12.2 **Initial Calibration Verification (ICV)**
An Initial Calibration Verification (ICV) standard containing all of the target analytes reported in this method (refer to section 10.11.1) shall be analyzed immediately after the completion of the initial calibration. The ICV shall be purchased from or prepared from second source standards to verify analyte concentrations.

12.3 **Continuing Calibration Verification (CCV)**
A CCV standard containing all of the target analytes reported in this method (refer to section 10.11.2) shall be analyzed after every tenth sample. The CCV standard shall be at a different concentration than the ICV, and shall be used to confirm the system is in calibration.

12.4 **Laboratory Control Sample (LCS)**
The LCS is used to evaluate the performance of the total analytical system, including all preparation and analysis steps. The LCS shall be prepared once per preparation batch of 20 or less samples per matrix type. If more than 20 samples are prepared a second LCS shall be prepared after the twentieth sample. The LCS shall be processed through all preparatory steps used for the samples, including cleanup procedures. The LCS shall be analyzed using the same instrument and conditions as the samples. Refer to section 10.10 for LCS analytes and concentrations.

12.5 **Duplicates**
Duplicates of field samples or of the LCS must be prepared in compliance with the method requirements and client directives. Note: the analysis of the Matrix Spike Duplicate (MSD) is used as a substitute for the laboratory duplicate. In those cases when there is insufficient sample to perform either a duplicate analysis or MSD analysis or the sample cannot be divided (e.g., wipes), the duplicate analysis of the LCS (LCS/LCSD) is used to judge the precision of the analytical results.

12.6 **Matrix Spike and Matrix Spike Duplicate (MS/MSD)**
MS/MSDs indicate the effect of the sample matrix on the precision and accuracy of the results generated using the selected method. This information does not determine the validity of the entire batch. MS/MSDs must be analyzed at a minimum of 1 per 20 samples per matrix per preparation procedure, or as specified by the required test method. If an MS/MSD pair is not analyzed in the preparation batch, an LCS/LCSD pair is analyzed. Samples chosen for matrix spiking are rotated among different clients and/or different client projects. This is accomplished through communication between the Department Manager and the analyst. In addition, designated samples, as indicated by client request or

contract requirement, are matrix spiked. The MS/MSD pair shall be processed through all preparatory steps used for the samples. They shall be analyzed using the same instrument and conditions as the samples. Refer to section 10.10 for MS analytes and concentrations. Some clients may require different spiking levels and/or target analytes. These specific needs are documented on the request for analysis forms.

12.7 **Internal Standards**

The internal standards for this method are used to monitor physical and matrix interferences and they are added to all samples, standards, and blanks. Refer to section 10.5 for preparation and concentration instructions.

12.8 **Interference Check Solutions**

The interference check solution (ICS) is prepared to contain known concentrations of interfering elements that will demonstrate the magnitude of interferences and provide an adequate test of any corrections. Chloride in the ICS provides a means to evaluate software corrections for chloride-related interferences such as $^{35}Cl^{16}O^{+}$ on ^{51}V and $^{40}Ar^{35}Cl^{+}$ on 75As+. Iron is used to demonstrate adequate resolution of the spectrometer for the determination of manganese. Molybdenum serves to indicate oxide effects on cadmium isotopes. The other components are present to evaluate the ability of the measurement system to correct for various molecular-ion isobaric interferences. The ICS is used to verify that the interference levels are corrected by the data system within quality control limits. The ICS pair, solutions A and AB, is analyzed after calibration, every twelve hours of analysis, and at the end of the analytical batch. Refer to Section 10.9 for the preparation of these solutions.

Note: For ambient air filters, the ICS pair is analyzed every eight hours of analysis, and at the end of the analytical batch.

12.9 **Serial Dilutions**

If the analyte concentration is within the linear dynamic range of the instrument and sufficiently high (minimally, a factor of at least 100 times greater than the concentration in the reagent blank, an analysis of a fivefold (1+4) dilution must agree within 10% of the original determination. If not, an interference effect must be suspected. One dilution test may be included for each twenty samples (or less) in a batch.

12.10 **Post-Digestion Spike**

This test may be applied for new or unusual matrices. An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 75 to 125 %R of the known value or within the laboratory derived acceptance criteria. The spike addition should be based on the indigenous concentration of each element of interest in the sample. If the spike is not recovered within the specified limits, the sample must be diluted and reanalyzed to compensate for the matrix effect. Results must agree to within 10% of the original determination. The use of a standard-addition analysis procedure may also be used to compensate for this effect.

13.0 CALIBRATION AND STANDARDIZATION

Calibrate the instrument after tuning to generate an acceptable Tune Report (section 14.2.1), and setting the Pulse/Analog factors for each analyte.

Note: Generating a tune report and setting the Pulse/Analog factors needs to be done only once each day. After calibration the software goes immediately into sample analysis. Step by step instructions to calibrate are listed in the procedure in section 14.

Initial Calibration (ICAL)
In addition to achieving the reference method requirements for the minimum number of calibration standards and the acceptance criteria (statistics) for calibration curve fit, the following ICAL criteria also apply:

13.1 The ICAL must be a minimum of two standards, not including a blank. Flush the system with the rinse blank between each standard solution. Use the average of at least three integrations for both calibration and sample analyses. All masses that could affect data quality should be monitored to determine potential effects from matrix components on the analyte peaks.
13.2 The ICAL must be verified with a second source standard (ICV) prior to the analysis of samples.
13.3 Results of samples not within the linear range of the instrument must be qualified on the final report. Dilute the sample and reanalyze in order to achieve a result within the linear range of the instrument.
13.4 The lowest calibration standard may establish the reporting limit: see Attachment 1 for analyte reporting limits (RL). The RL must be greater than the detection limit.

Initial Calibration Verification (ICV)
In addition to the method requirements, the following ICV criteria also apply:

13.5 Must be a second source standard from the ICAL standards or from a different manufacturer lot number.
13.6 Must be traceable to NIST when available.

13.7 Initial Calibration Blank (ICB): (2% HNO_3) Analyzed immediately after the ICV. Acceptance limits are ± RL.

Continuing Calibration Verification (CCV)
In addition to the method requirements, the following CCV criteria also apply:

13.8 Must be analyzed every 10 samples and at the end of each analytical batch.
13.9 Continuing Calibration Blank (CCB): (2% HNO_3 Analyze immediately after the CCV. Acceptance limits are ± RL.
13.10 If the CCV results obtained are outside the acceptance criteria, corrective actions must be performed. If routine corrective actions fail to produce an acceptable second consecutive CCV, then sample analyses cannot continue until a new ICAL is established and verified with an ICV.
NOTE: For calibration verification purposes, the CCV/CCB is analyzed as a set.

However, sample data associated with an unacceptable CCV may be reported as qualified data under the following special conditions:

13.10.1 When the acceptance criteria for CCV are exceeded high, i.e., high bias, and there are associated samples that are non-detects, then those non-detects may be reported. Otherwise the samples affected by the unacceptable calibration verification must be reanalyzed after a new ICAL has been established, evaluated and accepted.

13.10.2 When the acceptance criteria for the CCV are exceeded low, i.e., low bias, those sample results may be reported if they exceed a maximum regulatory limit/decision level. Otherwise the samples affected by the unacceptable verification must be reanalyzed after a new ICAL is established and verified with an ICV.

13.10.3 When the acceptance criteria for the CCV are exceeded and it is not possible to reanalyze the sample due to limited sample quantity AND a new sample cannot be obtained by the laboratory, the data may be reported with the appropriate data qualifiers if the client has been contacted and agrees, in writing, to accept the qualified data.

13.11 Records: Initial and Continuing Calibration Records will contain, at a minimum, the following:

1. Calibration date
2. Test method
3. Instrument
4. Analysis date
5. Each analyte name
6. Analyst's initials or signature
7. Standard Concentration (appropriate units) and number of standards
8. Response (appropriate units)
9. Calibration curve or response factor
10. Statistics for ICAL curve fit in order to judge calibration curve acceptance
11. Acceptance Limits for ICV analysis in order to judge calibration curve acceptance
12. Acceptance Limits for CCV analysis in order to judge continuing calibration acceptance
13. Calibration Standards and Reagent Solutions ID's

Table 5 Calibration Requirements

QCL	Frequency	Standards	Control Limits	Corrective Action
ICAL	Daily or as needed	Minimum of two standards, see Table 2 for concentrations	r = 0.995	Correct problem then repeat initial calibration
ICV	After each new ICAL	25µg/L, 50 µg/L, 500 µg/L	± 10% of true value	Correct problem then repeat ICV or initial calibration
ICB	After each new ICV	Reagent Blank (2% HNO_3)	< RL	Correct problem then repeat ICB
CCV	Every 10 samples, and end of the batch	50 µg/L, 100 µg/L, 1000 µg/L	± 10% of true value	Correct problem then repeat CCV and associated samples, or repeat initial calibration
CCB	After each CCV	Reagent Blank (2% HNO_3)	< RL	Correct problem then repeat CCB and associated samples

Support Equipment
Autopipettes - Check autopipette to ensure standardization is within control limits (see SOP 1040 General Laboratory Practices for Pipette Calibration).

Dispensing Pipettes Check pipette to ensure standardization is within control limits (see SOP 1040 General Laboratory Practices for Pipette Calibration

14.0 PROCEDURE

14.1 Sample Preparation

14.1.1 Acid Digestion: Samples requiring digestion must be prepared by one of the following methods prior to ICP-MS analysis.

Matrix	SOPs
Water	3005
Soil/sediment/Waste	3110
TSP/PM10 filters	3115

14.1.2 Direct Analysis
For Dissolved Metals Analysis:
Filtering the Sample Through a 0.45 Micron Filter.
Wash the filter paper or filter disk with 5 mL of 2% nitric acid followed by 2-3 mL of sample before filtering the aliquot to be tested. Record this procedure in the comments section of the ICP-MS Preparations logbook. Take a 10 ml aliquot of the filtered sample and acidify with 0.2 mL of concentrated HNO_3. Filter a MB and LCS to be analyzed with the batch.

Also prepare a MS/MSD (if sample amount permits, otherwise prepare an LCS/LCSD), by spiking 10 mL of the filtered sample with 0.2 mL of LCS/MS stock (section 10.10) and analyze with the samples. Report results as dissolved metals.

For Drinking Water Analysis - Take a 10 ml aliquot of the sample and acidify with 0.4 mL of 1:1 HNO_3. Report results as total metals.

14.2 ICP-MS Analysis

Turn on the argon flow (100 psi minimum) from the Dewar. Turn on the water chiller. Connect all pump tubing. Double click ICP-MS Top icon. A message will appear "Is ISIS power on?" Turn it on if not already on. Click <yes>, <instrument>, <instrument control>, <plasma>, and <plasma on> to ignite the plasma and allow at least 30 minutes for warm up.

14.2.1 TUNING:
Click <ALS> in the instrument control screen, and <Go To>, to move the sipper probe to the tune solution. Put the internal standard tubing into reagent water. Close the Instrument Control Window. Open the tune screen by clicking <Instrument> and <Tune>. The tune window will open. Click <start> to monitor the counts per 0.1 seconds, and give a visual display of the RSD for counts for ^{7}Lithium, ^{89}Yttrium and ^{205}Thallium. The tune screen also displays the settings for

the Plasma Orientation, Gas Flows, Peripump RPMs, Lens settings, Q-Pole settings and Detector Parameters.

Tune the Agilent 7500 for sensitivity to ensure that the instrument produces the best results for the masses being analyzed. Achieve good sensitivity by running a recommended tuning solution of 10 parts per billion (ppb) of Li, Y, Ce and Tl. [ICP-MS Working Tuning Solution, 10.6]. If necessary adjust the tune parameters for maximum sensitivity, reducing Oxide Ions, and Doubly Charged Ions.

Operating conditions: Attachment 4 lists the affects of adjusting the parameters in the tune window on the tune of the instrument. Once you have adjusted the parameters satisfactorily, generate a Tune Report.

NOTE: A Tune Report MUST be generated prior to analyzing samples every day, whether the parameters have been changed or not.

TUNE SPECIFICATIONS:
Sensitivity:
Li > 5,000 cts/0.1sec @10 ppb concentration
Y > 10,000 cts/0.1 sec @ 10 ppb concentration
Tl > 5,000 cts/0.1sec @ 10ppb concentration

Precision:
Li < 15% RSD (0.1 sec integration time)
Y < 10% RSD (0.1 sec integration time)
Tl < 10% RSD (0.1 sec integration time)

Oxides: < 1.2 %

Double Charged: Ce ++/Ce+ < 5.0%

Background:
Li < 30 cps
Y <15 cps
Tl < 15 cps

Mass Resolution: W-10% 0.65 – 0.8 AMU

Mass Axis: nominal mass +/- 0.1 AMU for ^{7}Li, ^{89}Y and ^{205}Tl

After generating an acceptable tune report insert the sample tube for internal standards into the Internal Standard working solution and place the sipper probe for the sample line into 2% v/v HNO_3 rinse solution. Allow the system to rinse out the lines for at least five minutes.

14.2.2 SETTING P/A FACTORS:
ChemStation automatically switches between pulse and analog mode. For linear calibration curves, these two modes should be adjusted by using P/A Factor tuning.

The counts of each element must range from 400,000 to 4,000,000 cps to get accurate P/A Factors. The P/A factor adjustment must be performed everyday to get accurate results in a sample with a wide concentration range where both the pulse and analog mode are used.

Determine the P/A Factors by

1. Moving the sipper probe in the lowest concentration P/A solution.
2. After the solution has rinsed through into the plasma, click <tune> <adjust P/A factors>. 3. Click on <Load masses from acq. method> in the window that pops up.4. Click <run>. After about 20 seconds a message appears saying, "accept current P/A factors?" Check the clipboard window behind the message. Either a number (the P/A factor) or a message that states "sensitivity is too low" appears next to each mass. Click <yes> to accept the P/A factors and close out the clipboard window. If a message appears that states "sensitivity is too high" you can accept the P/A factor but will need to P/A with a lower concentration solution to get the P/A factor for the mass that gave "sensitivity too high."

Repeat steps 1, 2, and 4 for successively higher analyte concentrations until you have P/A factors for all masses of interest. Check the box "Merge in the current data" if not already checked. This will add in successive P/A factors without deleting the P/A factors for the masses, which have P/A factors already.

DO NOT REPEAT STEP 3 (click on <Load masses from acq. method> for each successive solution). This clears out all your P/A factors and should only be clicked on before you first start to P/A.

14.2.3 Load the appropriate method. (IO35.M for ambient airs samples, or 6020G.M for all other analyses.

14.2.4 TUNE CHECK:

Prior to calibration and analysis the tune conditions must be verified by analyzing a Tune Check Solution at least five times with relative standard deviations of < 5% for the analytes contained in the tuning solution.

Conduct mass calibration and resolution checks in the mass regions of interest. The mass calibration and resolution parameters are required criteria, which must be met prior to any samples being analyzed. If the mass calibration differs more than 0.1 amu from the true value, then the mass calibration must be adjusted to the correct value. The resolution must also be verified to be less than 0.9 amu full-width at 10 percent peak height.

14.2.4.1 After tuning and P/A adjustments go to ICPMS top and click on <sequence>, <edit>, in the dropdown box on the left select TUNE, CCV, CALIB, or ICS, to edit the comment section in each of these screens. Enter any new solution preparation numbers for standards, ICV, CCV, ICB, ICS A, etc. in the comment column. Click <OK> at the bottom to save changes.

14.2.4.2 Click on <sequence>, <edit> again and select "SMPL" from the dropdown box to open up the sample sequence table. Edit inserting information under the column headings, VIAL (vial position), METHOD, SAMPLE (sample ID), COMMENT (sample test code), and Dil/Lv (dilution factor) for all samples to be analyzed. Click <print> to print out the list to refer to when placing the sample tubes in the racks and checking the order for correctness before starting analysis. Then click <save> to save the sample table. Samples are analyzed in order as they appear in the sample table.

14.2.4.3 Uncap and place all standards, tune check, and check standards in their proper places in rack #1. Racks #2-4 are for sample tubes.

14.2.4.4 Start the calibration and running of samples by clicking <sequence>, <run>. "Full Method'" and "Overwrite Existing Data Files," should be checked. Enter the instrument ID and your initials in the box for operator name and click <run sequence>. The software will run a blank, tune check, then the calibration followed by samples. After all samples have run the software will analyze a final ICS A, ICS AB, blank, CCV, and CCB. The plasma will then shut off and the ISIS program will stop. If additional samples will be analyzed later it will be necessary to insert blanks into the sample table to keep the instrument running.

14.2.4.5 Verify the Tune Check when complete. RSDs for Li, Co, In, and Tl must be < 5% and the mass calibration for each mass must be within 0.1 AMU of the mass number and <0.9 AMU at 10% peak height. If not abort the run and restart to rerun the Tune Check.

14.2.5 Initial Calibration and Quality Control Checks

14.2.5.1 Check each standard to determine if all internal standard cps are within 20% of the calibration blank's cps. If not abort the run and restart.

14.2.5.2 Check the ICV and ICB to determine if masses of interest are within tolerance. If they are continue with sample analysis. Rinse time before and after the samples are programmed into the method as well as analysis of CCV and CCB after every ten samples.

14.2.5.3 If an internal standard fails for any mass in a sample the system will run a blank before proceeding with analysis.

14.2.5.4 Perform all qualitative and quantitative measurements as described in Sections 14.4 and 14.5. After analysis, store the digests at room temperature.

14.2.6 The analytical sequence for Initial Calibration is:
(Tune Check)
Blank
Calibration Blank
Calibration standard (S1)
Calibration standard (S2)
Calibration standard (S3)
Calibration standard (S4)
Blank
Initial Calibration Verification Standard (ICV)

Initial Calibration Blank (ICB)
Interference Check Solution A (ICS A)
Interference Check Solution AB (ICS AB)
Blank

A typical analytical sequence for Sample Analysis is:
Method Blank (MB)
LCS
(LCS Duplicate optional)
Sample #1
Sample #1 Matrix Spike (MS)
Sample #1 Matrix Spike Duplicate (MSD)
Samples #2, #3, etc. up to 10 analytical samples
CCV
CCB
10 analytical samples (which may include, MB, LCS, MS, MSD, samples)
CCV
CCB
....
ICS A
ICS AB
blank
CCV
CCB

14.3 Data Interpretation - Qualitative Analysis

To obtain analyte data of known quality, it is necessary to measure more than the analytes of interest in order to apply corrections or to determine whether interference corrections are necessary. If the concentrations of interference sources (such as C, Cl, Mo, Zr, W) are such that, at the correction factor, the analyte is less than the limit of quantification and the concentration of interferents are insignificant, then the data may go uncorrected. Note that monitoring the interference sources does not necessarily require monitoring the interferent itself, but that a molecular species may be monitored to indicate the presence of the interferent. When correction equations are used, all QC criteria must also be met. Extensive QC for interference corrections are required at all times. The monitored masses must include those elements whose hydrogen, oxygen, hydroxyl, chlorine, nitrogen, carbon and sulfur molecular ions could impact the analytes of interest. Unsuspected interferences may be detected by adding pure major matrix components to a sample to observe any impact on the analyte signals. When an interference source is present, the sample elements impacted must be flagged to indicate (a) the percentage interference correction applied to the data or (b) an uncorrected interference by virtue of the elemental equation used for quantitation. The isotope proportions for an element or molecular-ion cluster provide information useful for quality assurance.

NOTE: Only isobaric elemental, molecular, and doubly charged interference corrections that use the observed isotopic-response ratios or parent-to-oxide ratios are acceptable corrections for use in this method.

14.4 Data Interpretation - Quantitative Analysis

Calculations including appropriate interference corrections, internal-standard normalization, and the summation of signals at 206, 207, and 208 m/z for lead (to compensate for any differences in the abundances of these isotopes between samples and standards), are performed automatically by the instrument during analysis.

14.5 Records

Record the following information in the appropriate logbook or data file. Include any deviations from this procedure. Analyst initials, date of analysis, sample number or ID, initial sample volume or weight processed, calibration standard, sample, or solution identifier, QC sample or solution identifier, internal standard solution identifier, any dilution information, readings from support equipment, data file name, instrument method name, visual observations, and any other information as deemed necessary.

14.6 Troubleshooting

The sample line tubing and internal standard tubing should be checked for even flow when the instrument is first started by observing and air bubble passing through the line. Adjust the tension on the tubing so that it is just tight enough to allow the air to evenly move through the tubing without any pulsing.

Check for leaks and air bubbles at tubing connections, tee connectors and fittings. The majority of problems you encounter occur somewhere along the sample introduction path.

Ensure that the argon Dewar has enough argon to maintain a pressure of 100 psi throughout the run.

14.7 Routine Mainte nance

Record all maintenance in the instrument logbook. For non-routine maintenance record the problem, what was done to correct it and whether the correction solved the problem.

14.7.1 Daily, or as needed according to sample throughput, examine the tubing
14.7.2 Clean the sample and skimmer cones on an as needed basis (loss of sensitivity).
14.7.3 Inspect the pump tubing for wear and replace as necessary. Check the Argon gas supply; replace as necessary.

14.8 Calibration of the Polypropylene Volumetric Flasks

(Yearly, independently check flask volume with reagent water using a balance to monitor weight of water volume: tolerance is stated volume ± 0.1%). Perform this check every year.

14.8.1 Initially check the volume of each flask. Using an analytical balance, record the weight of the empty and dry flask.
14.8.2 Add room temperature de-ionized reagent water.
14.8.3 Fill to mark and re-weigh.
14.8.4 Subtract initial weight from final weight.
14.8.5 Divide the result by the volume of the flask and multiply by 100.
14.8.6 The percent recovery should be ±0.1%.
14.8.7 Record this information and label the flask for reference.

15.0 DATA REDUCTIONS, CALCULATIONS, AND LOADING

15.1 The data system prepares a calibration curve by plotting response versus standard concentration. Sample concentration is calculated from the regression equation.

NOTE: The LIMS program will convert µg/L to the appropriate reporting units.

15.2 Report only those values that fall between the lowest calibration standard and the linear range of the instrument. Samples exceeding the linear range must be diluted and reanalyzed.

15.3 For sample results greater than the linear range, dilute the sample in a 15 mL centrifuge tube using 2% HNO_3. Pipette in the appropriate volume of sample into the tube and dilute to volume with 2% HNO_3. Dilution Factor = (10 mL/ digestate volume analyzed in mL). Use the dilution factor and calculate the concentration in the digestate as follows:

Concentration in mg/L = readout * 0.001 (10 mL/ digestate volume analyzed in mL)

15.4 Air Samples: calculate the concentration as follows:

Conc. in $\mu g/m^3$ = readout in µg/L * (10 mL/ initial sample air volume in m^3) * 1 L/1000 mL

NOTE: $1m^3$ = 1000 Liters

15.5 TSP/ PM10 Ambient Air Samples

15.5.1 Each filter should have an associated volume of air sampled, average temperature and pressure. This value is corrected to the EPA standard volume using the equation listed below.

$$V_{std} = V_{avg} (P_{avg}/760\text{mm Hg})(298K/T_{avg})$$

Where:
V_{avg} is the calculated average flow rate during the elapsed sampling time (field data)
P_{avg} is the average barometric pressure in mm Hg during the sample run (field data)
T_{avg} is the average temperature in K during the sample run (field data)

15.5.2 Metals concentration in the air samples can then be calculated as follows:

$$C = [(\mu g \text{ metal/L}) \times (\text{Digestion volume, L/strip})(9) - F_m]/V_{std}$$

where:
C = concentration, µg metal/m3.
µg metal/L =determined metal concentration determined
final extract volume (L)/strip = total sample extraction volume from extraction procedure
9 = Useable filter area, [20 cm x 23 cm (8" x 9")]
Exposed area of one strip, [2.5 cm x 20 cm (1" x 8")].
F_m = average concentration of blank filters, µg.

V_{std} = standard air volume pulled through filter, std. m^3 (@25°C and 760 mm Hg).

15.5.3 When corrected average volume, average pressure and average temperature are NOT provided for a given filter, calculate µg metal/filter using the following equation

µg metal/ filter =[(µg metal/L) x (Digestion volume, L/strip)(9) - F_m]

15.5.4 Reported values should be blank subtracted for filters that STAT Analysis supplies to the client.

15.6 Wipe Samples: calculate the concentration as follows:

Conc. in µg/ft^2 = readout in µg/L * (50 mL/ initial wipe area in ft^2) * 1 L/1000 mL

NOTE: 1 ft^2 = 144 in^2 = 12 in * 12 in

15.7 Aqueous Samples: The concentration readout for aqueous sample digestates is µg/L. It does not need further data reduction unless the initial sample volume was less than 50 mL. If less than 50 mL sample was digested, calculate the concentration as follows:

Concentration in mg /L = readout *0.001 *(50mL/ initial sample volume digested in mL)

15.8 Soil Samples: The concentration readout for soil samples must be multiplied by the following factor: Factor = (50 / sample weight in g). Calculate the concentration in soil samples as follows:

Conc. in mg/Kg = readout * 0.001 (50 mL/ sample weight in g) * 1 L/1000 mL * 1000 g /1 Kg

15.9 Soil samples reported on a dry weight basis: The concentration is divided by the decimal equivalent of the percent residue of the soil after oven drying at 105 °C.

15.10 Report results in the appropriate units.

15.11 The procedure for uploading data into the LIMS system is detailed in SOP 1400 LIMS.

16.0 METHOD PERFORMANCE

Demonstration of Capability (DOC)
All parameters of interest must meet the method acceptance criteria before actual sample analysis begins. See SOP 1230 Training for the procedure to perform and document the DOC. The DOCs for the analysts performing this method are located in the analysts' training form folders located in the QA office files.

A QC reference concentrate is required containing each analyte at a concentration of either 10 or 100 mg/L. The QC reference sample used is a ten-fold dilution of the CCV solution. The QC

reference sample is made using stock standards prepared independently from those used for calibration.

For each analyte calculate the mean recovery (X) and standard deviation (s) and the average % Recovery (%R). Compare X and s and %R with the corresponding acceptance criteria for accuracy and precision, respectively. X must be within 9/90 and 11/110 µg/L, respectively, and s must be less than 1.0/10.0 µg/L, respectively, and %R must be within 100 ± 10%.

These limits are taken from established in-house criteria. If X and s and %R for all analytes meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual X or %R falls outside the range for accuracy or any individual s exceeds the precision limit, then the system performance is unacceptable for that analyte and corrective action must be taken.

Comparison to Reference Method Data:
EPA Method 6020 Table 4, aqueous samples, provides guidance for the establishment of control limits for the LCS samples.

EPA Method 6020 Table 5, solid samples, provides guidance for the establishment of control limits for the LCS samples.

EPA Method IO-3.5, Table 7, solid samples, provides guidance for the establishment of control limits for the LCS samples.

In-House Control Limits: Method performance data is on file in the laboratory QC department. Comparison of method performance data for the laboratory to the reference method criteria occurs when laboratory in-house acceptance limits are generated. In-house generated data is compared to the specifications of the reference method. If the in-house limits are within the specifications of the reference method, the control limits are updated in LIMS. If the in-house limits are not within specifications, an investigation is performed to determine the cause(s) of the problem and a corrective action is completed. The analysis may continue until enough data points are collected to regenerate new control limits. Any QC data generated outside of reference method limits during that time frame is flagged.

The laboratory maintains performance records to document the quality of data that is generated. Method accuracy for samples is assessed and records maintained.

Control limits for the method parameters are generated by the QC staff and distributed to the analysts via updates to the LIMS control charts. The control limits are calculated based on in-house performance data. At a minimum, these limits are reviewed annually.

17.0 POLLUTION PREVENTION

The preparation of excessive volumes of laboratory reagents and standards shall be avoided so that waste and potential for pollution are minimized. Samples, reagents and standards shall be disposed in compliance with the lab waste disposal program, SOP 1130 Waste Disposal. With the consent of the client, the samples may be returned to their origin for treatment.

Uncontaminated paper waste, glass and cans should be separated for recycling. Laboratory staff is required to protect the laboratory and our clients' business information when disposing of recycled paper or waste from the facility.

18.0 DATA ASSESSMENT AND CRITERIA FOR QUALITY CONTROL MEASURES

Data assessment includes review of: proper sample condition, preservation, and storage; analysis within holding time limitations; deviations from the SOP, evaluation of performance based on in-house control limits, reference method limits or project specific limits.

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a calibration verification standard is used to confirm the measurements were performed in an in-control mode of operation. The data review is conducted according to SOP 1250 Data Review.

18.1 Blanks

If the Method Blank, ICB or CCB exceeds the RL the source of contamination must be investigated and corrective actions taken. The analyte concentrations in the method blank of a digestion batch must be less than the RLs listed in Attachment 1. If these criteria are exceeded, re-analyze the method blank. If after re-analysis, the blank criteria are still exceeded, then the entire digestion batch must be re-digested or qualified. Always refer to a client specific QAPP for additional guidance.

Affected samples must be reprocessed and reanalyzed or Data must be appropriately qualified if:

1) The concentration of a targeted analyte in the blank is at or above the reporting limit as established by the SOP or by regulation, AND is greater than 1/10 of the amount measured in any sample.
2) The blank contamination otherwise affects the sample results as per the test method requirements or the individual project data quality objectives.

18.2 Laboratory Control Samples (LCS)

The results of the individual batch LCS are calculated in percent recovery (%R). Results are compared to established acceptance criteria: 100 ± 20% for all samples. If the LCS is outside the acceptance criteria the analytical system is "out-of-control." Any affected samples associated with an out of control LCS must be reprocessed and reanalyzed or the results reported with appropriate data qualifiers. If after re-analysis the control criteria have not been met, the entire digestion batch must be redigested for the out of control analytes of interest. Always refer to a client specific QAPP for additional guidance.

18.3 Duplicates

The results from laboratory duplicates are designed to assess the precision of analytical results in a given matrix and are expressed as relative percent difference (RPD). See the STAT QAM, Section 5.4 for the calculation for RPD. Results are compared to established

acceptance criteria as listed in the MS/MSD. For duplicates results outside established criteria corrective action must be documented or the data reported with appropriate data qualifying codes.

For this test method, the analysis of the MS/MSD pair is used for determination of method precision. Duplicate LCS samples will be analyzed for all matrices where it would be impractical to perform a MS/MSD, such as wipe samples. Precision limits of 20% will be used for RPD acceptance criteria for MS/MSD and LCS/LCSD.

18.4 Matrix Spikes

The results from MS/MSD are primarily designed to assess the precision and accuracy of analytical results in a given matrix and are expressed as percent recovery (%R) and relative percent difference (RPD). See the STAT QAM, Section 5.4 for the calculation for RPD. Results are compared to established acceptance criteria: 100 ± 25%R and 20% RPD for all samples. For matrix spike results outside established criteria corrective action must be documented or the data reported with appropriate data qualifying codes. The RPD control limits are for analyte values greater than 100 times the instrumental detection limit. If this limit is exceeded, the reason for the out-of-control situation must be found and corrected.

NOTE: The %R limits will not apply to samples with analyte concentrations that are greater than four times the spike level.

Post Digestion Spike (PDS): This test may be applied for new or unusual matrices. An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 75 to 125 %R of the known value or within the laboratory derived acceptance criteria. The spike addition should be based on the indigenous concentration of each element of interest in the sample. If the spike is not recovered within the specified limits, the sample must be diluted and reanalyzed to compensate for the matrix effect. Results must agree to within 10% of the original determination. The use of a standard-addition analysis procedure may also be used to compensate for this effect.

18.5 Internal Standards

The results of the individual Internal Standard compounds on all samples, blanks, and spikes are calculated in percent recovery (%R) and are compared to established acceptance criteria. For instrument method 6020G.M, if the Internal Standard recovery in the test sample is outside the acceptance criteria, 30 to 120% of the response of the applicable internal standard in the ICAL Blank, corrective action must be taken. For ambient air samples, instrument method IO35.M, this limit is 60-125 %R. A dilution test (1+4) may be performed to minimize the matrix effect. Report the results from the diluted sample if internal standard recovery is acceptable.

NOTE: If the Internal Standard recovery in the calibration standards, ICV, ICB, CCV, or CCB is outside the acceptance criteria, 80 to 120% of the response of the applicable internal standard in the ICAL Blank, corrective action must be taken and affected samples must be reanalyzed.

18.6 Dilution Test

If the analyte concentration is within the linear dynamic range of the instrument and sufficiently high (minimally, a factor of at least 100 times greater than the concentration in the reagent blank, an analysis of a fivefold (1+4) dilution must agree within 10% of the original determination. If not, an interference effect must be suspected. One dilution test may be included for each twenty samples (or less) in a batch.

18.7 ICS

Verify the magnitude of elemental and molecular-ion isobaric interferences and the adequacy of any corrections at the beginning of an analytical run and once every 12 hours for instrument method 6020G.M. For ambient air sample, instrument method IO35.M, the ICS pair is analyzed at the beginning of the analytical run and once every eight hours. The ICS pair is analyzed at the end of the run as well for both methods. Do this by analyzing the interference check solutions A and AB. The analyst should be aware that precipitation from solution AB may occur with some elements, specifically silver. The recovery of each element in the ICS solution should be 100 ± 20%.

18.8 Instrument Detection Limits

IDLs in µg/L can be estimated by calculating the average of the standard deviations of the three runs on three non-consecutive days from the analysis of a reagent.blank solution with seven consecutive measurements per day. Each measurement must be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples). IDLs must be determined at least every three months and kept on file.

19.0 CORRECTIVE ACTIONS FOR OUT-OF-CONTROL DATA

The process for handling unacceptable and out of control data is found in SOP 230 Corrective Action.

If the ICV, ICB, CCV, CCB, MB, LCS/LCSD, MS/MSD, PDS, lab duplicate, or internal standard recovery of any parameter falls outside the designated acceptance range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrective action taken. The analytical result for that parameter in the samples is suspect and is only reported for regulatory compliance purposes with the appropriate corrective action. Immediate corrective action includes reanalyzing all affected samples by using any retained sample before the expiration of the holding time. Final data results must be qualified in the client report for reported results not meeting the laboratory-defined criteria.

1) Review standards preparation logbooks. Check all calculations and ensure dilution factors are properly recorded.
2) Re-prepare the suspected standard or QC sample to identify possible preparation errors of the standard or QC sample.
3) Re-Analyze the samples when the CCV or LCS is not within acceptable limits.
4) Perform routine preventative maintenance following manufacturer's specification. Record all maintenance in the instrument logbook.

20.0 CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

Every effort is made to prevent problems from occurring. When out of control or unacceptable data occurs the first option is to identify the problem and reanalyze the samples within the holding times. When this is not possible, the QA Manager and/or the Laboratory Director will review data and discuss options with the client. Reanalysis or reporting the data with qualification are alternatives. Out of control or unacceptable data reported to the client must include the data qualifier, flag and discussion on the rationale for reporting.
Holding time exceedence, improper preservation and improper sample condition or storage are noted on the corrective action form and included on the final report.
Review the CCV standard response, LCS result, ICS results, and internal standard recovery for acceptable performance for each batch of samples. Record any trends or unusual performance on a corrective action form. Final data results must be qualified in the client report for results not meeting the laboratory-defined criteria.

20.1 The process for handling unacceptable and out of control data is found in the Laboratory QAM Section 11. The reporting of data that is out of control must be approved and documented by Quality Assurance Manager and either the Technical Manager or the Laboratory Director.

20.2 Client Requested Modifications:
- 20.2.1 Clients must request modifications from the laboratory SOP in writing to the lab.
- 20.2.2 The lab director, technical manager and quality assurance manager will evaluate the requested client deviations, determine the feasibly of the deviation and the potential effects on the data.
- 20.2.3 If it is determined that the lab will perform the requested deviations, lab director, technical manager and quality assurance manager will decide if a method validation study is required.
- 20.2.4 The designated project manager will retain all documentation concerning the requested deviation, including all correspondence with the client, in the client folder.
- 20.2.5 The final analytical report must include the statement "This report has analyses performed using client requested modifications."

21.0 WASTE MANAGEMENT

The STAT Analysis Corporation Waste Disposal SOP 1130 identifies proper waste management practices for the chemicals and biological materials used in this procedure. Samples are stored and discarded accordance with SOP 1130 Waste Disposal.

22.0 REFERENCES

22.1 Method 6020, Revision 0, December 1996; U.S. EPA SW-846 "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods" Update III, December 1996

22.2 Compendium Method IO-3.5 Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air: Determination of Metals in Ambient Particulate Matter Using Inductively Coupled Plasma/ Mass Spectrometry (ICP/MS), U.S. EPA, June 1999.

22.3 STAT Analysis Corporation Quality Assurance Manual
22.4 STAT SAP 003 Chemical Hygiene Plan
22.5 STAT SOP 230 Corrective Actions
22.6 STAT SOP 1000 Control and Use of Laboratory Notebooks
22.7 STAT SOP 1010 Standard and Reagent Preparation
22.8 STAT SOP 1040 General Laboratory Procedures
22.9 STAT SOP 1130 Waste Disposal
22.10 STAT SOP 1210 Method Detection Limits (MDLs)
22.11 STAT SOP 1230 Training
22.12 STAT SOP 1250 Data Review
22.13 STAT SOP 1400 LIMS
22.14 STAT SOP 3005 SW846 3005A Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by FLAA, ICP, or ICP-MS
22.15 STAT SOP 3110 SW846 3050B Acid Digestion of Sediments, Sludges, and Soils for Metals Analysis by FLAA, ICP, or ICP-MS
22.16 STAT SOP 3115 Acid Digestion of High Volume Filters
22.17 Manufacturers' Equipment Instruction Manuals

23.0 FORMS, FIGURES, TABLES, DIAGRAMS, FLOWCHARTS, ATTACHMENTS OR VALIDATION DATA

Attachment 1: MDLs and Reporting Limits
Attachment 2: Concentrations of ICS Solutions
Attachment 3: Concentrations of Spike Solutions
Attachment 4: Tune adjustment Parameters

ATTACHMENT 1: MDLs and REPORTING LIMITS FOR ELEMENTS

				Aqueous		Soil		Air	
CAS #	**Element**	**Mass (Isotope) *, ******	**IDL (µg/L)**	**MDL (mg/L)**	**RL (mg/L)**	**MDL (mg/Kg)**	**RL (mg/Kg)**	**MDL (µg/ filter)**	**RL (µg/ filter)**
7429-90-5	Aluminum	27	0.235	0.00309	0.02	0.3271	2	NA	NA
7440-36-0	Antimony	**121***, 123	0.606	0.00249	0.003	0.1099	0.2	0.75	5
7440-38-2	Arsenic	75	0.063	0.00097	0.002	0.0429	0.1	0.69	5
7440-39-3	Barium	135, **137***	0.007	0.00140	0.002	0.0260	0.1	27	200
7440-41-7	Beryllium	9	0.004	0.00027	0.001	0.0074	0.05	0.25	5
7440-43-9	Cadmium	**111***, 114	0.015	0.00021	0.001	0.0078	0.05	0.20	5
7440-47-3	Chromium	**52***, 53	0.027	0.00054	0.002	0.0260	0.1	1.4	10
7440-48-4	Cobalt	59	0.019	0.00011	0.002	0.0051	0.1	0.18	5
7440-50-8	Copper	**63***, 65	0.080	0.00158	0.005	0.0404	0.25	0.52	5
7439-92-1	Lead	**206,207, 208****	0.019	0.00059	0.001	0.0065	0.05	0.40	5
7439-96-5	Manganese	55	0.020	0.00029	0.002	0.0114	0.1	0.82	10
7440-02-0	Nickel	**60***, 62	0.186	0.00107	0.002	0.0434	0.1	0.54	10
7782-49-2	Selenium	82	0.210	0.00172	0.002	0.0646	0.1	0.44	5
7440-22-4	Silver	**107***, 109	0.050	0.00079	0.002	0.0278	0.1	0.071	5
7440-28-0	Thallium	205, **203***	0.096	0.00026	0.002	0.0080	0.1	0.17	5
7440-32-6	Titanium	46, 47*		0.00057	0.005	.0261	0.25	1.1	10
7440-66-6	Zinc	**66***, 67, 68	0.080	0.00160	0.01	0.1157	0.5	2.2	25
7440-23-5	Sodium	23	0.671	0.07706	0.15	1.0965	6	NA	NA
7439-95-4	Magnesium	**24***, 25	0.193	0.00832	0.05	0.4429	3	NA	NA
7440-09-7	Potassium	39	0.585	0.03922	0.05	0.7043	3	NA	NA
7440-70-2	Calcium	44	2.698	0.07448	0.10	6.3708	6	NA	NA
7440-62-2	Vanadium	51	0.009	0.00087	0.002	0.0959	0.1	0.52	5
7439-89-6	Iron	**57***, (54)	0.611	0.01154	0.05	0.6888	3	4.6	50
7439-98-7	Molybdenum	92,94,96,97, **98***	0.020	0.00033	0.005	0.0405	0.5	0.37	5
7440-31-5	Tin	**120***, 118	0.026	0.00054	0.01	0.0772	0.5	0.24	5
7440-42-8	Boron	**11***, 10	.332	0.00551	0.02	0.2322	1	NA	NA

NOTES:

* Primary mass used for quantitation. Other masses are optionally used if proper instrument QC is available.

** The summation of all three lead masses is used for quantitation.

NA = not applicable

ATTACHMENT 2: CONCENTRATIONS of ICS SOLUTIONS

Solution A: Concentration in mg/L

Element	Stock	Working
Al	500	100
C	1000	200
Ca	500	100
Cl	3600	720
Fe	500	100
K	500	100
Mg	500	100
Mo	10	2
Na	500	100
P	500	100
S	500	100
Ti	10	2

Solution AB: Concentration in mg/L

Element	Stock	Working		Element	Stock	Working
Al	500	100		Ag	0.100	0.020
C	1000	200		As	0.100	0.020
Ca	500	100		Cd	0.050	0.010
Cl	3600	720		Co	0.200	0.040
Fe	500	100		Cr	0.100	0.020
K	500	100		Cu	0.100	0.020
Mg	500	100		Mn	0.100	0.020
Mo	10	2		Ni	0.200	0.040
Na	500	100		Se	0.100	0.020
P	500	100		V	0.200	0.040
S	500	100		Zn	0.100	0.020
Ti	10	2				

ATTACHMENT 3: CONCENTRATIONS OF LCS/MS SPIKING SOLUTION

Element	Concentration (mg/L)
Aluminum	25
Antimony	12.5
Arsenic	25
Barium	25
Beryllium	25
Boron	25
Cadmium	25
Chromium	25
Cobalt	25
Copper	25
Lead	25
Manganese	25
Molybdenum	12.5
Nickel	25
Selenium	25
Silver	10
Thallium	25
Titanium	12.5
Tin	12.5
Vanadium	25
Zinc	25
Calcium	100
Iron	100
Magnesium	100
Potassium	100
Sodium	100

ATTACHMENT 4: Tune Adjustment Parameters

Plasma conditions:
Higher RF Power generally increases the sensitivity.

Sample Depth
Shortening sample depth increases sensitivity and raises oxide levels.

To reduce Oxide Ions <1.2%

- Increase the sampling depth
- Decrease the carrier gas flow
- Increase the RF power
- Decrease the sample flow rate

To Reduce the Doubly Charged Ions < 5%

- Increase the sampling depth
- Decrease the carrier gas flow
- Increase the RF power
- Decrease the sample flow rate

Resolution and Mass Axis
Peak width at 10 % should be 0.65 – 0.8 AMU
Mass Axis should be within +/- 0.1 AMU of the selected mass

AMU Gain - Adjusts the peak width. The higher the value the narrower the peak width for heaver masses

AMU Offset - Adjusts the peak width. The higher the value the narrower the peak width for ALL masses

Axis Gain - Adjusts mass calibration. Higher value shifts the peak of heavier masses towards higher mass

Axis Offset - Adjusts mass calibration. Higher value shifts the peak of ALL masses towards higher mass

QP Bias - Controls the speed of ions as they pass through the Q-Pole.

STAT Analysis Corporation

Standard Operating Procedure 4530:

Mercury In Water, Solid Or Semisolid Water (Manual Digestion/Automated Analysis Cold-Vapor Technique)

(EPA METHODS 7470A & 7471A)

Revision 03
Effective Date: January 9, 2003

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This Standard Operating Procedure has been prepared for the sole use of STAT Analysis Corporation.

Copy Number: _____

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1.0 Identification of Test Method

Mercury In Water, Solid Or Semisolid Water (Manual Digestion/Automated Analysis Cold-Vapor Technique) - EPA METHODS 7470A & 7471A

2.0 Applicable Matrix or Matrices

This method is applicable to the following matrices: non-potable water, solid and chemical waste.

3.0 Detection Limits

The lab follows the procedure found in 40CFR Part 136B to determine the MDL for each matrix type on an annual basis. See the STAT Analysis SOP 1210 for the MDL Procedure, frequency and acceptance criteria. The MDLs measured by the laboratory and all supporting documentation are in the laboratory QA files for review.

The laboratory determined MDL must always be less than the reporting limit (RL). The RLs will usually range from three to ten times the laboratory measured MDLs, but this relationship may vary dependent on dilution of sample aliquots, matrix interferences, moisture adjustments (in solid samples), or method specific requirements.

The reporting limits for this method is 0.00025 mg/L for waters and 0.025 mg/kg for soils. The method detection limits for these methods are 0.000015 mg/L for waters and 0.0022 mg/kg for soils. Reporting limits are based upon the lowest calibration standard

4.0 Scope and Application

This method is a cold-vapor atomic absorption procedure for determining the concentration of mercury in mobility-procedure extracts, aqueous wastes, and ground waters (EPA Method 7470A) as well as measuring total mercury (organic and inorganic) in soils, sediments, bottom deposits, and sludge-type materials (EPA Method 7471A). All samples must be subjected to an appropriate dissolution step prior to analysis. If this dissolution procedure is not sufficient to dissolve a specific matrix type or sample, then this method is not applicable for that matrix.

NOTE: Each analyst must demonstrate the ability to generate acceptable results with this method.

5.0 Summary of Test Method

5.1 Prior to analysis, the liquid samples and the solid or semi-solid samples must be prepared according to the procedures discussed in this method.

5.2 The cold-vapor absorption method is based on the absorption of radiation at the 253.7-nm wavelength 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 spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration.

5.3 **Method modifications from Reference** - This procedure utilizes an automated cold-vapor technique, mixing stannous chloride with an aliquot of the sample digestion at the instrument. Digestions take place in graduated 50-ml tubes.

6.0 Definitions

The STAT Analysis Corporation Quality Assurance Manual (QAM) contains the definitions of standard terms used in this SOP.

7.0 Interferences

7.1 Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 ppm of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from reagent water.

7.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 ppm had no effect on recovery of mercury from spiked samples.

7.3 For liquid analysis: seawaters, brines, and industrial effluents high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine hydrochloride reagent. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater by using this technique.

7.4 For solid analysis: samples high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidations step, chlorides are converted to free chlorine, which also absorbs radiation of 253 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). In addition, the dead air space in the digestion vessel must be purged before adding stannous chloride.

7.5 Certain volatile organic materials that absorb at this wavelength may also cause interference. A preliminary run without reagents should determine if this type of interference is present.

8.0 Safety

8.1 General laboratory protection (safety glasses, lab coat, disposal latex/nitrile gloves) should be worn at all times when handling samples or reagents.

8.2 The digestion, and all reagent additions, must be performed in a fume hood.

8.3 The potential health hazards from the samples cannot be determined. Therefore, exposure to the samples should be minimized to the extent possible. Other safety precautions must be conducted in accordance with the Chemical Hygiene Plan. Other actions can also be applied if deemed necessary.

8.4 A reference file of material safety data sheets (MSDS) is available in each room for personnel involved in an analysis using chemicals.

9.0 Equipment and Supplies

The following apparatus is recommended for performing this procedure. Equivalent items can be used, if with their use, the analytical and QA/QC requirements in this SOP can be met.

9.1 Cetac M-6000A Mercury Analyzer with ASX-500 autosampler. This instrument utilizes cold vapor atomic absorption to measure mercury concentration. Manufacturer recommended settings are used during operation.

9.2 Water Bath or Hot plate – adjustable and capable of maintaining a temperature of 90-95°C.

9.3 Analytical balance, capable of measuring 0.001 g.

9.4 Argon gas supply: high-purity grade (99.99%).

9.5 Graduated 50 mL centrifuge tubes, with screw caps

9.6 Thermometer capable of measuring 90-100 °C with suitable precision and accuracy.

9.7 Disposable tubes, approximately 14 mL

9.8 Autopipettor: 0.010 to 0.10 mL, 0.10 to 1.0 mL, 1.0 to 5.0 mL

9.9 Dispensing pipets: 1-5 mL, 1-10 mL, 1-20 mL

10.0 Reagents and Standards

The following reagents and standards are required to perform this procedure. When instructions are given on how to prepare a specific volume of a reagent or standard, larger or smaller volumes can be prepared as needed so long as the final concentrations remain the same. Any other deviations from the reagents or standards listed in this SOP could be detrimental to the quality of the data produced. Such deviations would have to be approved and documented.

10.1 Instructions for labeling and record keeping of reagents and standards are contained in SOP 1010 Standard and Reagent Preparation.

10.2 Reagents – In methods where the purity of reagents is not specified, analytical reagent grade shall be used. Reagents of lesser purity than those specified by the test method shall not be used.

10.3 Standards

10.3.1 At least one of the standards must be traceable to a NIST traceable source when available The manufacturer should include a certificate of analysis for each standard. If one is not provided, contact the manufacturer. Retain all certificates in the designated binder (see SOP 1010 Reagent Receiving).

10.3.2 Intermediate and Working standards (Sections 10.20 – 10.23) must be prepared volumetrically using class A volumetric glassware, calibrated micro-pipettes, or gas tight syringes. Do not use disposable pipettes to prepare standards.

10.3.3 The use of alternative standards will be allowed as long as the analytical and quality objectives of the SOP can be met.

10.4 Reagent Water: Reagent water will be interference free. All references to water in this method will refer to reagent water unless otherwise specified.

10.5 Sulfuric acid (H_2SO_4), concentrated: Trace Metal grade.

10.6 Hydrochloric Acid (HCl), concentrated: Trace Metal grade.

10.7 Nitric Acid (HNO_3), concentrated: Trace Metal grade.

10.8 Aqua Regia: Prepare immediately before use by carefully adding three volumes of concentrated HCl to one volume of concentrated HNO_3.

10.9 Stannous Chloride, Dihydrate ($SnCl_2 \cdot 2H_2O$): Reagent Grade

10.10 Stannous chloride, 10% solution (w/v): Dissolve 100 g of $SnCl_2$ in 70 mL of concentrated HCl and dilute to 1 liter with reagent water.

10.11 Sodium Chloride (NaCl): Reagent Grade.

10.12 Hydroxylamine Hydrochloride: Reagent Grade, "Suitable for Mercury Determination".

10.13 Sodium chloride – hydroxylamine hydrochloride solution: dissolve 120 g of sodium chloride and 120 g of hydroxylamine hydrochloride in reagent water and dilute to 1 liter.

10.14 Potassium Permanganate ($KMnO_4$): Reagent Grade, "Suitable for Mercury Determination".

10.15 Potassium permanganate ($KMnO_4$), 5% solution (w/v): Dissolve 50 g of $KMnO_4$ in 1 liter of reagent water.

10.16 Potassium persulfate ($K_2S_2O_8$): Reagent Grade.

10.17 Potassium persulfate ($K_2S_2O_8$), 5% solution (w/v): Dissolve 50 g of $K_2S_2O_8$ in 1 liter of reagent water.

10.18 2%HNO_3/2%HCl rinse: Add 40mL of concentrated HNO_3 and 40 mL of concentrated HCl in reagent water and dilute to 2 liters.

10.19 Ottawa Sand

10.20 Stock Standard Solutions: 1000 mg/L mercury standards are purchased commercially. Standards from two separate sources are purchased, one to be used for calibration and the second to be used for calibration verification.

10.21 Intermediate Calibration Standard Solution: (CAL STD 10 mg/L) Add approximately 80 mL of reagent water to a 100 mL volumetric flask, add 0.500 mL of Nitric Acid, add 1.00 mL of Stock Standard Solution (1000 mg/L), dilute to final volume. Prepare fresh every 28 Days.

10.22 Intermediate Calibration Verification Standard Solution: (ICV/CCV 10 mg/L) Add approximately 80 mL of reagent water to a 100 mL volumetric flask, add 0.500 mL of Nitric Acid, add 1.00 mL of the second source Stock Standard Solution (1000 mg/L), dilute to final volume. Prepare fresh every 28 Days.

10.23 Working Calibration Standard Solution: (100.0 µg/L) Add approximately 80 mL of reagent water to a 100 mL volumetric flask, add 0.500 mL of Nitric Acid, add 1.00 mL of Intermediate Calibration Standard Solution (10.0 mg/L, Section 10.20), dilute to final volume. Prepare fresh weekly (Expires in 7 days).

10.24 Working Calibration Verification Standard Solution: (ICV/CCV 100.0 µg/L) Add approximately 80 mL of reagent water to a 100 mL volumetric flask, add 0.500 mL of Nitric Acid, add 1.00 mL of Intermediate Calibration Verification Standard Solution (10.0 mg/L, Section 10.21), dilute to final volume. Prepare fresh weekly (Expires in 7 days).

10.25 ICV Standard: Into a 50.0 mL centrifuge tube spike 0.30 mL of Working Calibration Verification Standard Solution: (ICV/CCV 100 µg/L, Section 10.23). Dilute to 30 mL with reagent water, **TV= 1.0 µg/L**.

10.26 CCV Standard: Into a 50.0 mL centrifuge tube spike 0.750 mL of Working Calibration Verification Standard Solution: (ICV/CCV 100 µg/L, Section 10.23). Dilute to 30 mL with reagent water, **TV= 2.50 µg/L**.

10.27 LCS/MS/MSD Spiking Solution: Spike 0.750 mL of Working Calibration Verification Standard Solution: (ICV/CCV 100 µg/L, Section 10.23) per sample.

10.28 Prepare Calibration Standards in 50.0 mL centrifuge tubes from the Working Calibration Standard Solution (100 µg/L Section 10.21) by dilution to 30.0 mL as follows:

Table 1 Mercury Calibration Standards

Calibration Standard Concentration, µg/L	Amount of solution to add to graduated tube, mL	Concentration of solution added to graduated tube, µg/mL	Final Volume, mL	µg Hg per 30 mL
7.00	2.10	100	30	0.21
5.00	1.50	100	30	0.15
2.50	0.75	100	30	0.075
1.00	0.30	100	30	0.03
0.50	0.15	100	30	0.015
0.25	0.075	100	30	0.075

11.0 Sample Collection, Preservation, Shipment and Storage

11.1 All samples are stored away from all standards, reagents, food, and other potentially contaminating sources in order to prevent cross contamination.

11.2 The following table summarizes the requirements for proper sample collection, preservation, shipment and storage.

Matrix	**Bottle Type**	**Preservation**	**Shipping & Storage**	**Minimum Sample Amount**	**Prep/Analysis Hold Time**
Solid	P, G	Chill to 4°C	Chill to 4°C	4 Oz.	28 days
Liquid	P, G	Acidify with HNO_3 to pH < 2		250 mL	28 days

[P= Polyethylene, G = Glass, AG = Amber Glass, etc.].

11.3 All sample containers should be pre-washed with detergents, acids, and reagent water. Plastic and glass containers are both suitable.

11.4 Aqueous samples must be acidified to a pH < 2 with HNO_3.

11.5 The maximum holding time for mercury is 28 days.

11.6 Non-aqueous samples shall be refrigerated, when possible, and analyzed as soon as possible.

11.7 It can be difficult to obtain a representative sample with wet or damp materials. Wet samples may be dried, crushed, and ground to reduce sub-sample variability as long as drying does not affect the extraction of the analytes of interest in the sample.

11.8 Sample Storage

11.8.1 Non-aqueous samples must be chilled to 4°C.

12.0 Quality Control

The following details the QC requirements that apply to this analysis. Each Quality Control Indicator (QCI) provides information pertaining to either method or individual sample performance. Our goal is to produce defensible data of known and documented quality.

The results of these QCI samples are used to assess the acceptability of data.

12.1 Blanks

The Method Blank analysis is performed to determine if any contamination is present in the analytical process and is used to evaluate acceptance of the batch of samples. The method blank must be processed along and under the same conditions as the associated samples, including cleanup procedures. The method blank must be analyzed at a minimum of 1 per preparation batch (see Section 8 for definition of a prep batch). The method blank is of a similar matrix (e.g., reagent water, Ottawa sand, glass beads, etc.) to the associated samples and is known to be free of the analytes of interest.

12.2 Laboratory Control Sample (LCS)

The LCS is used to evaluate the performance of the total analytical system, including all preparation and analysis steps. The LCS is a controlled matrix (e.g., reagent water, Ottawa sand, glass beads, etc.), known to be free of analytes of interest, spiked with known and verified concentrations of analytes. Alternatively the LCS may consist of a media containing known and verified concentrations of analytes or as Certified Reference Material (CRM). All LCS analyte concentrations must be within the calibration range. The LCS must be analyzed at a minimum of 1 per preparation batch (see Section 8 for definition of a prep batch).

12.3 Matrix Spike and Matrix Spike Duplicate (MS/MSD)

MS/MSDs indicate the effect of the sample matrix on the precision and accuracy of the results generated using the selected method. This information does not determine the validity of the entire batch. MS/MSDs must be analyzed at a minimum of 1 per 20 samples per matrix per preparation procedure, or as specified by the required test method. If an MS/MSD pair is not analyzed in the preparation batch, an LCS/LCSD pair is analyzed.

Samples chosen for matrix spiking are rotated among different clients and/or different client projects. This is accomplished through communication between the Department Manager and the analyst. In addition, designated samples, as indicated by client request or contract requirement, are matrix spiked.

12.4 Duplicates

Duplicates are defined as replicate aliquots of the same sample taken through the entire analytical procedure. The results from this analysis indicate the precision of the results for the specific sample using the selected method. The duplicate provides a usable measure of precision only when target analytes are found in the sample chosen for duplication. Duplicates are performed on replicate aliquots of actual samples. The duplicate analysis may be analyzed at a frequency of 1 per 20 samples per matrix per preparation procedure.

Samples chosen for duplicate analyses are rotated among different clients and/or different client projects. This is accomplished through communication between the Department Manager and the analyst.

Note: For this test method, the analysis of the Matrix Spike Duplicate (MSD) is used as a substitute for the laboratory duplicate. In those cases when there is insufficient sample to perform a MS and MSD analysis, the duplicate analysis is used to judge the precision of the analytical results. In those cases when there is insufficient sample to perform either a duplicate analysis or MSD analysis, the duplicate analysis of the LCS (LCS/LCSD) is used to judge the precision of the analytical results.

12.5 Post Digestion Spikes (PDS)

Post Digestion Spikes are used to check for matrix interference on a given matrix. Added after sample preparation, they provide a measure of recovery for every sample matrix. They may be analyzed at a frequency of 1 per 20 samples per matrix per preparation procedure.

13.0 Calibration and Standardization

Initial Calibration (ICAL)

In addition to achieving the reference method requirements for the minimum number of calibration standards and the acceptance criteria (statistics) for calibration curve fit, the following ICAL criteria also apply:

13.1 The ICAL must be a minimum of 5 standards, not including a blank.

13.2 The ICAL must be verified with a second source standard (ICV) prior to the analysis of samples.

13.3 Results of samples not bracketed by the ICAL range must be qualified on the final report. If possible, dilute the sample or extract and reanalyze in order to achieve a result within the calibrated range of the instrument.

13.4 The lowest calibration standard may establish the reporting limit. The reporting limit may also be based upon another point in the calibration curve. It must be greater than the detection limit.

13.5 The ICAL is digested weekly, and analyzed daily with the preparation batch. The digested standards are stored near the instrument and are labeled with the standard concentration, the matrix (S or W), and the date the standard was digested.

Initial Calibration Verification (ICV)

In addition to the method requirements, the following ICV criteria also apply:

13.6 Must be a second source standard from the ICAL standards or from a different manufacturer lot number.

13.7 Must be traceable to NIST when available.

13.8 Must be digested/analyzed every day a preparation batch is performed.

Continuing Calibration Verification (CCV)

In addition to the method requirements, the following CCV criteria also apply:

13.9 Must be digested/analyzed every day a preparation batch is performed.

13.10 Must be analyzed after every 10 samples and at the end of each analytical batch.

13.11 If the CCV results obtained are outside the acceptance criteria, corrective actions must be performed. If routine corrective actions fail to produce an acceptable *second consecutive (immediate)* CCV, then either the lab has to demonstrate performance after corrective action with two consecutive successful CCVs, or a new ICAL must be performed. If the instrument has not demonstrated acceptable performance, sample analyses cannot continue until a new ICAL is established and verified with an ICV. However, sample data associated with an unacceptable CCV may be reported as qualified data under the following special conditions:

13.11.1 When the acceptance criteria for CCV are exceeded high, i.e., high bias, and there are associated samples that are non-detects, then those non-detects may be reported. Otherwise the samples affected by the unacceptable calibration verification must be reanalyzed after a new ICAL has been established, evaluated and accepted.

13.11.2 When the acceptance criteria for the CCV are exceeded low, i.e., low bias, those sample results may be reported if they exceed a maximum regulatory limit/decision level. Otherwise the samples affected by the unacceptable verification must be reanalyzed after a new ICAL is established and verified with an ICV.

13.11.3 When the acceptance criteria for the CCV are exceeded and it is not possible to reanalyze the sample due to limited sample quantity AND a new sample cannot be obtained by the laboratory, the data may be reported with the appropriate data qualifiers if the client has been contacted and agrees, in writing, to accept the qualified data.

13.12 Records: Initial and Continuing Calibration Records will contain, at a minimum, the following:

Calibration date
Instrument
Analysis date
Analyst's initials or signature
Standard Concentration (appropriate units) and number of standards
Response (appropriate units)
Calibration curve
Evaluation of and Statistics for ICAL curve fit in order to judge calibration curve acceptance

Initial/Continuing Calibration Blank (ICB/CCB – Reagent Blank)

In addition to the method requirements, the following ICB/CCB criteria also apply:

13.13 Must be digested/analyzed every day a preparation batch is performed.

Note: For aqueous digestions, the Method Blank may act as the ICB/CCB.

13.14 Must be analyzed after Initial Calibration Verification (ICV).

13.15 Must be analyzed after every Continuing Calibration Verification (CCV).

Calibration Acceptance Summary (see Table 2):

Table 2 Quick reference of instrument Calibration Requirements

QCI	Frequency	Standards	Control Limits	Corrective Action
ICAL	Digested weekly, analyzed daily	Minimum 5 standards, see Table 1 for concentrations	r ≥0.995	Correct problem then repeat initial calibration
ICV	Digested and analyzed daily	1.00 µg/L	± 10% of true value	Correct problem then repeat ICV or repeat initial calibration
CCV	Digested and analyzed daily	2.50 µg/L	= 20% of true value	Correct problem then repeat CCV or repeat initial calibration
ICB/CCB	Digested daily, and analyzed after each ICV and CCV		< RL	Correct problem then repeat ICB/CCB or repeat initial calibration

Support Equipment

Autopipettes - Check autopipette to ensure standardization is within control limits (see SOP for Pipette Calibration).

Balances - Be sure the balance is checked prior to use and performance criteria are met (see SOP for Calibration of Balances).

Thermometers - Check the thermometer to ensure the calibration is not expired (see SOP for Thermometer Calibration). Check the thermometer during the analysis and record the corrected temperature in the analysis logbook.

14.0 Procedure

14.1 Digestion Procedure for Aqueous Samples (EPA METHOD 7470A)

14.1.1 Measure 30 ml of sample aliquot (or portion of sample diluted to 30 mL) into a 50 ml centrifuge tube. **Addition of all reagents should be done in the hood.**

14.1.2 Add 1.5 ml of concentrated H_2SO_4.

14.1.3 Add 0.75 ml of concentrated HNO_3.

14.1.4 Add 4.5 ml of $KMNO_4$ solution, cap, invert to mix, and let sit for at least 15 minutes. If samples are no longer purple after 15 minutes, (i.e. brown or clear) re-prepare sample at dilution.

14.1.5 Add 2.4 ml of $K_2S_2O_8$ solution, screw cap on tube and invert to mix.

14.1.6 Heat for two hours at 90-95°C in water bath or hot block. Record time in/time out in prep logbook. Record thermometer ID and bath/block temperature in prep logbook.

14.1.7 Cool and add 1.8 ml of Sodium Chloride - Hydroxylamine Hydrochloride solution to reduce excess $KMNO_4$. Invert to mix.

14.1.8 Samples are now ready for analysis on Cetac M-6000A according to method and instrument parameters.

14.1.9 Record all reagents used in prep logbook.

14.2 Digestion Procedure for Solid or Semisolid Samples (EPA METHOD 7471A)

14.2.1 Weigh approximately 0.3 g of sample into a 50 ml centrifuge tube. For Method Blank and LCS, weigh approximately 0.3 g of Ottawa sand.

14.2.2 Add 1.5 ml of DI H_2O

14.2.3 Add 1.5 ml Aqua Regia. **Add Aqua Regia and all other reagents in hood.**

14.2.4 Heat in a water bath or hot block at 90-95 °C for 2 minutes. Record time in/time out in prep logbook. Record thermometer ID and bath/block temperature in prep logbook.

14.2.5 Allow to cool for 5 minutes.

14.2.6 Add 15 ml DI H_2O.

14.2.7 Add 4.5 ml of $KMNO_4$, cap and invert to mix.

14.2.8 Heat in water bath at 90-95°C for 30 minutes. Record time in/time out in prep book.

14.2.9 Allow to cool for 15 minutes.

14.2.10 Add 1.8 ml Sodium Chloride – Hydroxylamine Hydrochloride solution to reduce excess $KMNO_4$.

14.2.11 Add 16.5 ml DI H_2O. Invert to mix.

14.2.12 Samples are now ready for analysis on Cetac M-6000A according to method and instrument parameters.

14.2.13 Standards for soils will be prepared as noted above in section 10.27 (Table 1). Before addition of reagents add 3 ml of DI H_2O to ensure the final volume is the same for samples and standards. Otherwise treat standards in the same manner as samples with regard to reagent addition, except add no additional water (omit steps 14.2.2, 14.2.6 and 14.2.11). Final volume of samples and standards should be 40.8 ml.

14.2.14 Record all reagents used in prep logbook.

14.3 Analysis

14.3.1 Turn on the gas.

14.3.2 Turn on the power to the instrument, the lamp, and the autosampler. Allow the lamp to warm up for at least 20 minutes.

14.3.3 Double click on the **Hg Analysis** icon on the desktop.

14.3.4 The main menu appears. Click on **Worksheet**, click on **Open**, and select an appropriate worksheet for analysis (currently **Daniel**).

14.3.5 Click on the **Filing** tab. Click on **Rename**, Click on **Yes**. Change the analyst, and the ICAL and QC solutions, as appropriate.

14.3.6 Disconnect the outlet gas (top tube) from the gas-liquid separator.

14.3.7 Attach the tubing to the pump – Stannous chloride solution on top, followed by the sample tubing, and finally the drain tubings.

14.3.8 Turn on the pump, and allow stannous chloride and rinse solution to start pumping into the gas-liquid separator. Pinch the drain tubing (or disconnect) to allow the gas-liquid separator to fill with solution. This process "wets" the center post of the gas-liquid separator. Once the center post has been sufficiently wetted, reconnect the drain tubing on the pump, and allow the gas-liquid separator to drain completely. Reattach the outlet gas tubing to the gas-liquid separator.

14.3.9 Click on the **Labels** tab. Type the samples into the table.

14.3.10 Load the samples into the autosampler tray.

14.3.11 Click on the **Analysis** tab. Click on **Instrument** on the menu and click on **Zero**. Click on the **Read** button, click on **Standard**, select **Standard 6**, and click **OK**. The instrument will now analyze the highest standard. Check for adequate response, and reproducibility.

14.3.12 Click on the **Start** button. Check the boxes for calibration (as necessary), instrument zero, and for report printing, and click **OK**.

14.3.13 Dilute and reanalyze any sample that exceeds the highest standard. Reanalyze any detectable sample if the %RSD exceeds 5 %.

14.3.14 After analysis, rinse the gas-liquid separator with an HNO_3 solution. Drain the gas-liquid separator completely. Turn off the gas, pump, autosampler, lamp, and then the instrument.

15.0 Data Reduction, Calculations and Loading

15.1 The data system will then prepare a calibration curve by plotting response versus standard concentration. Sample concentration is calculated from the regression equation.

NOTE: The LIMS program will convert µg/L (part per billion) concentrations from the instrument readout to mg/L or mg/Kg (part per million).

15.2 Report only those values that fall between the lowest and highest calibration standards. Samples exceeding the highest standard must be diluted and reanalyzed.

15.3 Aqueous samples - The concentration readout for aqueous sample distillates is µg Hg/L. It does not need further data reduction unless the initial sample volume was less than 30 mL. If less than 30 mL sample was digested, calculate the concentration as follows:

Concentration in mg Hg/L = readout * 0.001 (30 mL/ initial sample volume analyzed in mL)

15.4 Solid Samples – The concentration readout for soil and solid samples must be multiplied by the following factor: Factor = (30/ sample weight in g). Calculate the concentration of Hg in soil and solid samples as follows:

Concentration in mg Hg/L = readout * 0.001 (30 mL/ initial sample weight in g)

15.5 The procedure for uploading data into the LIMS system is detailed in SOP 1400 LIMS.

16.0 Method Performance

Demonstration of Capability (DOC)

All parameters of interest must meet the method acceptance criteria before actual sample analysis begins. See SOP 1230 Training for the procedure to perform and document the DOC. The DOCs for the analysts performing this method are located in the analysts' training form folders located in the QA office files.

A quality control (QC) reference concentrate is required containing each analyte at a concentration of 0.00025 mg/L for aqueous samples and 0.025 mg/Kg for soil samples using the ICV/CCV solution. The

QC reference sample is made using stock standards prepared independently from those used for calibration.

For each analyte calculate the mean recovery (X) and standard deviation (s) and the average % Recovery (%R). Compare X and s and %R with the corresponding acceptance criteria for accuracy and precision, respectively. Note: For aqueous samples, X must be within 0.00025 ± 0.00005 mg/L and s must be less than 0.00005 mg/L and %R must be within 100 ± 20%. Note: For soil samples, X must be within 0.025 ± 0.005 mg/Kg and s must be less than 0.005 mg/Kg and %R must be within 100 ± 20%. These limits are taken from established in-house criteria. If X and s and %R for all analytes meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual X or %R falls outside the range for accuracy, or any individual s exceeds the precision limit, then the system performance is unacceptable for that analyte and corrective action must be taken.

The Analyst performing the analysis on the Cetac Mercury Analyzer need only perform one DOC (either the aqueous or the soil DOC) to demonstrate capability in the analysis.

Comparison to Reference Method Data

There is no stated reference method criteria for LCS, Duplicates, or MS/MSD recoveries in EPA Methods 7470A or 7471A. EPA Method 7000 does require the recovery of an independent check standard (ICV) to be within ± 10% of the true value, and that the calibration check standard (CCV) be within ± 20% of the true value. EPA Methods 7470A and 7471A require a blank and 5 standards for the calibration curve. EPA Methods 7470A and 7471A recommend that the standards be digested daily. The laboratory digests the calibration standards weekly, but digests the ICV, CCV, and Reagent Blank with every preparation batch.

In-House Control Limits

Method performance data is on file in the laboratory QC department. Comparison of method performance data for the laboratory to the reference method criteria occurs when laboratory in-house acceptance limits are generated. In-house generated data is compared to the specifications of the reference method. If the in-house limits are within the specifications of the reference method, the control limits are updated in LIMS. If the in-house limits are not within specifications, an investigation is performed to determine the cause(s) of the problem and a corrective action is completed. The analysis may continue until enough data points are collected to regenerate new control limits. Any QC data generated outside of reference method limits during that time frame, is flagged.

The laboratory maintains performance records to document the quality of data that is generated. Method accuracy for samples is assessed and records maintained. After the analysis of 20 laboratory control samples, calculate the average percent recovery (R) and the standard deviation of the percent recovery (S).

Control limits for the method parameters are generated by the QC staff and distributed to the analysts via updates to the LIMS control charts. The control limits are calculated based on in-house performance data. At a minimum, these limits are reviewed annually.

17.0 Pollution Prevention

17.1 The preparation of excessive volumes of laboratory reagents and standards shall be avoided so that waste and potential for pollution are minimized. Samples, reagents and standards shall be disposed in compliance with the laboratory waste disposal program, SOP 1130. With the consent of the client, the samples may be returned to their origin for treatment.

17.2 Uncontaminated paper waste, glass and cans should be separated for recycling. Laboratory staff are required to protect the laboratory's and our clients' business information when disposing of recycling or waste from the facility.

18.0 Data Assessment and Criteria for Quality Control Measures

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of QC samples indicate atypical method performance, a calibration verification standard is used to confirm the measurements were performed in an in-control mode of operation. The data review is conducted according to SOP 1250 Data Review.

Method Blank (MB)

If the blank exceeds the RL (usually the lowest calibration standard), the source of contamination must be investigated and corrective actions taken.

Affected samples must be reprocessed and reanalyzed **or** Data must be appropriately qualified if:

1) The concentration of a targeted analyte in the blank is at or above the reporting limit as established by the SOP or by regulation, AND is greater than 1/10 of the amount measured in any sample.

2) The blank contamination otherwise affects the sample results as per the test method requirements or the individual project data quality objectives.

Laboratory Control Sample (LCS)

The results of the individual batch LCS are calculated in percent recovery (%R) and compared to established acceptance criteria (in-house limits). LCS %R limits are 100 ± 20% for both aqueous and soil samples. If the LCS is outside the acceptance criteria, the analytical system is "out of control". Any affected samples associated with an out of control LCS must be reprocessed and reanalyzed or the results reported with appropriate data qualifiers.

Note: An LCS consisting of a media containing known and verified concentrations, or a Certified Reference Material (CRM) may have limits different from the limits listed above.

Matrix Spikes

The results from MS/MSD are primarily designed to assess the precision and accuracy of analytical results in a given matrix and are expressed as percent recovery (%R) and relative percent difference (RPD). See the STAT QAM, Section 5.4 for the calculation for RPD. Results are compared to established acceptance criteria (in-house limits). For aqueous and soil samples, MS/MSD %R limits are 100 ± 25% and RPD limits are 20%. For matrix spike results outside established criteria corrective action must be documented, or the data for the spiked sample is reported with appropriate data qualifying codes.

> Note: If the original sample result is sufficiently high (greater than four times the MS/MSD spike level), then % R limits may not apply.

Duplicates

The results from laboratory Duplicates are designed to assess the precision of analytical results in a given matrix and are expressed as relative percent difference (RPD). See the STAT QAM, Section 5.4 for the calculation for RPD. Results are compared to established acceptance criteria (in-house limits). RPD limits are 20 %. For duplicates results outside established criteria corrective action must be documented, or the data for the duplicate sample is reported with appropriate data qualifying codes.

Post Digestion Spike

The results from PDS are primarily designed to assess the accuracy of analytical results in a given matrix and are expressed as percent recovery (%R). For aqueous and soil samples, PDS %R limits are 100 ± 15%. For post digestion spike results outside established criteria corrective action must be documented, or the data for the spiked sample is reported with appropriate data qualifying codes.

19.0 Corrective Actions for Out-of-Control Data

The process for handling unacceptable and out of control data is found in SOP 230 Corrective Action.

If the CCV, MB, LCS/LCSD, MS/MSD, lab duplicate, PDS, or some other QC sample recovery of any parameter falls outside the designated acceptance range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the samples is suspect and is only reported for regulatory compliance purposes with the appropriate corrective action form. Immediate corrective action includes reanalyzing all affected samples by using any retained sample before the expiration of the holding time. Final data results must be qualified in the client report for reported results not meeting the laboratory defined criteria.

1) Review standards preparation logbooks. Check all calculations and ensure dilution factors are properly recorded.
2) Re-prepare the suspected standard or QC sample to identify possible preparation errors of the standard or QC sample.
3) Re-Analyze the samples when the CCV or LCS are not within acceptable limits.

4) Perform routine preventative maintenance following manufacturer's specification. Record all maintenance in the instrument logbook.

20.0 Contingencies for Handling Out-of-Control or Unacceptable Data

Every effort is made to prevent problems from occurring. When out of control or unacceptable data occurs the first option is to identify the problem and reanalyze the samples within the holding times. When this is not possible, the QA Manager and/or the Laboratory Director reviews data and discusses options with the client. Reanalysis or reporting the data with qualification are alternatives. Out of control or unacceptable data reported to the client must include the data qualifier, flag and discussion on the rationale for reporting.

Holding time exceedence, or improper preservation are noted on the corrective action form and included on the final report.

20.1 The process for handling unacceptable and out of control data is found in the Laboratory QAM Section 11. The reporting of data that is out of control must be approved and documented by Quality Assurance Manager and either the Technical Manager or the Laboratory Director.

20.2 Client Requested Modifications:

20.2.1 Clients must request modifications from the laboratory SOP in writing to the lab.

20.2.2 The Laboratory Director, Technical Manager and Quality Assurance Manager will evaluate the requested client deviations, determine the feasibly of the deviation and the potential effects on the data.

20.2.3 If it is determined that the laboratory will perform the requested deviations, the Laboratory Director, Technical Manager and Quality Assurance Manager will decide if a method validation study is required.

20.2.4 The designated project manager will retain all documentation concerning the requested deviation, including all correspondence with the client, in the client folder.

20.2.5 The final analytical report must include the statement "*This report has analyses performed using client requested modifications* ".

21.0 Waste Management

The STAT Analysis Corporation Waste Disposal SOP 1130 identifies proper waste management practices for the chemicals and biological materials used in this procedure. Samples are stored and discarded in accordance with SOP 1130 Waste Disposal.

22.0 References

22.1 SW 846 3rd Edition, Method 7471A, Mercury in Solid or Semisolid Waste and 7470A Mercury in Liquid Waste.
22.2 STAT SOPs [sample prep]
22.3 STAT SOPs [support equipment, recordkeeping, MDLs, etc]
22.4 SOP 230 Corrective Actions
22.5 SOP 1010 Standard and Reagent Preparation
22.6 SOP 1400 LIMS
22.7 SOP 1130 Waste Disposal
22.8 SOP 003 Chemical Hygiene Plan
22.9 SOP 1250 Data Review
22.10 Manufacturers' Equipment Instruction Manuals
22.11 SOP 1230 Training
22.12 STAT Analysis Corporation Quality Assurance Manual
22.13 NELAC Chapter 5 Quality Systems, Approved May 25, 2001
22.14 Guidance for the Preparation of Standard Operating Procedures (G-6) EPA/240/B-01/004 March 2001

23.0 Forms, Figures, Tables, Diagrams, Flowcharts, Attachments or Validation Data.

23.1 Appendix A Prep Logbook

Appendix A – Prep Logbook

Mercury Prep LogBook (SOP# 4530)

Matrix: W = Water, S = Soil, T = TCLP

Time in Bath _____
Time out of Bath _____
Water Bath Temperature _____
Thermometer ID _____

Analyst(s)	Date	Sample ID	Bottle #	Matrix	Sample Wt./ Vol. (g or mls)	Final Volume (mls)	Spike Volume (mls)	Spike Solution ID#	Comments

Digestion Reagents

Potassium Permanganate _____
Potassium Persulfate _____
Hydroxylamine Hydrochloride _____

Sulfuric Acid _____
Hydrochloric Acid _____
Nitric Acid _____

Reviewed by _____

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