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NSWC CRANE
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Quality Assurance Project Plan

for

Mine Fill A (SWMU 12)
Mine Fill B (SWMU 13)
Cast High Explosives Fill/
B146 Incinerator (SWMU 16) and
Pyrotechnic Test Area (SWMU 19)
RCRA Facility Investigation

Volume 2 - Appendix I

Naval Surface Warfare Center
Crane

Crane, Indiana

Southern Division
Naval Facilities Engineering Command

Contract Number N62467-94-D-0888

Contract Task Order 0166

July 2002

APPENDIX I

LABORATORY STANDARD OPERATING PROCEDURES

STANDARD OPERATING PROCEDURE SUBMITTALS

Laucks Testing Laboratory, Triangle Laboratory, and NSWC Crane Laboratory Analytical Standard Operating Procedures (SOPs) have previously been submitted as part of other QAPPs. Laucks Testing Laboratory and Triangle Laboratory SOPs were submitted as part of the approved Quality Assurance Project Plan for Ammunition Burning Grounds Little Sulphur Creek and Jeep Trail Resource Conservation and Recovery Act Phase III RCRA Facility Investigation. NSWC Crane Laboratory analytical SOPs were submitted as part of the approved Work Plan for RCRA Facility Investigation Corrective Measures Study and Risk Assessment at Solid Waste Management Unit 2-Dye Burial Grounds. All analytical SOPs utilized for analysis of samples collected at SWMUs 12, 13, 16, and 19 are listed. However, analytical SOPs which have not changed are incorporated by reference and only SOPs which have been changed are included in this submission and are shown in italics in the Appendix I Table of Contents.

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SOP No.	REV No.	QAPP/WP	TITLE
LAUCKS TESTING LABORATORIES			
LTL-1001	4	126[1]	Elements of SOP and Method Formats
LTL-1002	5	126[1]	Document Tracking and Control
LTL-1003	2	126[1]	Chain-of-Custody and Documentation Procedures
LTL-1004	4	126[1]	Documentation of Analyst Competence and Training
LTL-1005	5	126[1]	Analytical Balances
LTL-1006	3	126[1]	Refrigerator, Freezer, and Oven Thermometer Calibration and Maintenance
LTL-1007	3	126[1]	Use of Instrument Records and Logbooks
LTL-1008	6	126[1]	QC Corrective Action
LTL-1009	3	126[1]	Blind Spike Program
LTL-1011	4	126[1]	Procedures for the Determination and Reporting of Detection Limits, Reporting Limits, Precision and Accuracy Studies, and Control Limits
LTL-1012	2	126[1]	Solvent QC Monitoring for Trace Residue Analysis
LTL-1013	4	126[1]	Preparation, Storage, Shelf Life and Traceability Documentation of Standards and Reference Materials
LTL-1017	1	126[1]	Internal Audit Procedures
LTL-1018	1	126[1]	Overview of Review and Approval Practices for Validatable Data Packages
LTL-1019	2	166[2]	Controlling, Maintaining, and Monitoring Laboratory Logbooks
LTL-1020	2	166[2]	Integration of IC, GC, HPLC and GCMS Peaks
LTL-2001	6	166[2]	Waste Segregation and Disposal
LTL-3000	12	166[2]	Extraction Method for Base, Acid and Neutral Compounds in Water (8270C by 3520C)
LTL-3001	4	166[2]	Extraction Method for Polynuclear Aromatics in Water (8270C by 3520C)
LTL-3011	2	166[2]	Extraction Method for Chlorinated Herbicides in Soil (8151A by 3550B)
LTL-3077	5	166[2]	Extraction Method for Ordnance Compounds in Water
LTL-3100	11	126[1]	Extraction Method for Base, Acid and Neutral Compounds in Soils (8270C by 3550B)
LTL-3161	5	166[2]	Extraction Method for Ordnance Compounds in Soils (8330)
LTL-3202	3	166[2]	Extraction Method for Organochlorine Pesticides and Polychlorinated Biphenyls in Water (8081A/8082 by 3510C)
LTL-3302	2	126[1]	Extraction Method for Organochlorine Pesticides and Polychlorinated Biphenyls in Soil (8081A/8082 by 3550B)

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LTL-3450	1	126[1]	Extraction Method for Polynuclear Aromatics in Soil (8270C by 3550B)
LTL-3510	8	166[2]	Extraction Method for Chlorinated Herbicides in Water (8151A by 3510C)
LTL-3550	5	166[2]	Extraction Method for Picric and Picramic Acids in Water (3510C)
LTL-3555	4	166[2]	Extraction Method for Piciric and Picramic Acids in Soil (3550B)
LTL-4002	6	126[1]	Electronic Sample Entry and Log-In
LTL-4103	0	126[1]	Reviewing a Sample Delivery Group (SDG) and Updating Projects in the LIMS
LTL-4201	0	126[1]	Package Deliverables for all Reporting Levels
LTL-6006	0	166[2]	Cation –Exchange Capacity of Soils (Sodium Acetate) by SW 846 Method 9081
LTL-6008	0	166[2]	The Determination of Acid Volatile Sulfides and Simultaneously Extracted Metals in Sediment
LTL-7003	2	126[1]	Inorganic Glass Cleaning Procedure
LTL-7009	3	126[1]	Microwave Assisted Acid Digestion of Aqueous Samples and Extracts Using SW846 Method 3015
LTL-7010	3	166[2]	Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by ICP Spectroscopy by SW846 Method 3010A
LTL-7012	1	126[1]	Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils Using SW846 Method 3015
LTL-7015	1	126[1]	Acid Digestion of Sediments, Sludges, and Soils Using SW846 Method 3050B
LTL-7202	4	126[1]	Metals Analysis Using Inductively Coupled Plasma – Mass Spectrometry (ICP/MS) SW846 Method 6020
LTL-7501	2	166[2]	Operation of the PE FIMS 400 for the Analysis of Hg
LTL-8000	2	126[1]	Determination of Retention Time Windows
LTL-8019	4	166[2]	Determination of Non-Halogenated Volatile Organics by SW 8015B
LTL-8084	5	166[2]	Analysis of Organochlorine Pesticides and PCBs by SW 846 Methods SW 8081A and 8082
LTL-8151	4	166[2]	Analysis of Chlorinated Herbicides by 8151A
LTI-8265	4	166[2]	Determination of Volatile Organic Compounds by Method 8260B
LTL-8277	2	166[2]	Determination of Polynuclear Aromatic Hydrocarbon Compounds by Selective Ion Monitoring (SIM) Method 8270C
LTL-8279	3	166[2]	Determination of Semivolatile Organic Compounds by Method 8270C and 8270D
LTL-8302	1	126[1]	HPLC Ordnance 8330 Data Review

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LTL-8303	5	166[2]	Determination of Picric and Picramic Acid
LTL-8330	11	166[2]	Determination of Nitroaromatics and Nitramines by SW-846 Method 8330
LTL-9104	3	166[2]	Preparation and Analysis of Total and Amenable Cyanide According to EPA Methods 335.1, 335.3, and SW 846 9012A
LTL-9110	8	166[2]	Determination of Anions by Ion Chromatography by Method 300.0A or 9056
LTL-9113	2	166[2]	pH in Soil and Waste Samples Using SW846 Method 9045C
LTL-9115	3	166[2]	The Determination of Total Organic Carbon in Water Samples by EPA415.1 and SW-846 9060
LTL-9116	6	166[2]	The Determination of Total Organic Carbon in Soil/Sediment Samples Using Modified SW-846 Method 9060
LTL-9136	0	166[2]	Determination of Perchlorate by Ion Chromatography by EPA Method 314.0
LTL-9202	3	166[2]	Total Suspended Solids (Non-Filterable Residue) Using EPA Method 160.2

TRIANGLE LABORATORY

2.04	6	166[2]	Nonconformance
5.01	10	166[2]	Sample Receipt, Identification, Handling, and Storage
DSP 105	16	166[2]	Extraction of PCDD/PCDF from Solids (not tissue) – 8290
DSP 161	18	166[2]	Extraction of PCDD/PCDF from Water for Methods 1613, 8290, and 551
DHR 182	9	166[2]	PCDDs and PCDFs by HRGC/HRMS – Method 8290
DPA 104	12	166[2]	Data Package Assembly and Shipping

NSWC CRANE LABORATORY

CR4052-PD-0001	1	166[2]	Quality Assurance and Control Plan
CR4052-PD-0100	3	166[2]	Document Control
CR4052-PD-0150	4	166[2]	Record Retention
CR4052-PD-0200	3	166[2]	Preventive Maintenance
CR4052-PD-0220	0	166[2]	Chemical/Supply Management
CR4052-PD-0250	1	166[2]	Calibration
CR4052-PD-0300	0	166[2]	Training Overview
CR4052-PD-0450	0	166[2]	Performance Evaluation
CR4052-PD-0500	1	166[2]	Chain of Custody: Soil and Water Samples
CR4052-PD-0600	2	166[2]	Customer Reports

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SOP No.	REV No.	QAPP/WP	TITLE
CR4052-PD-0700	0	166[2]	Glassware Cleaning Procedure
CR4052-PD-2500	0	010[3]	Determination of Organic Colorants in Environmental Matrices by HPLC

Shading indicates SOPs that have been revised or that have not been included in previous QAPPs.

1 "Quality Assurance Project Plan for Ammunition Burning Grounds Little Sulphur Creek and Jeep Trail Resource Conservation and Recovery Act Phase III RCRA Facility Investigation," NSWC Crane, April 2001.

2 "Quality Assurance Project Plan for Mine Fill A (SWMU 12), Mine Fill B (SWMU 13), Cast High Explosives Fill/B146 Incinerator (SWMU 16), and Pyrotechnic Test Area (SWMU 19) RCRA FRI Investigation," NSWC Crane, February 2002.

3 Risk Assessment Work Plan for Risk Assessment at SWMUs 4, 5, 9, and 10," August 2000.

SOP No.—standard operating procedure number.
REV No.—SOP revision number.
QAPP—quality assurance project plan.
WP—work plan.

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-1019

Title: **Controlling, Maintaining, and Monitoring Laboratory Logbooks**

Revision history:

Number	Date
0	4/11/96
1	5/13/98
2	11/17/00

Written by: Harry Romberg Date: 11-22-00
Harry Romberg, QA Officer

Approved by: Kathy E Kreps Date: 11-22-00
Kathy Kreps, Laboratory Director

Controlled Document
No. 20 Assigned to: Tetra

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1. Introduction and Scope

1.1 Scope

1.1.1 The maintenance of logbooks is essential to monitoring all aspects of laboratory operations including instrument and method performance and in tracking analyses. It is also important in confirming instrument performance at the time of specific analyses and in monitoring ongoing or periodic performance degradation and the steps taken to correct or prevent such occurrences. This document applies to all personnel involved in the preparation, control and use of laboratory notebooks.

1.1.2 More specific instructions for maintaining logbooks can be found in pertinent SOPs, such as LTL-1007 "Maintaining Instrument Records and Logbooks" or LTL-1005 "Analytical Balances" or others specific to other laboratory operations.

1.2 Purpose

1.2.1 The purpose of this SOP is to define the practices used to maintain control and use of laboratory logbooks. This SOP is not intended as a specific description of any particular logbook type but covers the practices that must be in place for all logbooks employed at Laucks.

1.3 Definition of Terms

1.3.1 Logbook - Any bound or unbound document that forms a record of activities and pertinent data regarding an activity including but not limited to maintenance logs, standards logs, reagent chemical logs, analysis logs including instrument outputs (computer generated or strip chart recordings), balance and temperature logs, or any other regularly maintained record of activity.

2. Requirements

2.1 Control

2.1.1 Documents that specify quality requirements or activities affecting quality or evidentiary activities shall be controlled to ensure that correct documents are being used and properly archived when completed. This insures that logbooks can be found at later dates rather than lost or prematurely disposed.

2.2 Maintenance

2.2.1 Quality assurance records (logbooks) shall be compiled and maintained in accordance with approved procedures.

2.3 Monitoring

2.3.1 Logbooks should be periodically monitored to ensure they are being properly maintained and information is being correctly recorded. Standard logbooks and run logs should be monitored at least semiannually by group supervisors or their designees. Pages from these logbooks, however, should be at least checked for accuracy and completeness as the individual data packages are reviewed. Maintenance and other logbooks need only be reviewed annually, unless previous review has demonstrated inadequacies in the logbook which require more frequent monitoring. At any time, whether during routine data review or specific logbook monitoring, if discrepancies are found, they should be corrected not only on the copies of logbook pages which may accompany a data package but on the original logbook page(s). If more systematic problems are found, the originator of the discrepancies must be re-trained in the proper documentation technique.

3. Responsibilities

3.1 Quality Assurance Manager

- Maintain the logs for control of laboratory notebooks and provide control numbers and labels as required.
- Approve format and proposed content of laboratory notebooks; minor changes to pre-printed forms do not need QA approval as long as their basic content does not change.
- Maintain master copies of notebook pages (in instances where pre-printed pages with a specific format are used); this may be in electronic or hardcopy form or both.
- Monitor satisfactory implementation of the requirements of this SOP

3.2 Responsible Supervisor

- Determine the format and content of notebooks used in their respective areas.
- Ensure that QA has been provided with an electronic version of all pre-printed logbook pages in order that they are later available for reprinting or editing.
- In coordination with QA and the respective analyst(s) ensure that all laboratory notebooks are properly labeled, including the appropriate control number.
- Ensure that personnel are adequately trained in the proper use of laboratory notebooks

- Periodically review laboratory notebooks to verify satisfactory implementation of the requirements of this SOP. Standard logbooks and run logs should be monitored at least semiannually by group supervisors or their designees. Maintenance and other logbooks need only be reviewed annually, unless previous review has demonstrated inadequacies in the logbook which require more frequent monitoring. This activity may be assigned to another individual but should not be the same individual who regularly completes the log itself.

3.3 Analyst

- Ensure that they are using the appropriate logbook and understand how to properly fill in the required fields. In general, this not only means entering correct information but that no pertinent information is left out or not entered in the assigned fields.

- Ensure that any new logbook has been given a logbook number by QA before beginning to use it.

- Ensure that the logbook is clearly identified with an instrument ID and purpose or other appropriate title which will enable the analyst to easily identify the logbook.

- Ensure that if pre-printed logbook pages need to be modified, the modifications are approved by their supervisor and that an electronic copy or, if requested an original hardcopy have been provided to QA.

4. Procedure

4.1 Notebook Structure

4.1.1 Laboratory notebooks may be either bound or unbound as described below. Most logbooks should be bound in some fashion but it is recognized that this is not always possible, such as for vendor service records. These records may be stored in 3-ring binders or other suitable notebooks but they may NOT be stored loose-leaf or in a simple manila folder.

4.1.2 In some instances, logbooks may be created from instrument printouts or other pages that do not lend themselves to being pre-bound. In these instances, the log sheets may be stored in a 3-ring binder or other storage until enough sheets have been accumulated to have them bound with the laboratory comb binder.

4.1.3 All logbooks whether bound or unbound must be controlled by QA as designated by the appropriate QA Book Number label (see example in Appendix 1).

4.1.4 Bound notebooks shall conform to the following:

- Where feasible, binding will be of a type that will make the removal and reinsertion of pages readily noticeable.
- If pre-printed and bound, all pages will be sequentially pre-numbered. If the format of the notebook permits the use of the reverse side of the pages, both sides of each page will contain a sequential page number.
- Each page of the pre-printed bound notebook will contain, as a minimum, the laboratory name, logbook title, and sequential page number. Other elements may also be necessary for any specific logbook.

4.1.5 Unbound notebooks shall conform to the following:

- Unbound pages will be contained in a binder or folder that prevents loss and provides protection from damage.
- Each unbound page will contain a unique identifier (e.g., run number/date). For identification purposes, a continuous printout on fanfold computer paper requires only one identifier unless the sheets are separated.
- As noted above in 4.1.2, some unbound logbooks may eventually be bound if practical.

4.1.6 All notebooks will contain the following information on the cover:

- Laboratory name, Laucks Testing Laboratories, Inc.
- Control number assigned by the Quality Assurance Officer
- The department to which the logbook was issued
- The use of the logbook (i.e. balance calibration, instrument run-log, etc.)
- The department book number or title uniquely identifying that book, as required to identify the specific use of the book. This may include an instrument number or other logbook ID (such as a standards logbook ID). This is in addition to the QA logbook number.
- Start Date, the date on which the first entry was made
- End date, the date on which the last entry was made

4.2 Control of Logbooks

4.2.1 The QA Officer will maintain a master log of laboratory notebooks that contains as a minimum, the following information:

- Unique control number for each logbook
- Logbook title, which should reflect the type of information to be entered.
- Department to whom issued, for accountability only. A logbook will generally be assigned to a work station or function, and in no way is a laboratory notebook to be considered a "personal" notebook.
- Date issued, for accountability only.
- Date closed, for accountability.

4.2.2 Master sheets for each logbook will be maintained by the QA Officer in cooperation with the responsible supervisor and analysts and will be utilized for producing notebooks when required.

4.3 Use of Laboratory Logbooks

4.3.1 The notebook is the basic document for recording information. Entries should be made into the notebook in real time, not written on scratch paper and transferred later.

4.3.2 Handwritten entries should be legible and entered in black or blue indelible ink.

4.3.3 Computer-generated data should be printed out and collected at appropriate times to represent the activities being recorded.

- Computer printouts may be either placed in unbound notebooks as described above, or inserted into bound notebooks.
- Computer printouts or other material inserted into bound notebooks must be securely fastened (tape is preferred) in such a way that removal and insertion of material can be determined readily.

4.3.4 When information from related activities is recorded in more than one notebook, provide adequate cross-reference information in all affected notebooks so that all pertinent data can be readily accessed.

4.3.5 Do not skip pages when entering data. For example, if data is not readily available for entry, do not leave space for later entry. Enter the data when it becomes available and provide adequate cross-references if required.

4.3.6 In cases where partial or complete pages must be left blank and not used, indicate the unused portion by placing a horizontal line at the beginning and end of the unused portion and connecting opposite ends of the horizontal lines with a diagonal, resulting in a Z-shaped figure. The individual striking out the blank area will initial and date the diagonal.

4.3.7 Errors or other changes must be deleted in a similar fashion or with a single-line cross-out which has been initialed and dated. **No erasures, overwriting, white-out or multiple-line cross-outs (blacking out) are acceptable.**

4.3.8 When pre-printed formats are used and all possible entries are not required, the remaining blanks may be struck out with a Z as described above, or entries such as N/A may be placed in the unused blanks.

4.3.9 The individual entering information into the notebook shall initial and date each page used, or in the case of logbooks with ongoing records which do not occupy the entire page, such as maintenance logs or balance logs, each individual entry.

4.4 Supervisory Monitoring of Laboratory Logbooks

4.4.1 Standard logbooks and run logs should be monitored at least semiannually by group supervisors or their designees. Maintenance and other logbooks need only be reviewed annually, unless previous review has demonstrated inadequacies in the logbook which require more frequent monitoring. This activity may be assigned to another individual but should not be the same individual who regularly completes the log itself.

4.4.2 Logbooks should be reviewed using the review items provided in Appendix II, although it is not necessary to actually document the review using this checklist.

4.4.3 Errors should be formally brought to the attention of the responsible individual through the use of Corrective Action Forms. If errors are correctable or items can be corrected for legibility problems, they should be corrected using the proper error correction technique.

4.4.4 Logbooks that have been reviewed are marked with a fluorescent yellow or other colorful label that looks similar to the label in Appendix III.

4.5 QA Monitoring of Laboratory Logbooks

4.5.1 The QA Officer will verify during periodic audit and surveillance activities that notebooks are properly completed and maintained. This will generally be done approximately annually as part of routine audits. This observation does not preclude the requirement for supervisory review.

Appendix I

Example QA Logbook Label

Laucks
Testing Laboratories, Inc.

QA Book No.: _____

Issued To: _____

Used For: _____

Dept. Book No.: _____

Start Date: _____

End Date: _____

Appendix II

Example Logbook Review Items to be Observed

- Have all pertinent fields been filled or marked not applicable (N/A)?
- Has empty space been crossed out properly initialed and dated?
- Have errors been corrected with single-line crossouts, initialed and dated (no obliterations or overwrites)?
- Are all entries clear and easy to read and comprehend?
- If calculations are involved, check several random calculations for error.
- If traceability is involved (as for standards) check several random entries to confirm that the logbook entries can be tracked back to the original entry.
- If standards log, observe some actual standards and compare them against logbook entries for accuracy.
- Are all handwritten entries initialed and dated?
- If the book is beginning to deteriorate, it should be repaired or retired and replaced before it completely falls apart.

Appendix III

Example Logbook Review Label

Logbook pages _____ through _____
have been reviewed for completeness and
spot-checked for accuracy.

Initials:_____ Date:_____

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-1020

Title: **The Integration of IC, GC, HPLC, and GC/MS Peaks**

Revision history:

Number	Date
0	08/26/96
1	08/21/97
2	05/02/02

Revised by: Monica Carr, Organics Division Manger Date: 5/9/02

Reviewed by: Harry Romberg, QA Officer Date: 5-9-02

Approved by: Kathy Kreps, Laboratory Director Date: 5/9/02

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1. Introduction and Scope

1.1 Method Description

1.1.1 This SOP describes the integration process for chromatographic data, the procedures for manual integration, and the procedures for documenting manual integration.

1.1.2 Integration identifies peaks found in the data collected during data acquisition and characterizes them. The software uses the integrated peaks to determine the identity and quantity of compounds in the samples. The peak area, peak height, peak type, baseline, and retention time of each peak in a chromatogram are determined by integration. It is expected that situations will arise when the automated quantitation provide inappropriate quantitations. This normally occurs when there is compound co-elution, baseline noise, or matrix interference. Some peaks, due to limitations of the software, will need to be manually integrated. The manual integration process must be documented as outlined in section 5 of this SOP.

1.1.3 Manual integrations have been a source of serious concerns throughout the laboratory industry as a tool of fraud. There have been labs as well as individuals who have been penalized due to improper manual integration, or inadequate documentation that their actions were appropriate. Therefore, it is imperative that proper and honest and completely documented procedures are followed.

1.1.4 This method is restricted to use by, or under the supervision of analysts experienced in the technique described. Each analyst performing this method must have demonstrated the ability to perform the described analysis.

1.2 Definition of Terms

1.2.1 Manual Integration - any intervention by an analyst or supervisor to change the peak area, peak height, baseline, peak type, or retention time of a chromatographic peak.

2. Software

2.1.1 GC Acquisition-HP/EZChrom
2.1.2 GC/MS-Teknivent/EnviroQuant/Chemstation
2.1.3 GC-Target

3. Responsibilities

3.1 Analyst

3.1.1 The analyst is responsible for reading and understanding this SOP and that which is applicable to the method of analysis. The analyst must also perform and document all manual integrations as specified in this SOP.

3.2 Supervisor

3.2.1 The supervisor or designated data reviewer must verify that all manual integrations are performed according to this SOP. The supervisor or designated data reviewer must document that this verification has occurred per the applicable Data Review, Validation, and Reporting SOP.

4. Operation Procedures

4.1 Integrator operation

4.1.1 The ideal chromatogram has perfectly symmetric peaks separated from each other with periodic baseline points. It is common to encounter split peaks, deformed peaks, merged peaks, sloping baselines, noise, spikes, shoulders on peaks, and a host of other calamities.

4.1.2 To maximize the chances of obtaining ideal chromatograms, first optimize the chromatography.

4.1.3 Peak recognition and integration sequence - As the integrator scans the data, it examines the slope (vertical distance between points) and curvature (positive or negative). So long as these remain within preset bounds data is interpreted as the baseline. If the bounds are exceeded, a peak may be starting. If the condition persists, the integrator decides that it is on the upslope of a peak.

4.1.4 The curvature changes to negative about halfway up the peak. This is the inflection point where the peak starts to round over approaching the apex. Passing the top, the slope becomes negative and the integrator is on the downslope. Another inflection point comes on the downslope and finally the peak returns to the baseline (Figure 1).

4.1.5 Finite width of integration slices - The slope changes from positive to negative at the top of the peak. However for area slices having finite width the integrator can only determine which slice contains the peak apex. To get better values for the retention time and peak height, the

integrator takes the slice containing the-apex and one slice on either side, fits them to a quadratic equation, and solves the equation to find the highest point (Figure 2).

4.1.6 Optimizing peak recognition - The best conditions for recognizing isolated symmetric peaks on a quiet baseline is to match the peak width parameter to the measured width of the peaks at half height. Threshold should be a few units less than the highest value still capable of detecting the peak. When peaks cluster together or the baseline slopes or is noisy, these ideal values must be modified. Figure 3 shows the effects of changing the values.

4.1.7 Manual integration - It is important that the analyst is familiar with the compounds that are routinely analyzed. Knowing the response and peak shape of the standard is important for consistency in integration. It is best to optimize the method to process data so that manual intervention is minimized and peak integration is more consistent. If manual integration is performed, it is important to be consistent for a given analyte in the standards, blanks, spikes, and samples.

4.1.8 Allowable manual integrations - Some common reasons for manual integration are:

4.1.8.1 Split peaks (attachment 1)

4.1.8.2 Tailing (attachment 2)

4.1.8.3 Retention time shifts (attachment 3)

4.1.8.4 Mis-identification (attachment 3)

4.1.8.5 Merged peaks (attachment 3)

4.1.8.6 Secondary ions or qualifier ions (attachment 4)

4.1.8.7 Baseline shifts (attachment 5)

4.1.8.8 Skimming versus dropped baseline (attachment 6)

4.1.9 Improper manual integrations - These practices are not allowed and warnings up to and including termination of employment will follow any documented cases of improper manual integration. If you are unsure about a manual integration ask your supervisor or QA.

4.1.9.1 Adding area by including other peaks. (attachment 7)

4.1.9.2 Improper baseline - this includes the practice of having the baseline moved up the side of a peak to decrease the area. (attachment 8)

4.1.9.3 Changing a proper integration to make the peak "in".

4.1.10 Special rules for fuel analyses (*e.g.*, gasoline, diesel) - The integration of these multi-component analytes requires special integration rules. The area of all peaks (with the exception of the surrogates) and the area of the non-resolved components (hump) are grouped together to determine the quantity of the analyte. The baseline is fixed at the start and held at a constant level for the entire run. When integration of the baseline for fuel analyses is performed, the quantitation report will not be dated and initialed by the analyst. Instead an explanation of the baseline integration will be documented on the quantitation report or in the appropriate SOP and discussed in the sample narrative. Some acceptable multi-analyte integrations are shown in attachment 9.

5. Documentation

5.1.1 When any manual integration is performed, a graphic copy of the peak with the integration marks is generated and put into the folder with the chromatograms and quantitation reports for that sample. The three different software systems used in the laboratory are listed below with the commands for generating the copy. On the quantitation report the analyst must initial, date, and give a brief description of the reason for the manual integration (table 1). In addition, the analyst must provide chromatograms from both before and after the manual integration. The manual integration must also be documented in the associated sample narrative. The supervisor or his/her designee will look at each manual integration during data review and complete the summary on the data review or QC checklist.

5.1.2 Target: After changing the integration, exit and save in Target Review.

5.1.3 GC/MS Teknivent EnviroQuant/Chemstation: After using Qedit to change the peak click on 'Graphics Report to Printer'

5.1.4 EZChrom: After changing the integration, toggle the "Reanalyze" key and print.

Table 1

Manual Integration Key

M = Manual integration due to missed peak or irregular peak shape.
MS = Manual integration due to split peak.
MR = Manual integration due to retention time shift.
MI = Manual integration of correct isomer.
MT = Manual integration due to peak tailing.

MB = Manual integration due to irregular baseline.

6. REFERENCES

6.1.1 Target Manual, Thru-Put Systems, Inc., Target Compound Analysis Software User's Guide, 1994.

6.1.2 Envirolink User's Manual, TEKNIVENT, 1994

6.1.3 HP Chemstation, Version B.01.00

6.1.4 EZChrom Chromatography Data System, Scientific Software, Rev. 6.6, 1995.

6.1.5 Wisconsin DNR Newsletter, October 1994.

6.1.6 SOP# LTL-1018, Standard Operating Procedure for Review and Approval Practices for Validatable Packages.

6.1.7 SOP # LTL-8005, Standard Operating Procedure for GC Gas/BTEX Data Review.

6.1.8 SOP #LTL-8004, Standard Operating Procedure for GC Volatiles Data Review.

6.1.9 SOP #LTL-8001, Standard Operating Procedure for GC Hydrocarbons Data Review.

6.1.10 SOP #LTL-8301, Standard Operating Procedure for HPLC Aromatics 8310 Data Review.

6.1.11 SOP #LTL-8302, Standard Operating Procedure for HPLC Ordnance 8330 Data Review.

6.1.12 SOP #LTL-8201, Standard Operating Procedure for GC/MS VOA Data Review.

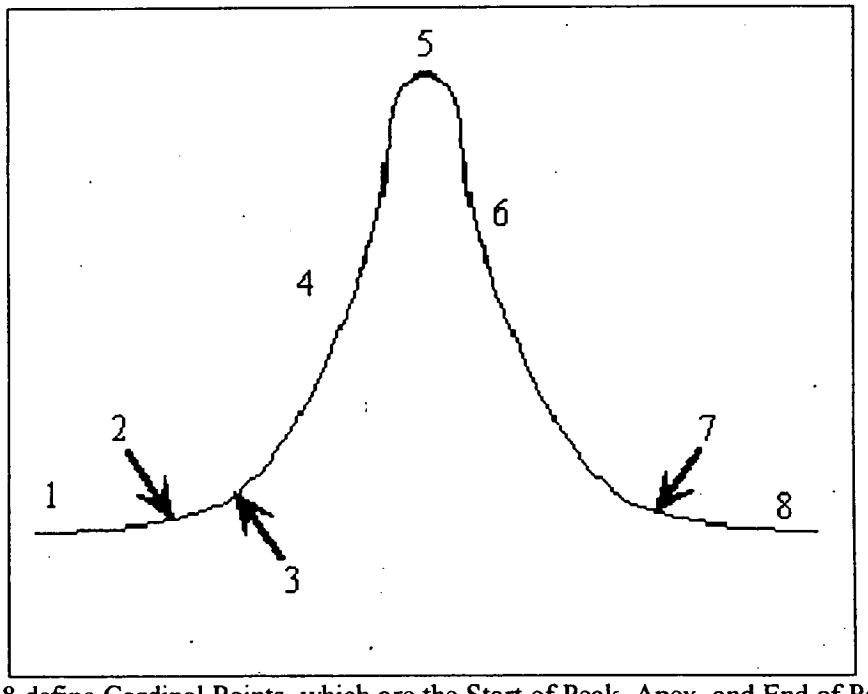
6.1.13 SOP #LTL-8202, Standard Operating Procedure for GC/MS Semivolatile Data Review.

Appendix I

Fig 1.

The sequence for finding a positive peak is:

1. Slope and curvature within limits	track baseline
2. Slope and curvature above limits	perhaps a peak?
3. Slope remains above limit	here's a peak!
4. Curvature becomes negative	front inflection point
5. Slope becomes negative	top of peak
6. Curvature becomes positive	rear inflection point
7. Slope and curvature within limits	approaching end of peak
8. Slope and curvature remain within limits	end peak, track baseline



Steps 3,5, and 8 define Cardinal Points, which are the Start of Peak, Apex, and End of Peak Respectively

Fig 2.

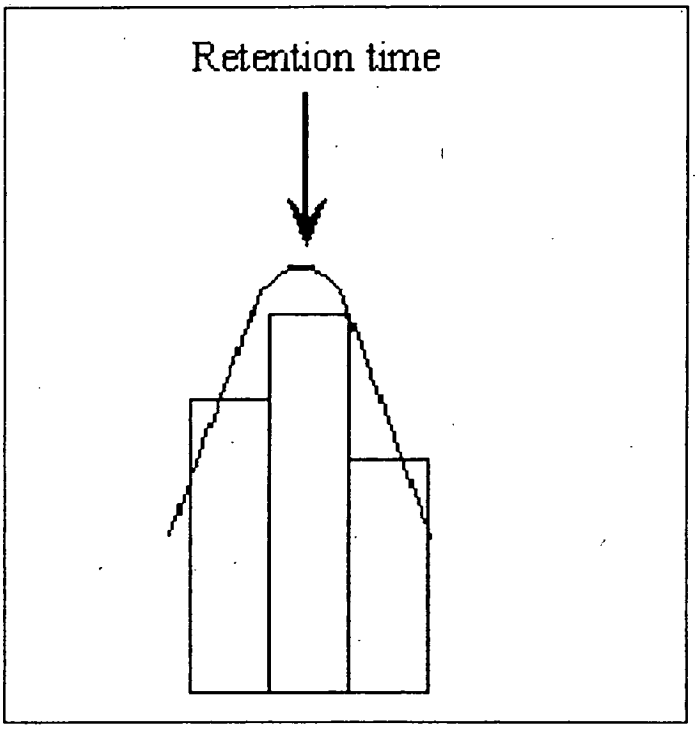
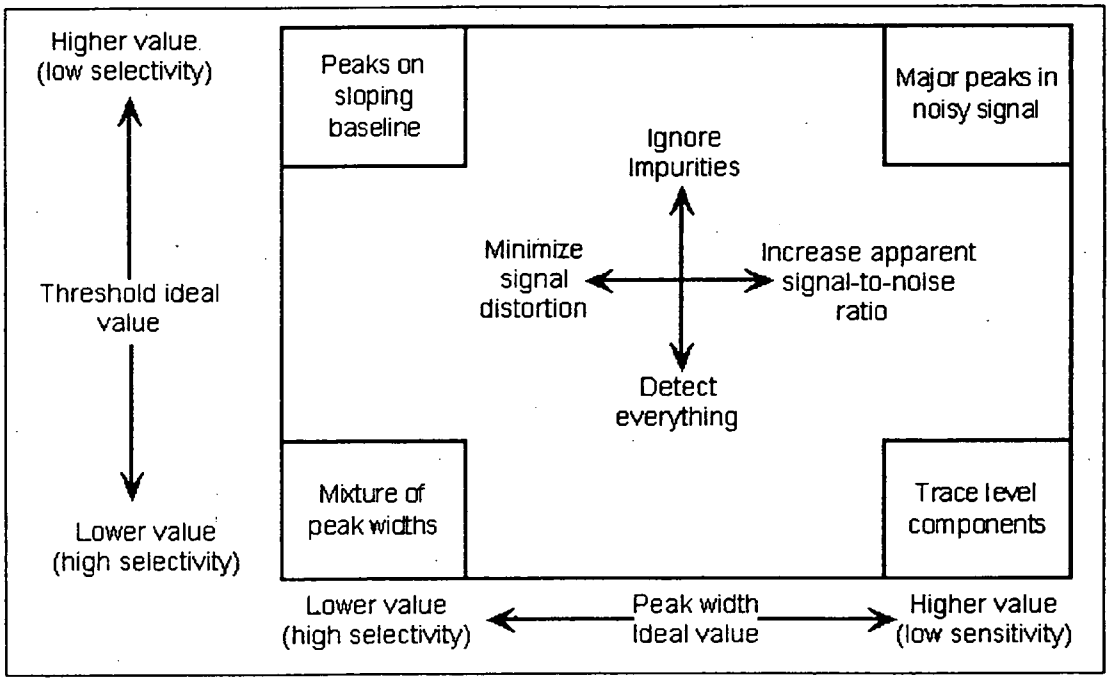
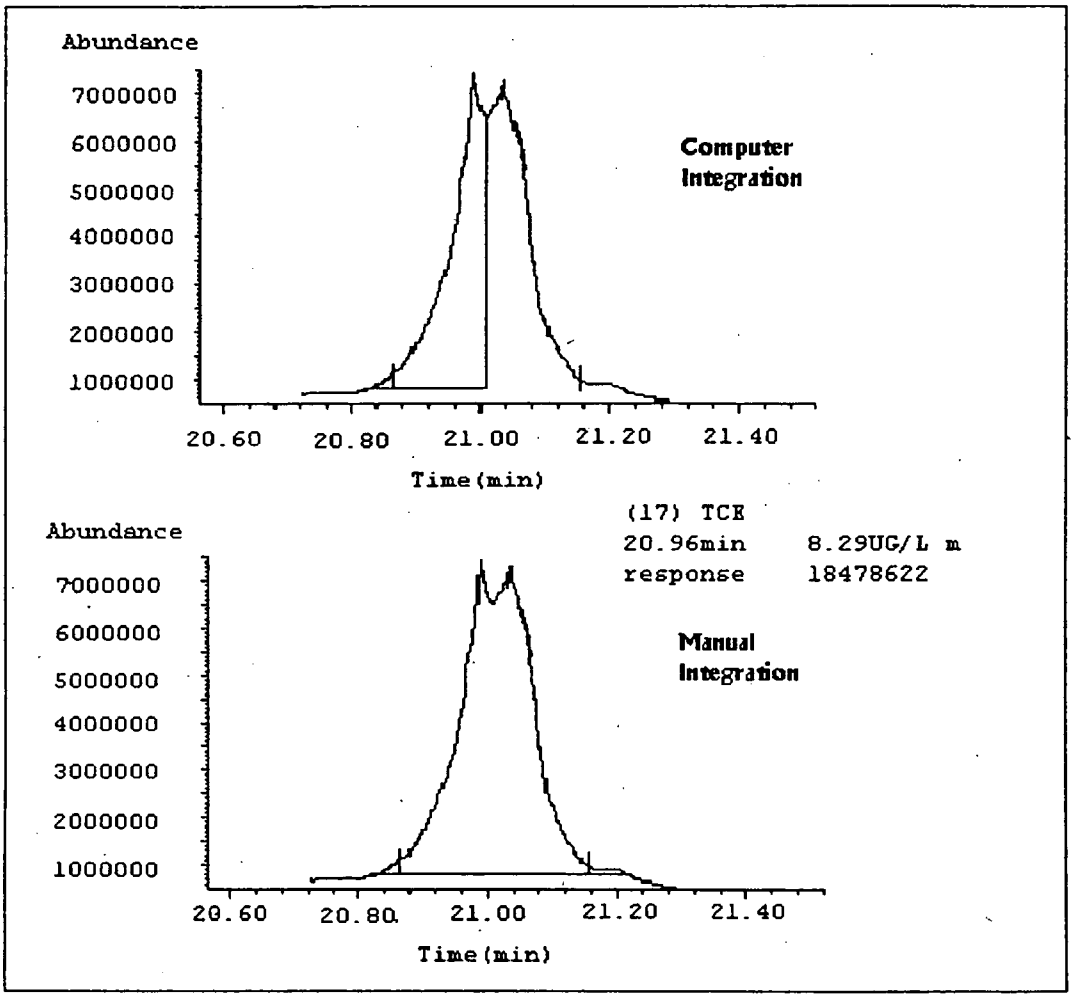


Fig 3.


Higher value
(low selectivity)
Threshold ideal value
Lower value
(high selectivity)
Peaks on sloping baseline
Major peaks in noisy signal
Ignore Impurities
Minimize signal distortion
Increase apparent signal-to-noise ratio
Detect everything
Mixture of peak widths
Trace level components
Lower value
(high selectivity)
Peak width
Ideal value
Higher value
(low sensitivity)

Appendix II

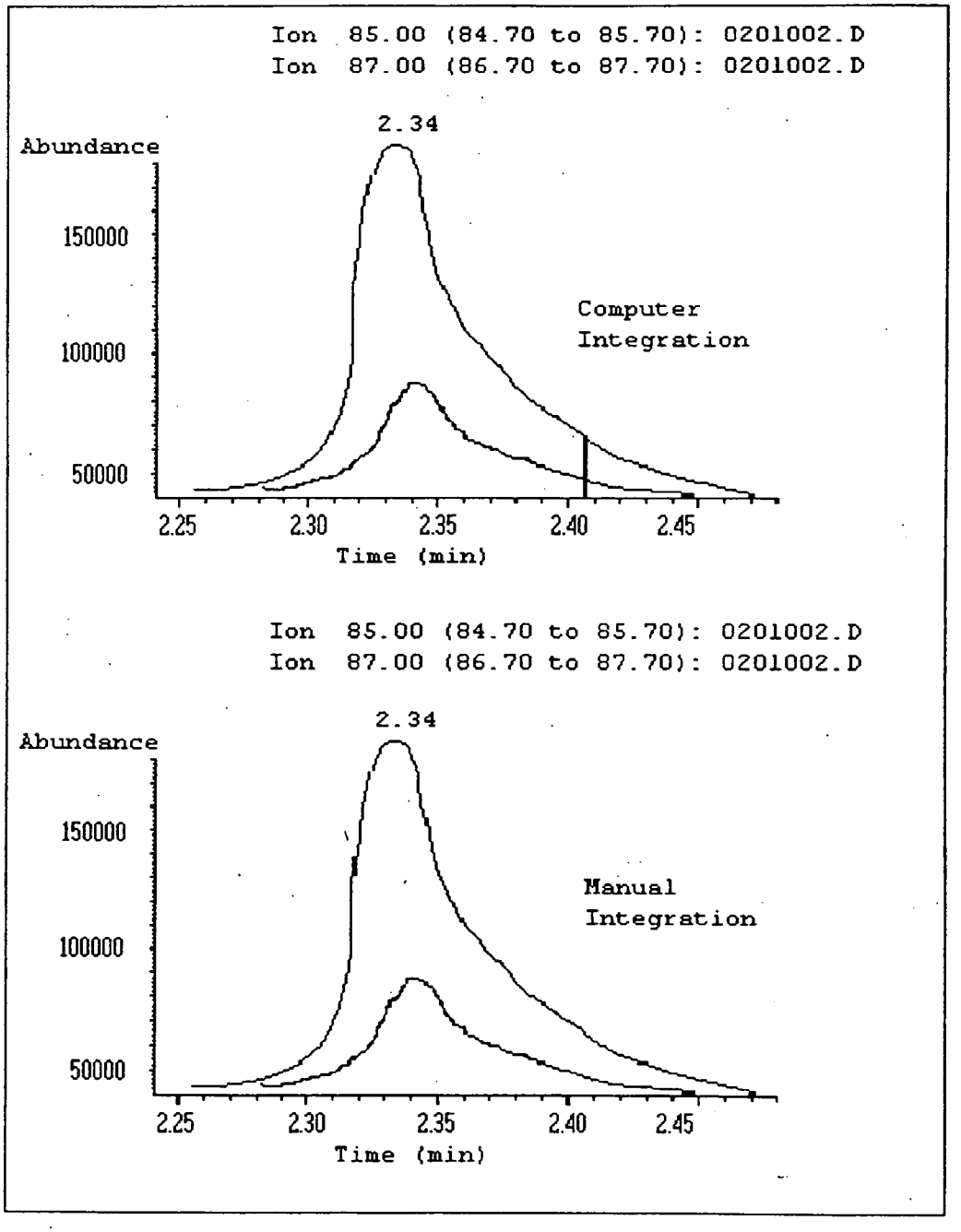
Attachment 1



Allowable Integration

Split Peaks

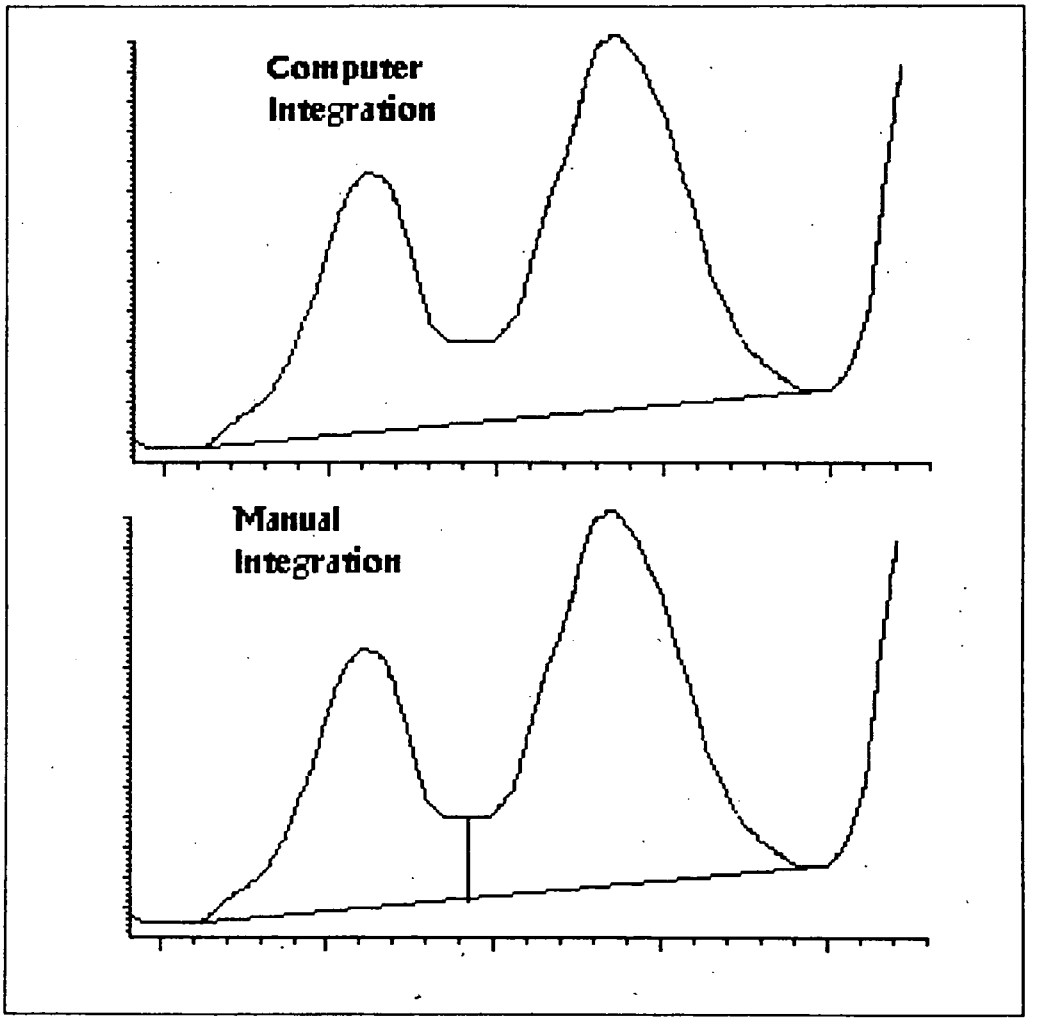
Attachment 2



Allowable Integration

Tailing

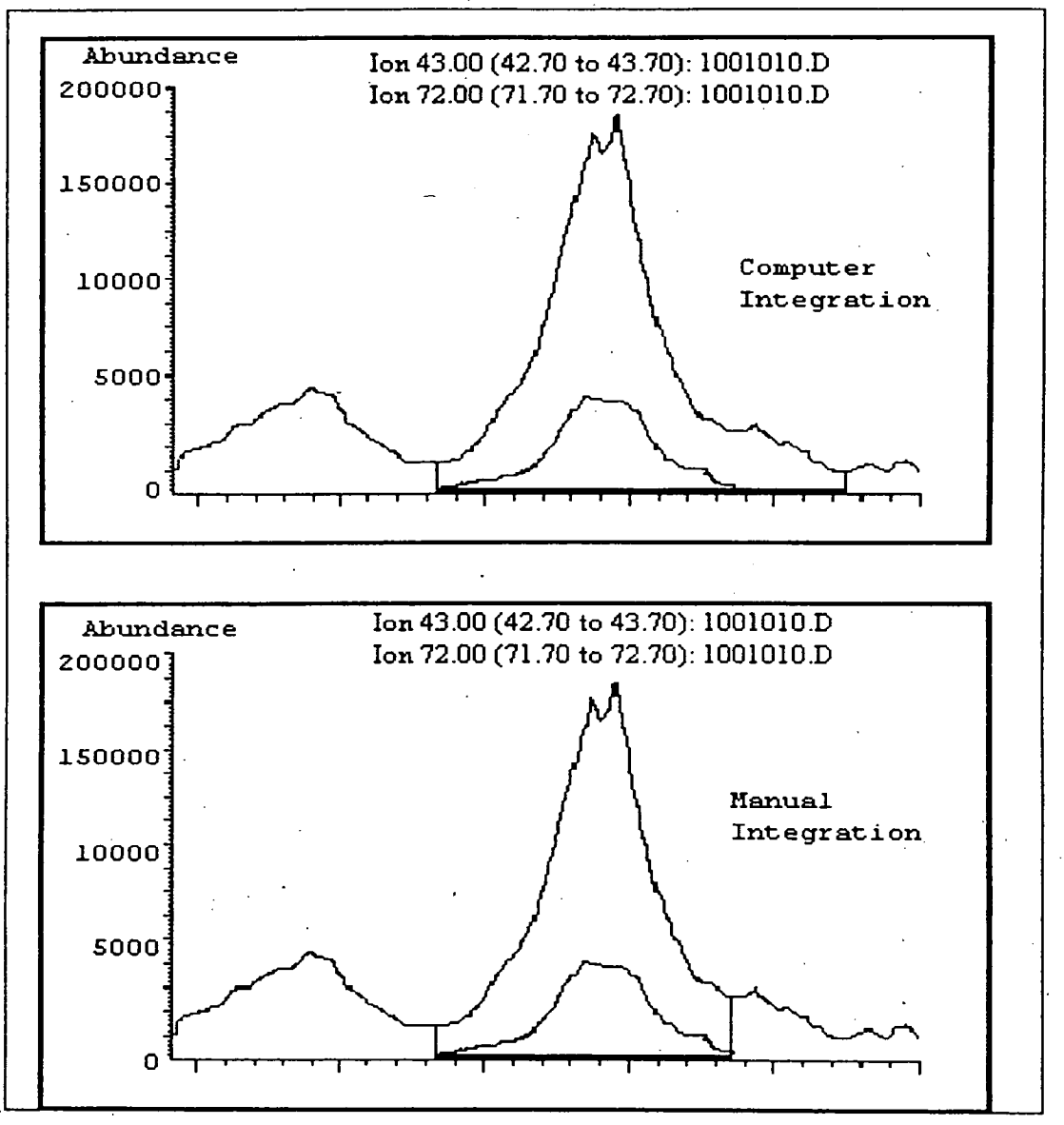
Attachment 3



Allowable Integration

Retention Time Shift - Mis-Identification - Merged

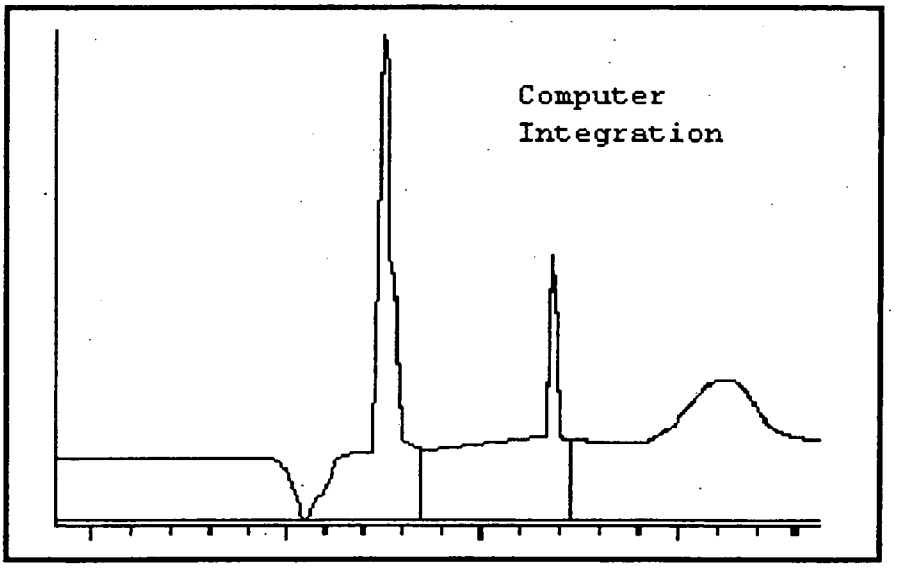
Attachment 4

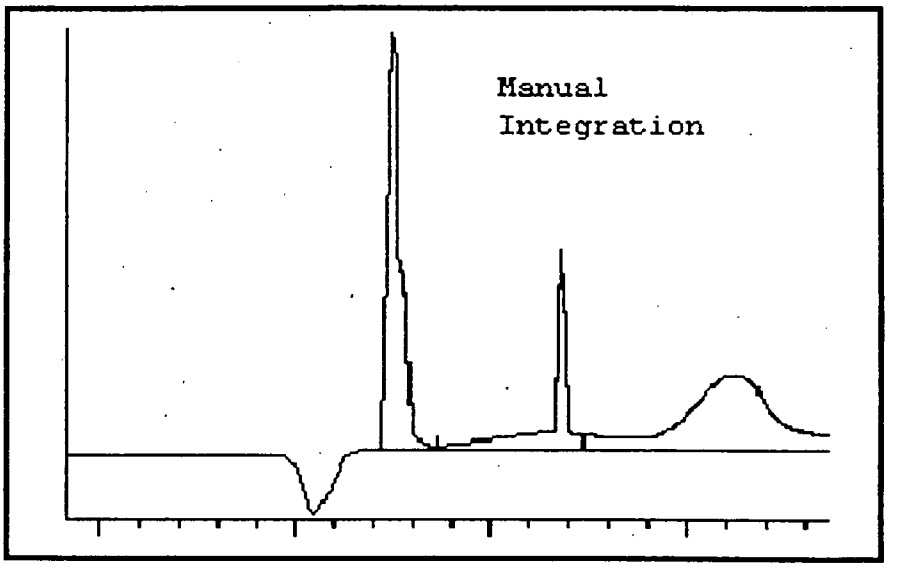


Allowable Integration

Secondary or Qualifier Ions

Attachment 5

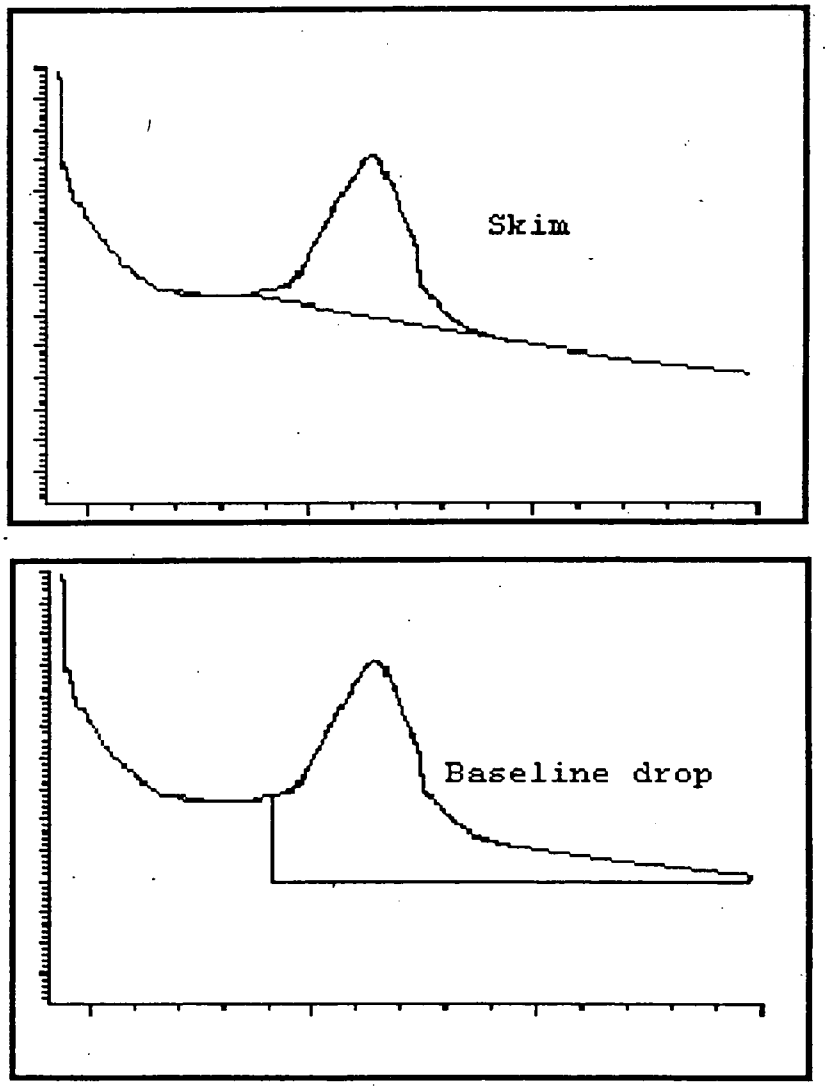




Allowable Integration

Baseline Shift

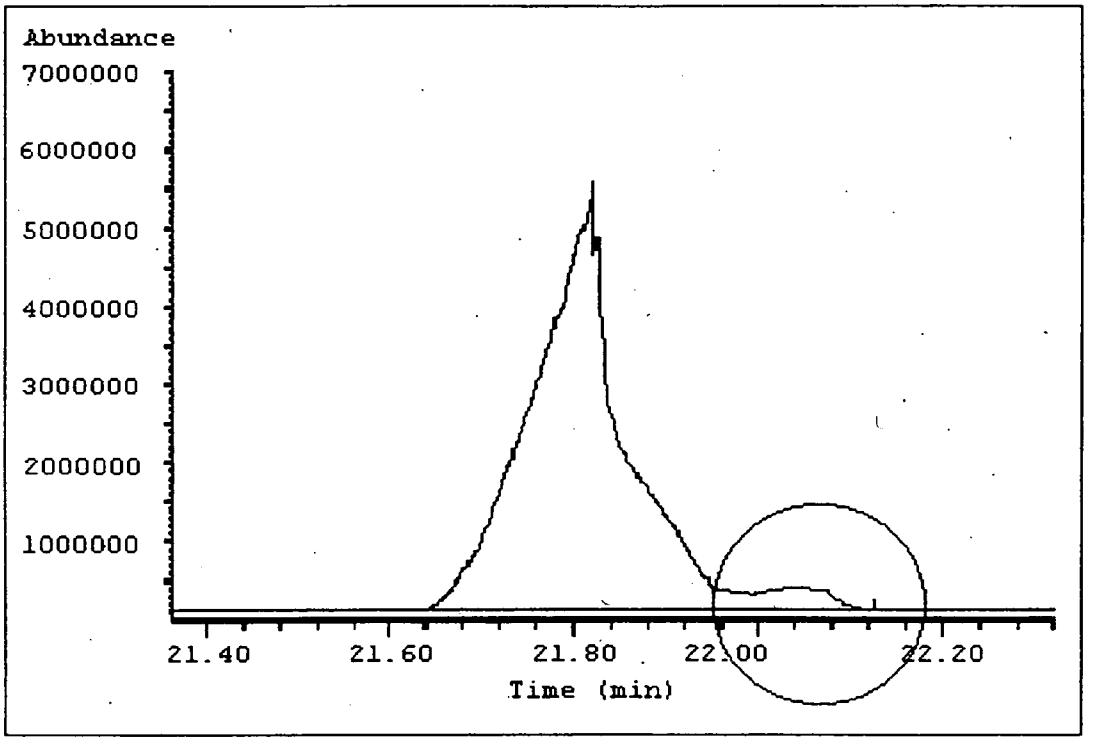
Attachment 6



Allowable Integration

Skimming (manual) vs. Baseline Drop (computer)

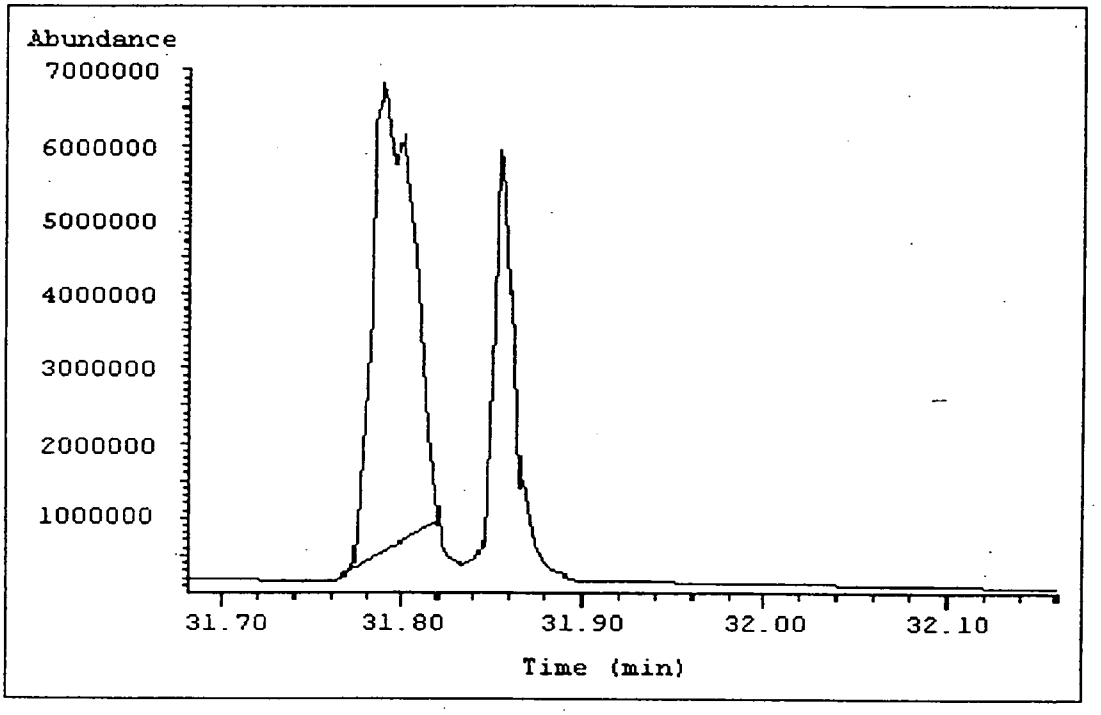
Attachment 7



Improper Integration

Adding Area by Including Other Peaks

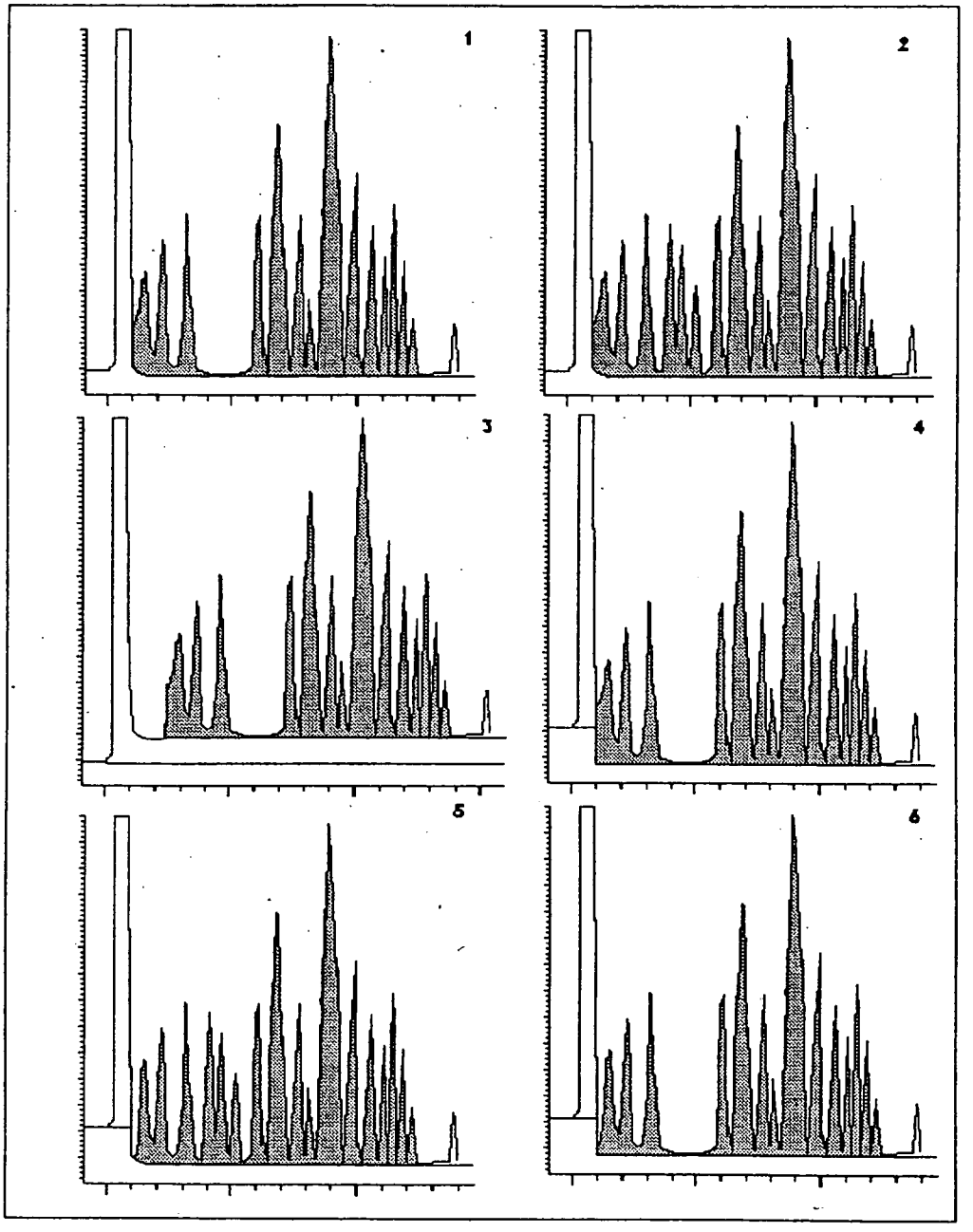
Attachment 8



Improper Integration

Baseline Moved To Decrease Peak Area

Attachment 9



Acceptable Methods of Integration
Grouped Peaks

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-2001

Title: **Waste Segregation and Disposal**

Revision history:

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Written by: Harry Romberg Date: 10-10-01
Harry Romberg, Quality Assurance Officer

Approved by: Kathy Kreps Date: 10-16-01
Kathy Kreps, Laboratory Director

Controlled Document
No. 20 Assigned to: TeTC

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1. Introduction and Scope

1.1 Method Description

1.1.1 The purpose of this SOP is to describe the laboratory waste disposal scheme currently in place at Laucks. The primary waste streams described include solvents, PCB oil wastes, COD waste, soil samples, aqueous acidic waste, and fluorescent light bulbs. This SOP only covers handling of the waste from the point of collection.

1.1.2 This method is restricted to use by, or under the supervision of analysts experienced in the techniques described. As part of their training for analytical tasks which generate related wastes, each analyst must be trained to properly dispose of the waste or to consolidate it at the appropriate collection point.

1.1.3 This SOP generally does not cover handling of the waste up to the point of disposal.

1.1.4 Appendix III, entitled *"A Quick Primer on Hazardous Waste Management"* contains a brief description of what is expected of individuals in the laboratory in terms of hazardous waste disposal. This is primarily to be used as a reminder and may be handed out independently of the entire SOP. Staff members who handle hazardous waste should also read this SOP.

2. Equipment List

2.1 Equipment

2.1.1 The equipment necessary to properly dispose of laboratory wastes varies with the type of waste. In general, an appropriate container, packing material, and safety equipment (including clothing, eye wear, and respirators) is required.

3. Safety precautions

3.1 Safety Precautions

3.1.1 Solvent wastes may contain materials flammable at room temperature or lower. Caution should be taken to avoid flames and sparks when in the presence of or handling these wastes.

3.1.2 COD and other acidic or alkaline wastes may contain materials which will burn the skin, eyes, and/or mucous membranes if improperly handled. Precautions should be taken to avoid accidental contact.

3.1.3 All wastes may contain materials which can have both known and unknown long-term health effects. COD wastes, for instance, contain high levels of mercury and

chromium salts. Direct contact should be avoided through the use of proper clothing and eye wear, even if no immediate danger is obvious. In the case of volatile solvents and other materials, handling should be done in a well-ventilated area and the exposure to vapors minimized. Where strong fumes are unavoidable, a carbon-filter or other respirator should be worn.

3.1.4 All people who handle waste products or the original reagents should be aware that the laboratory provides safety equipment and has a file containing Material Safety Data Sheets (MSDSs) on all laboratory chemicals in support of OSHA and other safety programs.

4. Operation procedures

4.1 Operations Appropriate to All Collection Areas

4.1.1 Land Disposal Restriction Forms (LDRs), manifests and other paperwork are not extensively discussed in this SOP because the disposal vendor deals with this aspect of the paperwork. It will only be necessary for the person who will be asked by the vendor to sign these forms (usually QA) to check that the information on the forms is accurate and to sign the form.

4.1.2 All waste requiring a Hazardous Waste disposal sticker and manifest will be marked with one of two EPA Hazardous Waste Site numbers. All waste transported from the 921 facility will be numbered WAD981762024 and all waste transported from the 940 facility will be numbered WAD027446608. It is only necessary that these numbers appear on the containers before they are shipped. It is not necessary on drums which have yet to be transported. The labels themselves, however, must be placed on the containers prior to use.

4.1.3 The Hazardous Waste Sticker must be labeled with the proper DOT shipping name, even though the disposal company will usually replace the label before shipping. The proper shipping names are listed below in the applicable sections of this SOP. This item **IS** necessary on all drums as soon as any waste at all is dumped into them.

4.1.4 All collection drums **must** be marked with an appropriately filled out Hazardous Waste sticker (see Appendix A). It is only necessary for Laucks staff to fill in the date that collection was **started** and the contents of the drum in the appropriate space. Hazardous Waste cannot be accumulated for longer than 90 days before it must be disposed. Therefore, do **not** mark the date on the drum until collection is started so as to maximize the allowable time until disposal. This applies to the 55 gal. drums of solvent in the 921 building and the 30 gallon drum in the 940 solvent locker. All other containers are considered satellite collection points and need only be dated when the

containers are **filled**. This sticker will be replaced by the transporter when they arrive to transport the waste to an approved disposal facility. The replacement sticker will contain all of the information required for transport and disposal.

4.1.5 All collection drums containing liquids should have secondary containment. That is, the primary collection drum should sit in a tub or bermed space so that if the container suffered partial or complete failure, there would be sufficient space in the secondary container to hold all of the liquid and not allow it to drain to the sewer.

4.1.6 In addition, corrosive and flammable waste collection drums must have a sticker which indicates their corrosive (8) or flammable nature (3) (see Appendix B). Soil drums are designated with a general hazard (9) label.

4.1.7 Once a material has been designated as waste and disposed into the designated drum, that drum must not be stored for longer than 90 days from the date marked on the drum as designated above. This is rarely of concern at Laucks because transport is generally scheduled for most wastes within much less time than the required maximum storage time. Note that Laucks is currently considered a medium quantity generator by the WA Dept. of Ecology and subsequently has 180 days to dispose of full waste containers but we will strive to meet the 90-day clock to insure we are even meeting requirements if we inadvertently exceed the large quantity generator threshold of 2200 lbs./mo.

4.1.8 When collection drums are full or the 90-day limit is approaching, the Quality Assurance (QA) Department must be notified. This department, at the time of this writing, is responsible for contacting the appropriate approved transporter and insuring proper disposal takes place. The preferred lead-time for pickup is 10 working days so QA should actually be contacted 80 days after the first drum is dated. QA does weekly inspections of the laboratory with the express purpose of observing the hazardous waste areas and making safety related observations. However, it should never be assumed that QA or a substitute will automatically take care of a particular accumulation.

4.1.9 All questions or concerns regarding hazardous waste operations should first be directed to QA who will determine the appropriate course of action.

4.1.10 QA or the designated waste manager will also be responsible for insuring that signed manifests are received from the disposal facility within 90-days of shipment. This is easily done by the organization of our hazardous waste files for both of our facilities.

4.2 Mixed Solvent Waste

4.2.1 This waste stream is primarily composed of methylene chloride with some acetone and hexane and potentially small quantities of other solvents or dissolved products. The collection point for all of this waste in the 921 facility (Extractions) are the 55 gallon drums in the solvent locker. In the 940 facility, they are designated 30 gallon drums in the 940 solvent locker

4.2.2 Small, 5 gallon or less containers of other mixed solvent waste may be collected as satellite accumulation units in the inorganics or organics instrument preparation areas but these **must** be transported to the primary drums when full. Likewise, waste solvent bottles are kept in some hoods in the 921 Extractions facility. Satellite accumulation containers must be kept closed when not in use and must be marked with the words "Hazardous Waste" or with other words that identify the contents of the container. This will most conveniently be done by using a blank Hazardous Waste Sticker. Open solvent containers are not allowed except when actually in use.

4.2.3 When new materials are collected in the primary drum, a Hazardous Waste sticker should be affixed with an initial collection date. The Hazardous Waste stickers should be marked with a DOT shipping name of "**Waste Flammable Liquids**".

4.2.4 Although methylene chloride is non-flammable, other components of these waste drums may be highly flammable. Thus, all of the waste solvent containers must be labeled with the flammable hazard (3) sticker.

4.2.5 At least 2 inches of headspace must be left between the top of the liquid and the top of the drum to allow for expansion.

4.2.6 When 3 or more full 55 gallon drums of this waste have been accumulated at 921, or 1 30-gallon drum at 940, or 80 days have passed since the beginning of collection of the oldest accumulated drum, QA must be contacted to arrange for transport and disposal.

4.2.7 At the time of this writing, Laucks uses Safety Kleen as the facility of choice for handling this waste stream, although this could be changed at the discretion of QA on either a one-time or ongoing basis.

4.3 Chemical Oxygen Demand (COD) Waste

4.3.1 The primary constituents of this waste are sulfuric acid, water, mercury, silver, and chromium (both tri- and hexavalent). The collection point for this waste is in the inorganics area where CODs are analyzed. These analyses are conducted in small pre-packaged tubes. The reacted tubes are not considered to be waste until they are poured out of the tubes into a collection container.

4.3.2 Collection containers must be labeled with a Hazardous Waste sticker as previously noted. The Hazardous Waste Sticker should be marked with a DOT shipping name of "**Waste Corrosive Liquids, Acidic, Inorganic**".

4.3.3 In addition to the hazardous waste sticker, these containers should be labeled with a corrosive (8) sticker as previously noted.

4.3.4 The waste may not be held for more than 90 days from filling of the satellite 5-gallon collection container. Immediately upon filling the container it must be tightly closed, dated, and transported to the acid storage locker. QA must be immediately contacted to arrange for transport and disposal within the allowable timeframe. While being filled, the 5-gallon collection container must be in secondary containment which consists of a washtub in which the collection container sits.

4.3.5 At least 2 inches of headspace must be left between the top of the liquid and the top of the drum to allow for expansion.

4.3.6 At the time of this writing, Laucks uses Safety Kleen as the facility of choice for handling this waste stream. This vendor can be changed at the discretion of QA on either a one-time or ongoing basis.

4.4 Soil Sample Disposal

4.4.1 Soil waste drums must be labeled with a hazardous waste label and identified as "**soil contaminated with lead**". It must also have a general hazard (9) sticker placed right next to the hazardous waste label on the upper half of the drum.

4.4.2 State law allows a laboratory to store samples indefinitely, until they are considered waste and disposed. The laboratory is also allowed to store a 55 gallon drum for at least 90-days (depending on our generator status) after it has been **filled and dated**. The drum must be tightly sealed and an accumulation date written on the hazardous waste label immediately after it has been filled.

4.4.3 Each drum used for soil waste disposal must be clearly marked with an identifying number which will be used to track which drum contained which samples. When samples are signed-out from their storage areas for disposal, the log sheet must be marked with the appropriate assigned drum number. This will enable the laboratory to track which samples were disposed in which drum.

4.4.3.1 The drums should be marked with the year the accumulation is STARTED, location from which they originate, and sequential number. Thus drums for which accumulation began in 1998 from the extractions laboratory would be marked 98-921-01. The -01 being a sequential number that would be incremented with each

additional drum -02, -03, etc. throughout 1998. A drum from the main lab would be designated 98-940-01, etc.

4.4.3.2 When samples are transferred from the storage locations to the drums, the Secure Storage Custody Log must be marked to indicate into which drum they were disposed. This should include any bottle identifiers, if necessary to identify just what was disposed. Thus, it will be necessary for personnel disposing of samples to check the drums to make sure there is enough room for the designated samples. Soil samples will generally have their lids removed and disposed in the regular garbage. If the contents of the jar are easily poured into the drum, this is done and the jar disposed in the waste glass. If not, jar and all will then be disposed in the waste drum. If the lids themselves contain client identifying marks or locations or have significant amounts of adhering material (oil, etc.) which cannot be readily dumped into the drum the lid will also be disposed into the waste drum.

4.4.3.3 When the drums are disposed, it will be necessary for the laboratory representative who signs the manifest to mark the drum identity on the manifest, although this only needs to be on the laboratory copy if the transporter does not want this information to appear on their copy of the record.

4.4.4 QA must be notified 80 days after the drum is full in order to arrange for disposal in a timely manner. This timeframe is not of major concern because there are always Hazardous Waste pickups scheduled within any 90 day time period.

4.4.5 At the time of this writing, Laucks uses Safety Kleen as the vendor of choice for handling this waste stream, although this could be changed at the discretion of QA on either a one-time or ongoing basis. This vendor solidifies these soils prior to landfilling in an approved landfill.

4.5 Acidic Waste

4.5.1 All acidic waste must be neutralized before disposal. This includes acid-preserved samples, digests, acid-washings or soaking bathes, etc. unless they contain high levels of heavy metals (which can be disposed with our COD waste if they are not too voluminous, <500 mLs.).

4.5.2 The wastes are poured into a stoppered sink and neutralized with sodium bicarbonate. The resulting neutralized liquid is flushed down the domestic sewer with large quantities of tap water.

4.5.3 Their neutralization and disposal must be documented as it impacts Laucks hazardous waste generator status. This is done in a designated logbook kept near the neutralization sink where the date and final volume disposed are recorded. Note, this

volume should not include the volume of the water used to flush the neutralized solution down the drain.

4.6 Fluorescent Lights

4.6.1 Fluorescent light bulbs are also disposed as hazardous materials. They are in a category termed "universal waste" and are collected in a well marked box similar to that in which they were purchased. When the box is full, it is sent to our hazardous waste vendor or to another recycling firm. This waste stream does not need to be disposed within any particular time frame but should be properly taken care of as soon as the box of bad bulbs is full. Care must be taken to not break the bulbs as they are coated on the inside with hazardous fluorescent material often containing high levels of mercury.

4.7 PCB Oil Waste Disposal

4.7.1 Laucks no longer analyzes many oil samples for PCBs. Thus, this is a very small and infrequent waste stream. However, discussion is presented here in order that there be some documented course of action when it is necessary to dispose of these materials.

4.7.2 All oil samples which are analyzed for PCBs or otherwise known to contain PCBs are treated as PCB oils. No effort is made to distinguish those that actually do contain PCBs.

4.7.3 These oils are accumulated in a 5 gal. drum located in the Extractions laboratory warehouse. This metal drum is stored inside of the lower half of a cut-off plastic 55 gal. drum which fulfills the federal requirements for secondary containment during storage.

4.7.4 When a full drum has been accumulated, Eastern Electric is contacted for pickup and disposal. A signed receipt must be obtained as proof of disposal. Eastern Electric sends a manifest in subsequent mail within 35 days of waste pick-up and must also send a certificate of disposal within 30 days after the actual disposal date.

4.7.5 No annual report to the Department of Ecology is required because the level of PCBs is considered so high as to fall outside of the state's responsibility to monitor. At such levels the federal government regulates the disposal under TSCA. For this reason, it also does not fall within the federal requirement for RCRA governed waste disposal within 90 days. Eastern Electric is responsible for filing appropriate reports. TSCA regulations require that manifests and certificates of disposal be kept on file for a minimum of 3 years.

5. Reports

5.1 Disposal Paperwork

5.1.1 Our current vendor produces all of the required paperwork and insures all of the appropriate container markings (stickers, etc.) are in place prior to shipment. Since Laucks' waste streams are consistent from time to time, our vendors already have the information required to properly fill out the paperwork and Hazardous Waste stickers.

5.1.1.1 The paperwork includes the manifests, land disposal restriction forms and other shipping paperwork. Thus the only requirements of the laboratory are to insure the paperwork is accurate and to sign the appropriate forms.

5.1.2 After the waste has been transported to the disposal or accumulation facility, a signed manifest is returned to the laboratory. This is kept with the permanent record.

5.1.3 All certificates of disposal later provided by the disposal vendor are also associated with any waste shipment and kept with the permanent record.

5.1.4 All records are retained for at least 5 years from the date of shipment of the waste.

5.2 Annual Reporting Requirements

5.2.1 The laboratory must file an annual report with the Washington Department of Ecology (WDOE) for legal and tax purposes. This report is due on March 1 each year. Reports are filed for both the 940 and the 921 facilities (both EPA ID numbers). All waste transported from the 921 facility will be numbered WAD981762024 and all waste transported from the 940 facility will be numbered WAD027446608.

5.2.1.1 The only exception to this reporting requirement is the reporting of the PCB waste oil which is a federally regulated waste and is thus not reported to the WDOE.

5.2.2 The format of this report is defined by WDOE in books provided to the laboratory several months in advance of the due date. Details of this report are not provided in this SOP.

5.2.3 In addition, as part of a WDOE program to reduce hazardous waste in general, Laucks files an annual pollution prevention plan update by September 1 of each year. This report is more loosely defined and the only major requirement is that it be filed. Details of this report are not part of this SOP.

Appendix I

Hazardous Waste Sticker

See directions in this SOP for proper filling out of this sticker.

HAZARDOUS WASTE

FEDERAL LAW PROHIBITS IMPROPER DISPOSAL

IF FOUND, CONTACT THE NEAREST POLICE, OR
PUBLIC SAFETY AUTHORITY, OR THE
U.S. ENVIRONMENTAL PROTECTION AGENCY

PROPER D.O.T.
SHIPPING NAME_____ UN OR NA#_____

GENERATOR INFORMATION:

NAME_____

ADDRESS_____

CITY_____ STATE_____ ZIP_____

EPA ID NO._____ EPA WASTE NO._____

ACCUMULATION START DATE_____ MANIFEST DOCUMENT NO._____

HANDLE WITH CARE!

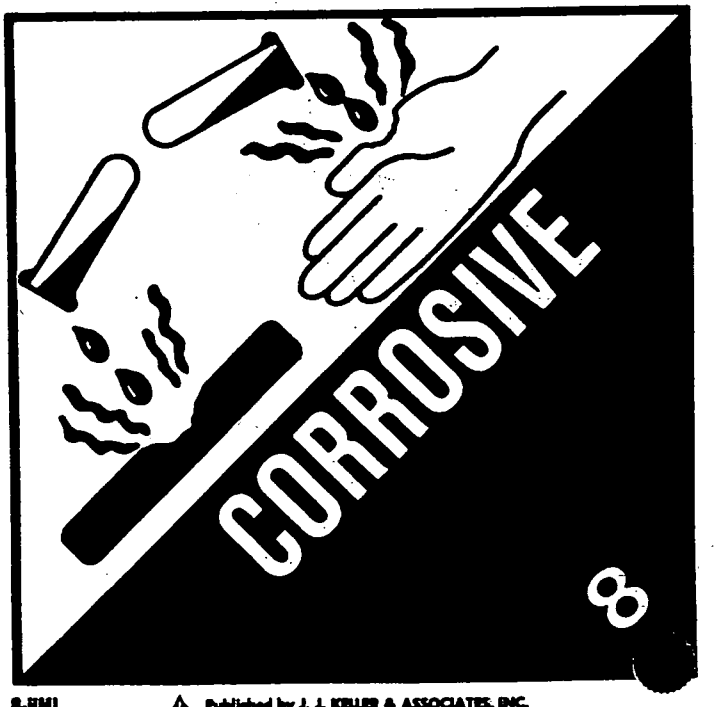
CONTAINS HAZARDOUS OR TOXIC WASTES

STYLE WM-6

Printed by LABELMASTER, Div. of AMERICAN LABELMARK CO., INC., CHICAGO, IL 60646

Appendix II

Example Hazard Class Stickers



8-HML

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Appendix III

A Quick Primer on Hazardous Waste Management

A Quick Primer on Hazardous Waste Management

Laucks is concerned and is indeed obligated by Washington State, to properly manage hazardous waste generated by the laboratory. This document is a quick overview for staff outlining the processes of which individuals should be aware. Everything is outlined in greater detail in Laucks SOP LTL-2001 *Waste segregation and Disposal*.

We currently manage 6 recurring hazardous waste streams at our 940 site and 4 at our 921 site. All individuals should be aware of the need to properly manage hazardous waste and those that need to know more should consult the aforementioned SOP. Any waste not covered in this document or in the SOP or which is not a regularly recurring waste stream must be discussed with QA for proper disposal.

940 Site:

- Solvent Waste – ALL solvent waste is collected in the 30 gallon drum in the solvent locker clearly labeled "Hazardous Waste". Solvent is collected in satellite containers located under the organic standards hood and in the waste solvent containers from the HPLC. Waste solvent should not be accumulated anywhere else without permission from QA. All other areas where solvent might be used should be immediately transferring the solvent to the 30 gallon container. Solvent is not to be dumped into any drum until it has been properly labeled.

- COD Waste – This is waste from the analysis for Chemical Oxygen Demand and is not only acidic but contains high concentrations of several metals, including Cr^{+6} and Hg. It is collected in a clearly labeled 5 gallon carboy underneath the sink where CODs are analyzed. There should be no other collection point. When the container is filled to 2 inches from the top, it should be tightly capped, the current date marked under the "accumulation start date" on the Hazardous Waste label, and the carboy transferred to the acid storage locker. A new 5 gallon container should be started and QA should be contacted for the required labeling. Waste is not to be dumped into any carboy until it has been properly labeled.

- Soil – Waste soil samples are assumed to contain hazardous metals, specifically lead. Unless a soil is known to have been an agricultural soil or is known not to contain hazardous substances, it is treated as though it is hazardous. The soil samples are dumped into a 55 gallon drum in the 940 warehouse. When the drum is full, it is sealed, the current date marked under the "accumulation start date" on the Hazardous Waste label, and QA notified in order to arrange transport to a disposal facility. A new drum will be labeled by QA. Soil is not to be dumped into any drum until it has been properly labeled.

- Extract Vials – Extract vials are collected in the covered, labeled 5 gallon bucket in the organic standards hood. When the bucket is full to the point that it can just be closed and sealed, it should be. The current date should then be marked on the Hazardous Waste label and QA contacted to arrange for disposal. A new 5 gallon container should be started and QA should be contacted for the required labeling. Waste is not to be dumped into any container until it has been properly labeled.

- Acidic Waste – Acidic waste containing significant amounts of metals should be disposed separately. QA should be consulted to make appropriate arrangements. Waste which is only acidic MUST first be neutralized with bicarbonate and then can be poured down the drain into the domestic sewer. This waste, however, must be recorded in a logbook kept for that purpose. The SOP should be consulted for further information.

- Fluorescent Lights – Fluorescent lights are considered "Universal Waste" and must never be disposed in the garbage. They must be collected and shipped to a recycling or hazardous waste disposal facility. These are collected in the boxes in which the replacement bulbs come, located in the 940 warehouse.

921 Site:

- Solvent Waste – ALL solvent waste is collected in the 55 gallon drum in the solvent locker clearly labeled "Hazardous Waste". Solvent may be collected in satellite containers located under some hoods but should NOT be allowed to sit uncovered and any such containers must be dumped into the 55 gallon container each night before the last analyst leaves. Solvent is not to be dumped into any drum until it has been properly labeled. Labeling instructions are in the SOP and labels are located in a drawer underneath the PCB hood.

- Soil – Waste soil samples are assumed to contain hazardous metals, specifically lead. Unless a soil is known to have been an agricultural soil or is known not to contain hazardous substances, it is treated as though it is hazardous. The soil samples are dumped into a 55 gallon drum in the 921 warehouse. When the drum is full, it is sealed, the current date marked under the "accumulation start date" on the Hazardous Waste label, and QA notified in order to arrange transport to a disposal facility. A new drum will be labeled by QA. Soil is not to be dumped into any drum until it has been properly labeled.

- Fluorescent Lights – Fluorescent lights are considered "Universal Waste" and must never be disposed in the garbage. They must be collected and shipped to a recycling or hazardous waste disposal facility. These are collected in the boxes in which the replacement bulbs come, located in the 940 warehouse.

- PCB Oil Waste – This waste is collected in a 5 gallon pail located in a blue plastic half-drum in the 921 warehouse. Only oil known or suspected to contain PCBs should be placed in this pail. Since we rarely get these oils anymore, the use of this container should be very infrequent. When it is full, QA is contacted to arrange for disposal and a new pail.

Extraction Method for Polynuclear Aromatics in Water
(8270C by 3520C)

Method # LTL-3001

January 26, 2001

Revision Number: #4

Written by: [illegible] Date: 1.26.01

Reviewed by: Harry Romberg Date: 4-30-01

Approved by: Kathy Grapp Date: 04-30-01

Controlled Document

No. 20 Assigned to: TETR

1. **PURPOSE** - In this method, polynuclear aromatics are extracted at pH <2 with methylene chloride using a continuous liquid-liquid extractor. Extracts are dehydrated and concentrated in a Kuderna-Danish (K-D) apparatus for analysis by GC/MS. This method also includes low concentration (SIM) method.

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 while executing this method. The company will provide any protective equipment or clothing to assure employee safety.

3. **REAGENTS**

3.1. All reagents shall be of AR grade or better.

3.2. All solvents shall be distilled in glass unless otherwise indicated.

3.3. The following special reagents shall be prepared:

3.3.1 1:1 Sulfuric Acid - measure equal volumes of concentrated sulfuric acid and DIW. Note: Observe proper acid preparation techniques.

3.3.2. Anhydrous Sodium Sulfate - prepared by muffling AR grade sodium sulfate for four hours at 400° C.

3.3.3. Alumina, Neutral, Brockman Activity I - activate 60-325 mesh alumina by heating for 16 hours at 130° C.

3.3.4. Surrogate solution prepared in methanol:

1-Fluoronaphthalene	250 ug/ml
Fluorene-d10	250 ug/ml
Pyrene-d10	250 ug/ml

Low Concentration (SIM) surrogate solution prepared in methanol:

1-Fluoronaphthalene	12.5 ug/ml
Fluorene-d10	12.5 ug/ml
Pyrene-d10	12.5 ug/ml

3.3.5. Matrix spiking solution and Low Concentration (SIM) matrix spiking solution prepared in methanol:

Acenaphthene	50 ug/ml
Acenaphthylene	50 ug/ml
Anthracene	50 ug/ml

Benzo(a)anthracene	50 ug/ml
Benzo(a)pyrene	50 ug/ml
Benzo(b)fluoranthene	50 ug/ml
Benzo(ghi)perylene	50 ug/ml
Benzo(k)fluoranthene	50 ug/ml
Chrysene	50 ug/ml
Dibenzo(a,h)anthracene	50 ug/ml
Fluoranthene	50 ug/ml
Fluorene	50 ug/ml
Indeno(1,2,3-cd)pyrene	50 ug/ml
Naphthalene	50 ug/ml
Phenanthrene	50 ug/ml
Pyrene	50 ug/ml
2-Methylnaphthalene	50 ug/ml

4. **EQUIPMENT**

4.1. Continuous liquid-liquid extractor with 500 ml round, flat-bottom boiling flask

4.2. Organomations Assoc., Inc. - N-EVAP, (nitrogen evaporator), Model 112

4.3. Teflon thistle tube

4.4. Standard laboratory glassware to include:

4.4.1. K-D apparatus: 500 ml. K-D flask, 10 ml or 25 ml ampule and three-ball snyder column.

4.4.2. Monstr-pette disposable pipettes.

4.5. All glassware to be rinsed as follows, prior to use:

4.5.1. Technical grade acetone (if the glassware is wet).

4.5.2. Triple rinsed with methylene chloride.

4.6. Volumetric measurements are to be made with a calibrated fixed or adjustable volume microdispenser and individually calibrated vials.

5. **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.

6. METHODOLOGY

6.1. Sample Extraction:

6.1.1. Mix sample thoroughly in its original container and place labeling tape at sample level. Mark meniscus of sample on the tape.

6.1.2. Transfer entire contents of container into a liquid-liquid extractor. Rinse container with methylene chloride and add to extractor. Fill sample container to the mark on tape with water. Measure volume of sample used in a calibrated 1000 ml cylinder.

6.1.3. Prepare a blank and a blank spike with 1000 ml DIW.

6.1.4. Prepare two additional aliquots of one sample if Quality Control is required.

6.1.5. Pipet 200 ul surrogate solution into each extractor.
(Low Conc: 100 ul of low conc. surrogate solution.)

6.1.6. Pipet 500 ul matrix spiking solution into each QC extractor.
(Low Conc: 25 ul of matrix spiking solution.)

6.1.7. Adjust the sample to pH <2 with 1:1 sulfuric acid.

6.1.8. Add 300 ml methylene chloride and boiling chips to a round, flat-bottom boiling flask.

6.1.9. Turn on the water recirculator and extract samples for 18 hours.

6.1.10. Allow the assembly to cool and collect all solvent in the boiling flask.

6.2. Solvent Dehydration

6.2.1. Prepare a glass funnel by plugging with glass wool, and filling 1/2-2/3 full with sodium sulfate.

6.2.2. Pre-rinse the sodium sulfate by passing 40 ml methylene chloride through the prepared funnel.

6.2.3. Pass the extract from step 6.1.10. through the funnel and collect in an assembled K-D apparatus.

6.2.4. Rinse the collection vessel with several 10 ml methylene chloride rinses.

6.2.5. Rinse the sodium sulfate with 40 ml of methylene chloride.

6.3. Solvent Evaporation

6.3.1. Assemble the full K-D apparatus with a snyder column prewet with 2-3 ml of methylene chloride.

6.3.2. 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 8 ml. Regulate the evaporation time to take one to one and a half hours.

6.3.3. Reduce the volume to 4-5 ml, remove the apparatus from the water bath and cool to room temperature.

6.3.4. Rinse joint and remove the snyder column. Allow rinse solvent to drain into ampule.

6.3.5. Remove the ampule clamp, and wipe the joint with a Kimwipe. Separate the ampule and rinse the joint with a small amount of methylene chloride.

6.3.6. Reduce the extract volume to 1.0 ml in a warm water bath with nitrogen. Rinse internal walls of ampule several times during blowdown.

6.3.7. Transfer extract to a 1.8 ml vial. The final volume is then adjusted to 1.0 ml (as compared to a measured volume) in methylene chloride.

Low Conc: Final volume adjusted to 0.5 ml. in methylene chloride.

6.3.8. Proceed to 6.4.10.

NOTE: If there is significant color in the extract, an alumina cleanup (Method 3610B) is indicated.

6.4. Alumina Cleanup

6.4.1. Prepare a Monstr-pette column by plugging with a small amount of glass wool.

6.4.2. Pack column with a minimum of 3 gm. of activated alumina. Top with 1/2 cm of sodium sulfate.

6.4.3. Pre-elute column with 10 ml methylene chloride.

6.4.4. Add entire extract directly to top of the sodium sulfate and allow to elute onto the column.

6.4.5. Rinse the ampule twice with a small amount of methylene chloride and add to top of column.

6.4.6. Attach a Teflon thistle tube to the column and add a minimum of 10 ml methylene chloride.

6.4.7. Elute into a 16 x 125 mm culture tube.

6.4.8. Reduce the extract volume to 1.0 ml in a warm water bath with nitrogen. Rinse internal walls of the culture tube several times during blowdown.

6.4.9. Transfer extract to a 1.8 ml vial. The final volume is then adjusted to 1.0 ml (as compared to a measured volume) in methylene chloride.

Low Conc: Final volume adjusted to 0.5 ml. in methylene chloride.

6.4.10. Label the extract and deliver to 940.

6.4.11. Complete all paperwork and bench sheet. Bench sheet should include cleanup method if indicated, alumina lot #, date and time of transfer to 940 and extract location. Clip T-card on the folder and place in GC/MS room extraction folder box. File folder color is dark blue and blank name ____MPNWL_.

7. **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.

3520C (1996), 8270C (1996), 3610B (1996)

LAUCKS TESTING LABORATORIES INC.	EXTRACTION	DATE	METHOD	ANALYST	CHECKER	ANALYSIS
JOB NUMBER: 0101367 MATRIX: H2O	MSPNA	1-25-01	3520C	LS/AGH	BJD 1-27-01	MSPNA

Sample #	wt./vol.	Final Vol				Ext #	SDG #	Bkl #
0101367-1	1020	1.0 ml				3	T1008	62
2	1010					4		73
3	980					5		79
4	1040					6		84
4MS	1010					7		85
4MSD	1000					8		86
5	1010					9		90
S012501MPNWLS	1000					10		
B012501MPNWLS	1					11		

BJD 1-25-01

COMMENTS:

Ext & Final Sol: MeCl2 - Bag # BZ743 - GN <3 - Liq/Liq on 1330; off 0730 1-26-01

SURROGATES:

200 ul of: Ex 8-46.1

ul of:

SPIKES:

500 ul of: Ex 8-38.3

ul of:

STANDARDS:

ul of:

ul of:

ul of:

Fraction and Method	Extraction		Transferred from 921 to 940		Extract Location	Analysis	
	Time out	Time in	Time out	Time in	Tray #	Time out	Time in
MSPNA	0830	Empty	1320	—	1542		
	Date	Initials	Date	Initials	C4-C12	Date	Initials
	1-25-01	LS	1-27-01	AGH			
	Time out	Time in	Time out	Time in		Time out	Time in
			—				
	Date	Initials	Date	Initials		Date	Initials

Extraction Method for Chlorinated Herbicides in Soil
(8151A by Modified 3550C)

Method # LTL-3011

October 16, 2001

Revision Number: #2

Written by: _____ Date: 10-16-01

Reviewed by: Harry Bomberg Date: 10-16-01

Approved by: Kathy Freeps Date: 10-16-01

Controlled Document

No. 20 Assigned to: Tetr

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. **MATERIALS**

3.1. All reagents are to be AR grade or better.

3.2. All solvents are to be distilled in glass unless otherwise noted.

3.3 The following special reagents should be prepared:

3.3.1. 37% Potassium Hydroxide - prepared by dissolving 370 grams potassium hydoxide pellets and diluting to one liter with DIW.

3.3.2. Concentrated Sulfuric Acid

3.3.3. 10% Hydrochloric Acid - measure 100 ml concentrated hydrochloric acid and dilute to 1000 ml with DIW. Note: Observe proper acid preparation techniques.

3.3.4. Anhydrous Sodium Sulfate - prepared by muffling AR grade sodium sulfate for four hours at 400°C.

3.3.5. 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.

3.3.6. 10 M Potassium Hydroxide - prepared by dissolving 56.1 grams potassium hydoxide pellets and diluting to 100 ml with DIW.

3.3.7. Diethylene Glycol Monoethyl Ether (Carbitol) – (Sigma – catalog # D-1265)

3.3.8. Diazald® (Aldrich - catalog # D2,800-0).

3.3.9. Activated Silicic Acid - activate 100 mesh silicic acid powder by heating for 16 hours at 130°C.

3.3.10. Surrogate solution prepared in methanol:

2,4 - Dichlorophenyl Acetic Acid	5.0 ug/ml

3.3.11. Matrix Spiking solution prepared in methanol:

2,4,5-TP	0.8 ug/ml
2,4,5-T	0.8 ug/ml
Dicamba	0.8 ug/ml
Pentachlorophenol	4.0 ug/ml
Dinoseb	4.0 ug/ml
Picloram	8.0 ug/ml
2,4-DB	8.0 ug/ml
2,4-D	8.0 ug/ml
Dichloroprop	8.0 ug/ml
Dalapon	20.0 ug/ml
MCPP	800.0 ug/ml
MCPA	800.0 ug/ml

4. EQUIPMENT

4.1. Organomations Assoc., Inc. - N-EVAP, (nitrogen evaporator), Model 112

4.2. Standard laboratory glassware to include:

4.2.1. 40 ml Teflon culture tubes

4.2.2. 16 x 100 mm culture tubes

4.3. All glassware to be used shall be rinsed in the following manner:

4.3.1. 10% hydrochloric acid

4.3.1. Reagent grade acetone

4.4. Volumetric measurements are to be made with a calibrated fixed or adjustable volume microdispenser and individually calibrated vials.

5. **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.

6. METHODOLOGY

6.1. Sample Extraction:

6.1.1. Mix the sample thoroughly in its original container if there is space available, otherwise mix in solvent rinsed aluminum tray.

6.1.2. Weigh 15.0 grams of soil (wet weight) into an Teflon culture tube. Cover sample with DIW.

6.1.3. Prepare two additional aliquots of a sample if Quality Control is required.

6.1.4. Prepare a blank and a blank spike with 10 ml. DIW.

6.1.5. Pipet 100 ul surrogate solution into each tube.

6.1.6. Pipet 100 ul matrix spiking solution into each QC tube.

6.1.7. Pipet 1.0 ml 37% potassium hydoxide into each culture tube, mix and loosely cap with teflon screw cap.

6.1.8. Immerse tubes in a 60-65°C water bath for a minimum of 90 minutes.

6.1.9. Remove from bath and cool to room temperature.

6.1.10. Add 6-7 mls 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.

6.1.11. Draw off and discard ether layer.

6.1.12. Repeat from step 6.1.10. two additional times using 3 ml ethyl ether.

6.1.13. Adjust pH to <2 by slowly adding 500µl concentrated sulfuric acid to each tube. Mix and check pH.

6.1.14. Repeat step 6.1.10 three times using 3 ml ethyl ether and save ether into a 16 x 100 culture tube.

6.2. Dehydration of the extract:

6.2.1. Adjust volume to 5-6 mls in the nitrogen blowdown.

6.2.2. Add 3 gm of acidified sodium sulfate to each tube, cap and shake.

6.2.3. Tap the tubes to settle the sodium sulfate and let stand at least 60 minutes and may stand overnight.

6.2.4. Transfer ether extract to 16 x 100 culture tube.

6.2.5. Add 1-2 mls ether to acidified sodium sulfate, cap and shake to break up sodium sulfate.

6.2.6. Transfer rinse to tube containing the ether extract.

6.2.7. Repeat from step 6.2.5. two additional times.

6.2.8. Gently reduce the volume to approx. 1 ml in the nitrogen blowdown.

6.2.9. Add 0.5 ml iso-octane and bring to 2.0 ml with ethyl ether.

6.3. Derivatization:

6.3.1. To tube A (the first tube in the train), add 1.0 ml methanol, and bring to 8.0 ml with ethyl ether.

6.3.2. To tube B add:

6.3.2.1. 2.0 ml 10 M potassium hydoxide (to the first marked line)

6.3.2.2. 1.4 ml Carbitol (diethylene glycol monoethyl ether) to the second marked line.

6.3.3. Place 10 ul micro-pipet in each sample tube from step 6.2.8.

6.3.4. Connect nitrogen line to the apparatus and regulate so that tube A bubbles actively but not violently.

6.3.5. 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.

6.3.6. Bubble the generated diazomethane into the tube for 90 seconds. (Extract will turn bright yellow.)

6.3.7. Let extract stand for 15 minutes.

6.3.8. 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.

6.3.9. Adjust the final volume to 5.0 ml (as compared to a measured volume) with hexane and centrifuge.

6.3.10. Label the extract and deliver to 940.

6.6.11. Complete all the necessary paperwork and bench sheet. Bench sheet to include date derivatized, time and date of transfer to 940 and extract location. Clip the T-card on the folder and place in the GC room extraction folder box. The file folder color will be yellow, and the blank name will be ____GHB.SL_.

7. **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)

LAUCKS TESTING LABORATORIES INC.	EXTRACTION	DATE	METHOD	ANALYST	CHECKER	ANALYSIS
JOB NUMBER: 0106262	Herb	6-18-01	mod 3550C	YL	SD 6-19-01	8151A
MATRIX: Soil						

Sample #	wt./vol.	% Lipid					SDG #	Lab #
0106262-1	15.0g	5.0ml			–		T5904	32
2								33
3								34
4								35 & 36
4MS								
4MSD								
5								37
6								38
S061801GNBS4P								
B061801GNBS4P								

YL 6-18-01

COMMENTS:

Ext Sol: Ethyl Ether - BGS # C3192
Hexane Sol: Hexane - EM# 40163
Derivatized - 6-20-01

SURROGATES:

100 ul of: Ext 8-51-5
ul of:

SPIKES:

100 ul of: Ext 8-47-1
ul of:

STANDARDS:

ul of:
ul of:
ul of:

Fraction and Method	Extraction		Transferred from 921 to 940		Extract Location	Analysis	
	Time out	Time in	Time out	Time in	Tray #	Time out	Time in
Herb	0900	1230	1450	—	6-19-01		
	Date	Initials	Date	Initials	D2-E1	Date	Initials
	6-18-01	SD	6-20-01	YL			
	Time out	Time in	Time out	Time in		Time out	Time in
			—	1450			
	Date	Initials	Date	Initials		Date	Initials
			6-20-01	SMS			

Extraction Method for Ordnance Compounds in Water
(8330A)

Method # LTL-3077

May 4, 2001

Revision Number: #5

Written by: B. O Quell Date: 5-4-01

Reviewed by: Harry Pinkney Date: 5-7-01

Approved by: Bailey Grapes Date: 5-8-01

Controlled Document

No. 20 Assigned to: TETR

1. **PURPOSE** - In this method the ordnance compounds are extracted from neutral water with acetonitrile. The extract is salted-out and analyzed by HPLC.

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 while executing this method. The company will provide any protective equipment or clothing needed to assure employee safety.

3. **REAGENTS**

3.1. All reagents shall be of AR grade or better.

3.2 . All solvents shall be distilled in glass unless otherwise indicated.

3.3. The following special reagents shall be prepared:

3.3.1. Sodium Chloride - prepared by muffling AR grade sodium chloride for four hours at 400°C.

3.3.2. Salt Water - prepared by weighing 325 grams muffled sodium chloride, dissolving in DIW and bringing to 1000 ml.

3.3.3. Surrogate solution prepared in methanol:

1,2-Dinitrobenzene	400 ug/ml

3.3.4. Matrix spiking (MS) solution prepared in methanol:

1,3-Dinitrobenzene	80 ug/ml
2,4-Dinitrotoluene	80 ug/ml
2,6-Dinitrotoluene	80 ug/ml
HMX	80 ug/ml
RDX	80 ug/ml
Nitrobenzene	80 ug/ml
2-Nitrotoluene	80 ug/ml
3-Nitrotoluene	80 ug/ml
4-Nitrotoluene	80 ug/ml
Tetryl	80 ug/ml
TNT	80 ug/ml
1,3,5-Trinitrobenzene	80 ug/ml
2-amino-4,6-dinitrotoluene	80 ug/ml
4-amino-2,6-dinitrotoluene	80 ug/ml

3.3.5. Special Matrix spiking solution for PETN/NG in methanol:

PETN	50 ug/ml
Nitroglycerin	100 ug/ml

3.3.6. Special Matrix spiking solution for 6 Attenuation compounds in methanol:

2,4-DA-6-NT	80 ug/ml
2,6-DA-4-NT	80 ug/ml
3,5-DNA	80 ug/ml
MNX	80 ug/ml
TNX	80 ug/ml
4,4'-TN-AZOXY	80 ug/ml

3.3.7. Special Matrix spiking solution for MNX in methanol:

MNX	80 ug/ml

4. **EQUIPMENT**

4.1. Magnetic stirrer with stirring bar

4.2. Standard laboratory glassware to include:

4.2.1. 1000 ml volumetric flask and various sizes of graduated cylinders

4.3. All glassware to be rinsed as follows, prior to use:

4.3.1. Technical grade acetone (if the glassware is wet).

4.3.2. Triple rinsed with methylene chloride.

4.4. Volumetric measurements are to be made with a calibrated fixed or adjustable volume microdispenser and individually calibrated vials.

4.5. PTFE 0.45µm syringe filter.

5. **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.

6. METHODOLOGY

6.1. Sample Extraction

6.1.1. Bring sample to room temperature and mix thoroughly in its original container.

6.1.2. Measure 770 mls sample into a 1000 ml volumetric flask placed on a magnetic stirrer.

6.1.3. Prepare two additional aliquots of one sample if Quality Control is required.

6.1.4. Prepare a blank and blank spike with DIW.

6.1.5. Pipet 50 ul surrogate solution to each flask.

6.1.6. Pipet 250 ul matrix spiking solution to each of the QC flasks. (When indicated, use 250 ul special matrix spiking solution.)

6.1.7. Add 251.3 gm sodium chloride to the flask with the stirring bar at maximum speed and stir until sodium chloride is completely dissolved.

6.1.8. Add 164 mls acetonitrile to each flask and stir for 15 minutes.

6.1.9. Turn off the stirrer and let set for 10 minutes.

6.1.10. Remove acetonitrile with a Pasteur pipet and transfer to a 100 ml flask.

6.1.11. Add 10 ml acetonitrile to the sample and stir for 15 minutes.

6.1.12. Turn off stirrer and let set for 10 minutes.

6.1.13. Transfer acetonitrile to flask with extract from step 6.1.10. Discard sample in 1000 ml flask.

6.1.14. Add 84 mls salt water to extract in flask.

6.1.15. Stir for 15 minutes and let stand for 10 minutes.

6.1.16. Transfer acetonitrile to a 10 ml graduated cylinder.

6.1.17. Add 1.0 ml acetonitrile to flask and repeat steps 6.1.15 and 6.1.16.

6.1.18. Record total final volume to 0.1 ml.

6.1.19. Transfer final extract to a 4.0 ml **amber** vial. Any remaining extract may be discarded. If extract is cloudy or turbid, filter through a PTFE 0.45μm syringe filter into amber vial.

6.1.20. Label the extract and deliver to 940.

6.1.21. Complete all paperwork and bench sheet. Bench sheet to include date and time of transfer to 940 and extract location. Clip the T-card on the folder and place in GC room extraction folder box. The file folder color will be red and the blank name will be ____HOR.WL_.

7. **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,

8330A (1998).

Neymen

LAUCKS TESTING LABORATORIES INC.	EXTRACTION	DATE	METHOD	ANALYST	CHECKER	ANALYSIS
JOB NUMBER: 0101514	8330	1-30-01	8330A	BJ	BJ 1-30-01	8330A
MATRIX: H2O						

Sample #	wt./vol.	Final vol	To 940				SDu #	Bt #
0101514-1	470 ml	4.0 ml	~4.0 ml				CH010	36
2		4.9						38
3		5.3						40
4		7.9						42
5		6.4						44
SMS		8.2						45
SMSD		7.6						46
S013001HORWLC		5.4						
B013001HORWLC		4.9						

BJ 1-30-01

COMMENTS:

Ext & Final Sol: Acetonitrile - Bag # BZ347

SURROGATES:

50 ul of: Ex 8.42-1A

ul of:

SPIKES:

250 ul of: Ex 8.40-10

ul of:

STANDARDS:

ul of:

ul of:

ul of:

Fraction and Method	Extraction		Transferred from 921 to 940		Extract Location	Analysis	
8330/H2O	Time out 0730	Time in 1130	Time out 0825	Time in —	Tray # 2-148	Time out	Time in
	Date 1-30-01	Initials BJ	Date 1-31-01	Initials AGH	F1-F9	Date	Initials
	Time out	Time in	Time out	Time in		Time out	Time in
	Date	Initials	Date	Initials		Date	Initials

Extraction Method for Ordnance Compounds in Soils (8330A)

Method # LTL-3161

May 4, 2001

Revision Number: #5

Written by: B. O Gill Date: 5.4.01

Reviewed by: Harry Pombey Date: 9-13-01

Approved by: Gatty Grieps Date: 9-13-01

Controlled Document

No. 20 Assigned to: Tetc

1. **PURPOSE** - In this method the ordnance compounds are extracted from neutral soil with acetonitrile. The sample is air dried, sonicated, and extract salted-out and analyzed by HPLC.

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 while executing this method. The company will provide any protective equipment or clothing needed to assure employee safety.

3. **REAGENTS**

3.1. All reagents shall be of AR grade or better.

3.2 . All solvents shall be distilled in glass unless otherwise indicated.

3.3. The following special reagents shall be prepared:

3.3.1. Ottawa Sand - prepared by soxhleting for 8 hours with methylene chloride and muffling for four hours at 400°C.

3.3.2. 0.045 M Calcium Chloride - prepared by dissolving 5.0 gm in 1000 ml of DIW.

3.3.3. Surrogate solution prepared in methanol:

1,2-Dinitrobenzene	400 ug/ml

3.3.4. Matrix spiking (MS) solution prepared in methanol:

1,3-Dinitrobenzene	80 ug/ml
2,4-Dinitrotoluene	80 ug/ml
2,6-Dinitrotoluene	80 ug/ml
HMX	80 ug/ml
RDX	80 ug/ml
Nitrobenzene	80 ug/ml
2-Nitrotoluene	80 ug/ml
3-Nitrotoluene	80 ug/ml
4-Nitrotoluene	80 ug/ml
Tetryl	80 ug/ml
TNT	80 ug/ml
1,3,5-Trinitrobenzene	80 ug/ml
2-amino-4,6-dinitrotoluene	80 ug/ml
4-amino-2,6-dinitrotoluene	80 ug/ml

3.3.5. Special Matrix spiking solution for PETN/NG in methanol:

PETN	50 ug/ml
Nitroglycerin	100 ug/ml

3.3.6. Special Matrix spiking solution for MNX in methanol:

MNX	80 ug/ml

4. EQUIPMENT

4.1. Ultrasonic bath

4.2. #30 mesh sieve

4.3. Disposable cartridge filters - 0.45 µm Teflon filter

4.4. Standard laboratory glassware to include:

4.4.1. 20 x 150 mm culture tubes

4.5. Volumetric measurements are to be made with graduated serological pipets or a calibrated fixed volume microdispenser and individually calibrated vials.

5. QUALITY CONTROL

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.

6. METHODOLOGY

6.1. Sample Extraction

6.1.1. Mix sample thoroughly in its original container if there is space available (otherwise mix in solvent rinsed aluminum tray).

6.1.2. Weigh approximately 20-30 grams into a labeled, large aluminium weighing tin. Place in hood and air dry for 48 hours or until a constant weight is attained.

6.1.3. Grind and sieve.

6.1.4. Weigh 2.0 grams of air dried soil into a 20 x 150 mm culture tube.

6.1.5. Prepare two additional aliquots of one sample if Quality Control is required.

6.1.6. Prepare a blank and blank spike with 2.0 grams Ottawa sand.

6.1.7. Pipet 100 ul surrogate solution to each culture tube.

6.1.8. Pipet 500 ul matrix spiking solution to each of the QC culture tubes.

6.1.9. Add 9.9 ml acetonitrile to each sample culture tube and blank and 9.4 mls to QC and blank spike.

6.1.10. Sonicate the samples for 18 hours in a sonic bath packed with ice in the cold room.

6.2. Salting Out

6.2.1. Remove samples from ice bath and allow to come to room temperature.

6.2.2. Transfer 5.0 mls of supernatant to a 16 x 100 mm culture tube.

6.2.3. Add 5.0 ml calcium chloride solution to each sample.

6.2.4. Shake and let stand for 15 minutes.

6.2.5. Centrifuge each sample.

6.2.6. Filter through a 0.45µm PTFE syringe filter into 4 ml **amber** vial, discarding first 3 mls.

6.2.7. Label the extract and deliver to 940.

6.3.8. Complete all paperwork and bench sheet. Bench sheet to include PTFE filter lot #, date and time of transfer to 940 and extract location. Clip the T-card on the folder and place in GC room extraction folder box. The file folder color will be red and the blank name will be ____HOR.SM_.

7. **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

8330A (1998)

LAUCKS TESTING LABORATORIES INC.	EXTRACTION	DATE	METHOD	ANALYST	CHECKER	ANALYSIS
JOB NUMBER: 0105180 MATRIX: Soil	8330	5-4-01	8330A	SD	SD 5-3-01	8330A

Sample #	wt./vol.	Final Add #1	To CaCl2	Final Add #2	To 940		SDG#	Bkt#
0105180-1	2.0 g	10.0 ml	5.0 ml	10.0 ml	~4.0 ml		T5901	28
2								29
3								30
4								31
5								32
5MS									
5MSD									
6								35
7								36
8								37
S050401HORSMG								
B050401HORSMG								

SD 5-4-01

COMMENTS:

Ext Sol: Acetonitrile - B&J # CB512
Final Sol: Acetonitrile - B&J # CB512 / 0.5% CaCl2
Samples airdried prior to extraction
Sonic Bath - On - 1545 - 5-4-01
Off - 1000 5-5-01

SURROGATES:
100 ul of: Ex 8-49-6
ul of:

SPIKES:
500 ul of: Ex 8-49-6
ul of:

STANDARDS:
ul of:
ul of:
ul of:

Fraction and Method	Extraction		Transferred from 921 to 940		Extract Location	Analysis	
8330	Time out 1130	Time in 1305	Time out 1520	Time in —	Tray # 2-163 D1-D12	Time out	Time in
	Date 5-3-01	Initials SD	Date 5-6-01	Initials SD		Date	Initials
	Time out	Time in	Time out —	Time in 1531		Time out	Time in
	Date	Initials	Date 5-6-01	Initials SB		Date	Initials

Extraction Method for Organochlorine Pesticides and Polychlorinated Biphenyls in Water (8081A/8082 by 3510C)

Method # LTL-3202

May 7, 2001

Revision Number: #3

Written by: B. O Jiel Date: 5-7-01

Reviewed by: Harry Rombey Date: 5-11-01

Approved by: Kathy Kreps Date: 5-11-01

Controlled Document

No. 20 Assigned to: IETR

1. **PURPOSE** - In this method, organochlorine pesticides and polychlorinated biphenyls are extracted from neutral water with methylene chloride. The extracts are dehydrated, concentrated in a Kuderna-Danish apparatus and exchanged into hexane. If necessary, the pesticide/PCB extracts may be SPE Florisil cleaned prior to GC analysis. PCB only extracts may be acid cleaned prior to GC analysis.

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 extractionist to exercise due care and caution while executing this method. The company will provide any protective equipment or clothing needed to assure employee safety.

3. **REAGENTS**

3.1. All reagents shall be of AR grade or better.

3.2. All solvents shall be distilled in glass unless otherwise indicated.

3.3. The following special reagents shall be prepared:

3.3.1. 10 N Sodium Hydroxide - weigh 400 grams sodium hydroxide, dissolve and dilute to one liter with DIW.

3.3.2. 1:1 Sulfuric Acid - measure equal volumes of concentrated sulfuric acid and DIW. Note: Observe proper acid preparation techniques.

3.3.3. Anhydrous Sodium Sulfate - prepared by muffling AR grade sodium sulfate for four hours at 400°C.

3.3.4. Surrogate solution prepared in acetone:

2, 4, 5, 6-Tetrachloro-m-xylene	1.0 ug/ml
Decachlorobiphenyl	1.0 ug/ml

3.3.5. Pesticide and/or PCB matrix spiking solution prepared in acetone:

Gamma-BHC	2.5 ug/ml
Heptachlor	2.5 ug/ml
Aldrin	2.5 ug/ml
Arochlor 1260	25.0 ug/ml

4. **EQUIPMENT**

4.1. Glas-Col mechanical separatory funnel shaker

4.2. Organomations Assoc., Inc. - N-EVAP, (Nitrogen Evaporator), Model 112

4.3. Vortex mixer

4.4. Standard laboratory glassware to include:

4.4.1. 2000 ml Teflon separatory funnels

4.4.2. 300 ml Fleakers

4.4.3. K-D apparatus: 250 ml. K-D flask, 10 ml or 25 ml ampule and three-ball snyder column.

4.5. All glassware to be rinsed as follows, prior to use:

4.5.1. Technical grade acetone (if the glassware is wet).

4.5.2. Triple rinsed with methylene chloride.

4.6. Volumetric measurements are to be made with a calibrated fixed or adjustable volume microdispenser and individually calibrated vials.

5. **QUALITY CONTROL** - The normal level of quality control will consist of blank, blank spikes 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.

6. **METHODOLOGY**

6.1. Sample Extraction

6.1.1. Mix sample thoroughly in its original container and place labeling tape at sample level. Mark meniscus of sample on the tape.

6.1.2. Transfer entire contents of container into a 2000 ml separatory funnel. Rinse container with methylene chloride and add to funnel. Fill sample container to the mark on tape with water. Measure volume of sample used in a calibrated 1000 ml cylinder.

6.1.3. Prepare a blank and a blank spike with 1000 ml DIW.

6.1.4. Prepare two additional aliquots of one sample if Quality Control is required.

6.1.5. Pipet 200 ul surrogate solution into each funnel.

6.1.6. Pipet 200 ul matrix spiking solution into each QC funnel.

6.1.7. Adjust pH to 7 ± 2.

6.1.8. Add 60 ml methylene chloride to the separatory funnel.

6.1.9. Shake the samples hard for three minutes on the mechanical shaker, with the stopcocks closed.

6.1.10. Replace the funnels in rack and allow to stand for 10 minutes.

6.1.11. Drain and collect the lower methylene chloride layer in a fleaker.

6.1.12. Repeat from 6.1.8. until a total of three extractions have been performed.

6.2. Solvent Dehydration

6.2.1. Prepare a glass funnel by plugging with glass wool, and filling 1/2-2/3 full with sodium sulfate.

6.2.2. Pre-rinse the sodium sulfate by passing 40 ml methylene chloride through the prepared funnel.

6.2.3. Pass the extract from Step 6.1.12. through the funnel and collect in an assembled K-D apparatus.

6.2.4. Rinse the collection vessel with several 10 ml methylene chloride rinses.

6.2.5. Rinse the sodium sulfate with 40 ml of methylene chloride.

6.3. Solvent Evaporation

6.3.1. Assemble the full K-D apparatus with a snyder column prewet with 2-3 ml of methylene chloride.

6.3.2. 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 8 ml. Regulate the evaporation time to take one to one and a half hours.

6.3.3. Reduce the volume to 4-5 ml, and exchange into hexane as follows:

6.3.3.1. 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.

6.3.3.2. Repeat 6.3.3.1. two additional times.

6.3.4. Remove the apparatus from the water bath and cool to room temperature.

6.3.5. Rinse joint and remove the snyder column. Allow rinse solvent to drain into ampule.

6.3.6. Remove the ampule clamp, and wipe the joint with a Kimwipe. Separate the ampule and rinse the joint with a small amount of hexane.

6.3.7. Reduce the extract volume to less than 2 ml on a nitrogen blowdown. Transfer extract to a 16 x 100 mm culture tube, and adjust to 10.0 ml final volume (as compared to a measured volume) with hexane.

6.3.8. Label the extract and deliver to 940.

6.3.9. Complete all necessary paperwork and bench sheet. Bench sheet to include cleanup method #, if applicable, extract location, time and date of transfer to 940. Clip the T-card on the folder and place in GC room extraction folder box. The file folder color will be purple and the blank name will be ____GPXWL_.

7. **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, (1996).

8081A, 8082, 3510C

LAUCKS TESTING LABORATORIES INC.	EXTRACTION	DATE	METHOD	ANALYST	CHECKER	ANALYSIS
JOB NUMBER: 0101862	Pest / PCB	1-30-01	3510C	LS	BD 1-31-01	8081A / 8082
MATRIX: H2O						

Sample #	wt./vol.	Final vol					SDG #	Std #
0101862-1	1020 ml	10.0 ml					LA 492	1
1MS	1000							2
1MSD	1060							3
2	980							5
3	1050							7
4	1030							9
5	1040							11
S013001GPX WLG	1000							
B013001GPX WLG	1							

BD/LS 1-30-01

COMMENTS:

Ext Sol: MeCl2 - B&J # BZ743
Final Sol: Hexane - EM # 40163

SURROGATES:

200 ul of: Ex 8-45-9A
ul of:

SPIKES:

200 ul of: Ex 8-39-4
ul of:

STANDARDS:

ul of:
ul of:
ul of:

Fraction and Method	Extraction		Transferred from 921 to 940		Extract Location	Analysis	
Pest / PCB	Time out: 0910	Time in: Empty	Time out: 1550	Time in: —	Tray # 2-15-01	Time out:	Time in:
	Date: 1-30-01	Initials: LS	Date: 2-1-01	Initials: AGH	B1-B9	Date:	Initials:
	Time out:	Time in:	Time out: —	Time in: 1555		Time out:	Time in:
	Date:	Initials:	Date: 2-1-01	Initials: SO		Date:	Initials:

Extraction Method for Chlorinated Herbicides in Water
(8151A by Modified 3510C)

Method # LTL-3510

May 3, 2001

Revision Number: #8

Written by: B. O Gill Date: 5-3-01

Reviewed by: Harry Romley Date: 5-3-01

Approved by: Kathy Greps Date: 05-03-01

Controlled Document

No. 20 Assigned to: TETR

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 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. **MATERIALS**

3.1. All reagents are to be AR grade or better.

3.2. All solvents are to be distilled in glass unless otherwise noted.

3.3 The following special reagents should be prepared:

3.3.1. 37% Potassium Hydroxide - prepared by dissolving 370 grams potassium hydoxide pellets and diluting to one liter with DIW.

3.3.2. Concentrated Sulfuric Acid

3.3.3. 10% Hydrochloric Acid - measure 100 ml concentrated hydrochloric acid and dilute to 1000 ml with DIW. Note: Observe proper acid preparation techniques.

3.3.4. Anhydrous Sodium Sulfate - prepared by muffling AR grade sodium sulfate for four hours at 400°C.

3.3.5. 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.

3.3.6. 10 M Potassium Hydroxide - prepared by dissolving 56.1 grams potassium hydoxide pellets and diluting to 100 ml with DIW.

3.3.7. Diethylene Glycol Monoethyl Ether (Carbitol) – (Sigma – catalog # D-1265)

3.3.8. Diazald® (Aldrich - catalog # D2,800-0).

3.3.9. Surrogate solution prepared in methanol:

2,4 - Dichlorophenyl Acetic Acid	5.0 ug/ml

3.3.10. Matrix Spiking solution prepared in methanol:

2,4,5-TP	0.8 ug/ml
2,4,5-T	0.8 ug/ml
Dicamba	0.8 ug/ml
Pentachlorophenol	4.0 ug/ml
Dinoseb	4.0 ug/ml
Picloram	8.0 ug/ml
2,4-DB	8.0 ug/ml
2,4-D	8.0 ug/ml
Dichloroprop	8.0 ug/ml
Dalapon	20.0 ug/ml
MCPP	800.0 ug/ml
MCPA	800.0 ug/ml

4. EQUIPMENT

4.1. Organomations Assoc., Inc. - N-EVAP, (nitrogen evaporator), Model 112

4.2. Standard laboratory glassware to include:

4.2.1. 25 x 200 mm Pyrex culture tubes

4.2.2. 16 x 100 mm culture tubes

4.3. All glassware to be used shall be rinsed in the following manner:

4.3.1. 10% hydrochloric acid

4.3.1. Reagent grade acetone

4.4. Volumetric measurements are to be made with a calibrated fixed or adjustable volume microdispenser and individually calibrated vials.

5. QUALITY CONTROL

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.

6. METHODOLOGY

6.1. Sample Extraction:

6.1.1. Mix sample thoroughly in its original container.

6.1.2. Measure 50 ml sample into 25 x 200 culture tube.

6.1.3. Prepare a blank and a blank spike with 50 ml DIW.

6.1.4. Prepare two additional aliquots of a sample if Quality Control is required.

6.1.5. Pipet 10 ul surrogate solution into each tube.

6.1.6. Pipet 10 ul matrix spiking solution into each QC tube.

6.1.7. Pipet 1.0 ml 37% potassium hydoxide into each culture tube, mix and loosely cap with teflon screw cap.

6.1.8. Immerse tubes in a 60-65°C water bath for a minimum of 90 minutes.

6.1.9. Remove from bath and cool to room temperature.

6.1.10. Add 6-7 mls ethyl ether to each culture tube, cap tightly and shake for two minutes. If emulsions occur, centrifuge tubes.

6.1.11. Draw off and discard ether layer.

6.1.12. Repeat from step 6.1.10. two additional times using 3 ml ethyl ether.

6.1.13. Adjust pH to <2 by slowly adding 500µl concentrated sulfuric acid to each tube. Mix and check pH.

6.1.14. Repeat step 6.1.10 three times using 3 ml ethyl ether and save ether into a 16 x 100 culture tube.

6.2. Dehydration of the extract:

6.2.1. Adjust volume to 5-6 mls in the nitrogen blowdown.

6.2.2. Add 3 gm of acidified sodium sulfate to each tube, cap and shake.

6.2.3. Tap the tubes to settle the sodium sulfate and let stand at least 60 minutes and may stand overnight.

6.2.4. Transfer ether extract to 16 x 100 culture tube.

6.2.5. Add 1-2 mls ether to acidified sodium sulfate, cap and shake to break up sodium sulfate.

6.2.6. Transfer rinse to tube containing the ether extract.

6.2.7. Repeat from step 6.2.5. two additional times.

6.2.8. Adjust volume to 5-6 mls in the nitrogen blowdown.

6.3. Derivatization:

6.3.1. To tube A (the first tube in the train), add 1.0 ml methanol, and bring to 8.0 ml with ethyl ether.

6.3.2. To tube B add:

6.3.2.1. 2.0 ml 10 M potassium hydoxide (to the first marked line)

6.3.2.2. 1.4 ml Carbitol (diethylene glycol monoethyl ether) to the second marked line.

6.3.3. Place 10 ul micro-pipet in each sample tube from step 6.2.8.

6.3.4. Connect nitrogen line to the apparatus and regulate so that tube A bubbles actively but not violently.

6.3.5. 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.

6.3.6. Bubble the generated diazomethane into the tube for 90 seconds. (Extract will turn bright yellow.)

6.3.7. Let extract stand for 15 minutes.

6.3.8. Reduce extract to near dryness on nitrogen blowdown. Add 5 ml hexane.

6.3.9. Reduce the extract volume to less than 0.5 ml in a nitrogen blowdown.

6.3.10. Adjust the final volume to 0.5 ml (as compared to a measured volume) with hexane.

6.3.11. Label the extract and deliver to 940.

6.3.12. Complete all the necessary paperwork and bench sheet. Bench sheet to include date derivatized, date and time of transfer to 940 and extract location. Clip the T-card on the folder and place in the GC room extraction folder box. The file folder color will be yellow, and the blank name will be ____GHB.WL_.

7. **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

8151A (1996), 3510C (1996)

LAUCKS TESTING LABORATORIES INC.	EXTRACTION	DATE	METHOD	ANALYST	CHECKER	ANALYSIS
JOB NUMBER: 0104123	Web	4-10-01	mod 3510C	YL	4-11-01	8151A
MATRIX: H_2O						

Sample #	wt./vol.	% val					SDG#	Bot#
0104132-1	50 ml	0.5ml					LI143	13
2								14
3								15
3MS								16
3MSD								17
4								18
5								20
6								22
S010401GHBWLG								
B010401GHBWLG								

4-10-01 YL

COMMENTS:

Ext Sol: Ethyl Ether - B&J # CB192
Final Sol: Hexane - EM # 40163
Derivatized: 4-11-01

SURROGATES:

10 ul of: Ex 8.44-5
ul of:

SPIKES:

10 ul of: Ex 8-44-8
ul of:

STANDARDS:

ul of:
ul of:
ul of:

Fraction and Method	Extraction		Transferred from 921 to 940		Extract Location	Analysis	
Web	Time out: 0900	Time in: 1000	Time out: 1350	Time in: —	Tray # 1564 A1 – A10	Time out:	Time in:
	Date: 4-10-01	Initials: YL	Date: 4-12-01	Initials: AGH		Date:	Initials:
	Time out:	Time in:	Time out: —	Time in: 1400		Time out:	Time in:
	Date:	Initials:	Date: 4-12-01	Initials: SO		Date:	Initials:

Extraction Method for Picric and Picramic Acids in Water
(3510C)

Method # LTL-3550

April 12, 2001

Revision Number: #5

Written by: B. O'Neill Date: 4-12-01

Reviewed by: Harry Romberg Date: 4-26-01

Approved by: Kathy Krepp Date: 04-30-01

Controlled Document

No. 20 Assigned to: TETR

1. **PURPOSE:** In this method, the ion pairing reagent, tetrabutylammonium dihydrogen phosphate (TBAP), is added to a water sample, pH adjusted to slightly basic and extracted with methylene chloride. Extracts are dehydrated and concentrated in a Kuderna-Danish (K-D) apparatus and exchanged to methanol prior to analysis by HPLC.

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 while executing this method. The company will provide any protective equipment or clothing needed to assure employee safety.

3. **REAGENTS**

3.1. All reagents shall be of AR grade or better.

3.2 . All solvents shall be distilled in glass unless otherwise indicated.

3.3. The following special reagents shall be prepared:

3.3.1. 10 N Sodium Hydroxide - prepared by weighing 400 grams sodium hydroxide, dissolve and dilute to one liter with DIW.

3.3.2. 1:1 Sulfuric Acid - measure equal volumes of concentrated sulfuric acid and DIW. Note: Observe proper acid preparation techniques.

3.3.3. Tetrabutylammonium Dihydrogen Phosphate (TBAP) - prepared by weighing 1.0 gm TBAP, dissolve and dilute to one liter with DIW.

3.3.4. Anhydrous Sodium Sulfate - prepared by muffling AR grade sodium sulfate four hours at 400°C.

3.3.5. Surrogate Solution prepared in methanol:

4,6-Dinitro-*o*-cresol	80.0 ug/ml

3.3.6. Matrix Spiking Solution prepared in methanol:

Picric Acid	40.0 ug/ml
Picramic Acid	40.0 ug/ml

4. **EQUIPMENT**

4.1. Glas-Col mechanical separatory funnel shaker

4.2. Organomations Assoc., Inc. - N-EVAP, (nitrogen evaporator), Model 112

4.3. Standard laboratory glassware to include:

4.3.1. 2000 ml Teflon separatory funnels

4.3.2. 300 ml Fleakers

4.3.3. K-D apparatus: 250 ml. K-D flask, 10 ml or 25 ml ampule and three-ball snyder column.

4.4. All glassware to be rinsed as follows, prior to use:

4.4.1. Technical grade acetone (if the glassware is wet).

4.4.2. Triple rinsed with methylene chloride.

4.5. Volumetric measurements are to be made with a calibrated fixed or adjustable volume microdispenser and individually calibrated vials.

5. **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.

6. **METHODOLOGY**

6.1. Sample Extraction

6.1.1. Mix sample thoroughly in its original container and place labeling tape at sample level. Mark meniscus of sample on the tape.

6.1.2. Transfer entire contents of container into a 2000 ml separatory funnel. Rinse container with methylene chloride and add to funnel. Fill sample container to the mark on tape with water. Measure volume of sample used in a calibrated 1000 ml cylinder.

6.1.3. Prepare a blank and a blank spike with 1000 ml DIW.

6.1.4. Prepare two additional aliquots of one sample if Quality Control is required.

6.1.5. Add 100 ml TBAP solution to each funnel.

6.1.6. Pipet 100 ul surrogate solution into each funnel.

6.1.7. Pipet 100 ul matrix spiking solution into each QC funnel.

6.1.8. Adjust pH to 8.5 - 9.

6.1.9. Add 60 ml methylene chloride to each separatory funnel.

6.1.10. Shake the samples hard for three minutes on the mechanical shaker, with the stopcocks closed.

6.1.11. Replace the funnels in rack and allow to stand for 10 minutes.

6.1.12. Drain and collect the lower methylene chloride layer in a Fleaker.

6.1.13. Repeat from 6.1.9. until a total of three extractions have been performed.

6.2. Solvent dehydration

6.2.1. Prepare a glass funnel by plugging with glass wool, and filling 1/2-2/3 full with muffled sodium sulfate.

6.2.2. Pre-rinse the sodium sulfate by passing 40 ml methylene chloride through the prepared funnel.

6.2.3. Pass the extract from 6.1.13. through the funnel and collect in an assembled K-D apparatus.

6.2.4. Rinse the collection vessel with several 10 ml methylene chloride rinses.

6.2.5. Rinse the sodium sulfate with 40 ml of methylene chloride.

6.3. Solvent evaporation

6.3.1. Assemble the full K-D apparatus with a snyder column prewet with 2-3 ml of methylene chloride.

6.3.2. 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 8 ml. Regulate the evaporation time to take one to one and a half hours.

6.3.3. Reduce the volume to 4-5 ml, and exchange into methanol as follows:

6.3.3.1. Add 2-3 ml methanol through the top of the snyder column while the ampule is still immersed in the water bath. Reduce to 4-5 ml.

6.3.3.2. Repeat 6.3.3.1. two additional times.

6.3.4. Remove the apparatus from the water bath and cool to room temperature.

6.3.5. Rinse joint with methanol and remove the snyder column. Allow rinse solvent to drain into ampule.

6.3.6. Remove the ampule clamp, and wipe the joint with a Kimwipe. Separate the ampule and rinse the joint with a small amount of methanol.

6.3.7. Reduce the extract volume to below 0.5 ml in a warm water bath with nitrogen to insure that there has been a complete exchange to methanol. Rinse internal walls of ampule several times during blowdown.

6.3.8. Transfer extract to a 1.8 ml vial. The final volume is then adjusted to 1.0 ml (as compared to a measured volume) in methanol.

6.3.9. Label the extract and deliver to 940.

6.3.10. Complete all paperwork and bench sheet. Bench sheet to include date and time of transfer to 940 and extract location. Clip the T-card on the folder and place in GC room extraction folder box. The file folder color will be neon green and the blank name will be ____HSV.WL_.

7. **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

3510C (1996)

LAUCKS TESTING LABORATORIES INC.	EXTRACTION	DATE	METHOD	ANALYST	CHECKER	ANALYSIS
JOB NUMBER: 0104217	Pic/Pic	4/12/01	3510C	LS.	LS 4/12/01	Picric/ Picramic
MATRIX: H_2O						

SDG LE001

Sample #	wt./vol.	Final Vol.						Btl #
0104217-1	1000ml	1.0ml						1
-2								3
-2ms								4
-2msD								5
-3								9
-4								11
-5								13
-6								15
S041201HSVWLS								
B041201HSVWLS								

4/12/01 LS.

COMMENTS:

- Ext. Solvent: MeCl2 B+J CA561
- Final Solvent: MeOH Em # 39022
- pH 8.5-9

SURROGATES:

100 ul of: EX8-39-5

_____ ul of: _____

SPIKES:

100 ul of: EX8-43-4

_____ ul of: _____

STANDARDS:

_____ ul of: _____

_____ ul of: _____

_____ ul of: _____

Fraction and Method	Extraction		Transferred from 921 to 940		Extract Location	Analysis	
Pic/Pic-H_2O	Time out: 0900	Time in: Empty	Time out: 1600	Time in: —	Tray # 1565 AA0-AA9	Time out:	Time in:
	Date: 4/12/01	Initials: LS.	Date: 4/12/01	Initials: AGH		Date:	Initials:
	Time out:	Time in:	Time out: —	Time in: 1610		Time out:	Time in:
	Date:	Initials:	Date: 4/12/01	Initials: SO		Date:	Initials:

Extraction Method for Picric and Picramic Acids in Soil (3550B)

Method # LTL-3555

November 29, 1999

Revision Number: #4

Written by: B. O'Neill Date: 11-29-99

Reviewed by: Harry Rosberg Date: 12-13-99

Approved by: Kathy Grieps Date: 12-13-99

Controlled Document

No. 20 Assigned to: Tetra

1. **PURPOSE:** In this method, picric/picramic acids are extracted from soil with 80:20 DIW/methanol. Ion pairing reagent, tetrabutylammonium dihydrogen phosphate (TBAP), is added to the water sample, pH adjusted to slightly basic and extracted with methylene chloride. Extracts are dehydrated, concentrated in a Kuderna-Danish (K-D) apparatus and exchanged to methanol prior to analysis by HPLC.

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 while executing this method. The company will provide any protective equipment or clothing needed to assure employee safety.

3. **REAGENTS**

3.1. All reagents shall be of AR grade or better.

3.2. All solvents shall be distilled in glass unless otherwise indicated.

3.3. The following special reagents shall be prepared:

3.3.1. 10 N Sodium Hydroxide - prepared by weighing 400 grams sodium hydroxide, dissolve and dilute to one liter with DIW.

3.3.2. 1:1 Sulfuric Acid - measure equal volumes of concentrated sulfuric acid and DIW. Note: Observe proper acid preparation techniques.

3.3.3. Tetrabutylammonium Dihydrogen Phosphate (TBAP) - prepared by weighing 1.0 gm TBAP, dissolve and dilute to one liter with DIW.

3.3.4. Anhydrous Sodium Sulfate - prepared by muffling AR grade sodium sulfate four hours at 400°C.

3.3.5. Surrogate solution prepared in methanol:

4,6-Dinitro-o-cresol	80.0 ug/ml

3.3.6. Matrix Spiking solution prepared in methanol:

Picric Acid	40.0 ug/ml
Picramic Acid	40.0 ug/ml

4. **EQUIPMENT**

4.1. Heat Systems Ultrasonic Processor - Model XL2020, 550 watts - Maintain per manufacturer's instructions.

4.1.1. 3/4 inch titanium horn (#208).

4.2. Organomations Assoc., Inc. - N-EVAP, (nitrogen evaporator), Model 112

4.3. Standard laboratory glassware to include:

4.3.1. 8 ounce extraction bottles

4.3.2. 300 ml Fleakers

4.3.3. 1000 ml Teflon separatory funnels

4.3.3. K-D apparatus: 250 ml. K-D flask, 10 ml or 25 ml ampule and three-ball snyder column.

4.4. All glassware to be rinsed as follows, prior to use:

4.4.1. Technical grade acetone (if the glassware is wet).

4.4.2. Triple rinsed with methylene chloride.

4.5. Volumetric measurements are to be made with a calibrated fixed or adjustable volume microdispenser and individually calibrated vials.

5. **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.

6. **METHODOLOGY**

6.1. Sample Extraction

6.1.1. Mix sample thoroughly in its original container.

6.1.2. Weigh 30.0 grams of soil into an extraction bottle.

6.1.3. Prepare two additional aliquots of one sample if Quality Control is required.

6.1.4. Prepare a blank and blank spike with 60 grams sodium sulfate.

6.1.5. Pipet 100 ul surrogate solution to each bottle.

6.1.6. Pipet 100 ul matrix spiking solution to each of the QC bottles.

6.1.7. Add 80 ml DIW to each extraction bottle.

6.1.8. Adjust pH to 8.5 - 9.0.

6.1.9. Add 20 ml methanol to each bottle.

6.1.10. Sonicate the bottles for 3 minutes using the sonic horn, set at 50% duty cycle and full output (10).

6.1.11. Centrifuge the samples for 20 minutes at 2000 rpm.

6.1.12. Decant off and collect the supernatant in a 1000 separatory funnel.

6.1.13. Adjust pH to 8.0 - 8.5.

6.1.14. Add 100 ml TBAP solution.

6.1.15. Add 60 ml methylene chloride to each separatory funnel.

6.1.16. Shake the samples hard for three minutes on the mechanical shaker, with the stopcocks closed.

6.1.17. Replace the funnels in rack and allow to stand for 10 minutes.

6.1.18. Drain and collect the lower methylene chloride layer in a Fleaker.

6.1.19. Repeat from step 6.1.15. until a total of three extractions have been performed.

6.2. Solvent dehydration

6.2.1. Prepare a glass funnel by plugging with glass wool, and filling 1/2-2/3 full with muffled sodium sulfate.

6.2.2. Pre-rinse the sodium sulfate by passing 40 ml methylene chloride through the prepared funnel.

6.2.3. Pass the extract from step 6.1.19. through the funnel and collect in an assembled K-D apparatus.

6.2.4. Rinse the collection vessel with several 10 ml methylene chloride rinses.

6.2.5. Rinse the sodium sulfate with 40 ml of methylene chloride.

6.3. Solvent evaporation

6.3.1. Assemble the full K-D apparatus with a snyder column prewet with 2-3 ml of methylene chloride.

6.3.2. 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 8 ml. Regulate the evaporation time to take one to one and a half hours.

6.3.3. Reduce the volume to 4-5 ml, and exchange into methanol as follows:

6.3.3.1. Add 2-3 ml methanol through the top of the snyder column while the ampule is still immersed in the water bath. Reduce to 4-5 ml.

6.3.3.2. Repeat 6.3.3.1. two additional times.

6.3.4. Remove the apparatus from the water bath and cool to room temperature.

6.3.5. Rinse joint with methanol and remove the snyder column. Allow rinse solvent to drain into ampule.

6.3.6. Remove the ampule clamp, and wipe the joint with a Kimwipe. Separate the ampule and rinse the joint with a small amount of methanol.

6.3.7. Reduce the extract volume to below 0.5 ml in a warm water bath with nitrogen to insure that there has been a complete exchange to methanol. Rinse internal walls of ampule several times during blowdown.

6.3.8. Transfer extract to a 1.8 ml vial. The final volume is then adjusted to 1.0 ml (as compared to a measured volume) in methanol.

6.3.8. Label the extract and deliver to 940.

6.3.9. Complete all paperwork and bench sheet. Bench sheet to include date and time of transfer to 940 and extract location. Clip the T-card on the folder and place in GC room extraction folder box. The file folder color will be neon green and the blank name will be ____HSV.SL_.

7. **ANALYSIS TIME** - Based on experience in the laboratory, it is anticipated that a single sample may be completed in about six hours. If it is possible to batch similar samples, it is expected that about ten samples could be completed in approximately 18 hours. About one hour of actual hands on time will be expended by the extractionist. These approximate times are based on the assumption that the samples are "average", and will not require additional time beyond normal operations. Additional time must be allocated for samples which are very dirty or are extraordinary.

8. **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

3550B (1996), 3510C (1996)

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-6006

Title: Cation-Exchange Capacity of Soils (Sodium Acetate) by SW 846 Method 9081

Revision history:

Number	Date
0	1/25/99

UNCONTROLLED

Written by: Harry Romberg Date: 1-25-99
Harry Romberg, Quality Assurance Officer

Reviewed by: Raul N Date: 1/25/99
Raul Nino, Analyst

Approved by: Kathy Kreps Date: 1/25/99
Kathy Kreps, Laboratory Director

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APPENDIX I 8

QC SUMMARY TABLE 8

APPENDIX II 10

FLOW CHART 10

1. Introduction and Scope

1.1 Scope

1.1.1 LTL-6006 (SW 846 Method 9081) is applicable to most soils, including calcareous and noncalcareous soils. This method only applies to the Cation Exchange Capacity extraction. The actual analysis method should be referred to for quantitation of sodium in the extract.

1.2 Method Description

1.2.1 The soil sample is mixed with an excess of sodium acetate solution, resulting in an exchange of the added sodium cations for the matrix cations. Subsequently, the sample is washed with isopropyl alcohol. An ammonium acetate solution is then added, which replaces the adsorbed sodium with ammonium. The concentration of displaced sodium is then determined by flame atomic absorption spectroscopy or ICP.

1.2.2 This method is restricted to use by, or under the supervision of analysts experienced in the technique described. Each analyst performing this method must have demonstrated the ability to perform the described analysis.

1.3 Sample Collection, Sample Storage, Holding Times

1.3.1 No holding times or preservation are specified for this method.

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.

1.4.2 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. This is followed by the date, analysis, matrix and sequence number (i.e. BmmddyyCECS01).

1.4.3 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 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.

1.4.4 DIW - Deionized water - Lab reagent water. This water should be free of virtually all analytes.

1.4.5 RPD - Relative percent difference, in this case between duplicate analyses, calculated as the difference between replicate sample determinations divided by the average calculated as a percent.

2. Equipment List and Standards

2.1 Equipment

- 50 mL centrifuge tubes and stoppers
- mechanical shaker
- 100 mL class A volumetric flasks

2.2 Reagents

2.2.1 Sodium acetate (NaOAc), 1.0 N: Dissolve 136 g of $NaC_2H_2O_2 \cdot 3H_2O$ (or 82 g anhydrous $NaC_2H_2O_2$) in water and dilute it to 1,000 mL. The pH of this solution should be 8.2. If needed, add a few drops of acetic acid or NaOH solution to bring the reaction of the solution to pH 8.2.

2.2.2 Ammonium acetate (NH_4OAc), 1 N: Dilute 114 mL of glacial acetic acid (99.5%) with water to a volume of approximately 1 liter. Then add 138 mL of concentrated ammonium hydroxide (NH_4OH) and add water to obtain a volume of about 1,980 mL. Check the pH of the resulting solution, add more NH_4OH, as needed, to obtain a pH of 7, and dilute the solution to a volume of 2 liters with water.

2.2.3 Isopropyl alcohol: 99%.

3. Safety precautions and Waste Disposal

3.1 Safety Precautions

3.1.1 All standards, samples and sample solutions should be handled as if they are 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.

3.2 Waste Disposal

3.2.1 Isopropyl alcohol solutions should be disposed of in the solvent waste container.

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 Method Blanks

4.1.1 Method blanks are used to verify contamination free reagents and apparatus. They are prepared with every set of samples prepared at the same time or at least one blank every 20 samples which ever is more frequent. Any analyte response above the reporting limit is reported. Method blank control limits are that contamination should not exceed the reporting limit.

4.1.2 Corrective action

4.1.2.1 Corrective action may necessitate re-preparation and re-analysis of the sample set. For example if an analyte were found in the blank but not in any of the associated samples then sample group may not require re-analysis. In addition, if sample levels exceed 20 times the blank, the level of contamination may be considered insignificant. In any case, if re-preparation and re-analysis is not being undertaken, the analyst must first discuss the issue with the Quality Control Officer. It is the laboratory's responsibility to ensure that method interferences caused by contaminants in acids, solvents, reagents, glassware, and other sample processing hardware leading to discrete artifacts and/or elevated baselines in the analytical run 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.

4.2 Sample Duplicate

4.2.1 Criteria

4.2.1.1 At least one duplicate sample per 10 samples is required. RPD values are calculated in a manner similar to MS/MSD RPDs:

$$RPD = \frac{|S1 - S2| * 100}{(S1 + S2)/2}$$

where:
S1 = measured concentration in the initial analysis
S2 = measured concentration in the duplicate analysis

4.2.1.2 The RPD control limits are detailed in the Quality Control Database (QC_DB) and will change from time to time.

4.2.2 Corrective action

4.2.2.1 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. Generally, if recoveries are in control and no analyte of interest was detected in any of the samples, no immediate action will be taken on that sample set. If integrity of reported sample values is in doubt, re-analysis may be called for. Corrective actions should be discussed with the Quality Control Officer.

5. Operation procedures

5.1 Extraction Procedure

5.1.1 Weigh 4 g of medium or fine-textured soil or 6 g of coarse-textured soil and transfer the sample to a 50-mL, round-bottom, narrow-neck centrifuge tube. (A fine soil has >50% of the particles <0.074 mm, medium soil has >50% >0.425 mm, while a coarse soil has more than 50% of its particles >2 mm.

5.1.2 Add 33 mL of 1.0 N NaOAc solution, stopper the tube, shake it in a mechanical shaker for 5 min, and centrifuge it until the supernatant liquid is clear.

5.1.3 Decant the liquid, and repeat Paragraph 5.1.2 three more times.

5.1.4 Add 33 mL of 99% isopropyl alcohol, stopper the tube, shake it in a mechanical shaker for 5 min, and centrifuge it until the supernatant liquid is clear.

5.1.5 Repeat the procedure described in Paragraph 5.1.4 two more times.

5.1.6 Add 33 mL of NH_4OAc solution, stopper the tube, shake it in a mechanical shaker for 5 min, and centrifuge it until the supernatant liquid is clear. Decant the washing into a 100-mL volumetric flask.

5.1.7 Repeat the procedure described in Paragraph 5.1.6 two more times.

5.1.8 Dilute the combined washing to the 100-mL mark with ammonium acetate solution and determine the sodium concentration by atomic absorption, emission spectroscopy, or an equivalent method.

5.2 Instrumental Analysis

5.2.1 Specifics of the instrumental analysis are contained in the appropriate SOP.

6. Reports

6.1 Data Packet Organization

6.1.1 Sample reports vary depending upon the needs of the client. They may be as simple as a standard laboratory report with only a QC summary (generated from QC_DB) or they may be more thorough and include instrument calibration information and raw data if a full data package is required.

6.2 Quality Control Reports

6.2.1 All results for quality control tests are entered into the lab data base using the QC_DB program. Printouts of all data entered must be included in the data packet. The routine minimum for this analysis is a method blank report and a duplicate 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 limit of detection indicated.

Appendix I

QC Summary Table

Laucks Testing Laboratories

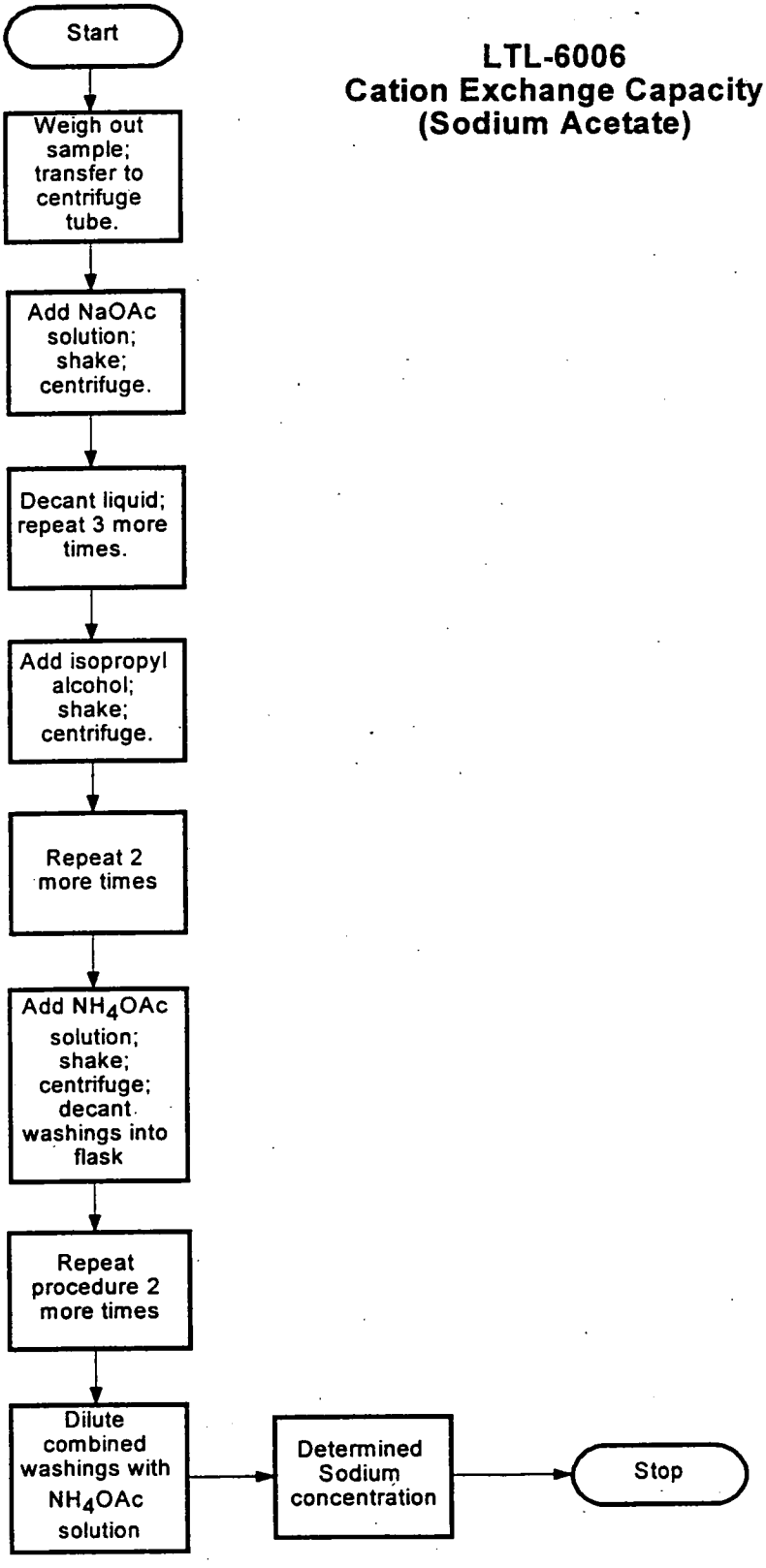
Method LTL-6006 QA Requirements and Corrective Actions

QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
Method Blank	None	No blank above reporting limit	1 per 20 samples or one per batch	reanalyze unless samples >20X blank	QC_DB and sample report
Duplicate % Difference or RPD	None	See QC_DB database	1 per 10 samples or one per batch	Discuss with QC Officer	QC_DB and sample report

Appendix II

Flow Chart

LTL-6006
Cation Exchange Capacity
(Sodium Acetate)



LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-6008

Title: **Determination of Acid Volatile Sulfides (AVS) and Simultaneously Extractable Metals (SEM) in Sediment**

Revision history:

Number	Date
0	10/03/01

Written by: Raul J. Nino, Chemist Date: 10/10/01

Approved by: Harry Romberg, QA Officer Date: 10-8-01

Approved by: Kathy Kreps, Laboratory Director Date: 10-8-01

Controlled Document

No. 20 **Assigned to:** Tetr

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Assigned to _____ No. _____

1. Scope, Summary of Method, Interferences, and Definitions

1.1 Scope and Application

1.1.1 This method describes procedures for the determination of acid volatile sulfides (AVS) and for metals that are solubilized during the acidification step (simultaneously extracted metal, SEM). The conditions used have been reported to measure amorphous or moderately crystalline monosulfides. As a precipitant of toxic heavy metals, sulfide is important in controlling the bioavailability of metals in anoxic sediments. If the molar ratio of toxic metals measured by SEM to AVS exceeds one, the metals are potentially bioavailable. Because the relative amounts of AVS and SEM are important in the prediction of potential metal bioavailability, it is important to use the SEM procedure for sample preparation for metal analysis. This uses the same conditions for release of both sulfide and metal from the sediment and thus provides the most predictive means of assessing the amount of metal associated with sulfide.

1.2 Summary of Method

1.2.1 The AVS in the sample is first converted to hydrogen sulfide (H_2S) gas by acidification with hydrochloric acid at room temperature. The H_2S is then purged from a sample and trapped as silver sulfide (Ag_2S). The amount of Ag_2S formed is determined gravimetrically, and calculated as µmoles/g DB of AVS.

1.2.2 The SEM part of the analysis is determined after the H_2S gas has been released from the sample in the reaction vessel. The acidified solution is then filtered and analyzed by inductive coupled plasma (ICP) for metals, and reported as µmoles/g DB for each metal.

1.2.3 The sum total of all the metals found in the SEM analysis divided by the sulfide found in the AVS analysis is then used to determine the bioavailablity of the sample, reported as µmoles/g of SEM/AVS .

1.3 Interferences

1.3.1 Oxygen in the reagents and apparatus is the primary interference reported. Special precautions must be taken to insure that the analytical system is adequately purged with oxygen-free nitrogen.

1.3.2 The pH of the sample after the addition of the acid and during the purge process must be below 3. Typically, the pH is below 2.

1.4 Sample Collection, Preservation and Storage

1.4.1 The samples should be collected in a wide mouth jar with minimum air space above the sediment and sealed with a Teflon lined lid or a polyethylene lined lid.

1.4.2 If possible, the headspace should be purged with oxygen free nitrogen, otherwise there are no other sample preservation required.

1.4.3 Samples should be cooled to 4°C as soon as possible after collection and be kept at 4°C until sample analysis. Holding time for the samples should not exceed 14 days from the date of collection.

1.5 Definition of Terms

1.5.1 This section defines terms and acronyms as they are used in this SOP.

Acid Volatile Sulfides (AVS)	Amorphous, moderately crystalline monosulfide, and other sulfides that form hydrogen sulfide under the conditions of this test.
Simultaneously Extracted Metals (SEM)	Metals, commonly cadmium, copper, lead, mercury, nickel and zinc, which form less soluble sulfides than do iron or manganese, and which are at least partially soluble under the conditions of this test.
DIW	Deionized water. Lab reagent water.

2. Safety precautions and Waste Disposal

2.1 Routine Safety Precautions

2.1.1 All samples and solutions should be handled as if they contain hazardous substances.

2.1.2 Some of the reagents used may causes irritation and/or be harmful if swallowed or inhaled. Read the MSDS for proper handling and storage of the reagents used.

2.1.3 Hydrogen sulfide is a highly poisonous, gaseous compound having a characteristic odor of rotten eggs. It is detectable in air by humans at a concentration of 0.002 ppm. However, the human nose quickly adjusts to the presence of sulfide up to the point that it can actually become hazardous. Thus, ventilation is necessary and caution must be exercised.

2.1.4 Refer to the instrument manufacturer's manual for routine instrument precautions.

2.1.5 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 and have the potential to do harm if not used properly.

2.1.6 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

2.1.7 Grounded power outlets, turning off the instrument and disconnecting the instrument from the electrical power supply before working on any electrical components, etc.

2.2 Waste disposal

2.2.1 Any unused or used acidic solutions must be neutralized with sodium bicarbonate prior to disposal down the sink and flushed with copious amounts of water.

2.2.2 Waste segregation and disposal from the point of collection is further covered in the Laucks SOP on Waste Segregation and Disposal.

3. Equipment List and Solutions

3.1 Equipment List

3.1.1 Assorted Calibrated Pipettes and Volumetric Flasks.

3.1.2 Nitrogen Gas – 99.999% pure.

3.1.3 Flow Controller.

3.1.4 250 mL Erlenmeyer Flasks.

3.1.5 Rubber Stoppers – Two and three holed.

3.1.6 125 ml Separatory Funnel.

3.1.7 Filtering Flask with 47 mm Filter Holder.

3.1.8 Pre-Weighted 47 mm Glass Fiber Filter.

3.1.9 Drying Oven – Capable of maintaining a constant temperature of 100°C ± 5°C.

3.1.10 Course (2.7 micron) Glass fiber filters (Whatman GF/D)

3.1.11 Analytical Balance – A balance sensitive to 0.0001 grams.

3.1.12 Magnetic Stirrer (thermally insulated) and Teflon-Coated Stirring Bars.

3.2 Solutions

3.2.1 Hydrochloric Acid, 6M – Dilute 500 mL of concentrated hydrochloric acid to 1 L with DIW. Purge with oxygen free nitrogen gas for 30 minutes before use.

3.2.2 Potassium Acid Phthalate, 0.05M – Dissolve 10.2 gm of potassium acid phthalate in DIW and dilute to 1 L.

3.2.3 Silver Nitrate, 1M – Dissolve 17 gm of silver nitrate in DIW and dilute to 1 L. Store in a dark bottle.

3.2.4 Starch Indicator – Dissolve 20 gm soluble starch in 1 L of boiling DIW, after the solution has cooled add 2 gm of buffered aspirin to preserve the solution.

3.2.5 Potassium Bi-iodate, 0.025N – Potassium bi-iodate solution is purchased as a pre-made certified solution. If necessary, it can be made by dissolving 0.8124 gm of potassium bi-iodate in DIW and diluting it to 1000 mL.

3.2.6 Sodium Thiosulfate, 0.025N – Dissolve 12.41 gm of sodium thiosulfate 5-hydrate into about 900 mL of DIW in a 1000 mL volumetric flask, add 1.5 mL or 0.4 gm of sodium hydroxide, and fill the volumetric flask to 1000 mL with DIW. Standardize with the potassium bi-iodate solution.

3.2.6.1 Standardization – Dissolve approximately 2 gm of potassium iodide (free from iodate) in an erlenmeyer flask with 100 to 150 mL of DIW. Add 1 mL of 6N hydrochloric acid and 20 mL of 0.025N potassium bi-iodate. Dilute to 200 mL and titrate liberated iodine with the sodium thiosulfate solution. Add starch toward the end of the titration, when a pale yellow is reached. Adding starch will make the solution dark blue to light blue, depending on how close to the end of the titration. Continue titrating until the solution is colorless. 20 mL of the sodium thoisulfate would be necessary to neutralize 20 mL of 0.025N potassium bi-iodate. If not then adjust the sodium thiosulfate solution, until they match.

3.2.7 Iodine, 0.025N – Dissolve 22.5 gm of potassium iodide, in a small volume of DIW (<100 mL). Add 3.2 gm iodine. Wait for the iodine to dissolve then dilute to 1000 mL with DIW. Standardize against the standardized 0.025N sodium thiosulfate solution before each use.

3.3 Standards

3.3.1 Sodium Sulfide – Dissolve about 15 gm of sodium sulfide crystals and 0.2 gm of sodium hydroxide into approximately 900 mL of DIW. Dilute to 1000 mL. This solution should be calibrated with the standardized sodium thiosulfate and iodine solutions before each use.

4. Quality Control

4.1 Quality Control

4.1.1 The minimum requirement for this method is an MDL study, and the analysis of laboratory reagent blanks, fortified blanks, duplicate sample analyses, and fortified matrix samples.

4.1.2 See Appendix I for QC Summary Table

4.2 Initial Demonstration of Performance

4.2.1 The initial demonstration of performance is used to characterize instrument performance, method detection limits, and linear calibration ranges.

4.2.2 Method detection limit (MDL) – The method detection will be established for each analyte, using DIW (blank) fortified at a concentration two to five times the estimated detection limit. To determine the MDL values, analyze at least seven replicate aliquots of the fortified reagent water and process though the entire analytical method. Perform all calculations and report the concentration in the appropriate units. Calculate the MDL as follows:

$$MDL = t * s$$

where:

t = Students' t value for 99% confidence level and a standard deviation estimate with n-1 degrees of freedom (t = 3.14 for seven replicates).

s = Standard deviation of the replicate analyses.

4.2.3 The MDL study for the AVS analysis will be determined gravimetrically.

4.2.4 The MDL study for the SEM analysis will be analyzed as outlined in Laucks SOP LTL-7105 (for ICP metals analysis by SW-846 method 6010) and LTL-7501 (for mercury cold vapor analysis by SW-846 method 7471).

4.3 Laboratory Reagent Blank (LRB)

4.3.1 Criteria

4.3.1.1 Method blanks are used to verify contamination free reagents and apparatus. They are prepared with every set of samples prepared at the same time or at least one blank every 20 samples which ever is more frequent. Any analyte response above the detection limit is reported. Method blank control limits are that contamination should not exceed half of the reporting limit.

4.3.1.2 The estimated reporting limits in µmoles/gm for AVS and SEM are listed in the table below:

Analyte	Reporting Limit
AVS	
Sulfide (S^{-2})	0.008
SEM	
Cadmium (Cd)	0.001
Copper (Cu)	0.002
Lead (Pb)	0.003
Mercury (Hg)	0.0001
Nickel (Ni)	0.006
Zinc (Zn)	0.005

4.3.2 Corrective action

4.3.2.1 Corrective action may necessitate re-preparation and re-analysis of the sample set. For example if an analyte were found in the blank but not in any of the associated samples then sample group may not require re-analysis. In addition, if sample levels exceed 20 times the blank, the level of contamination may be considered insignificant. In any case, if re-preparation and re-analysis is not being undertaken, the analyst must first discuss the issue with the Quality Control Officer. It is the laboratory's responsibility to ensure that method interferences caused by contaminants in acids, solvents, reagents, glassware, and other sample processing hardware leading to discrete artifacts and/or elevated baselines in the analytical run 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.

4.4 Laboratory Fortified Sample Matrix (LFM)

4.4.1 Criteria

4.4.1.1 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 preparation. The analyst should attempt to avoid selecting sample which are identified by the client as blanks. The LFM is analyzed exactly as a sample including exposure to all glassware, equipment, and reagents that are used with samples. The LFM is used to determine if sample matrix contributes to the bias of the analytical

results. The LFM is also known as a Matrix Spike. One matrix spike per 10 samples.

$$\% \text{ REC} = \frac{(R1 - S1) * 100}{TV}$$

where:

R1 = measured concentration in the spiked sample
S1 = measured concentration in the sample
TV= True Value concentration of analytes spiked in sample

4.4.1.2 The current %REC control limits for AVS and SEM are listed in the table below:

Analyte	% Recovery
AVS	
Sulfide (S^{-2})	50 – 150
SEM	
Cadmium (Cd)	75 – 125
Copper (Cu)	75 – 125
Lead (Pb)	75 – 125
Mercury (Hg)	75 – 125
Nickel (Ni)	75 – 125
Zinc (Zn)	75 – 125

4.4.2 Corrective action

4.4.2.1 If a trend in out of control %REC 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 recovery. Generally, if recoveries are out of control and no analytes of interest are detected in any of the samples, no immediate action will be taken on that sample set. If integrity of reported sample values is in doubt, re-analysis may be called for. Corrective actions should be discussed with the Quality Control Officer.

4.4.2.2 If both the matrix spike and blank spike are out of control low and there was no recoveries in the sample(s), then the sample results may be considered false negatives and re-analysis may be required or spike recovery limits may need to be re-evaluated.

4.5 Laboratory Fortified Blank (LFB)

4.5.1 Criteria

4.5.1.1 A method 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. The LFB is analyzed exactly as a sample including exposure to all glassware, equipment, and reagents that are used with samples. The LFB is used to determine if method analytes are recovering within the acceptable limits. The LFB is also known as a Blank Spike. One blank spike per 20 samples.

$$\% \text{ REC} = \frac{R2 * 100}{TV}$$

where:

R2 = measured concentration in the spiked blank
TV= True Value concentration of analytes spiked in blank

4.5.1.2 The current %REC control limits for AVS and SEM are listed in the table below:

Analyte	% Recovery
AVS	
Sulfide (S^{-2})	85 – 105
SEM	
Cadmium (Cd)	75 – 125
Copper (Cu)	75 – 125
Lead (Pb)	75 – 125
Mercury (Hg)	75 – 125
Nickel (Ni)	75 – 125
Zinc (Zn)	75 – 125

4.5.2 Corrective action

4.5.2.1 If a trend in out of control %REC 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 recovery. Generally, if recoveries are out of control and no analytes of interest are detected in any of the samples, no immediate action will be taken on that sample set. If integrity of reported sample values is in doubt, re-analysis may be

called for. Corrective actions should be discussed with the Quality Control Officer.

4.5.2.2 If both the matrix spike and blank spike are out of control low and there was no recoveries in the sample(s), then the sample results may be considered false negatives and re-analysis may be required or spike recovery limits may need to be re-evaluated.

4.6 Sample Duplicate

4.6.1 Criteria

4.6.1.1 At least one duplicate sample per 20 samples per matrix is required. RPD values are calculated as follows:

$$RPD = \frac{|S1 - S2| * 100}{(S1 + S2)/2}$$

where:
S1 = measured concentration in the initial analysis
S2 = measured concentration in the duplicate analysis

4.6.1.2 The current % RPD control limits for AVS/SEM are listed in the table below:

Analyte	%RPD
AVS	
Sulfide (S^{-2})	30
SEM	
Cadmium (Cd)	20
Copper (Cu)	20
Lead (Pb)	20
Mercury (Hg)	20
Nickel (Ni)	20
Zinc (Zn)	20

4.6.2 Corrective action

4.6.2.1 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. Generally, if recoveries are out of control and no analytes of interest are detected in any of the samples, no immediate action will be taken on

that sample set. If integrity of reported sample values is in doubt, re-analysis may be called for. Corrective actions should be discussed with the Quality Control Officer.

5. Operation Procedures

5.1 Sample Preparation

5.1.1 Assemble glassware as illustrated in Appendix II.

5.1.2 Add a measured amount, approximately 10.0 gm, of wet sample to the reaction flask (first flask), magnetic stirring rod, and 100 mL of DIW. If the AVS concentration is expected to be high, less sample maybe used. It is not recommended to use less than 2.0 gm, due to sulfide oxidation and sample heterogeneity.

5.1.3 Add 25 mL of the 6M hydrochloric acid solution to the separatory funnel.

5.1.4 Fill the second flask with 175 – 200 mL of potassium acid phthalate solution. This solution is to buffer the hydrochloric acid from the reaction flask, as it would interact with the silver nitrate solution.

5.1.5 Fill the third and fourth flask with 175 – 200 mL of the silver nitrate solution.

5.1.6 Make sure that all of the rubber stoppers are on tight and start the magnetic stirrer.

5.2 Sample Analysis (AVS)

5.2.1 Purge the system for 10 minutes with 100 cc/min of nitrogen gas. Reduce the flow to 40 cc/min and continue purging for 10 minutes.

5.2.2 Begin to add the hydrochloric acid to the sample in the reaction flask. Do not drain all of the acid into the reaction flask, leave approximately 2 mL in the separatory funnel.

5.2.3 Reduce the flow of nitrogen to 20 cc/min and continue purging for 1 hour.

5.3 Sulfide Analysis

5.3.1 After the sample has been purged for one hour, check the fourth flask for precipitate. If there is precipitate in the fourth flask then the sample will need to be re-analyzed with less sample weight. If there is no precipitate in the fourth flask, then continue.

5.3.2 Filter the solutions from the third and fourth flask on to a preweighted 1.2 micron filter. Dry at 105°C, cool in a desiccators, and weigh.

5.3.4 Calculate the amount of silver sulfide (in gm) as the difference between the weight of dried silver sulfide with filter minus the weight of the preweighed filter.

5.4 AVS Calculations

5.4.1 Calculate the amount of sulfide in the sample (µmoles):

$$\text{Sulfide in Wet Sediment, } \mu\text{moles} = \frac{\text{Silver sulfide (gm)}}{247.8} * 10^6$$

5.4.2 Calculate the sulfide (AVS) concentration per gram of sample (µmoles/gm):

$$\text{AVS, } \mu\text{moles/gm DB} = \frac{S}{T * W}$$

Where,

S = Sulfide in Wet Sediment, µmoles
T = Total Solids (ratio of dry weight to wet weight)
W = Sample Weight (gm) as received

5.5 Simultaneously Extracted Metals Analysis (SEM)

5.5.1 After the generation of sulfide has been completed, filter the sediment suspension remaining in the reaction flask through a fast fiberglass filter (Whatman GF/D).

5.5.2 Transfer the solution to a 250 mL volumetric flask. Rinse the filtering flask 3 times with DIW and add the rinses to the volumetric flask. Dilute to volume with DIW.

5.5.3 Metals (cadmium, copper, nickel, lead, and zinc) will be analyzed by ICP as outlined in Laucks' SOP LTL-7105.

5.5.4 Mercury will be analyzed as outlined in Laucks' SOP LTL-7501.

5.6 SEM Calculations

5.6.1 Below are the calculations for the SEM portion of the analysis. "Metal" indicates only one of the target metals of interest and all of the metals of interest will need to be calculated.

5.6.2 Convert metal results from ug/L to µmoles/L:

$$X, \mu moles/L = \frac{U}{Y}$$

Where,

X = Metal result in µmoles/L
U = Metal result in ug/L
Y = Molecular weight of metal

5.6.3 Convert metal results from µmoles/L to µmoles:

$$Z, \mu moles = \frac{X}{V}$$

Where,

Z = Metal in Wet Sediment, µmoles
X = Metal result in µmoles/L
V = Final Volume in L

5.6.4 Convert metal results from µmoles to µmoles/gm DB and report value:

$$M, \mu moles/gm\ DB = \frac{Z}{T * W}$$

Where,

M = Metal in Dry Sediment, µmoles/gm
Z = Metal in Wet Sediment, µmoles
T = Total Solids (ratio of dry weight to wet weight)
W = Sample Weight as received

5.7 SEM to AVS Calculation

5.7.1 Calculate the ratio of SEM to AVS

$$SEM/AVS, \mu moles/gm\ DB = \frac{A}{B}$$

Where,

A = Is the sum of all the metals (cadmium, copper, lead, mercury, nickel, and zinc) results, µmoles/gm DB
B = The AVS result is determined in Section 5.4.2, µmoles/gm DB

5.7.2 A SEM:AVS ratio greater than one suggests that toxicity is possible while a ratio less than one suggests that the metals in the sediment are not toxic.

5.8 Bench Sheets

5.8.1 A copy of the bench sheets can be found Appendix III

5.9 Quality Control Reports

5.9.1 All results for quality control tests are entered into the lab database. If the data is for a data packet, copies of the printouts will be included in the data packet. Otherwise, their entry ID will be noted on the QC_DB Report Form. The routine minimum is a duplicate, if there is sufficient sample.

6. References

Draft Analytical Method for the Determination of Acid Volatile Sulfides in Sediment, EPA 821/R-91-100, December 1991

H.E. Allen and F. Gongmin, University of Delaware, Newark, Delaware

W. Boothman, Environmental Research Laboratory – Narragansett, U.S. Environmental Protection Agency, Narragansett, Rhode Island

D. Ditoro and J.D. Mahony, Bronx, New York

APPENDIX I

QC Summary Table

Laucks Testing Laboratories

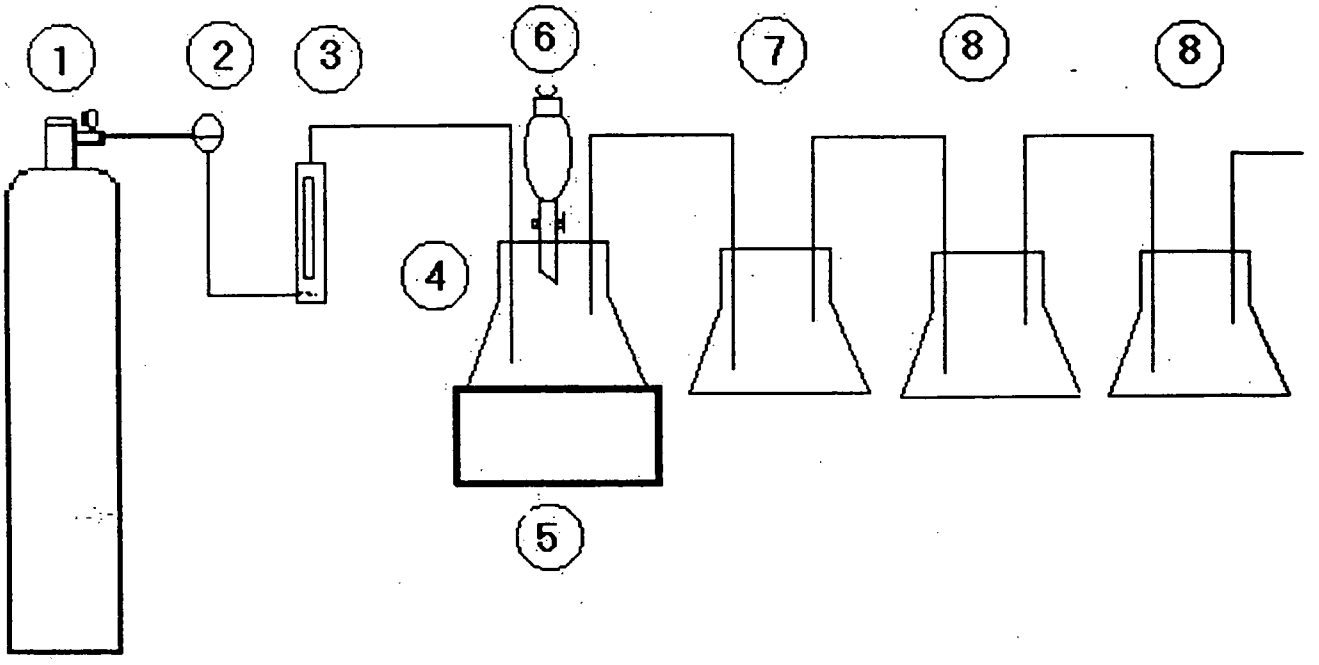
AVS/SEM QC Requirements and Corrective Actions

QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
Method Blank for AVS	<MDL	<½ of the Reporting Limit	1 per 20 sample matrices	Re-analyze or use narrative comments	Corrective Action Form and/or narrate
Method Blank for SEM	<MDL	<½ of the Reporting Limit	1 per 20 sample matrices	Re-analyze or use narrative comments	Corrective Action Form and/or narrate
Blank Spike for AVS % REC	85 – 105 %	85 – 105 %	1 per 20 sample matrices	Re-analyze or use narrative comments	Corrective Action Form and/or narrate
Blank Spike for SEM % REC	None	75 – 125 %	1 per 20 sample matrices	Re-analyze or use narrative comments	Corrective Action Form and/or narrate
MS for AVS % REC	None	50 – 150 %	1 per 10 sample matrices	Re-analyze or use narrative comments	Corrective Action Form and/or narrate
MS for SEM % REC	None	75 – 125 %	1 per 10 sample matrices	Re-analyze or use narrative comments	Corrective Action Form and/or narrate
Duplicate Analysis, for AVS % RPD	None	± 30	1 per 10 sample matrices	Re-analyze or use narrative comments	Corrective Action Form and/or narrate
Duplicate Analysis, for SEM % RPD	None	± 20	1 per 10 sample matrices	Re-analyze or use narrative comments	Corrective Action Form and/or narrate

APPENDIX II

Glassware Assembly

Glassware Assemblely



1 – Nitrogen Gas, 99.999%
2 – Regulator
3 – Flow Meter/Controller
4 – Reaction Flask
5 – Magnetic stirrer
6 – Separatory Funnel
7 – Potassium Acid Phthalate Solution Flask
8 – Silver Nitrate Solution Flasks

APPENDIX III

Bench Sheets

Laucks Testing Laboratories, Inc.

AVS Analysis Bench Sheet

Item	Date	Analyst	Checker
Prep #1	/ /		
Analysis	/ /		

Sulfide Standardization

Solution ID	Sulfide Spiked (L)	0.025 N Iodine (mL)	0.025N $Na_2S_2O_5$ (mL)	Sulfide Conc. (mg/L)	Average Sulfide Conc. (mg/L)
P. Blank	0.	10.			
aa					
bb					

AVS Bench sheet

Sample ID	Container ID	Sample Weight (gm)	Tare (gm)	Silver Sulfide + Tare (gm)	Silver Sulfide (gm)	Sulfide in Wet Sediment (µmoles)	AVS Result (µmoles/gm DB)

$$S, \mu mole = \frac{g}{247.8} * 10^6$$

Sulfide conc., mg/L = {[(a)(b) - (c)(d)] x 16.03} - e / f

$$AVS, \mu moles/gm\ DB = \frac{S}{T * W}$$

a = Normality of Iodine
b = Iodine (mL)
c = Normality of Sodium Thiosulfate
d = Sodium Thiosulfate (mL)
e = P. Blank Correction, mg = [(a)(b) - (c)(d)] x 16.03
f = Spiked Sulfide (L)

g = Silver Sulfide (gm)
S = Sulfide in Wet Sediment, µmole
T = Total Solids
W = Sample Weight (gm)

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

Method #: LTL-7010

Title: **Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by ICP Spectroscopy by SW846 Method 3010A**

Revision history:

Number	Date
1.	12/14/94
2.	06/03/96
3	2/1/01

Revised by: Stan Dittrick — Date: 2/1/01
Stan Dittrick, Chemist

Reviewed by: Paul Swift — Date: 02/01/01
Paul Swift, Inorganics Manager

Approved by: Harry Romberg — Date: 2-2-01
Harry Romberg, QA Officer

Approved by: Kathy Kreps — Date: 2-2-01
Kathy Kreps, Laboratory Director

Controlled Document
No. 20 Assigned to: Tetra

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1. Introduction and Scope

1.1 This digestion procedure is used for the preparation of aqueous samples, TCLP and mobility-procedure extracts, and wastes that contain suspended solids for analysis by inductively coupled argon plasma spectroscopy (ICP). The procedure is used to determine total metals.

1.2 Samples prepared by Method 3010A may be analyzed by ICP for the following:

Aluminum	Calcium	Magnesium	*Silver
*Antimony	Chromium	Manganese	Sodium
Arsenic	Cobalt	Molybdenum	Thallium
Barium	Copper	Nickel	*Tin
Beryllium	Iron	Potassium	Vanadium
Cadmium	Lead	Selenium	Zinc

* Although antimony, silver and tin are not listed in the original SW846 document as analytes that may be analyzed from samples prepared by Method 3010A, Laucks has demonstrated adequate recovery for these analytes from this digestate.

1.3 This digestion procedure is not suitable for samples which will be analyzed by ICP-MS because hydrochloric acid can cause interference. Consult Method LTL-7008 for samples requiring ICP-MS analysis.

2. Summary of Method

2.1 A mixture of nitric acid and the material to be analyzed is refluxed in a covered beaker. This step is repeated with additional portions of nitric acid until the digestate is light in color or until its color has stabilized. After the digestate has been brought to a low volume, it is refluxed with hydrochloric acid and brought up to volume. If a sample goes to dryness, it must be discarded and prepared again.

3. Safety Procedures

3.1 These procedures involve the use of strong and/or hot acid solutions. The analyst must wear eye protection, a lab coat, and gloves to protect against burns.

3.2 These procedures involve hot plates or hot blocks which may present the danger of burns from heated surfaces and electrical hazards. The analyst must take appropriate caution to avoid injury from these sources.

3.3 Samples and spiking solutions may contain high levels of toxic metals and other unknown constituents. The analyst must take every precaution to avoid contact with these potentially hazardous materials and should wash hands thoroughly before eating or going home for the day.

4. Equipment

- Plastic digestate bottles, precleaned
- 100-mL graduated cylinder, acid-washed
- Eppendorf or other micropipets
- Block digester at 90-95° C.
- Glass funnels, acid-washed
- Filter paper, Whatman No. 41 or equivalent
- Thermometer

Note: All glassware used for this digestion must be prepared by the method stated in Inorganics Glass Cleaning Procedures, LTL-7003.

5. Reagents

5.1 Reagent Water. Reagent water will be interference-free. All references to water in the method refer to reagent water unless otherwise specified.

5.2 Nitric acid (concentrated), HNO_3, Trace Metals analyzed

5.3 Hydrochloric acid (concentrated), HCl, Trace Metals analyzed.

The method blank, prepared along with the samples, is used as a contamination check. Since the holding time for all analytes associated with this method have a holding time of 6 months, repreparation would not be an issue if contamination was traced to a specific reagent.

6. Acid Digestion Procedure

See Appendix A for digestion log.
See Appendix B for flowchart.
See Appendix C for Quality Control solutions.
See Appendix D for Procedure Checklist
See Appendix E for Page from Standards Logbook

6.1 Transfer a 100-mL representative aliquot of the well-mixed sample to a digestate bottle and add 3 mL of concentrated HNO_3. If only one graduated cylinder is used for all

samples, the preparation blank is to be the last sample dispensed to assure the absence of sample carry-over. Place the digestate bottle on the block digester and carefully evaporate to 5 mL, making certain that the sample does not boil and that no portion of the bottom of the bottle is allowed to go dry. Make several holes in the top of one digestate bottle and suspend a thermometer in the lid. Place this digestate bottle full of water on the block digester. Make sure the thermometer does not touch the bottom. Record the temperature achieved during the digest on the digest log. Cool the digestate and add another 3-mL aliquot of HNO_3. Return the digestate bottle to the block digester and adjust the temperature, if necessary, so that a gentle reflux action occurs.

6.2 Continue heating, adding additional HNO_3 as necessary until the digestion is complete, indicated when the digestate is light in color or does not change in appearance upon additional heating. Evaporate the samples to 3 mL, not allowing any portion of the bottom of the beaker to go dry. After allowing the beakers to cool, add 5 mL of concentrated HCl and 5 mL reagent water. Reflux the samples for an additional 15 minutes to dissolve any precipitate or residue resulting from evaporation.

Note: If a sample is allowed to go to dryness at any stage of the digestion procedure, low recoveries will result. The sample must be discarded and prepared again.

6.3 After cooling the digestate bottles, add 5mL concentrated HCl to obtain a final acid concentration of approximately 10%. Bring the digestate to a final volume of 100 mL. If silicates or other insoluble material that could clog the nebulizer are present in the samples, the samples should be allowed to settle overnight prior to analysis. Filtration should be performed only if there is concern that the insoluble material will not settle out of solution. Place a funnel over the digestate funnel and use a Whatman no. 41 filter. Pour the sample in the filter. Acid wash filter apparatus to avoid sample contamination. Dilute the samples to a final volume of 100 mL. Samples should be stored in digestate bottles.

6.4 The prepared samples are then transferred to the metals analysis department. The digestion log is to reflect the time at the start and finish of the digest. In order to maintain strict chain of custody, the time and date when the digestates are relinquished to the analysis department, as well as the initials of the analyst accepting the digest, are recorded on the digestion log.

7. Quality Control

7.1 In each batch or SDG consisting of no more than 20 samples, a preparation blank is created. This consists of 100 mL of reagent water and the appropriate amounts of nitric and hydrochloric acid, digested in exactly the same way as the samples. If only one graduated cylinder is used for all samples, the preparation blank is to be the last sample dispensed to assure the absence of sample carry-over. The blank should be labeled on

the digestate bottle in the following way: B, date, instrument, S or W (for soil or water) and the sequence number of the digestion. Example: B111794ICPW01.

7.2 Spiked samples should be employed to determine accuracy. In each batch or SDG consisting of no more than 20 samples, either matrix spike / sample duplicate (MS/Dup) or matrix spike / matrix spike duplicate (MS/MSD) samples will be prepared. For SW846-specified quality control measures, MS/Dup samples will be prepared in the following way. Dispense one sample in triplicate. Two will be digested exactly as any other sample. The third must be spiked with the appropriate spike solutions determined by the analyst, and then treated as any other sample. **Spike additions must be witnessed by a second individual and initialed on the bottom of the digest log.** All glassware and digestate bottles must be marked appropriately. If MS/MSD samples are required instead of the SW846-specified MS/Dup, both the second and third aliquots must be spiked and all glassware and digestate bottles marked appropriately.

7.3 Determine the analytes required for analysis by consulting sample work order information. Each spiking solution is given its own unique number according to the page and line of the standards logbook which it is entered into. This number and the volume dispensed must be clearly recorded on the digestion log. A sample page from the standards logbook is included in Appendix E.

7.4 In each batch or SDG consisting of no more than 20 samples, either a Blank Spike (BLK SPK) or a Laboratory Control Sample (ICP LCSW) must be digested in exactly the same manner as a sample. A Blank Spike consists of 100 mL of reagent water spiked at the levels determined by the analyst as outlined in Section 7.3.

8. References

8.1 USEPA, Test Methods for Evaluating Solid Waste Physical/Chemical Methods, USEPA SW846, most recent version, Method 3010A.

Appendix A, Sample LTL-7010 Digestion Logs

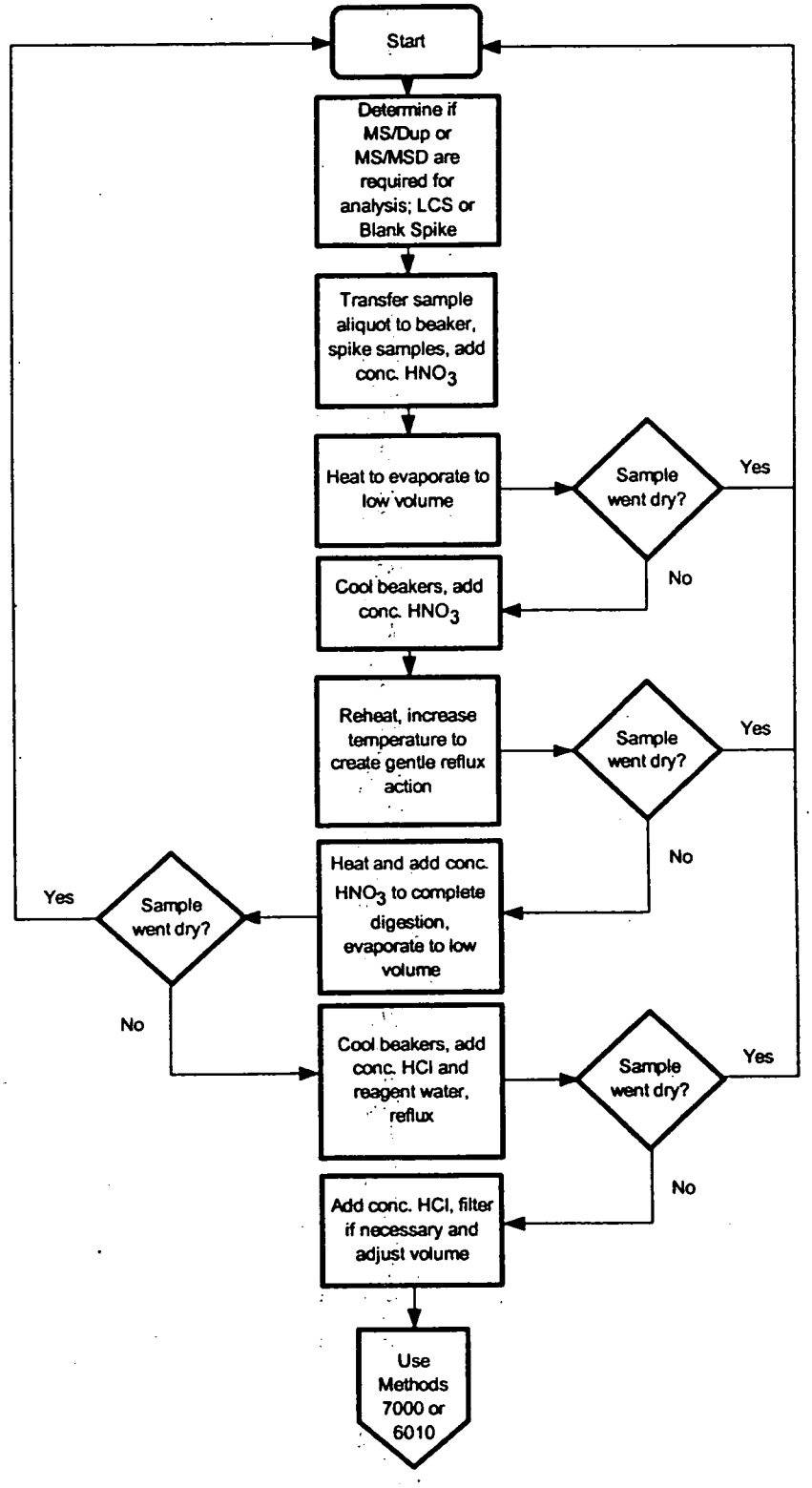
LAUCKS TESTING LABORATORIES, INC.		ICP DIGESTION LOG	Place a √ in the box next to the method performed.			
	Digest start : date/time	Digest finish : date/time	SW-846 3005A		ILM04.0-water	
SDG #: B0E749	01-17-01	1-17-01	SW-846 3010A	✓	ILM04.0-soil	
Analyst: DLS	9:20	15:10	SW-846 3050A		SW-846 3050B	

	Sample ID	Sample Size (g:mL)	Final Volume (mL)	Color Bef	Color Aft	Clarity Bef	Clarity Aft	Text	Art	Comments	Bottle #
01	B0170121pw02	100	100	11	11	1	1				N/A
02	ICP LCS.01			11						ME 13-11-8	1
03	010185-01			11							22
04	010185-02			9							23
05	-03			11							24
06	-04			1							25
07	-04D										25
☆ 08	-04S										25
09	-05										26
10	-06			1							27
11	-07	1	1	9	1	1	1				28
12											
13											
14											
15										01-17-01 DLS	
16											
17											
18											
19											
20											
21											
22											
23											
24											

Chain of Custody	Digest Relinquished Date / Time : Analyst	Digest Accepted Analyst	Digest Disposed Date	Hot Plate Temperature, °C
	1-17-01 15:15 DLS	R 01/17/01		92 °C
Reagents Lot Number	HNO_3 40161	HCl 40125	H_2O_2	

Color 1=Red, 2=Blue, 3=Yellow, 4=Green, 5=Orange, 6=Violet, 7=White, 8=Brown, 9=Grey, 10=Black, 11=Colorless
Clarity 1=Clear, 2=Cloudy, 3=Opaque
P:\metals\bnchshee\icpdig.doc
Texture F=Fine (powdery), M=Medium (sandy), C=Coarse (rocky) Artifacts: If "Yes", give description in the comments field.

Appendix B, Flowchart for LTL-7010


Start
Determine if MS/Dup or MS/MSD are required for analysis; LCS or Blank Spike
Transfer sample aliquot to beaker, spike samples, add conc. HNO_3
Heat to evaporate to low volume
Sample went dry?
Yes
No
Cool beakers, add conc. HNO_3
Reheat, increase temperature to create gentle reflux action
Sample went dry?
Yes
No
Heat and add conc. HNO_3 to complete digestion, evaporate to low volume
Sample went dry?
Yes
No
Cool beakers, add conc. HCl and reagent water, reflux
Sample went dry?
Yes
No
Add conc. HCl, filter if necessary and adjust volume
Use Methods 7000 or 6010

Appendix C, Quality Control Solutions

ICP LCSW

The LCSW for the ICP digest was made by diluting 10 mLs of CLP-SPIKE and 50 mLs of LTL-6 solutions, and 2 mLs of conc. HNO_3 to 1000 mLs with type II water. A 100 mL aliquot of this solution was then digested.

ICP Analytes

Analyte	Concentration in Digest (ppb)	Analyte	Concentration in Digest (ppb)
Al	20000	Pb	500
Ba	20000	Mg	500000
Be	500	Mn	1500
Cd	500	Ni	4000
Ca	500000	K	500000
Cr	1000	Ag	1000
Co	5000	Na	500000
Cu	2500	V	5000
Fe	10000	Zn	2000
Sb	6000		

Other Analytes

Analyte	Concentration in Digest (ppb)	Analyte	Concentration in Digest (ppb)
As	1000	Tl	1000
Se	500		

Tables based on a final volume of 100 mL.

ICP Spikes

- The CLP spike solution for ICP digest was made by diluting 10 mLs of CLPP-SPK-1™, 10 mLs of CLPP-SPK-2™, and 10 mLs of CLPP-SPK-3™ to 100 mLs with Type II water.

- Add 1000 µLs of CLP spike solution to water samples and 2000 µLs of CLP spike solution to soil samples prior to digestion.

ICP Analytes

Analyte	Concentration in Digest (ppb)	Analyte	Concentration in Digest (ppb)
Ag	50	Fe	1000
Al	2000	Mn	500
As	2000	Ni	500
Ba	2000	Pb	500
Be	50	Se	2000
Cd	50	Sb	500
Co	500	Tl	2000
Cr	200	V	500
Cu	250	Zn	500

Table based on a final volume of 100 mL for water digests, and 200 mL for soil digests.

ICP
CLP-LOW SPIKES

- Add the analytes from the two tables below into separate 100 mL volumetric flasks which contain ~50 mL of Type II water and 5 mL of HNO_3.

ICP-1

Analyte	Volume	Stock Concentration	Spike Concentration
Sb	500 µL	1000 ppm	5 ppm
Al	5000 µL	1000 ppm	50 ppm
Ba	2000 µL	1000 ppm	20 ppm
Be	100 µL	1000 ppm	1 ppm
Cr	500 µL	1000 ppm	5 ppm
Co	1000 µL	1000 ppm	10 ppm
Cu	500 µL	1000 ppm	5 ppm
Fe	2500 µL	1000 ppm	25 ppm
Mn	500 µL	1000 ppm	5 ppm
Ni	1000 µL	1000 ppm	10 ppm
V	1000 µL	1000 ppm	10 ppm
Zn	1000 µL	1000 ppm	10 ppm

ICP-2

Analyte	Volume	Stock Concentration	Spike Concentration
Ag	500 µL	1000 ppm	5 ppm

- Add 1000 µL of ICP-1 and 1000 µL of ICP-2 spike solutions to water samples prior to digestion. For soil samples, add 2000 µL of each spike solution prior to digestion. The final digest will contain:

Analyte	Concentration in Digest	Analyte	Concentration in Digest
Sb	50 ppb	Al	500 ppb
Ba	200 ppb	Be	10 ppb
Cr	50 ppb	Co	100 ppb
Cu	50 ppb	Fe	250 ppb
Mn	50 ppb	Ni	100 ppb
V	100 ppb	Zn	100 ppb
Ag	50 ppb		

Table based on final volume of 100 mL for water digests, and 200 mL for soil digests:

PDCA
SPIKES and LCSW

The LCSW for the PDCA extraction was make by adding 10 mL SPEX ICV-1™ solution to 100 mL of Type II water prior to extraction. The spike was made by adding 1000 µL of CLP SPK solution to a 100 mL aliquot of the sample prior to extraction.

ICP Analytes

Analyte	Concentration in Digest	Analyte	Concentration in Digest
Cd	50 ppb	Mn	500 ppb
Co	500 ppb	Ni	500 ppb
Cu	250 ppb	Ag	50 ppb
Fe	1000 ppb	V	500 ppb
Zn	500 ppb		

Graphite Furnace Analytes

Analyte	Concentration in Digest	Analyte	Concentration in Digest
Pb	500 ppb	Tl	2000 ppb
Se	2000 ppb		

Tables based on a final volume of 100 mL.

Appendix D, Procedure Checklist

SW846-3010A AQUEOUS DIGESTIONS (LTL-7010)

SWDIW*
ICP

QC: Blk, LCSW, Dup/Spk

- [ ] 100mL sample
- [ ] Add spikes
- [ ] 3mL HNO_3
- [ ] Reduce sample to 5 mL
- [ ] Cool 10 min
- [ ] Add 3 mL HNO_3
- [ ] Reduce sample to 3mL
- [ ] Cool 10 min
- [ ] Add 5 mL DIW and 5 mL HCl
- [ ] Heat 15 min
- [ ] Cool 10 min
- [ ] Add 5 mL HCl
- [ ] Final Volume 100mL

SWDFW
ICP-MS

QC: Blk, LCSW, Dup/Spk

- [ ] 100 mL sample
- [ ] Add spikes
- [ ] 0.5mL HNO_3
- [ ] 2 mL H_2O_2
- [ ] Reduce sample to 25-50mL
- [ ] Final Volume 100mL

* For SWDIW: If samples look clear use method SW846-3005A (LX_WM6).
For TCLP or dirty samples, use method SW846-3010A(SWDIW).

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Appendix E, Page from Standards Logbook

LAUCKS TESTING LABORATORIES, INC.
STANDARDS LOGBOOK

#	ANALYTE	ID or STOCK No.	STOCK CONC.	VOL/WT TAKEN	FINAL VOL.	FINAL CONC.	SOLVENT	PREP. DATE	INIT.	EXP. DATE	QC'D (Initials)
1	Hg Std	ME 12-98-2 11/1/01	998 µg/mL	100 µL	100 mL	1.0 ppm	0.15% HNO_3	11/17/00	EC	[illegible]	
2	Hg Std	ME 12-98-2 11/1/01	998 µg/mL	100 µL	100 mL	1.0 ppm	0.15% HNO_3	11/20/00	EC	11/21/00	
3	ICP MS LCSW	ME 12-98-05 11-1-01	1000 mL ~~500 mL 11/21/00~~	500 mL	1000 mL	various ~~various~~	2 mL HNO_3	11/21/00	DLH	11/1/2001	
4	Hg Std	ME 12-98-2 11/01/01	998 µg/mL	100 µL	100 mL	1.0 ppm	0.15% HNO_3	11/21/00	EC	11/22/00	
5	ICP LCSW	ME 12-99-05 07/01/01	LTL-6 various	100 mL	2000 mL	various	2% HNO_3	11/22/00	DLH	07/01/01	
↓	↓	ME 13-4-3 9/01/01	CLP spk various	20 mL	↓	↓	↓	↓	↓	09/01/01	
6	Hg Std	ME 12-98-2 11/1/01	998 µg/mL	100 µL	100 mL	1.0 ppm	0.15% HNO_3	11/22/00	EC	11/23/00	
7	Hg Std	ME 12-98-2 11/1/01	998 µg/mL	100 µL	100 mL	1.0 ppm	0.15% HNO_3	11/27/00	EC	11/28/00	
8	CCV	QC Std 7 6/30/01	various MW 12-57-10	2 ml	200 ml	various	5% HCl 1% HNO_3	11/27/00		6/30/01	
		QC Std 21 6/30/01	various	2 ml							
		SM 9/1/01	1000 µg/mL ME 12-79-1	200 µL							
		Stock std -	12-1/01 ME 12-91-02	10 ml							

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-7501

Title: **Operation of the PE FIMS 400 for the Analysis of Hg for EPA Methods SW-846 7470/7471, 245.1/245.5, and CLP ILM04.1**

Revision history:

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1. Introduction and Scope

1.1 Method Description:

1.1.1 This SOP covers the cold vapor analysis of Hg using the Perkin-Elmer Flow Injection Mercury System, Model 400 (FIMS 400). Sample handling and preparation are as required by SW-846 methods 7470/7471 and 245.1/245.5. This SOP is also valid for the preparation and analysis of samples under CLP protocol when used in conjunction with the SOW ILM04.1. Where the requirements of these procedures differ, the more stringent requirements are used. The requirement of analyzing soil samples in triplicate under 7471 is not used except upon request.

1.1.2 After preparation and digestion to convert Hg to its ionic form, 0.5 mL of sample is introduced into a stream of carrier solution (3% HCl), mixed with a $SnCl_2$ suspension to reduce the Hg ion to its metallic form, which is then carried into an absorption tube through which passes light at a wavelength of 253.7 nm. The absorption is then measured.

1.1.3 This method is restricted to use by, or under the supervision of analysts experienced in the technique described. Each analyst performing this method must have demonstrated the ability to perform the described analysis.

1.2 Sample Collection, Sample Storage, Holding Times

1.2.1 Samples are stored either in glass or plastic. The holding time is 28 days from collection. Soil samples are stored at 4° ±2° C. Water samples are stored at room temperature. Water samples are preserved by the addition of HNO_3 to a pH <2.

1.3 Interferences

1.3.1 This section covers interferences which may potentially occur with the FIMS associated with sample or standard preparation or gas or liquid flow through the system.

1.3.2 Foaming

1.3.2.1 If excess foaming results in liquid being transported into the quartz cell, the reagent stream should be stopped immediately, and the tubing and cell assemblies should be disassembled and cleaned.

1.3.3 Precipitates

1.3.3.1 All solutions used with the FIMS (samples, carrier solutions, and reducing agents) must be free of solid particles since they are transported through the narrow tubing and valve openings. In addition, the formation of precipitates during the course of a reaction must be avoided. When such a case occurs, an appropriate digestion or separation method should be used to remove the offending component.

1.3.4 Contamination

1.3.4.1 The detection limits obtainable using the FIAS-System are very often a function of the degree of contamination in the samples and the reagents rather than of instrument capabilities. Contamination is the main source of error when working at the nanogram levels typical for FIMS analyses. Careful operation of the instrument, selection of proper sample preparation techniques, and good laboratory cleanliness practices are the most important prerequisites for minimizing contamination.

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.

1.4.2 **LFB** - Laboratory Fortified Blank - A sample of DIW to which a known amount of Hg is added.

1.4.3 **CRA** – a sample of DIW to which a known amount of Hg is added. This is a low concentration to verify the curve is valid near the reporting limit of 0.2 µg/L.

1.4.4 **CCB** - Continuing Calibration Blank - This is the same acronym used in the CLP program. This is a blank which is analyzed immediately after the CCV (almost always after every 10 samples and at the end of the analytical run) during the analysis sequence to determine whether the instrument or system has maintained a stable baseline.

1.4.5 **CCV** - Continuing calibration verification. - This is the same acronym used in the CLP program. This is a standard analyzed at some prescribed frequency (almost always after every 10 samples and at the end of the analytical run) during the analysis sequence to determine whether the instrument or system has remained in calibration.

1.4.6 **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 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.

1.4.7 **Corr Coef, CC** - Correlation coefficient - A measure of the "goodness of fit" of a set of data to a linear regression model. The closer the value is to 1, the higher the degree of confidence in the correlation

1.4.8 **DIW** - Deionized water - Lab reagent water. This water should be free of virtually all analytes.

1.4.9 **ICB** - Initial calibration blank - This term is borrowed from CLP. An instrument blank is made up in the same way as calibration standards, without target analytes.

1.4.10 **ICV** - Initial calibration verification - is a standard which is analyzed at the start of each analytical run that is compared to the initial multi-point calibration to determine whether the instrument calibration is accurate. This verification standard is from a source different from that used to make the calibration standards

1.4.11 **IDL** - Instrument detection limit. The lowest concentration of a target analyte that will yield a signal:noise ratio of least 3x. Determined quarterly using blanks to which a known quantity of standard has been added. The IDL is determined by analyzing 7 replicates spiked at 2-5 times the expected IDL on three non-consecutive days. The sum of the standard deviations of the three runs is the IDL.

1.4.12 **MDL** - Method detection limit - The lowest concentration 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 annually.

1.4.13 **MDL** standard - Method detection limit standard - A standard prepared so that the concentration of Hg is 1-5 times the anticipated MDL

1.4.14 **LCS** - Laboratory Control Sample - A sample containing a known quantity of Hg used to verify digestion and analysis. LCSW indicates a water sample. It is used interchangeably with ICV. LCSS indicates a soil sample.

1.4.15 **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. A measure of the similarity of the values one to another.

1.4.16 **PBW** - A blank carried through the sample preparation and digest procedures.

2. Equipment, Standards and Reagents

2.1 Equipment

2.1.1 Equivalent equipment may be used where appropriate.

FIMS 400 automatic Hg analyzer
Perkin Elmer AS-90 autosampler
Epson LQ300 dot-matrix printer
Hot water bath
BOD bottles
Analytical balance
Micropipettes: 20, 50, 100, 200, 500 and 1000 µl
50 mL and 15 mL plastic centrifuge tubes

2.2 Standards

2.2.1 All standards must be prepared in 0.15% HNO_3.

2.2.2 **1000 ppm Hg stock solution**: Vendor supplied. Currently purchased from Inorganic Ventures.

2.2.3 **Working Hg solution**: Dilute 100 µl of 1000 ppm Hg stock solution to 100 mL in DIW to which 0.15 mL HNO_3 has been added. The identification number of the standard solution used and the dilution must be entered in the standards logbook. This solution must be prepared daily. The identification number of the working standard must also be recorded on the bench sheet (digestion log-Appendix II).

2.2.4 **0.2 µg/L standard** - Place 100 mL DIW in a BOD bottle. Add 20 µl working Hg solution.

2.2.5 **0.5 µg/L standard** - Place 100 mL DIW in a BOD bottle. Add 50 µl working Hg solution.

2.2.6 **1.0 µg/L standard** - Place 100 mL DIW in a BOD bottle. Add 100µl working Hg solution.

2.2.7 **2.0 µg/L standard** - Place 100 mL DIW in a BOD bottle. Add 200 µl working Hg solution.

2.2.8 **5.0 µg/L standard** - Place 100 mL DIW in a BOD bottle. Add 500 µl working Hg solution.

2.2.9 **10.0 µg/L standard** - Place 100 mL DIW in a BOD bottle. Add 1000 µl working Hg solution.

2.2.10 **100 ppm Hg stock solution**: Vendor supplied. Currently purchased from Spex Certiprep.

2.2.11 **ICV Standard** - Dilute 1000µl of 100 ppm Hg stock solution to 100 mL in DIW to which 0.15 mL HNO_3 has been added. The identification number of the standard solution used and the dilution must be entered in the standards logbook and the digestion log (Appendix II). This solution must be prepared monthly from an independent stock solution, ie a different vendor than the stock solution used to prepare the calibration and quality control samples.

2.2.12 **ICV solution** - Add 100 mls DIW to a BOD bottle. Add sufficient ICV solution to produce a concentration of 1.0 to 5.0 µg/L. Currently a concentration of 4.0 µg/L is in use.

2.2.13 **CCV/CCB/Blank Spike (Soils only)** - In setting up the run, use the 5.0 µg/L standard for the CCV and Blank Spike; for the CCB use the calibration blank.

2.2.14 **MS/MSD or MS/Duplicate** - Add 500 µl of the working Hg solution to the samples being spiked. When performing Hg under CLP protocols use 100 µl of the working Hg solution and perform MS/Duplicate.

2.2.15 **LCSS** - Laboratory control soil sample. Concentrations and limits are certified by the vendor.

2.3 **Reagents**:

2.3.1 DIW - deionized water free of impurities.

2.3.2 H_2SO_4 (sulfuric acid) - concentrated, reagent grade

2.3.3 HNO_3 (nitric acid) - concentrated, reagent grade

2.3.4 HCl (hydrochloric acid) - concentrated, reagent grade

2.3.5 Stannous chloride - Add 27.5 g. $SnCl_2 \cdot 2H_2O$ (stannous chloride dihydrate) to 2.5 L DIW to which has been added 75 mL concentrated HCl.

2.3.6 $KMnO_4$ (potassium permanganate) - Dissolve 100 g. $KMnO_4$, marked "suitable for Hg determination", in 2 L DIW. This is a saturated solution. Sufficient undissolved $KMnO_4$ should be allowed remaining in the bottom of the bottle to assure a saturated solution.

2.3.7 $K_2S_2O_8$ (potassium persulfate) - Dissolve 50 g. $K_2S_2O_8$, marked "suitable for Hg determination", in 1 L DIW. This is a saturated solution. Sufficient undissolved $K_2S_2O_8$ should remain in the bottom of the bottle to assure a saturated solution.

2.3.8 $NaCl/NH_2OH{\cdot}HCl$ (sodium chloride/hydroxylamine hydrochloride) - Dissolve 240 g NaCl (table salt is generally used) and 240 g $NaCl/NH_2OH{\cdot}HCl$ (reagent grade marked "suitable for Hg determination") in 2 L DIW. Contamination has been experienced with this solution. For this reason a 50% solution should be analyzed by the FIMS 400 whenever a new bottle is made up. If the absorbance (peak height) exceeds .004 the solution of $NaCl/NH_2OH{\cdot}HCl$ should be disposed and remade.

2.3.9 Carrier solution - The carrier is a 3% HCl solution.

3. Safety Precautions and Waste Disposal

3.1 Safety Precautions

3.1.1 All standards, samples and sample solutions should be handled as if they are 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 Because of the toxic nature of Hg vapor, inhalation or skin contact should be avoided.

3.1.6 The usual precautions should be taken in handling acids.

3.1.7 $SnCl_2$ is a skin and eye irritant; avoid contact.

3.1.8 The addition of hydroxylamine after digestion may release gas including chlorine. Avoid inhalation; use hood if necessary.

3.1.9 Waste disposal – See SOP LTL-2001 for general information on waste disposal. In addition, sample digestates are acidic in nature and must be neutralized prior to disposal.

4. Calibration and Quality Control

4.1 Method Detection Limit Study (MDL).

4.1.1 The estimated MDL for waters is currently 0.05 µg/L. The estimated MDL for soils is currently 0.04 mg/kg.

4.1.2 Prior to the analysis of any samples, it is necessary to establish method detection limits. This procedure is fully described in 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. MDL studies for Hg water samples and soil samples are performed annually.

4.2 Initial Multi-Point Calibration:

4.2.1 Concentrations:

Standard Name	Concentration
S0	0.0 µg/L
S0.2	0.2 µg/L
S0.5	0.5 µg/L
S1.0	1.0 µg/L
S2.0	2.0 µg/L
S5.0	5.0 µg/L
S10.	10.0 µg/L

Standards are prepared fresh daily from the working standard in 0.15% HNO_3. See section 2.2.2 through 2.2.8 for the preparation details.

4.2.2 The calibration blank, the ICV, the LCS, the Blank Spike, the ICB and all standards are digested along with the samples being analyzed.

4.3 Calibration Criteria

4.3.1 Calibration curve – "best fit" of points in calibration curve. Linear correlation coefficient (R) must be equal to or greater than 0.995.

4.3.2 ICV - This is run immediately following a successful curve. This is to verify from a source of mercury independent from the calibration source that the curve is valid. For CLP and EPA 245.1/245.5 analyses the recovery limits are 80-120 %, for SW-846 7470/7471 the limits are 90-110%. If recovery is outside of the control limits an immediate reanalysis is permitted. If still out of control the curve must be reanalyzed followed by another ICV otherwise continue with an ICB.

4.3.3 ICB – This is run immediately following a successful ICV. This is to verify that there is no contamination and that the curve is valid. Limitations presently in use are ±0.1 µg/L (1/2 of the reporting limit). If recovery is outside the limit an immediate reanalysis is permitted. If still out of control, a corrective action must follow and a reanalysis of the curve.

4.3.4 A PBW and an LFB are run immediately following the successful calibration. The limitations on the PBW are the same as the limitation on the ICB. The limitations on the LFB are as set forth in the laboratory QC database (80-120%).

4.3.5 If the above criteria are not met, recalibration must be performed.

4.4 Continuing Calibration:

4.4.1 A CCV followed immediately by a CCB must be run every 10 samples and after the last sample. The ICB, PBW and Blank Spike count as samples for this purpose.

4.4.2 Criteria - For CCV's the recovery limitations are 80% to 120%. For blanks the limitations are ±0.1 µg/L.

4.4.3 Corrective action - If a CCV or CCB is out of control, an immediate reanalysis is permitted. However if the reanalysis is out of control a reanalysis of all samples since the previous successful CCV and/or CCB must be performed.

4.5 Matrix Spike

4.5.1 A sample is chosen at random from the samples to be analyzed, and 500 µl of the working standard is added (100µl for CLP). The spike level is then 5.0 µg/L(1.0 µg/L for CLP). The analyst should attempt to avoid selecting samples which are identified by the client as blanks. As the purpose of the matrix spike is to test the system under "typical" conditions, the analyst may also avoid selecting the most difficult sample of the batch for spiking. It is not always required that a matrix spike analysis be performed with each preparation/analysis batch, however, the minimum frequency for MS analysis is 1 each per 20 samples per matrix. This will be best accomplished by running one with every batch for many analyses. 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:

$$\text{recovery,\%} = \frac{(SS - S)}{SA} * 100$$

where:
SS = concentration in spiked sample
S = native concentration in unspiked sample
SA = spiked added, the amount of spiking material actually added to the sample calculated on the sample basis

4.5.2 The recovery criteria are listed in the quality control database and will change from time to time. Current acceptable recovery limits are 85-116% for SW-7470. All other methods are 75-125%.

4.5.3 Corrective action

4.5.3.1 Samples with spike recoveries outside control limits will be reviewed for possible corrective action. Corrective action will first involve recalculation, followed by possible re-preparation, and/or reanalysis. This process should also look at the recovery of Hg from the LCS and/or blank spike analysis. In all cases a narrative explanation of the condition is required to detail the corrective actions taken.

4.6 Matrix Spike Duplicate

4.6.1 The compound recovery criteria are identical to those for the matrix spike sample. In addition, the matrix spike duplicate is used 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:

$$RPD = \frac{|S1 - S2|}{(S1 + S2)/2} * 100$$

where:
S1 = measured concentration for MS sample
S2 = measured concentration for MSD sample

4.6.2 RPD control limits are listed in the quality control database and will change from time to time. The currently acceptable RPD limit is 20%.

4.7 Sample Duplicate

4.7.1 Sample duplicates are required when CLP practices are employed, or when the method specifically calls for duplicates. At least one duplicate sample per 20 samples per matrix is required when matrix spikes are being performed.

$$RPD = \frac{|S1 - S2|}{(S1 + S2)/2} * 100$$

where:
S1 = measured concentration in the initial analysis
S2 = measured concentration in the duplicate analyses

4.7.2 The RPD control limits listed in the quality control database and will change from time to time.

4.7.3 Corrective action

4.7.3.1 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. Generally, if recoveries are in control and no analyte of interest was detected in any of the samples, no immediate action will be taken on that sample set. If integrity of reported sample values is in doubt, re-analysis may be called for. Corrective actions should be discussed with the Quality Assurance Officer.

5. Operation Procedures

5.1 Digestion Set-up - BOD bottles - Soil or Water:

5.1.1 Digestion log (Appendix II): The digestion log should list the sample numbers, the date, the name of the analyst, the time placed in the hot water bath, the time when the temperature reached 95 ± 5° C, and the time removed from the hot water bath. One should be prepared for each run. An example is attached as Appendix II. The numbers of each BOD bottle must be placed in the leftmost column of this form to identify which sample is in each BOD bottle.

5.1.2 Preparation of standards:

5.1.2.1 Prepare a working standard daily by adding 100 µl of the 1000 mg/L stock standard to 100 mL of 0.15% HNO_3 in DIW, giving a concentration of 1.0 mg/L of Hg.

5.1.2.2 Place 100 mL DIW in each of 9 BOD bottles. Mark these BOD bottles with the concentration of each standard in µg/L, plus one marked "Blank", one marked "ICV", and one more marked ICB.

5.1.2.3 Add from the working standard the following amounts to the following bottles:

0 µg/L	0 µl
0.2 µg/L	20µl
0.5 µg/L	50 µl
1.0 µg/L	100 µl
2.0 µg/L	200 µl
5.0 µg/L	500 µl
10.0 µg/L	1000 µl

5.1.2.4 To the ICV BOD bottle add that amount of the ICV standard which will produce a concentration from 1.0 µg/L to 5.0 µg/L. Currently a contration of 4.0 µg/L is in use.

5.1.2.5 The standards, the ICV and the ICB must be digested along with the PBW, Blank Spike and samples.

5.2 Digestion - Water Samples

5.2.1 These procedures are for methods SW-846 7470 and EPA 245.1 unless noted otherwise.

5.2.2 Place 100 mL DIW in the PBW BOD bottle.

5.2.3 Place 100 mL DIW + 500 µl intermediate standard in the Blank Spike BOD bottle.

5.2.4 Place 100 mL sample in the BOD bottle designated for that sample, being sure to place 100 mL sample in the designated duplicate, MS and MSD BOD bottles for the sample involved. TCLP samples and spikes should be diluted 20 mL/100 mL (dilution factor of 5) in DIW. The TCLP spikes should be diluted 2 mL/100 mL (dilution factor of 50) in DIW.

5.2.5 Add the required quantity (See Sec. 4.5.1) of the working standard to the MS and MSD BOD bottles.

5.2.6 Add the following reagents to each BOD bottle (for all methods):

5 mL concentrated H_2SO_4
2.5 mL concentrated HNO_3
15 mL $KMnO_4$ solution
8 mL $K_2S_2O_8$ solution

5.2.7 The $KMnO_4$ color must persist for 15 minutes. If it does not, more $KMnO_4$ must be added.

5.2.8 Place all the BOD bottles, being careful to keep them in order, in the hot water bath in a hood, and record the time on the digest log. Monitor the temperature of the hot water bath and record the time when the temperature reaches 90°C. Continue to heat the water bath, keeping the bath at 95°C ± 5°C for two hours.

5.2.9 Remove the BOD bottles from the hot water bath and allow to cool.

5.2.10 Add 7 mL $NaCl/NH_2OH{\cdot}HCl$ solution and mix until the mixture clears. If some undissolved permanganate remains, it will usually disappear on standing after a few minutes.

5.3 Digestion - Soil samples

5.3.1 These procedures are (for Methods SW-846 7471 and EPA 245.5 unless noted otherwise):

5.3.2 Place 50 mL DIW in the calibration BOD bottles. Add appropriate working standard to each.

5.3.3 Place approximately 0.5 g, or for certain CLP and SW-846 analyses, approximately 0.2 g of sample in each of the sample BOD bottles to which that sample applies. Record the exact weight on the digestion log.

5.3.4 Add 3.75 mL HCl , 1.25 mL HNO_3 to all the BOD bottles and 10 ml DIW to each sample BOD bottle.

5.3.5 Place all sample BOD bottles in a hot water bath in a hood that is at 95°C ± 5°C. Maintain the heat at this level for 10 minutes.

5.3.6 Cool for 20-30 minutes and add 40 mL DIW and 15 mL $KMnO_4$ to all sample BOD bottles (also add 8 mL $K_2S_2O_8$ for CLP). Mix.

5.3.7 The $KMnO_4$ color must persist for 15 minutes. If it does not, more $KMnO_4$ must be added.

5.3.8 Place all BOD bottles in a hot water bath that is at 95°C ± 5°C. Record the time on the digestion log. Maintain the hot water bath at this temperature for 30 minutes. Remove the BOD bottles and allow to cool.

5.3.9 Add 7 mL $HCl/NH_4NH_2OH{\cdot}HCl$ solution to all BOD bottles and mix to remove color.

5.3.10 Add 50 mL DIW to all BOD bottles. Allow to cool.

5.4 Analysis on FIMS 400

5.4.1 This is a programmed analysis. This is a 6 point curve with a blank correction. The development of the calibration curve, including the ICV and ICB, is automatic. If the calibration is unsuccessful, recalibration is attempted. The 5.0 µg/L standard is used for CCV's; the calibration blank for CCB's, both of which are programmed to be run every 10 samples. If a CCV or a CCB fails to meet quality control specifications, the system stops and all samples since the last preceding valid CCV or CCB are reanalyzed. A CCV and a CCB are also run after the last sample in the run.

5.5 Sample Information sheet.

5.5.1 Click the basic functions button on the screen which appears after activating the program.

5.5.2 Click the "Sample Information" button on the toolbar.

5.5.3 A blank sample information sheet appears. Previous sample information sheets may be obtained by activating the File - Open menu, designating "Sample Information" from the dialog which appears. The sample information sheet should be filled in to tell the computer to which auto-sampler locations to go.

5.5.4 Sample ID column - Some typing can be saved by double clicking on the column title. On the resulting form the job order may be typed in and the sample numbers will then be incremented by 1 for the autosampler locations indicated. The sample ID's will then be filled in. Sample: "0102094-0001..0002. .".

5.5.5 Sample weight column - For soil samples the weight of the samples should be filled in. At the top, the volume units should be filled in "mL", the weight units "g".

5.5.6 Sample units column - Typing may be saved by double clicking on the column title and indicating the units on the dialog box which appears, and indicating the AS locations

involved. In the case of water samples this will ordinarily by "µg/L ". For soil samples the button "weight:weight" should be clicked and the desired units specified in the dialog box selected. If the dialog box has been properly filled in, the machine is programmed to compute the proper units (e.g. mg/kg). It should be kept in mind that this is on an as received basis, not a dry basis.

5.5.7 User dilution column - Where a dilution is involved (e.g. TCLP analyses) the dilution factor should be entered. As in the sample weight and sample units columns, above, typing may be saved by double clicking the column title.

5.5.8 The autosampler tray being used at present is "Tray B".

Sampler Location	Size	Contents
1	50 mL tube	Calibration Blank
2	50 mL tube	0.2 µg/L standard
3	50 mL tube	0.5 µg/L standard
4	50 mL tube	1.0 µg/L standard
5	50 mL tube	2.0 µg/L standard
6	50 mL tube	5.0 µg/L standard
7	50 mL tube	10.0 µg/L standard
8	50 mL tube	ICV
9	15 mL tube	ICB
10	15 mL tube	LCSS/LCSW
11	15 mL tube	CRA
12	15 mL tubes	PBW
13-109	15 mL tubes	Samples

5.5.9 All tubes should be marked with their contents before being filled. Then the tubes are filled from the BOD bottles and placed in the autosampler locations designated either by the method or by the sample information sheet.

5.5.10 At the beginning of each day of analysis, the following steps are taken to prepare the instrument:

5.5.10.1 The flows of the carrier solution and the reductant solution (the stannous chloride solution) are measured by the methodology suggested in the Perkin-Elmer handbook "Setting Up and Performing Analyses", 2.4.2-2.4.4.

5.5.10.2 The rinse container (autosampler location 0) is rinsed and filled with 3% HCl solution. This is then analyzed using the location button in the analysis window of the automated analysis window, and the curve produced displayed through the curve button in the toolbar. The curve should be flat and less than 0.0004 absorbance units.

5.5.11 Analysis - The analysis is ordinarily started by clicking the "Analyze All" button in the Automated Analysis window. If only calibration is desired, the "Calibrate" button may be used. If samples are to be analyzed by an already existing calibration curve use the "Analyze Samples" button.

5.5.11.1 Once the analysis has been started, the autosampler places the sampling probe in the sample/calibration cup. The peristaltic pump begins pulling sample through the sample loop. After the line has been purged, the injection valve cycles and injects the sample into the carrier flow. This flow is then combined with the $SnCl_2$ and mixed. Next it goes to a liquid/vapor separator. The liquid goes to waste and the vapor is transported into the absorption cell of the spectrophotometer. All samples and standards are measured in duplicate.

5.5.11.2 Run log - A run log will be printed as the analysis progresses. The print program is designed to transmit the data to be printed to the printer one page at a time. Thus several autosampler locations will be analyzed before anything appears on the printer. If anything else is printed (e.g. the sample information sheet) while the automated analysis window is open, the computer must be rebooted, or a run log will not be printed.

5.5.11.3 Additional samples may be analyzed after the run designated on the sample information sheet by using the "Select Location" button on the "Analyze" page of the Automated Analysis window. The autosampler locations should be filled in the resulting dialog. The instrument will then analyze the samples indicated. This may be used to reanalyze the samples with questionable results, or to analyze diluted samples.

5.5.11.4 Dilution - Where analysis results are above the high standard (10.0 µg/L) an aliquot of the sample diluted with the calibration blank may be analyzed as set forth in 5.5.11.3 above.

6. Reports

6.1 Data Packet Organization

6.1.1 A report is prepared using the reformat procedure on the main menu. The reformatted design is entitled "Summary". It is transferred to a floppy disk, which is then imported to a spreadsheet using Microsoft Excel 2000. This must then be formatted into the form included in Appendix III.

6.1.2 The final data packet is to include the following:

1) The report (See Appendix III).
2) The quality control database Report Form
2) The digestion log (Appendix II).
4) The run log, if required.

6.1.3 All results for quality control tests are entered into the quality control database. A summary report of all data entered must be included in the data packet. The routine minimum is a method blank report, an MS/MSD or MS/duplicate report and a SRM/LCSW.

6.2 Data Qualifying Flags

Flag	Definition
U	The analyte of interest was not detected, to the limit of detection indicated.

6.2.1 Control charts

7. References

USEPA, Test Methods for Evaluating Solid Waste Physical/Chemical Methods, USEPA SW846, most recent version, Method 7470/7471

USEPA, Determination of Mercury in Water by cold vapor atomic absorption spectrometry, USEPA 245.1/245.5, most recent version, Method 245.1/245.5

CLP Inorganics Statement of Work, ILMO4.1

Appendix I - QC Summary Table

Laucks Testing Laboratories
Method 245.1/245.57471/7470, & CLP ILM04.1 QA Requirements and Corrective Actions

QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
Initial Calibration	R > 0.995	R > 0.995 6-point curve + blank	once per batch	recalibrate	run log
Initial Calibration Verification	SW846 90-110% EPA 245 and CLP 80-120%	Per the method	Once per batch	recalibrate	run log, report
Initial Calibration Blank	Below MDL	Below ½ R.L.	one per batch	recalibrate	run log, report
Method Blank (PBW)	Below R.L.	Below ½ R.L.	One per batch	Consult QC officer. Flag data or reanalyze.	Quality control database
Continuing Calibration Verification	80-120 %	80-120 %	every 10 samples and after the last sample	rerun samples since last CCV	run log
Continuing Calibration Blank	Below MDL	Below ½ R.L.	every 10 samples and after the last sample	rerun samples since last CCB	run log
Matrix Spike Recovery	See method	See quality control database	Every 20 samples	Consult QC officer. Flag data or reanalyze.	Quality control database
MS/MSD RPD	See method	See quality control database	Every 20 samples	Consult QC officer. Flag data or reanalyze.	Quality control database

QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
Duplicate % Difference	See method	See quality control database	Every 20 samples	Consult QC officer. Flag data or reanalyze.	Quality control database
Standard Reference Material (LCS) Recovery	Soil Vendor's limits Water See ICV	Vendor's limits	Once per 20	Recalibrate	Run log

Appendix - II - Sample Digestion Log

insert log here

Appendix III - Example Report Form

Hg in Water by SW-7470
Digested 11/13/2000
Analyzed 11/14/2000

Sample	Time	Value		% Rcvry	RPD	Flag
Calib Blank	11:49:54		µg/L			
S0.2	11:52:45		µg/L			
S0.5	11:55:38		µg/L			
S1.0	11:58:33		µg/L			
S2.0	12:01:30		µg/L			
S5.0	12:04:26		µg/L			
S10.0	12:07:22		µg/L			
ICV1 ME-13-4-1=4	12:10:26	3.951	µg/L	99%		
ICB	12:13:21	0.021	µg/L			
LCSW1	12:16:10	3.964	µg/L	99%		
CRA	12:19:03	0.199	µg/L			
PBW	12:21:57	0.017	µg/L			
0011185-01	12:24:51	0.023	µg/L			
011185-02	12:27:45	0.021	µg/L			
011185-03	12:30:42	0.024	µg/L			
011185-04	12:33:37	0.015	µg/L			
011185-04D	12:36:31	0.018	µg/L			
011185-04MS Spk=5	12:39:21	5.076	µg/L	102%		
CCV1=5	12:42:14	5.143	µg/L	103%		
CCB1	12:45:08	0.026	µg/L			
011185-05	12:47:58	0.017	µg/L			
011185-06	12:50:49	0.019	µg/L			
011185-07	12:53:40	0.021	µg/L			
011185-08	12:56:32	0.016	µg/L			
011185-09	12:59:24	0.017	µg/L			
011185-10	13:02:17	0.013	µg/L			
011185-11	13:05:12	0.009	µg/L			
0011143-02	13:08:05	0.016	µg/L			
011143-02MS Spk=5	13:10:59	5.160	µg/L	103%		
CCV2=5	13:13:54	5.143	µg/L	103%		
CCB2	13:16:46	0.028	µg/L			
011143-02MSD	13:19:39	5.150	µg/L	103%	0%	
0011149-02	13:22:34	0.018	µg/L			
0011167-02	13:25:31	0.016	µg/L			
011167-03	13:28:27	0.017	µg/L			
0011168-02	13:31:21	0.029	µg/L			
011168-03	13:34:10	0.017	µg/L			
0011196-02	13:37:01	0.021	µg/L			
011196-03	13:39:51	0.023	µg/L			
0011198-02	13:42:42	0.021	µg/L			
CCV3=5	13:45:34	5.163	µg/L	103%		
CCB3	13:48:28	0.026	µg/L			

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #: LTL-8019

Determination of Non-Halogenated Volatile Organics by SW 8015B

Revision history:

Number	Date
0	10/08/97
1	01/16/98
2	04/22/98
3	12/09/98
4	04/04/02

Revised by: Stacy Schulze, Analyst Date: 5/8/02

Approved by: Harry Romberg, QA Officer Date: 5-8-02

Approved by: Kathy Kreps, Laboratory Director Date: 5/9/02

Controlled Document

No. 20 **Assigned to:** TeTr

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1. Introduction and Scope

1.1 Method Description

1.1.1 Method 8015B is used in the determination of nonhalogenated volatile organic compounds and semivolatile organic compounds by gas chromatography. 8015B may also be applicable for the analysis of petroleum hydrocarbons, including gasoline range organics (GROs) and diesel range organics (DROs). However, this SOP is written strictly for the determination of nonhalogenated volatile organic compounds in soil, sediment, aqueous, and other matrices. This method employs sample introduction via a purge and trap sample concentrator.

1.1.2 A tabulated list of Laucks' typical analytes and their respective CAS numbers is located in Appendix I. The actual target analyte list may vary, depending on project-specific requirements.

1.1.3 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.

1.2 Method Deviations

Detailed below are any deviations from the published version of method SW8015. All deviations are followed as the standard operating procedure by Laucks Testing Labs.

1.2.1 At the time of this writing, the 3rd update of the 3rd edition to SW 846 requires that low level soils be collected in VOA vials and preserved with sodium bisulfate. This option is not currently available with our instrumentation; therefore, we follow the method as described in section 1.4.2.2 of this document.

1.2.2 Current instrumentation does not allow separation on both columns of acetonitrile from the solvent peak in high level soil samples. Therefore, the result cannot be confirmed and only results from low level analyses are reported.

1.3 Method Interferences/ Decision-making Process

In order to attain lab-wide consistency among staff members for decision-making processes with regard to laboratory anomalies, several common items have been addressed in this SOP. Any occurrences not covered in this SOP should be discussed with the supervisor prior to implementing a solution.

1.3.1 Any samples analyzed subsequent to a high level sample (which is defined as yielding one or more target analytes above the calibration range) should be thoroughly examined for potential carry-over of the same target analyte(s). Sample syringes are rinsed between samples, but contamination may still occur. Corrective action in the form of reanalysis for possible carry-over should be performed and documented in the narrative. Screening samples prior to analysis will also help prevent such contamination.

1.3.2 All sample chromatograms should be reviewed for analytes which may not show up on the sample quantitation report due to data system error or retention time shift. All peaks should be examined and evaluated based on the retention times and sample concentration in order to prevent reporting false negatives.

1.3.3 Samples may be contaminated by a single compound (such as a solvent or petroleum product) which is detectable within the analytes' retention times. The use of the dual detectors should enable the analyst to differentiate between the analyte list and stray compounds; however, alternative calibration, detection, or quantitation procedures may be necessary if the compound is a project concern.

1.3.4 Contamination by other volatile organic compounds during shipment and storage may occur. Trip blanks prepared from PFW (for water samples and non-field-preserved soils) or P&T grade methanol (for field-preserved soils) travel with sample vials throughout sampling and storage to check for such contamination. Storage blanks are also analyzed once a week to check conditions within storage refrigerators.

1.4 Sample Collection, Sample Storage, Holding Times

1.4.1 Waters

1.4.1.1 Samples are collected with zero headspace in 40 ml glass VOA vials containing 1:1 HCl preservative and sealed with Teflon-lined caps. After preservation to a pH of ≤2, all samples are stored at 4°C ± 2°C.

1.4.1.2 The holding time to analysis is 14 days from date of collection for acid-preserved samples and 7 days for non-preserved samples. The pH values for the water samples are measured at the time of sample preparation and are noted in the instrument logbook and the client report.

1.4.2 Soils

1.4.2.1 At the time of this writing, the 3rd update of the 3rd edition to SW 846 requires that low level soils be collected in duplicate using 5 grams and/or 1 gram aliquots which are to

be weighed out in the field. The soil samples are to be collected in a 40 ml vial containing water, sodium bisulfate, and a stir bar. 0.2 grams of sodium bisulfate are added for each gram of soil. Therefore, when collecting 5 grams of sample, the VOA vial should contain 1 gram of sodium bisulfate. The sodium bisulfate is added in order to ensure a sample pH of ≤2. The vials used for low level soils should have the tarred weight recorded on the label and be sealed with septum-lined screw caps. This procedure is not currently available for 8015B analysis due to instrument limitations.

1.4.2.2 Due to the previous technique's unavailability for 8015B analysis, Laucks uses the other option, which is the use of the EnCore™ sampler, the Purge-and-Trap Sampler™, or a cut plastic syringe to transfer the sample to the soil vial. If the EnCore™ sampler is used in the field, the samples may be stored for up to 48 hours. However, samples collected in this device should be transferred to the soil sample vials (and preserved) as soon as possible or analyzed within 48 hours. When preservation is not an option and soils must be analyzed straight from the EnCore™ sampler, a 7-day holding time to analysis may be negotiated with the client. The holding time for all other soils is 14 days from the date of collection.

1.4.2.3 At the time of this writing, the 3rd update of the 3rd edition to SW 846 requires that high level soils be collected by using one of the following options:

1.4.2.4 Option 1: Samples will be collected and preserved with methanol in the field. An aliquot of the methanol is then analyzed by method 5030B in the laboratory. The holding time for soil samples collected in this manner is 14 days from the date of collection.

1.4.2.5 Option 2: Samples will be collected using an EnCore™ type sampler or equivalent and extracted (preserved) at the laboratory. Samples collected in this fashion may be stored for 48 hours but should be preserved as soon as possible. Once preserved, the holding time for sample analysis is 14 days from the date of collection.

1.4.2.6 Option 3: Samples will be collected in 2- or 4-oz glass containers and sealed with Teflon-lined caps with zero headspace. Samples are then extracted (preserved) in the laboratory. The holding time for soil samples collected in this manner is 14 days from the date of collection.

1.5 Definition of Terms

This section defines terms and acronyms as they are used in this SOP. Not all of the terms are defined here since it is assumed that the user of this SOP already understands their general meaning.

Blank Spike	A background free matrix (PFW for water, clean sand for soils/sediments) to which known amounts of target analytes and surrogates are added each time samples or 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. A blank spike is analyzed at a rate of 5% per matrix per day.
Calibration Check Standard	A standard analyzed after an initial calibration to check the accuracy of that calibration. The solution must be from a different source than the one used for the initial calibration. This solution may be the blank spike or QC check standard. See also blank spike and QC check standard.
CCV	Continuing Calibration Verification. Also known as the calibration verification standard. This standard is 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, r^2	Correlation Coefficient. A measure of the "goodness of fit" of a set of data to a linear regression model. The closer the value is to 1, the higher the degree of confidence in the correlation. The correlation coefficient must be greater than 0.990 to be acceptable. (Specific projects may require a greater degree of confidence by using a correlation coefficient of 0.995.)
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. An instrument blank contains the method surrogates and is analyzed to monitor for carry over between samples or sample extracts.

ICV	Initial Calibration Verification. The ICV is used in the same capacity as a CCV to check for continuation of the calibration; however, this standard is also used to adjust the mid-point of the retention time window on extended QC periods. Calibration is set by the initial multi-point curve.
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.
Method Blank	A background free matrix (PFW for water, clean sand for soils/sediments) has surrogate added. This aliquot is taken through the entire analytical process. The purpose of the method blank is to demonstrate that interferences from the analytical system, glassware, laboratory contamination, and reagents are within tolerance. A method blank is analyzed at a rate of 5% per matrix per day.
MS/MSD	Matrix Spike and Matrix Spike Duplicate. A known amount of the target analytes and surrogates are added to a sample at a rate of 5% per matrix (1 MS/MSD set per 20 samples per matrix).
PFW	Purge-Free Water. Deionized water that has either been purged with high purity nitrogen for 15 minutes at 10 psi or has been boiled for 45 minutes in an environment free of all purgeable organics, cooled, and sealed for later use.
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 (BS). 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 samples or sample 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.
RF	Response Factor. The ratio of nanograms injected to peak response. This term is defined in the same way in both the CLP contract and SW 846.
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 the GC column.
RT window	Retention Time window. The +/- value applied to the ICV to establish the time range used to make tentative compound identifications.
Sequence	A set of samples, QC, 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

Gas Chromatograph:	Hewlett Packard, 5890 I or II employing a low-dead-volume interface from the sample concentrator to the GC injection port.
Data System:	EZChrom data acquisition system, revision 6.6, Target/NT data processing system, revision 4.0 capable of off-line data storage or equivalent.
Detectors:	Dual FID detectors from Hewlett Packard or equivalent.
Purge and trap:	Tekmar LSC 2 or equivalent.
Autosampler:	Dynatech PTA-30W/S or equivalent.
Trap:	Tenax/OV1 (Supelco G Trap). Other packings for the trap may be substituted if equivalent or improved performance can be demonstrated.
Columns:	1) 30m x 0.45mm x 3.0 film bonded phase fused silica capillary (DB-624). 2) 30m x 0.45mm x 3.0 film bonded phase fused silica capillary (DB-VRX).

2.2 Supplies and Materials

Syringes:	5 and 10 ml Luerlok syringes.
Microsyringes:	10 and 25 µl syringes with a 0.006 in. I.D. needle (Hamilton 702N or equivalent) in addition to 50, 100, 500 and 1000 µl gas-tight syringes.
Volumetric flask:	Class "A" type volumetric flasks of assorted volumes ranging from 10 to 100 ml.
Micro reaction vials:	1 and 2 ml micro reaction vials with Mininert valves for storing current standard solutions.
VOA vials:	20 ml VOA vial with Teflon-lined caps.

Compressed gases:	Hydrogen 99.995% (high purity) or better. Helium 99.995% (high purity) or better. Air (breathing air grade without trace hydrocarbons) or purified air from the Balston 75-80 Zero Air Generator.
Reagent water:	Reagent water (also known as purge-free water) is deionized water that has been boiled for 45 minutes in an environment free of purgeable organics.
Methanol:	B&J Purge and Trap quality.
Disposable pipettes:	1, 5, and 10 ml disposable pipettes.
Stainless steel spatula	
Analytical balance:	Capable of accurately weighing to the nearest 0.0001 g for standard preparation and a top loading balance capable of weighing to the nearest 0.01 g for samples.
Note:	All of the above equipment may be substituted with equivalent or better equipment.

2.3 Standards

2.3.1 Preparation of Standards

2.3.1.1 The standards are currently prepared from either neat chemicals or commercially supplied premixed solutions. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at the concentration that the manufacturer guarantees if they are certified by the manufacturer or by an independent source.

2.3.1.2 The Neat/Standard Logbook is used for creating a discrete entry for each standard. The information entered into the book documents the traceability of all standards that are used (i.e., source, lot number, purity, date made, and expiration date). In addition, all standards are labeled with the standard concentration, the solvent, date prepared, expiration date, analyst's initials, and the standard reference number.

2.3.1.3 Quality control is maintained on all solutions by verifying the standard solutions prior to use. This verification is accomplished through analysis of the new solution against a current 5-point calibration. Analyte values within 85-115 percent of their nominal value are considered acceptable.

2.3.1.4 Spiking solutions for the blank spikes and MS/MSD analyses are prepared in the same manner as the calibration standards. They are also used to verify the integrity of working calibration standards and the accuracy of the calibration curve. The spiking solutions are produced from standards purchased from a different vendor than the one used to purchase calibration standards.

2.3.1.5 All standards and spikes are stored in the VOA freezer at -10°C or lower. The working standards and spikes are stored in Mininert capped vials for a time period not to exceed three months or the expiration date of the parent standard, whichever is sooner. Prepared stock standards are stored for six months or the expiration date of the parent standard, whichever is sooner. Commercially prepared stock standards are stored until the manufacturer's expiration date or one year from opening, whichever is sooner. Standards are removed from the freezer and allowed to warm to room temperature prior to use.

2.3.2 Preparation of Surrogate Standards

2.3.2.1 If starting with a neat material, a measured amount of the neat chemical is placed in a glass volumetric, diluted to volume with methanol, and then transferred to an appropriate storage vial. A common dilution is approximately 125 mg of neat material into 25 ml of methanol. This dilution yields an intermediate solution of 5000 ng/µl, which is stored in amber vials for a time period not to exceed six months or the manufacturer's expiration date, whichever is sooner. Currently, we purchase separate certified solutions from Restek at concentration levels of 10,000 ng/µl each; they expire one year from opening or the manufacturer's expiration date, whichever is sooner.

Surrogates	**Source***	**Concentration**
Bromofluorobenzene	Restek	10,000 ng/µl
Trifluorotoluene	Restek	10,000 ng/µl

* or equivalent.

2.3.2.2 For field preserved soil samples, each surrogate is individually diluted ten-fold for a resulting concentration of 1000 ng/µl. These standards are stored for six months or the expiration date of the parent solution, whichever is sooner.

2.3.2.3 Aliquots of the 10,000 ng/µl stock solutions are taken from the surrogate standards and then combined in a volumetric flask and diluted with methanol to yield a working level multi-component surrogate of 200 ng/µl (for laboratory soil extraction). This solution is stored in a Mininert capped vial for a time period not to exceed six months or the expiration date of the parent standard, whichever is sooner.

Surrogate	Initial Conc.	Aliquot	Vol.	Final Conc.
Bromofluorobenzene	10,000 ng/µl	200 µl	10 ml	200 ng/µl
Trifluorotoluene	10,000 ng/µl	200 µl	10 ml	200 ng/µl

2.3.2.4 An aliquot of the 200 ng/µl solution is taken and then diluted ten-fold with methanol in a volumetric flask to yield a working level multi-component surrogate of 20 ng/µl (for water and low-level soil analysis). This solution is stored in a Mininert capped vial for a time period not to exceed three months or the expiration date of the parent standard, whichever is sooner.

Surrogate	Initial Conc.	Aliquot	Vol.	Final Conc.
Bromofluorobenzene	200 ng/µl	1 ml	10 ml	20 ng/µl
Trifluorotoluene	200 ng/µl	1 ml	10 ml	20 ng/µl

2.3.2.5 Surrogate standards are kept in the VOA freezer at -10°C or lower, removed prior to use, and allowed to warm to room temperature. An aliquot of the working solution is injected into a 10 ml syringe containing PFW or sample. Below are the surrogate concentrations and the preparation for water and low-level soil analyses.

Surrogate	Initial Conc.	Aliquot	Vol.	Final Conc.
Bromofluorobenzene	20 ng/µl	10 µl	10 ml	20 ng/ml
Trifluorotoluene	20 ng/µl	10 µl	10 ml	20 ng/ml

2.3.3 Preparation of Matrix Spike Standards

2.3.3.1 Certified sets of solutions containing the target analytes are purchased premixed from a commercial supplier at concentrations of 2000 ng/µl (for isobutyl alcohol, propionitrile, and 1,4-dioxane) or 1000 ng/µl (for acetonitrile). These solutions are stored until the manufacturer's expiration date or one year from opening the ampule, whichever is sooner. The oxygenate compounds (TAME, ETBE, DIPE, and TBA) are currently purchased as neats and diluted appropriately. These solutions are stored until the manufacturer's expiration date or five years from opening the ampule, whichever is sooner.

Matrix Spike Solution	Source*	Concentration
Isobutyl alcohol	Accustandard	2000 ng/µl
Acetonitrile	Accustandard	1000 ng/µl
Propionitrile	Accustandard	2000 ng/µl
1,4-Dioxane	Supelco	2000 ng/µl
TAME	ChemService	neat
ETBE	ChemService	neat
DIPE	ChemService	neat
TBA	ChemService	neat

* or equivalent.

2.3.3.2 Aliquots of the premixed solutions are taken and then diluted with methanol in a volumetric flask to yield a working level multi-component spike of 100 ng/µl (for isobutyl alcohol, acetonitrile, and propionitrile) and a single component spike of 500 ng/µl (for 1,4-dioxane). Certified neat chemicals of TAME, ETBE, DIPE, and TBA are purchased from a commercial supplier. Stock solutions are prepared from the neat chemicals by diluting 0.20g of material with methanol in a 10 ml volumetric flask, yielding individual solutions with concentrations of 20,000 ng/µl. These solutions are then diluted and mixed in methanol to generate a multi-component working standard at concentrations of 10-50 ng/µl. The oxygenate intermediate solutions are stored for a period of time not to exceed six months or the expiration date of the parent standard, whichever is sooner. All working solutions are stored in Mininert capped vials for an extended period of time not to exceed three months or the expiration date of the parent standard, whichever is sooner.

Matrix Spike Solution	Initial Conc.	Aliquot	Vol.	Final Conc.
Isobutyl alcohol	2000 ng/µl	50 µl	1 ml	100 ng/µl
Acetonitrile	1000 ng/µl	100 µl	1 ml	100 ng/µl
Propionitrile	2000 ng/µl	50 µl	1 ml	100 ng/µl
1,4-Dioxane	2000 ng/µl	250 µl	1 ml	500 ng/µl
TAME	20,000 ng/µl	5 µl	10 ml	10 ng/µl
ETBE	20,000 ng/µl	5 µl	10 ml	10 ng/µl
DIPE	20,000 ng/µl	5 µl	10 ml	10 ng/µl
TBA	20,000 ng/µl	25 µl	10 ml	50 ng/µl

2.3.3.3 Spikes are kept in the VOA freezer at -10°C or lower, removed prior to use, and allowed to warm to room temperature. An aliquot of the working solution is injected into a 10

ml syringe containing PFW or sample and an appropriate amount of the surrogate solution. Below are the spike concentrations and the preparation for the blank spike and MS/MSD analyses.

Matrix Spike Solution	Initial Conc.	Aliquot	Vol.	Final Conc.
Isobutyl alcohol	100 ng/µl	10 µl	10 ml	100 ng/ml
Acetonitrile	100 ng/µl	10 µl	10 ml	100 ng/ml
Propionitrile	100 ng/µl	10 µl	10 ml	100 ng/ml
1,4-Dioxane	500 ng/µl	20 µl	10 ml	1000 ng/ml
TAME	10 ng/µl	10 µl	10 ml	10 ng/ml
ETBE	10 ng/µl	10 µl	10 ml	10 ng/ml
DIPE	10 ng/µl	10 µl	10 ml	10 ng/ml
TBA	50 ng/µl	10 µl	10 ml	50 ng/ml

2.3.4 Preparation of Initial Calibration Standards

2.3.4.1 Certified neat chemicals of acetonitrile, propionitrile, and isobutyl alcohol are purchased from a commercial supplier. Stock solutions are prepared from the neat chemicals by diluting 0.20g of material with methanol in a 10 ml volumetric flask, yielding individual solutions with concentrations of 20,000 ng/µl. The stock solution of 1,4-dioxane is purchased as a certified, premixed solution from a commercial supplier at 2000 ng/µl. The oxygenates (TAME, ETBE, DIPE, and TBA) are purchased in a certified multi-component solution from a commercial supplier. Purchased solutions are stored until the manufacturer's expiration date or one year from opening the ampule, whichever is sooner. If additional target analytes are requested, these analytes may be ordered separately, in solution or as a neat material, and diluted to appropriate working concentrations through the described method.

2.3.4.2 The individual solutions are then diluted and mixed in methanol to generate a multi-component working standard at a concentration of 100 ng/µl (for acetonitrile, propionitrile, and isobutyl alcohol) or diluted to generate a single-component working standard at a concentration of 500 ng/µl (for 1,4-dioxane). The premixed oxygenates are diluted with methanol to generate a multi-component working standard with concentrations of 10-50 ng/µl. All solutions are stored in Mininert capped vials for a period of time not to exceed three months or the expiration date of the parent standard, whichever is sooner. The creation of the working surrogate standard was described in section 2.3.2.

The working standards contain the following compounds in each solution:

Analytes	Working Solution
Isobutyl alcohol	Mix 1
Propionitrile	Mix 1
Acetonitrile	Mix 1
1,4-Dioxane	Mix 3
Tert-amyl-methyl ether (TAME)	Mix 5
Ethyl-tert-butyl ether (ETBE)	Mix 5
Diisopropyl ether (DIPE)	Mix 5
Tert-butyl alcohol (TBA)	Mix 5
Surrogates	
Trifluorotoluene	Mix 2
Bromofluorobenzene	Mix 2 and Mix 4

2.3.4.3 Standards are kept in the VOA freezer at -10°C or lower, removed prior to making up the initial calibration standards, and allowed to warm to room temperature before use.

2.3.4.4 The initial calibration standards range from 20 µg/l to 300 µg/l for the non-dioxane/non-oxygenate compounds, from 50 µg/l to 3000 µg/l for 1,4-dioxane, from 1 µg/l to 500 µg/l for oxygenates, and from 2 µg/l to 40 µg/l for surrogates. The standards are prepared by withdrawing aliquots of the working solutions and injecting them into a 10 ml syringe containing PFW and an appropriate amount of the surrogate solution. After the curve has been analyzed, a method blank and a blank spike are also analyzed. The blank spike is prepared from a source different from that used for the curve and must be within 15% of the true value in order to pass.

Working Solution Conc. (non-diox/non-oxy compounds)	Aliquot	Final Volume	Concentration
100 ng/µl	2 µl	10 ml	20 µg/l
100 ng/µl	4 µl	10 ml	40 µg/l
100 ng/µl	8 µl	10 ml	80 µg/l
100 ng/µl	10 µl	10 ml	100 µg/l
100 ng/µl	20 µl	10 ml	200 µg/l
100 ng/µl	30 µl	10 ml	300 µg/l

Working Solution Conc. (1,4-Dioxane)	Aliquot	Final Volume	Concentration
500 ng/µl	1 µl	10 ml	50 µg/l
500 ng/µl	2 µl	10 ml	100 µg/l
500 ng/µl	10 µl	10 ml	500 µg/l
500 ng/µl	20 µl	10 ml	1000 µg/l
500 ng/µl	40 µl	10 ml	2000 µg/l
500 ng/µl	60 µl	10 ml	3000 µg/l

Working Solution Conc. (Oxygenates)	Aliquot	Final Volume	Concentration
10-50 ng/µl	10 µl into 100ml	10 ml of solution	1-5 µg/l
10-50 ng/µl	2 µl	10 ml	2-10 µg/l
10-50 ng/µl	5 µl	10 ml	5-25 µg/l
10-50 ng/µl	10 µl	10 ml	10-50 µg/l
10-50 ng/µl	20 µl	10 ml	20-100 µg/l
10-50 ng/µl	50 µl	10 ml	50-250 µg/l
10-50 ng/µl	100 µl	10 ml	100-500 µg/l

Surrogates	Aliquot	Final Volume	Concentration
20 ng/µl	1 µl	10 ml	2 µg/l
20 ng/µl	2 µl	10 ml	4 µg/l
20 ng/µl	5 µl	10 ml	10 µg/l
20 ng/µl	10 µl	10 ml	20 µg/l
20 ng/µl	15 µl	10 ml	30 µg/l
20 ng/µl	20 µl	10 ml	40 µg/l
20 ng/µl	30 µl	10 ml	60 µg/l

2.3.5 Preparation of a Continuing Calibration Standard

The concentration of the continuing calibration standard is the mid-point of the initial calibration curve. Due to its volatility, this solution is not stored for any period of time. Occasionally, the concentration of this standard is varied to further check the calibration.

3. Safety precautions

3.1 Routine Safety Precautions

3.1.1 Many analytes in this method are known or suspected carcinogens. Analysts should handle all neat materials, standards, and samples as if they were potentially hazardous substances. Respirators and fume hoods should be employed for extremely hazardous materials.

3.1.2 Refer to the instrument manufacturer's manual for routine instrument precautions.

3.1.2 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.

3.1.3 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.

3.1.4 Methanol should be stored in a solvent locker and kept away from sources of heat and sparks. Contact should be avoided.

3.2 Waste disposal

3.2.1 All expired standards are discarded in the solvent waste container located in the prep area under the fume hood.

3.2.2 All high level samples are either returned to the client for disposal or are disposed into the appropriate waste container.

3.2.3 Soil samples are dumped into a 55 gallon drum in the warehouse where an outside source disposes of the waste.

3.2.4 Waste segregation and disposal from the point of collection is further covered in the Laucks SOP on Waste Segregation and Disposal.

4. Operation procedures

4.1 Analytical Conditions

4.1.1 Chromatographic Conditions

Initial GC Temperature:	40°C
Hold Time:	3.0 min.

Ramp Rate:	8°C/min.
Final Temperature:	220°C
Final Time:	2.5 min.
Carrier Gas Flow:	10 ml/min.
Hydrogen Flow:	38 ml/min
Makeup Flow:	20 ml/min
Air Flow:	270 ml/min

4.1.2 Purge & Trap Parameters

Purge Time:	11 min.
Desorb Time:	4 min.
Bake Time:	16 min.
Desorb Preheat Temperature:	160°C
Desorb Temperature:	160°C
Purge Flow:	40 ml/min.
Purge Temperature:	40°C
Bake Temperature:	180°C
Desorb Flow Rate:	10 ml/min.

Dynatech Autosampler

Selection	Selected	Choice	Comments
Program set up	Auto	Man	Select Auto (use the arrow)
Start Delay	0.0		
Cycle Time	0		May vary depending on the GC
Aux Output	0		
Last Water	0		NEVER select anything but 0
Last Soil	1-30		Set according to # of samples
Blank Last	No		
Flush Vol.	5 ml		
Purge Setup	Soil	Water	Select Soil (use the arrow)
Standard	No		
Flow Rate	38 cc		
Line Heat	110C		
Sample Heat	40C		
Pre-Heat	0.0 min.		
Water Vol.	0.0 ml		
Pre-purge	0.0 min.		
Purge Time	11 min.		
Flushes	0		

Soil Stir	No	Yes	Low-level soils are stirred
Desorb Time	4 min.		
Water Trap Vol.	0		
Purge Setup	Soil	Water	System is verifying setup
Program set up	Auto	Man	System is ready to start, AUTO

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 for MDL determinations. 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. The current MDL ranges at the time of this writing are located in Appendix VIII.

4.2.2 The above procedure is used whenever a major change of equipment occurs or a new method is developed. MDLs are checked quarterly by analyzing a standard at ½ the reporting limit.

4.3 Method Validation

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.

4.4 Method Reporting Limits

Method reporting limits are based on the low level calibration standard, in accordance with SW 846 (see Appendix VIII). The limits are current at the time of the updating of this document.

4.5 Retention Time Windows

4.5.1 Prior to the analysis of any samples, it is necessary to establish retention time windows for the method by analyzing standards for all target analytes over at least a 72-hour period. These standards should be intermixed with real sample extracts in order to mimic actual instrument operating conditions. Tabulate the retention times for all standard compounds, and compute the standard deviation for each set of retention times.

4.5.2 The retention time window half-width is set at +/-3 times the standard deviation as previously determined. This operation must be repeated whenever major equipment changes are made or whenever the chromatographic method is modified.

4.5.3 In some cases, particularly for narrow bore capillary column analyses, the calculated retention time window half widths may be an unrealistically small value or even zero. If that is the case, then substitute a retention time window of a close eluting, similar compound to develop a valid retention time window.

4.6 Initial Multi-Point Calibration

Analyze standard solutions using a minimum of 5 different concentration levels. The lowest concentration should define the reporting limit. The highest concentration should define the upper usable working range of the detector. Evaluation criteria are detailed in Section 6.1. Refer to Appendix III for a tabulated list of calibration standard concentrations.

4.7 Calibration Check Standard

4.7.1 After the instrument is calibrated, the accuracy of the calibration should be checked. A standard from a different source than the calibration standards is analyzed. The acceptance criteria are detailed in Section 6.

4.8 Continuing Calibration Verification (CCV)

4.8.1 Prior to sample analysis, a mid-range calibration standard is analyzed. The computed calibration factor (CF) must meet the criteria detailed in Section 6.2.

4.8.2 The midpoint of the retention time window is set to the retention time for each target analyte in the initial CCV standard of the QC period to be used for compound identification. The retention times for analytes in subsequent CCV standards must be within the retention time windows as set by the initial CCV of the QC period.

4.8.3 Calibration verification standards are analyzed at the frequency of no more than ten samples between standards. All analyses, whether they are instrument blanks, blank spikes, or dry purges, are considered samples. In addition, this standard must be the last analysis made in the analysis sequence. Evaluation criteria are detailed in Section 6.3.

4.9 Sample Analysis

The ICV criteria and method blank criteria must be met prior to analyzing samples.

4.9.1 Analysis sequence

4.9.1.1 See Appendix IV for a detailed sample analysis sequence.

4.9.2 Sample Preparation

4.9.2.1 The samples are removed from the VOA refrigerator and allowed to warm to room temperature.

4.9.3 Water Sample Preparation

4.9.3.1 A 10 ml aliquot of the water sample is transferred to a 10 ml Luerlock syringe, where 10 µl of the surrogate solution is added. The sample containing the surrogate solution is then transferred to a 25 ml fritted soil vial, loaded onto the autosampler, and analyzed by SW5030B.

4.9.3.2 The sample volume and pH are recorded in the instrument logbook. The remaining sample can be transferred into a 20 ml VOA vial with zero headspace and sealed with a Teflon-lined cap.

4.9.3.3 If the analyte concentration exceeds the upper calibration limit, the sample must be diluted and reanalyzed.

4.9.3.4 To dilute a sample, a smaller sample aliquot is analyzed with PFW replacing the remainder of the 10 ml volume.

4.9.4 Soil Sample Preparation

The sample consists of the entire contents of the sample container. Do not decant any of the supernatant liquids. All soil samples must be stirred gently before removing an aliquot.

4.9.4.1 Low Level Soils

4.9.4.1.1 1.0 g of soil is weighed in an appropriate purge vessel, or the entire contents from the EnCore sampler is used. A magnetic stir bar is added. The actual sample weight should be recorded to the nearest tenth of a gram. (For example, 0.95 and 1.05 g should be recorded as 1.0 g, not 1 g.)

4.9.4.1.2 10 ml of reagent water containing the surrogate solution are transferred to the vial containing the soil sample. Refer to the water preparation above for details on the surrogate amount.

4.9.4.1.3 If the analyte concentration exceeds the upper calibration limit, the sample must be diluted and reanalyzed.

4.9.4.1.4 To dilute a sample, analyze according to the high-level soil, laboratory preserved procedure.

4.9.4.2 High Level Soils

4.9.4.2.1 Field preserved samples:

4.9.4.2.2 The client is provided with a 4oz. weighed glass container along with a 25 ml aliquot of methanol that contains a field surrogate (bromofluorobenzene) at 0.8 ng/ul. The client weighs approximately 25 g of soil into the container and then adds the methanol with surrogate.

4.9.4.2.3 Upon receipt by the laboratory, the sample is warmed to room temperature, the weight is recorded, and then 20 ul of the laboratory surrogate (trifluorotoluene) is added to produce a concentration of 0.8 ng/ul. (Note: samples requiring analysis for 1,4-dioxane do not have trifluorotoluene added.) The methanol and soil are re-mixed and then allowed to settle. A 250 ul aliquot is transferred to 10 ml of PFW, but no additional surrogate is added.

4.9.4.2.4 If the analyte concentration exceeds the upper calibration limit, the sample must be diluted and reanalyzed.

4.9.4.2.5 To dilute a sample, a smaller aliquot of the sample/methanol extract is analyzed.

4.9.4.2.6 Laboratory preserved samples:

4.9.4.2.7 Weigh 5.0 g of soil (recorded to the nearest 0.1 g) into a 20 ml VOA vial (or the entire contents from the EnCore sampler); then, add 0.1 ml of surrogate solution and 9.9 ml of methanol to the vial. Shake the sample for 2 minutes, and let the suspended solids settle before use, preferably overnight.

4.9.4.2.8 Transfer 100 µl of the aliquot to 10 ml of PFW. Record the sample weight and the aliquot amount in the instrument logbook.

4.9.4.2.9 If the analyte concentration exceeds the upper calibration limit, the sample must be diluted and reanalyzed.

4.9.4.2.10 To dilute a sample, a smaller aliquot of the sample/methanol extract is analyzed.

4.9.5 The same GC conditions apply to soil samples as water samples.

4.9.6 Compound Identification

4.9.6.1 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 retention time window on a second column. Retention time windows are established as previously described and are updated each QC period. Compounds can only be identified if the ICV and CCV criteria detailed in Section 6 are strictly adhered to.

4.9.6.2 The experienced analyst's judgment weighs heavily in evaluating chromatograms for compound identification. For instance, as referenced in Part 1.3.2 under Method Interferences/Decision-making Process, the retention times of analytes and surrogates may be outside their expected windows due to sample matrix effects. The analyst may decide to readjust the target analytes' retention time windows on an ad hoc basis based on such an observed shift. If this corrective action is taken, it must be fully documented in the case narrative notes.

4.9.7 Compound Quantification

Target compound concentrations are calculated using the external standard calibration equations.

4.9.7.1 Aqueous samples

As expressed in SW846:

$$Concentrat\ ion(\mu g / L) = \frac{A_s \times V_t \times D}{CF_{avg} \times V_i \times V_s}$$

where:

CF_{avg} = Average CF from the initial calibration.

V_t = Total volume of the concentrated extract (µl). For purge-and-trap analysis, V_t is not applicable and therefore, is set at 1.

A_s = Area or height of the peak for the analyte in the sample.

V_i = Volume of extract injected (µl). For low level purge and trap analysis, $V_i = 1$. For medium level purge and trap analysis, Vi has a value.

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 a high level sample was diluted 100 µl to 10,000 µl and subsequently diluted an additional 100 µl to 10,000 µl, the expression would be: (10,000/100) * (10,000/100) = 100 * 100 = 10,000. If no dilution was made, D = 1.

V_s = Volume of the aqueous sample purged (ml). If units of liters are used for this term, multiply the results by 1000.

4.9.7.2 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.

$$Concentration(\mu g / kg) = \frac{A_s \times V_t \times D}{CF_{avg} \times V_i \times W_s}$$

where:

W_s = Dry weight of sample extracted or purged (g). To obtain the dry weight, the wet weight of the sample must be multiplied by percent total solids (TS) expressed as a decimal. Therefore,

$$W_s(dry) = W_s(wet) \times TS \quad \text{where} \quad TS = \frac{100 - \%\text{Moisture}}{100}$$

All other variables have the same definition as for aqueous samples. When a non-aqueous sample is extracted for purge and trap analysis, V_i = volume of methanol extract added to reagent water for analysis.

5. Reports

5.1 Data Packet Organization

See Appendix V for a checklist detailing data packet organization.

5.2 Quality Control Reports

5.2.3 All results for quality control tests are entered into the lab QC database. 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.

5.3 Sample Result Reports

5.4 Data Qualifying Flags

Sample report results are qualified with data qualifying flags. These flags have the following definitions:

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.

J: The analyte of interest was detected below the practical quantitation 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 GC technique is employed, this flag indicates that calculated results from the two columns differ by more than 25%. Generally, we report the higher value (unless matrix interference has elevated one of the results).

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. Quality Control

Refer to Appendix VI for detailed QA and corrective action requirements.

6.1 Initial Calibration

6.1.1 Criteria

6.1.1.1 Initial calibration data can be evaluated in one of two ways: %RSD of the calibration factors (CF) or correlation coefficient (r^2) of a linear regression analysis.

6.1.1.2 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 an unforced intercept.

6.1.1.3 CFs are calculated using the equation:

$$CF = \frac{\text{response}}{\text{ng injected}}$$

6.1.1.4 For a set of data points, the %RSD is determined by calculating the average calibration factor (CF_{avg}) and the standard deviation(σ). The %RSD is equal to 100 times the standard deviation divided by CF_{avg}:

$$\%RSD = \frac{100\sigma}{CF_{avg}}$$

6.1.1.5 Currently, Laucks employs the use of calibration factors. The %RSD must be less than 20% for all compounds.

6.1.1.6 To verify contamination free reagents and apparatus, a method blank is analyzed after the curve.

6.1.1.7 To verify the curve, a blank spike prepared from a second source is analyzed after the curve. It must be within 15% of the true value in order to pass.

6.1.2 Corrective action

If the criteria are not met, the instrument must be recalibrated.

6.1.3 Documentation

6.1.3.1 Copies of the calibration standards and the calculated %RSDs are stored with the raw data. If the initial calibration is not used, this information is noted in the instrument logbook.

6.2 Calibration Check Standard

6.2.1 Criteria

6.2.1.1 The calibration check standard is produced from a source different from the initial calibration standards and must be between 85 and 115 percent recovery.

6.2.2 Corrective action

6.2.2.1 If the percent recoveries are not acceptable, corrective action in the form of reanalysis or recalibration and reanalysis must be performed.

6.2.3 Documentation

6.2.3.1 Copies of the calibration check standard results and percent recoveries are stored with the initial calibration

6.3 Continuing Calibration Verification

6.3.1 Criteria

6.3.1.1 At the beginning of the QC period and after every ten injections, a CCV standard is analyzed. The CF for each compound is calculated and the percent difference is calculated as follows:

$$\%Difference = \frac{CF_v - CF_{avg}}{CF_{avg}} \times 100$$

where:

CF_v = CF from the analysis of the verification standard.
CF_{avg} = Average CF from the initial calibration.

Note: The %D results cannot exceed the detailed CCV criteria of +/-15%.

The retention times for all target analytes must fall within the RT windows.

6.3.2 Corrective action

6.3.2.1 Check calculations, examine the chromatogram, check the integration, analyze another CCV, or perform instrument maintenance. To validate the quantitation of target analytes in analytical samples, the samples must be bracketed by CCVs where the percent difference is within +/-15%.

6.3.2.2 If the average percent difference is less than 15%, then the CCV standard is considered to be acceptable. If one of the bracketed samples has a detectable amount of the analyte whose %D has exceeded the allowable limit, then just that sample needs to be re-analyzed.

6.3.3 Documentation

6.3.3.1 Copies of the continuing calibration standards and the calculated %Ds are stored with the raw data. If the continuing calibration standard cannot be used, this information is noted in the instrument logbook.

6.4 Method Blank

6.4.1 Criteria

6.4.1.1 A method blank is used to verify contamination free reagents and apparatus. A method blank is analyzed prior to sample analysis. Method blank control limits are ½ the reporting limits for all current analytes. If analysis of the method blank results in detection of an analyte between the reporting limit and ½ the reporting limit, the chromatography is examined, and the method blank may be used if either the analyte was not detected in the samples or the analyst finds that the higher result is due to an anomaly that will not affect sample analyses.

6.4.2 Corrective action

6.4.2.1 Corrective action in the form of reanalysis of the method blank prior to sample analysis is performed when target analytes are present above the reporting limit or surrogate recoveries are outside the control limits.

6.4.2.2 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, method blanks may have to be analyzed from each stage of the sample processing to determine the contamination source so it can be eliminated.

6.4.3 Documentation

6.4.3.1 Copies of all method blank analyses are stored with the sample analyses raw data. The results for the method blank analyses are reported electronically via the laboratory's LIMS database. If a method blank cannot be used, this information is noted in the instrument logbook.

6.5 Blank Spike or QC Check Sample (LCS)

6.5.1 Criteria

6.5.1.1 A blank spike is prepared by adding a known amount of analyte to an aliquot of PFW for aqueous sample analysis or a weighed amount of sand for soil/sediment analysis instead of an actual sample. A method blank with added analytes is a blank spike. An aqueous blank spike is the same as a QC check standard, and the same standard solution can be used as a calibration check standard. The recovery criteria can be found in Appendix VIII.

6.5.2 Corrective action

6.5.2.1 The blank spike is used to determine the method's accuracy without including any matrix problems. Sample reanalysis is triggered by an out of control blank spike.

6.5.3 Documentation

6.5.3.1 Copies of method blank spike analyses are stored with the sample analyses raw data. The results for the blank spike analyses are reported electronically via the laboratory's LIMS database. The analyte and surrogate recoveries are monitored in a control chart to look for trends in the recoveries. If data from the blank spike analysis cannot be used, this information is noted in the instrument logbook.

6.6 Matrix Spike/Matrix Spike Duplicate

6.6.1 Criteria

6.6.1.1 A sample is chosen at random from the samples to be analyzed at a rate of one in twenty (5%). Then, duplicate aliquots are prepared by adding aliquots of spiking solution prior to prep and/or analysis. The matrix spike sample is used to evaluate the matrix effect of the sample upon recovery of the analytes. The duplicate fortified analysis is to evaluate the precision of the method by monitoring the relative percent difference (%RPD). Recovery and RPD criteria can be found in Appendix VIII.

6.6.1.2 The recovery of spike analytes is calculated as follows:

$$\%Recovery = \frac{SSR - SR}{SA} \times 100$$

where:

SSR = Concentration in spiked sample.
SR = Native concentration in unspiked sample.
SA = Concentration of spike added.

The relative percent difference is calculated as follows:

$$RPD = \frac{S1 - S2}{\frac{(S1 + S2)}{2}} \times 100$$

where:

S1 = Measured concentration for MS sample.
S2 = Measured concentration for MSD sample.

6.6.2 Corrective action

6.6.2.1 Samples with spike recoveries and/or RPD values outside control limits will be reviewed for possible corrective action. Corrective action may involve recalculation and/or reanalysis. This process should also include evaluation of the recovery of surrogate compounds in the MS sample and recovery of matrix spiking compounds from the blank spike analysis. In all cases, a narrative explanation of the condition is required to detail the corrective actions taken. If a trend in out-of-control recoveries or 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.

6.6.3 Documentation

6.6.3.1 The raw data for the matrix spike and matrix spike duplicate analyses are stored with the sample analyses raw data. The results for the matrix spike analyses are reported electronically via the laboratory's LIMS database.

6.7 Surrogate Recovery

6.7.1 Criteria

6.7.1.1 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. Recovery limits are 70 – 130%. Surrogate compound recoveries are calculated as follows:

$$\%Recovery = \frac{S_m}{S_a} \times 100$$

where:

S_m = Concentration of surrogate measured in sample.
S_a = Concentration of surrogate added.

6.7.2 Corrective Action

6.7.2.1 Check calculations for possible error. Reanalysis is required for surrogate recoveries that exceed the established control limits, unless matrix interference is observed or surrogates are diluted out.

6.7.2.2 Out-of-control surrogate recoveries in the method blank require that the method blank be reanalyzed. Sample analyses are not performed until all criteria for the method blank analysis are met. Sample and QC analyses require reanalysis for out-of-control surrogate recoveries. If the sample analyses demonstrate out-of-control surrogate recoveries due to matrix interference, this corrective action is discussed in the narrative.

6.7.3 Documentation

Copies of all surrogate recoveries are stored with the sample analyses raw data. The surrogate recoveries for all samples, blanks, and QC analyses are reported electronically via the laboratory's LIMS database.

7. References

SW 846 - Test Methods for Evaluating Solid Waste - Method 8000B "Determinative Chromatographic Separations", USEPA - Office of Solid Waste and Emergency, Revision 2, December 1996.

SW 846 - Test Methods for Evaluating Solid Waste - "Non-Halogenated Organics using GC/FID", Method 8015B, USEPA - Office of Solid Waste and Emergency Response, Revision 2, December 1996.

SW 846 - Test Methods for Evaluating Solid Waste - "Purge and Trap", Method 5030B, U.S. EPA, Revision 2, December, 1996.

SW 846 - Test Methods for Evaluating Solid Waste - "Purge and Trap", Method 5035, U.S. EPA, December, 1996.

SW 846 - Test Methods for Evaluating Solid Waste - "Organic Analytes", Chapter Four, U.S. EPA, December, 1996.

APPENDIX I

Target Analytes And Surrogates

Analytes	CAS Registry Number
Isobutyl alcohol	78-83-1
Propionitrile	107-12-0
Acetonitrile	75-05-8
1,4-Dioxane*	123-91-1
Tert-butyl alcohol (TBA)	75-65-0
Diisopropyl ether (DIPE)	108-20-3
Ethyl-tert-butyl ether (ETBE)	637-92-3
Tert-amyl-methyl ether (TAME)	994-05-8
Surrogates	
Trifluorotoluene*	98-08-8
Bromofluorobenzene	460-00-4

APPENDIX II

Analyte Elution Order

Column: DB-624	Column: DB-VRX
Acetonitrile	Acetonitrile
Propionitrile	Propionitrile
Isobutyl alcohol	Isobutyl alcohol
Trifluorotoluene*	Trifluorotoluene*
1,4-Dioxane*	1,4-Dioxane*
Bromofluorobenzene	Bromofluorobenzene

* These two compounds co-elute. Therefore, when 1,4-dioxane is requested as a target analyte, the surrogate trifluorotoluene is omitted from the analysis.

Column: DB-624	Column: DB-VRX
Tert-butyl alcohol (TBA)	Tert-butyl alcohol (TBA)
Diisopropyl ether (DIPE)	Diisopropyl ether (DIPE)
Ethyl-tert-butyl ether (ETBE)	Ethyl-tert-butyl ether (ETBE)
Tert-amyl-methyl ether (TAME)	Tert-amyl-methyl ether (TAME)
Trifluorotoluene	Trifluorotoluene
Bromofluorobenzene	Bromofluorobenzene

Appendix III

Initial Calibration Concentrations (µg/l)*

Compound	STD1	STD2	STD3	STD4	STD5	STD6
Acetonitrile	20	40	80	100	200	300
Propionitrile	20	40	80	100	200	300
Isobutyl alcohol	20	40	80	100	200	300
1,4-Dioxane†	50	100	500	1000	2000	3000
Trifluorotoluene†	1	2	5	10	15	20
Bromofluorobenzene	1	2	5	10	15	20

* At the time of this writing, these are the current calibration standards, however, they are subject to change.
† Since these two compounds co-elute, the 1,4-dioxane calibration curve is analyzed separately.

Compound	STD1	STD2	STD3	STD4	STD5	STD6	STD7
Tert-amyl-methyl ether (TAME)	1	2	5	10	20	50	100
Ethyl-tert-butyl ether (ETBE)	1	2	5	10	20	50	100
Diisopropyl ether (DIPE)	1	2	5	10	20	50	100
Tert-butyl alcohol (TBA)	5	10	25	50	100	250	500
Trifluorotoluene	2	4	10	20	30	40	60
Bromofluorobenzene	2	4	10	20	30	40	60

APPENDIX IV

Analysis Sequence

Injection	Sample
1	Std 1
2	Std 2
3	Std 3
4	Std 4
5	Std 5
6	Std 6
	Method Blank
	A total of 10 samples and/or blanks, duplicates, or matrix spike samples.
	CCV
	A total of 10 samples and/or blanks, duplicates, or matrix spike samples.
	CCV (closing?)

or

Injection	Sample
1	ICV
	Method Blank
	A total of 10 samples and/or blanks, duplicates, or matrix spike samples.
	CCV
	A total of 10 samples and/or blanks, duplicates, or matrix spike samples.
	CCV (closing?)

APPENDIX V

Data Packet Check List

I. CLIENT DELIVERABLE - IF REQUESTED

II. QC Summary

_____ Surrogate Recovery Summary Report
_____ Blank Spike Report
_____ MS/MSD Report
_____ Method Blank Summary Report

III. Sample Data

(In numerical order)

_____ Organic Analysis Data Sheet
_____ Sample Confirmation Form
_____ Chromatogram/ Quantitation Report Primary
_____ Chromatogram/ Quantitation Report Secondary

IV. Standard Data

(In chronological order)

_____ Linearity Report Primary/Secondary
_____ CCV Reports, %Difference Primary/Secondary

Linearity Standards:
_____ Chromatograms/ Quantitation Reports Primary
_____ Chromatograms/ Quantitation Reports Secondary
Continuing Calibration Standards:
_____ Chromatograms/ Quantitation Reports Primary
_____ Chromatograms/ Quantitation Reports Secondary
Other Standards Used to Support Sample Data (if required):
_____ i.e., MDL Reports

V. Raw QC Data

_____ Method Blank Report
_____ Confirmation Form
_____ Chromatogram/ Quantitation Report Primary
_____ Chromatogram/ Quantitation Report Secondary

_____ Blank Spike Report
_____ Confirmation Form
_____ Chromatogram/ Quantitation Report Primary
_____ Chromatogram/ Quantitation Report Secondary

_____ Matrix Spike Report
_____ Confirmation Form
_____ Chromatogram/ Quantitation Report Primary
_____ Chromatogram/ Quantitation Report Secondary

_____ Matrix Spike Duplicate Report
_____ Confirmation Form
_____ Chromatogram/ Quantitation Report Primary
_____ Chromatogram/ Quantitation Report Secondary

VI. Bench Sheets

_____ SDG summary
_____ Injection Log
_____ Misc. Work Sheets: soil extraction, %TS, calculations, HTVR
_____ Standards Log for all standards used with work

VII. Reject Data

DO NOT COPY DO NOT PAGINATE

Acquired 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 VI

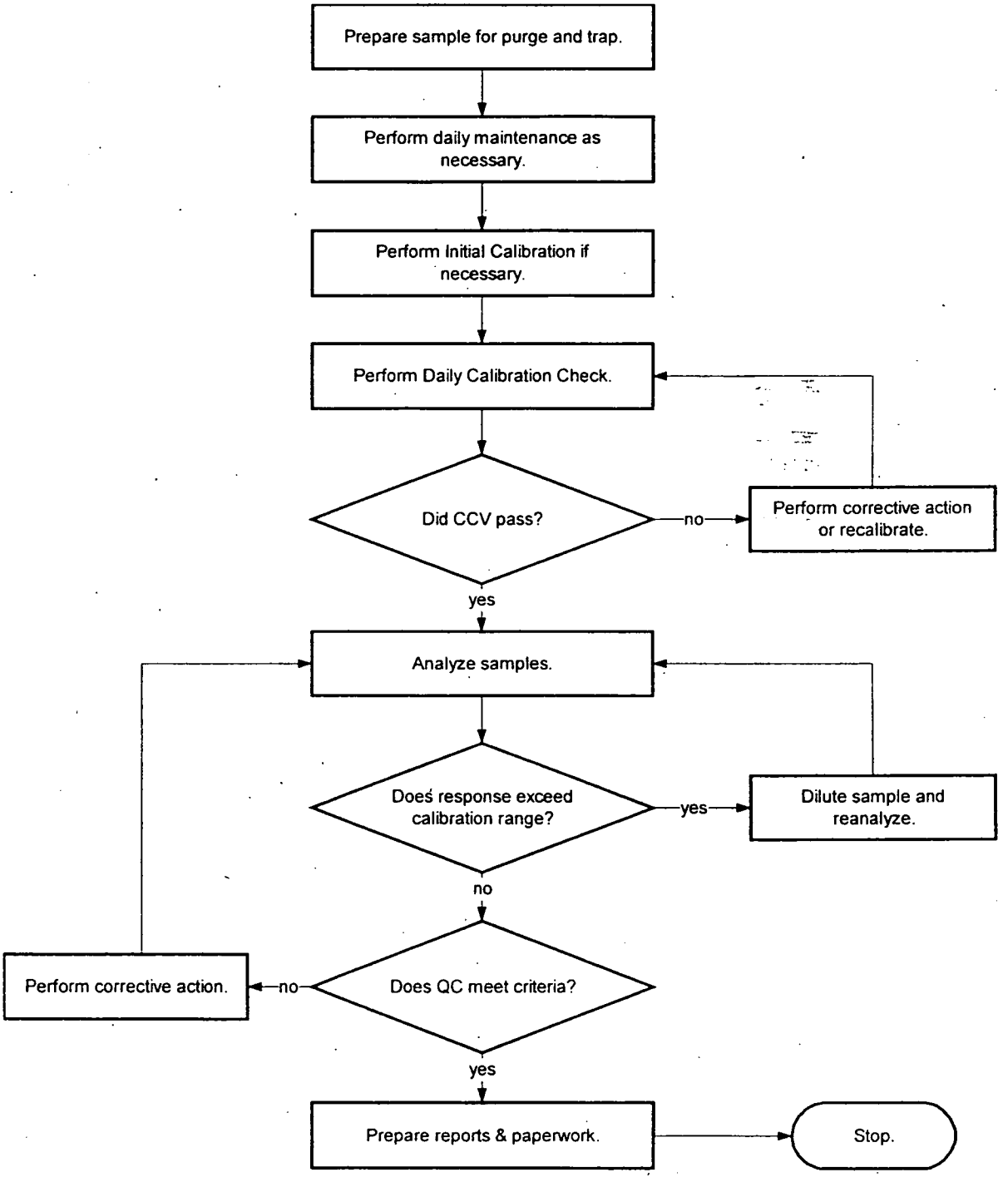
Method 8015B QA Requirements and Corrective Actions

QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
Holding Time	14 days from collection.	14 days from collection.	N/A	N/A	HTVR (holding time violation report) filed with data and noted in file and narrative.
Initial Calibration Curve	Minimum of 5 levels. If %RSD < 20, linearity assumed and average RF used. Alternatively, use linear regression to determine linearity.	Minimum of 5 levels. If %RSD < 20, linearity assumed and average RF used.	Initially and until ICV fails.	Reanalysis of out of control standards.	Copies of all raw data are filed.
Initial Calibration Verification	Mid-level calibration standard run every 10 samples. If not within ±15%, recalibrate.	Mid-level calibration standard run every 10 samples. If >15%D, reanalyze or recalibrate. RT are updated from this standard for all subsequent analyses.	At the beginning of every QC period.	Reanalysis of ICV 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.
Continuing Calibration Verification	Mid-level calibration standard run every 10 samples. If not within ±15%, recalibrate. Standard RT must fall within daily window or system is out of control.	Mid-level calibration standard run every 10 samples. If > 15%D, reanalyze for any out of control analyte which is detected in associated sample analysis. Standard RT must fall within daily window or system is out of control.	Every 10 samples.	Samples injected after criteria was exceeded must be reanalyzed.	Copies of raw data filed and notated in instrument logbook.
Internal Standards	Optional.	No internal standards are used at this time.			
Method Blank	One method blank per batch of up to 20 samples, or when there is a change in reagents, whichever is more frequent. Analysis of the method blank should demonstrate that interferences from the analytical system, glassware and reagents are under control.. Analytes present should be < MDL.	< 1/2RL for all analytes.	One method blank per batch of up to 10 samples.	Samples may not be analyzed until all criteria for the method blank are met.	Copies of raw data filed, and reported electronically. Daily control charts for all method blanks are recorded.

QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
Surrogate Standards	Add surrogates to encompass range of temperature program. Results must fall within laboratory established control limits.	4-Bromofluorobenzene and/or trifluorotoluene. Percent recoveries must meet established laboratory control limits. See QC database for laboratory established control limits. (Currently 70 – 130%)	Surrogates are used in all standards, blanks, samples, and QC.	Reanalysis if surrogate recoveries exceed the established control limits. If reanalysis produces similar surrogate recoveries, then it may be due to matrix interference.	Any out of control surrogates are documented in associated file.
MS/MSD & Blank Spike	One blank spike per analytical batch. One MS/MSD per 20 samples or each batch of samples, whichever is more frequent.	Blank spike recoveries, must meet control limits established by laboratory. See control limits database for laboratory established limits.	One blank spike daily; MS/MSD per 20 samples.	Reanalysis of blank spike if out of control. If MS/MSD out of control and blank spike in control, no further action required.	MS/MSD recoveries are stored electronically. Raw data is stored with file. Out of control events are notated in file.
Sample Preservation and Storage	Water samples: pH ≤ 2 with HCL. All samples: store at 4° C.	Water samples: pH ≤ 2 with HCL. All samples: store at 4°C.	All water samples are to be preserved. Any samples to be stored at 4°C.	The pH is measured for all water samples. Client is notified if aqueous samples are not acid-preserved. pH cannot be determined until after analysis in order to maintain sample integrity.	pH of all water samples recorded in instrument logbook.
Standard Solution Expiration	Stock standards: 6 months. Store at 4° C with minimum headspace, away from light. Aqueous calibration standards: 1 hour , 24 hours if stored with zero headspace.	Stock standards: 6 months; Stored -10° to -20° C. Aqueous calibration standard: daily.			All standard data recorded in standard logbook.
Field Sample Amount Required	Water samples: 2 40 ml vials with zero headspace. Soils: glass, with Teflon-lines lids.	Water samples: 2 40 ml vial with zero headspace. Soil samples: 2 oz. glass containers, Teflon-lined lids.			Bottles received by laboratory documented electronically.
Applicability	Groundwaters, soils, sludges, water-miscible and non-water miscible wastes.				

APPENDIX VII

Flow Chart



APPENDIX VIII

MDL Ranges / Reporting and Control Limits

For Aqueous Samples:

			Blank Spikes		Matrix Spikes	
Compound	**MDL**	**RL**	**LCL - UCL**	**RPD**	**LCL - UCL**	**RPD**
Acetonitrile	3.660	40	65 - 133	30	57 - 126	20
Propionitrile	4.626	40	77 - 121	30	73 - 124	15
Isobutyl Alcohol	6.258	40	68 - 131	30	63 - 130	18
1,4-Dioxane	43.88	100	-		-	
a,a,a-Trifluorotoluene(s)	N/A		-	N/A	-	N/A
p-Bromofluorobenzene(s)	N/A		-	N/A	-	N/A

RL - Reporting Limit (ug/L) LCL - Lower control limit. UCL - Upper control limit. RPD - Relative percent difference.
MDL - Typical range for MDL (ug/L). (s) - Indicates a surrogate.
The reporting limit is based on a ten ml sample volume purged. The actual reporting limit will vary.

For Low Level Soil / Sediment Samples:

			Blank Spikes		Matrix Spikes	
Compound	**MDL**	**RL**	**LCL - UCL**	**RPD**	**LCL - UCL**	**RPD**
Acetonitrile	14.18	400	60 - 140	30	60 - 140	30
Propionitrile	13.19	400	60 - 140	30	60 - 140	30
Isobutyl Alcohol	13.17	400	60 - 140	30	60 - 140	30
1,4-Dioxane	38.55	1000	60 - 140	30	60 - 140	30
a,a,a-Trifluorotoluene(s)	N/A		-	N/A	-	N/A
p-Bromofluorobenzene(s)	N/A		-	N/A	-	N/A

RL - Reporting Limit (ug/Kg) LCL - Lower control limit. UCL - Upper control limit. RPD - Relative percent difference.
MDL - Typical range for MDL (ug/Kg). (s) - Indicates a surrogate.
The reporting limit is based on one gram of sample purged. The actual reporting limit will vary.

For High Level Soil / Sediment Samples (field preservation):

			Blank Spikes		Matrix Spikes	
Compound	**MDL**	**RL**	**LCL - UCL**	**RPD**	**LCL - UCL**	**RPD**
Acetonitrile	*	1600	60 - 140	30	60 - 140	30
Propionitrile	93.29	1600	60 - 140	30	60 - 140	30
Isobutyl Alcohol	67.26	1600	60 - 140	30	60 - 140	30
1,4-Dioxane	359.9	4000	60 - 140	30	60 - 140	30
a,a,a-Trifluorotoluene(s)	N/A		-	N/A	-	N/A
p-Bromofluorobenzene(s)	N/A		-	N/A	-	N/A

RL - Reporting Limit (ug/Kg) LCL - Lower control limit. UCL - Upper control limit. RPD - Relative percent difference.
MDL - Typical range for MDL (ug/Kg). (s) - Indicates a surrogate.
The reporting limit is based on purging a 250ul aliquot of 25grams of sample preserved with 25ml of methanol. The actual reporting limit will vary.
* Acetonitrile is visible only on the DB-624 column and cannot be confirmed when a large amount of methanol is present.

For High Level Soil / Sediment Samples (laboratory preservation):

			Blank Spikes		Matrix Spikes	
Compound	**MDL**	**RL**	**LCL - UCL**	**RPD**	**LCL - UCL**	**RPD**
Acetonitrile	*	8000	60 - 140	30	60 - 140	30
Propionitrile	631.7	8000	60 - 140	30	60 - 140	30
Isobutyl Alcohol	777.2	8000	60 - 140	30	60 - 140	30
1,4-Dioxane	2396	20000	60 - 140	30	60 - 140	30
a,a,a-Trifluorotoluene(s)	N/A		-	N/A	-	N/A
p-Bromofluorobenzene(s)	N/A		-	N/A	-	N/A

RL - Reporting Limit (ug/Kg) LCL - Lower control limit. UCL - Upper control limit. RPD - Relative percent difference.
MDL - Typical range for MDL (ug/Kg). (s) - Indicates a surrogate.
The reporting limit is based on purging a 100ul aliquot of 5grams of sample preserved with 10ml of methanol. The actual reporting limit will vary.
* Acetonitrile is visible only on the DB-624 column and cannot be confirmed when a large amount of methanol is present.

Note: At the time of this revision, analysis of the oxygenates is still under development, and MDL ranges have yet to be determined. MDLs are based on the low standard, which is currently 1 µg/l for TAME, ETBE, and DIPE; and 5 µg/l for TBA.

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

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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.

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

**When chlordane is requested, a technical chlordane multicomponent standard is analyzed and response factors are calculated for 3-5 major peaks (including the alpha- and gamma-isomers). If these peaks are present in the sample at similar ratios to those found in the technical chlordane standard, an average concentration is calculated from the peaks chosen for calibration. If the peaks are present in the sample at dissimilar ratios to those found in the technical chlordane standard, a calibration factor will be calculated for the standard based upon the sum of the responses for each of the peaks and the sample concentration will be calculated based on the sum of the same peaks in the sample.

SW8082A COMPOUNDS	
Aroclor-1016	Aroclor-1221
Aroclor-1232	Aroclor-1242
Aroclor-1248	Aroclor-1254
Aroclor-1260	

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).

1.2.2 The continuing calibration standards' concentrations are varied per the Department of Defense (DOD) quality systems' requirement.

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 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. Blank spikes are required on all HAZWRAP and NFESC work. 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.
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 which 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. Equipment list:
Gas chromatograph (Hewlett-Packard 5890, 5890A, 6890 w/µECDs)
Autosampler (Hewlett-Packard 7673A, 7683)
2 electron-capture detectors (Hewlett-Packard)
2 capillary chromatographic columns of dissimilar phase (J&W DB5 and DB608, 30m x 0.45mm megabore, J&W DB-XLB, DB35ms 30m x 0.32mm, or equivalents).
Helium carrier gas
5% methane/95% argon detector make-up gas,
EZChrom Data Acquisition System version 6.6, Target Analytical Software for NT Operating System version 4.02, Pentium PCs, or equivalent.

2.2 Maintenance

2.2.1 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.

2.3 Standards

2.3.1 Commercially prepared, certified stock standards are used to prepare working solutions for all surrogates, calibration mixes, and spike mixes. The 2 calibration mixes (INDA and INDB) contain all of the individual pesticide analytes. The spike mix contains 3 representative individual pesticides and one Aroclor. These are ordered from Restek, Supelco or an equivalent supplier. Stock standards must be replaced by the manufacturers expiration date.

2.3.2 Calibration standards are prepared at 5 different concentration levels by dilution of the stock standards with hexane. High-level INDA and INDB mixtures are made at 16 times the PQL concentration. The lower levels are diluted by factors of 2, 4, 8 and 16. They must be replaced after 6 months or by the expiration date of the material they were made from, whichever is earlier.

2.3.3 Multicomponent analyte calibration standards (Aroclors, chlordane, Toxaphene), with the exception of Aroclors 1016 and 1260, are prepared at one concentration level, by dilution of commercially purchased stock solutions in hexane. Standards of the Aroclors 1016 and 1260 are combined in a mixture and prepared at five concentration levels. These must be replaced after 6 months or by the expiration date of the material they were made from, whichever is earlier.

2.3.4 A breakdown evaluation (EVAL) mix is prepared from dilution of stocks of 4,4'-DDT and endrin with hexane.

2.3.5 A surrogate mix is prepared from separate solutions which 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).

2.3.6 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.

2.3.7 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
Chlordane	±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

4.6.1.1 Analyze single component pesticide standards using at least 5 different concentration levels for linear calibrations. The lowest concentration should be at a concentration near, but above, the method reporting limit or PQL. The highest concentration should define the upper usable working range of the detector. After the initial calibration is complete, an additional standard is analyzed. This additional standard is prepared from

a source that differs from the source of standards used in the initial calibration. This standard is performed in order to verify the initial calibration.

4.6.1.2 Analyze multi-component pesticide and PCB standard solutions at one concentration level, with the exception of the Aroclor 1016/1260 mixed standard. This standard should be analyzed at 5 different concentration levels for linear calibration. This step can be omitted if analyzing for pesticides only.

4.6.1.3 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.

4.6.1.4 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. 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 20% for each analyte or averaged across all analytes in the calibration standard mix. Laucks uses 40% percent as the upper limit for all compounds as an internal guideline although it is not a requirement of SW 846.

4.7.4 Corrective action

4.7.4.1 If the criteria are not met, the instrument must be re-calibrated.

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.

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 Initial Calibration Verification

4.9.1 Concentration and/or CF Criteria

4.9.1.1 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.

4.9.1.2 Using the appropriate calculation technique (average CF) compute either CFs or concentration values. For linear calibrations the ICV standard can be verified by calculating either the percent difference or the percent drift.

4.9.1.2.1 The percent difference calculation compares the ICV 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

4.9.1.2.2 The percent drift calculation compares the ICV calculated concentrations to the

theoretical (or actual) concentration of the ICV 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

4.9.1.3 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.

4.9.2 Corrective action

4.9.2.1 If the ICV criteria are not met, no sample extracts can be analyzed. Perform system maintenance and re-check the ICV. If the criteria still cannot be met, the system must be recalibrated.

4.10 Updating Retention Time Windows

4.10.1 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.

4.11 Instrument Blank

4.11.1 Criteria

4.11.1.1 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.

4.11.2 Corrective action

4.11.2.1 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 of the analyte found in the IBLK.

4.12 Continuing Calibration Verification

4.12.1 The initial calibration is verified each 12 hours by injection of a calibration standard that alternates concentration levels. 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.

4.12.2 In accordance with DOD requirements, the concentration levels of the continuing calibration are varied approximately every 2 weeks when a new working solution is made. The concentration levels vary from the low level, mid-level and high level standards.

4.12.3 Criteria

4.12.4 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.

4.12.5 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.

4.12.6 The retention times for all target analytes must fall within the RT windows established by the mid-point of the initial calibration.

4.12.7 Corrective Action

4.12.8 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.

4.13 Method Blanks

4.13.1 Criteria

4.13.1.1 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.

4.13.2 Corrective action

4.13.2.1 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.

4.14 Blank Spikes

4.14.1 Criteria

4.14.1.1 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. It is recommended that all single component pesticide target analytes of concern and a minimum of one Aroclor be 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 per the USACOE Shell document. In addition, 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.

4.14.1.2 Blank spike recoveries must meet the criteria specified in the quality control database.

4.14.2 Corrective action

4.14.2.1 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.

4.15 Matrix Spike

4.15.1 Criteria

4.15.1.1 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

4.15.1.2 The recovery criteria are detailed in the QC database. 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 quality control database.

4.15.2 Corrective action

4.15.2.1 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.

4.16 Matrix Spike Duplicate

4.16.1 Criteria

4.16.1.1 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:

$$\%\text{RPD} = \frac{|\chi - \delta|}{(\chi + \delta)/2} \text{x}100$$

where:
χ = measured concentration for MS sample
δ = measured concentration for MSD sample

4.16.1.2 RPD control limits are detailed in the QC database.

4.16.2 Corrective action

4.16.2.1 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.

4.17 Surrogate Recovery

4.17.1 Criteria

4.17.1.1 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

4.17.1.2 Detailed surrogate recovery control limits are tabulated in the QC database.

4.17.2 Corrective Action

4.17.2.1 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.

4.17.2.2 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°C per min
Final temperature:	275°C
Final hold time:	9 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:

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.

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 gamma-BHC, Heptachlor, Aldrin, 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

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
Chlordane - technical					1000
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

Appendix I (Continued)

Calibration Stock Solutions, mg/L

Compound	Mix	Conc
alpha-BHC	A	5.0
beta-BHC	B	5.0
delta-BHC	B	5.0
gamma-BHC (Lindane)	A	5.0
alpha-Chlordane	B	5.0
gamma-Chlordane	B	5.0
Heptachlor	A	5.0
Aldrin	B	5.0
Heptachlor epoxide	B	5.0
Endosulfan I	A	5.0
Dieldrin	A	10.0
4,4'-DDE	B	10.0
Endrin	A	10.0
Endosulfan II	B	10.0
4,4'-DDD	A	10.0
Endosulfan sulfate	B	10.0
4,4'-DDT	A	10.0
Methoxychlor	A	50.0
Endrin aldehyde	B	10.0
Endrin ketone	B	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

*-The single component pesticides are contained in 2 separate mixes (A and B) when utilizing megabore (0.45mm ID) columns. These same components are combined into 1 mix when utilizing capillary (0.32mm ID) columns.

Breakdown Check Solution (CLP PEM solution), µg/L

Compound	**Concentration**
4,4'-DDT	100
Endrin	50

Surrogate Stock Solution, mg/L

Compound	**Concentration**
2,4,5,6-tetrachloro-m-xylene	10
Decachlorobiphenyl	10

APPENDIX II

Analysis Sequence

Injection	Sample
	hexane rinse
1	breakdown check standard (PEM)
2	ICV standard INDAM
3	ICV standard INDBM
4	ICV standard multi-components(for PCB only analysis - can replace above 3 stds)
5	up to 10 subsequent sample or QC extracts
15	solvent rinse or IBLK (optional - not required)
16	CCV standard INDAM
17	CCV standard INDBM
18	CCV standard multi-components (for PCB only analysis - can replace above 2 stds)
19	up to 10 subsequent sample or QC extracts
last	CCV standard INDAM
last	CCV standard INDBM
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

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

_____ Injection Sequence
_____ Target Method
_____ Extraction Bench Sheets
_____ Miscellaneous Work Sheets. i.e. %TS, SDG 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 ≤20% for each analyte or averaged across all analytes.	5 calibration stds for linear, 6 stds for quadratic, for all single and multi-components, %RSD ≤20% for each analyte or averaged across all analytes. A second source standard is analyzed to verify the initial calibration.	After performing major instrument maintenance or when persistent difficulties meeting CCV criteria occur.	Recalibrate or narrate faults if possible	Narrative
Initial Calibration Verification	Must be ±15% D for each analyte or averaged across all analytes.	Must be ±15% D for each analyte or averaged across all analytes.	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 or averaged across all analytes.	Must be ±15% D for each analyte or averaged across all analytes.	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

QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
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
Surrogate Recovery	Limits to be determined by the lab	Listed in QC database	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 QC 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	Limits not specified	Listed in QC 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	Limits not specified	Listed in QC 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
Standard Reference Material (SRM) Recovery	None required	None 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

	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

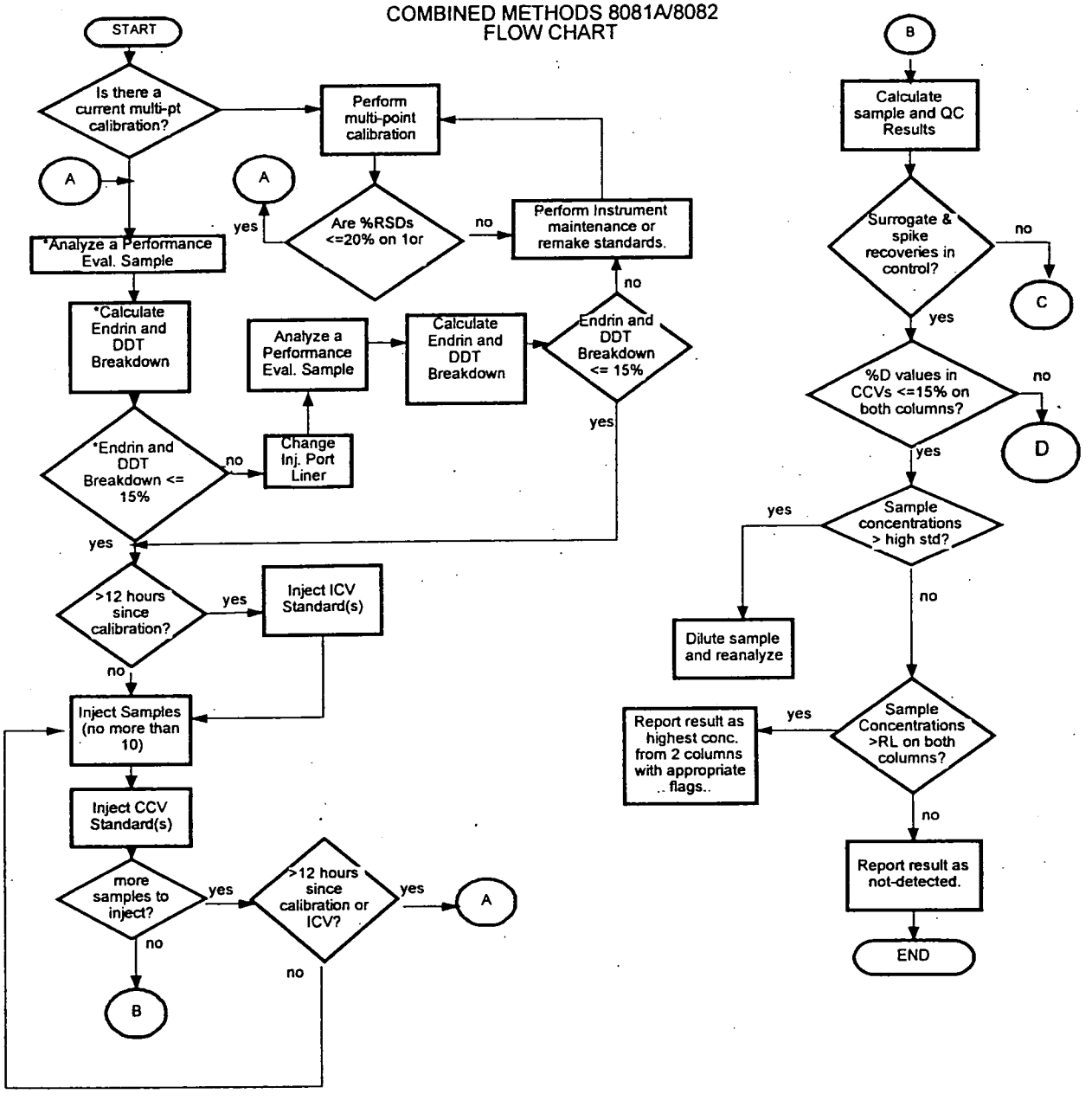
Compound Elution order on DBXLB and DB35ms Capillary (0.32 mm ID) Columns

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

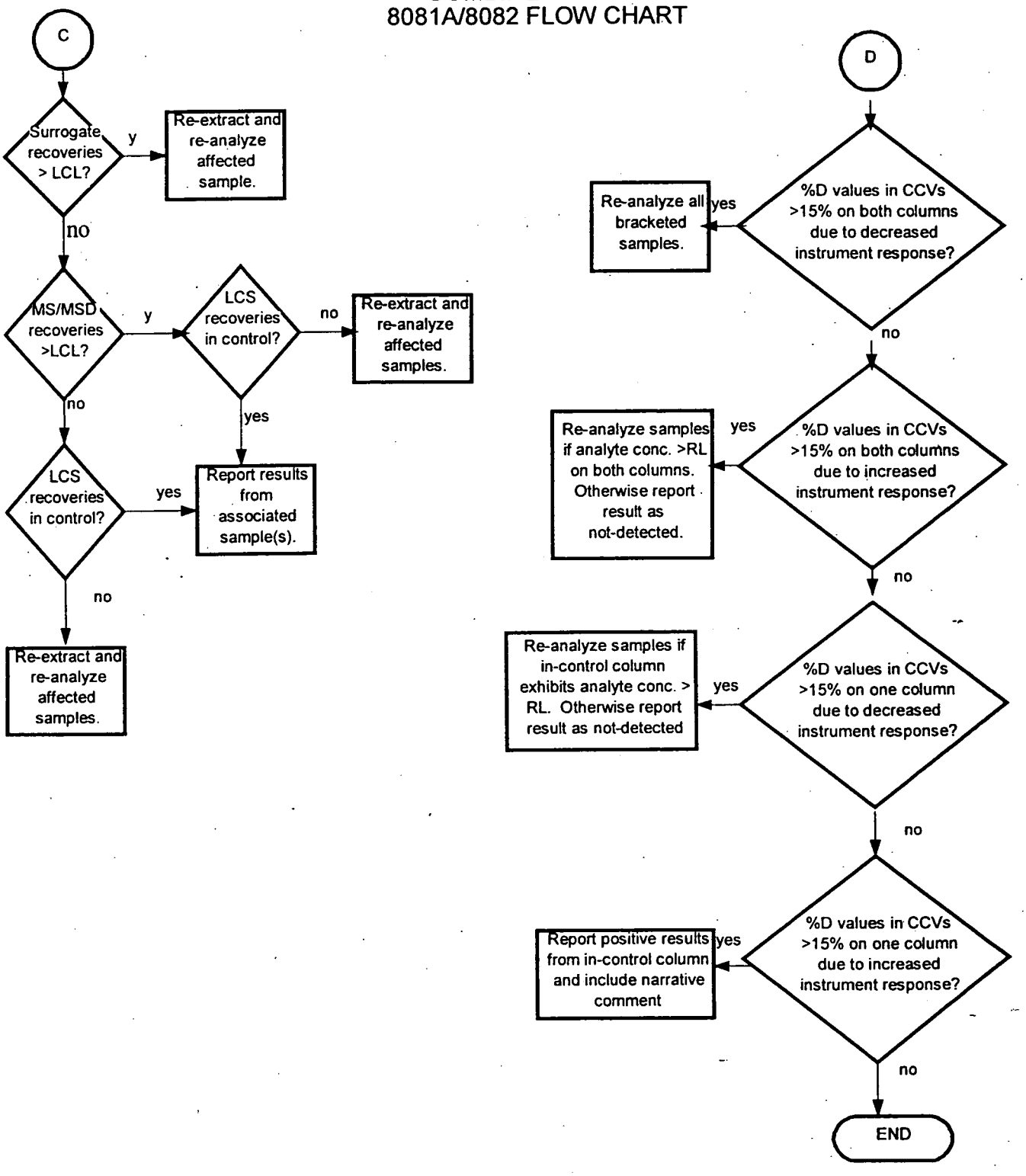
Flow Chart

COMBINED METHODS 8081A/8082
FLOW CHART



*These steps can be eliminated if analyzing for SW8082 compounds only

COMBINED 8081A/8082 FLOW CHART



LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-8151

Title: **Analysis of Chlorinated Herbicides by Method 8151A**

Revision history:

Number	Date
0	10/08/97
1	2/5/98
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Revised by: Monica Carr — Date: 3/22/02
Monica Carr, Organic Division Manager

Reviewed by: Harry Romberg — Date: 3-22-02
Harry Romberg, QA Officer

Approved by: Kathy Kreps — Date: March 22, 2002
Kathy Kreps, Laboratory Director

Controlled Document
No. 20 **Assigned to:** TeTr

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FLOW CHART 29

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

1.1.2 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.

1.2 Sample Collection, Sample Storage, Holding Times

1.2.1 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.

1.3 Definition of Terms

1.3.1 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. Blank spikes are required on all AIMTech and NFESC work. 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 term is borrowed from the CLP GC/MS protocol. It is a standard which 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.
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 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.

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 or equivalent.
Autosampler: Hewlett-Packard 7673 or equivalent.
Electron-capture detectors: Hewlett-Packard or equivalent.
Capillary chromatographic columns of dissimilar phase: J&W DB5 and DB608 or DB17, 30m x 0.45mm, 0.53mm, or 0.25mm megabore or equivalent.
Helium carrier gas and 5% methane/95% argon detector make-up gas
Data System: EZChrom Data Acquisition System version 6.6, Target Analytical Software for NT Operating System version 4.02, Pentium PCs, or equivalent.

2.2 Standards

2.2.1 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.

2.2.2 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.

2.2.3 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.

2.2.4 Appendix I details the compounds and concentrations contained in all solutions.

Primary	Manufacturer	Catalog Number	Comments
8 cmpds	Ultra	HBM-8152M	Methyl Ester
MCPA, MCPP	Restek	32059	Methyl Ester
PCP	Restek	31297	Acid
4-Nitrophenol	Restek	31296	Acid
Picloram	Restek	32266	Methyl Ester
Hexachlorophene	Ultra	PH270-1	Methyl Ester
2,4-DCPAA(surr)	Ultra	PPS-166	Methyl Ester
Second Source	**Manufacturer**	**Catalog Number**	**Comments**
10 cmpds	Supelco	47375	Methyl Ester
PCP	Supelco	48692	Methyl Ester
4-Nitrophenol	Supelco	48695	Methyl Ester
Picloram	Ultra	PS1108	Methyl Ester
Hexachlorophene	Supelco	40323	Methyl Ester
2,4-DCPAA(surr)	Supelco	47339	Methyl Ester

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. 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. Current MDLs are listed in the quality control database.

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. 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 standard has been defined as ± 20%.

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. There are no compound-specific criteria. All %RSDs must be within 20% for each analyte or averaged across all analytes in the calibration standard mix. Laucks uses 40% percent as the upper limit for all compounds as an internal guideline although it is not a requirement of SW 846.

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. 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:

$$y = ax^3 + bx^2 + cx + d$$

4.7.1.3 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, 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 greater than 0.900.

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 Initial 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. 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 ICV 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 ICV 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

CF = Mean Calibration Factor

4.8.1.2.2 The percent drift calculation compares the ICV calculated concentrations to the theoretical (or actual) concentration of the ICV 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 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.

4.8.2 Corrective action

4.8.2.1 If the ICV criteria are not met, no sample extracts can be analyzed. Perform system maintenance and re-check the ICV. If the criteria still cannot be met, the system must be recalibrated.

4.9 Updating Retention Time Windows

4.9.1 Due to the stability of the ECD, updating retention time windows is not normally required. However, the retention time windows for compound identification can be updated by using the retention times for each target analyte in the ICV standard 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.

4.10 Continuing Calibration Verification

4.10.1 A mid-range calibration standard is analyzed at the frequency of every 10 samples or 12 hours. In addition, this standard must be the last injection made in the analysis sequence.

4.10.2 Criteria

4.10.2.1 After every 10 sample extract injections, or 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.

4.10.3 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. Alternatively, if the average of the responses for all analytes is within 15%, then the

calibration has been verified. However, the average must include all analytes in the calibration, regardless of whether they are target analytes for a specific project, and the data must be provided with the calibration verification data.

4.10.3.1 The retention times for all target analytes must fall within the RT windows established by the ICAL.

4.10.4 Corrective action

4.10.4.1 Check calculations or perform instrument maintenance. To validate the quantification of target analytes in analytical samples, the samples must be bracketed by in-control CCVs. All samples bracketed by an out of control CCV must be reanalyzed unless the CCV demonstrates an increase in response and no analytes are detected above the RL in the associated samples.

4.11 Method Blanks

4.11.1 Criteria

4.11.1.1 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 quality control database.

4.11.2 Corrective action

4.11.2.1 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.

4.12 Method Blank Spikes

4.12.1 Criteria

4.12.1.1 A method 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 method blank spike. A method blank

spike is similar to a QC check standard. Method blank spike recoveries must meet the criteria specified in the quality control database.

4.12.2 Corrective action

4.12.2.1 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.

4.13 Matrix Spike

4.13.1 Criteria

4.13.1.1 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

4.13.1.2 The recovery criteria are detailed in the QC database. 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 quality control database.

4.13.2 Corrective action

4.13.2.1 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.

4.14 Matrix Spike Duplicate

4.14.1 Criteria

4.14.1.1 The compound recovery criteria are identical to those for the matrix spike sample. In addition, the matrix spike duplicate is used measure method precision. This is done by computing the relative percent difference (RPD) between the matrix spike and matrix spike duplicate recovery values.

4.14.1.2 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

4.14.1.3 RPD control limits are detailed in the QC database.

4.14.2 Corrective action

4.14.2.1 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.

4.15 Surrogate Recovery

4.15.1 Criteria

4.15.1.1 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

4.15.1.2 Detailed surrogate recovery control limits are tabulated in the laboratory QC database.

4.15.2 Corrective Action

4.15.2.1 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).

4.15.2.2 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.

Column flow	7-8 mL/min
Make-up gas	argon/methane (95%/5% High Purity Grade)
Make-up flow	70 mL/min
Injector	grob-type, split/splitless with 4mm wide bore deactivated liner
Injector temperature	205°C
Injection	on-column
Injection volume	1µl per column (2µl total)
Initial temperature	45°C
Initial hold time	1.0 min
Temperature ramp	25°C per min to 150°C
Hold time	1.0 min
Temperature ramp	5°C per min to 240°C
Hold time	0 min
Temperature ramp	25°C per min to 290°C
Final hold time	0 min
EC detectors temperature	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 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. 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.

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	0.040	0.080	0.160	0.200	0.400	.08	2.67
2,4-DB	0.008	0.016	0.040	0.080	0.160	0.200	0.400	.08	2.67
2,4,5-T	0.008	0.016	0.040	0.080	0.160	0.200	0.400	.08	2.67
2,4,5-TP (Silvex)	0.008	0.016	0.040	0.080	0.160	0.200	0.400	.08	2.67
Dicamba	0.008	0.016	0.040	0.080	0.160	0.200	0.400	.08	2.67
Dichlorprop (2,4-DP)	0.008	0.016	0.040	0.080	0.160	0.200	0.400	.08	2.67
Dinoseb	0.008	0.016	0.040	0.080	0.160	0.200	0.400	.08	2.67
Dalapon	0.008	0.016	0.040	0.080	0.160	0.200	0.400	.08	2.67
2,4-DCPAA(surr)	0.008	0.016	0.040	0.080	0.160	0.200	0.400	N/A	N/A
MCPA	4.00	8.00	20.00	40.00	80.00	100.00	200.00	40	1334
MCPP	4.00	8.00	20.00	40.00	80.00	100.00	200.00	40	1334
Hexachlorophene	0.05	0.10	0.25	0.50	1.00	5.00	10.00	0.5	16.7

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

APPENDIX II

Analysis Sequence

Injection	Sample
	rinse
1	ICV 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 Verification
Linearity Report
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

V. 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 or averaged across all analytes.	5 calibration std. for linear, 6 std. for quadratic, for all single and multi-components, %RSD ≤20% for each analyte or averaged across all analytes. Verification using a 2nd source ± 20%.	After performing major instrument maintenance or when persistent difficulties meeting CCV criteria occur.	recalibrate or narrate faults if possible	Narrative
Initial Calibration Verification	Must be ±15% D for all quantitated analytes (or average of %Ds ±15%).	Must be ±15% D for all quantitated analytes (or average of %Ds ±15%).	once per daily analytical sequence	rerun with new ICV, instrument maintenance, &/or recalibrate (or narrate if possible)	Narrative
Continuing Calibration Verification	Must be ±15% D for all quantitated analytes (or average of %Ds ±15%).	Must be ±15% D for all quantitated analytes (or average of %Ds ±15%).	Every 10 samples or every 12 hours.	rerun with new ICV, 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 reextracted

QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
Surrogate Recovery	Limits to be determined by lab	listed in QC database	every sample	if other QC is in control, narrate; otherwise re-extract	case narrative and corrective action form if re-extracted
Matrix Spike Recovery	every analytical batch or 1 per 20 samples, limits to be determined by lab	listed in QC 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 QC 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 QC 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

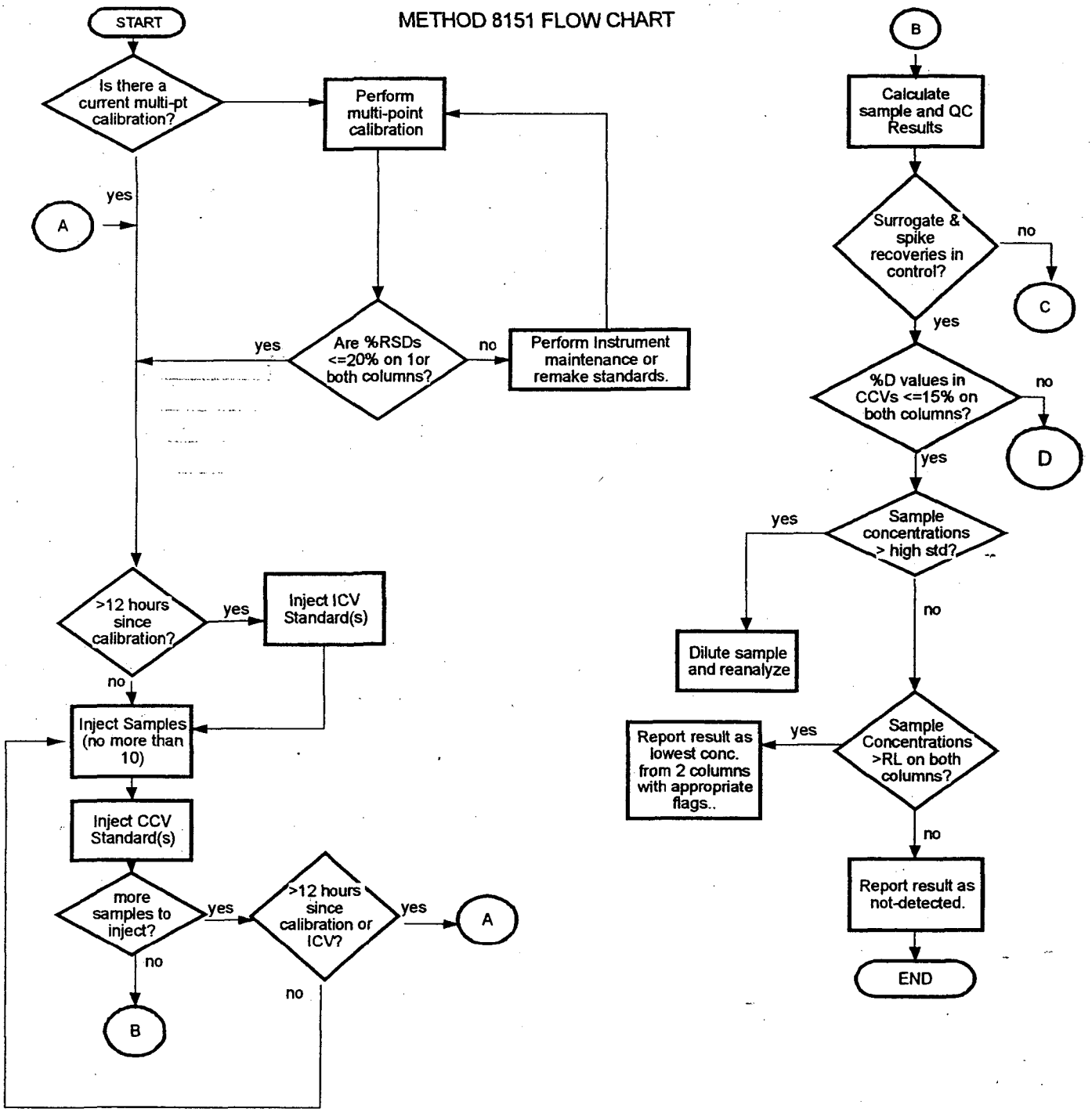
APPENDIX V

Compound Elution Order

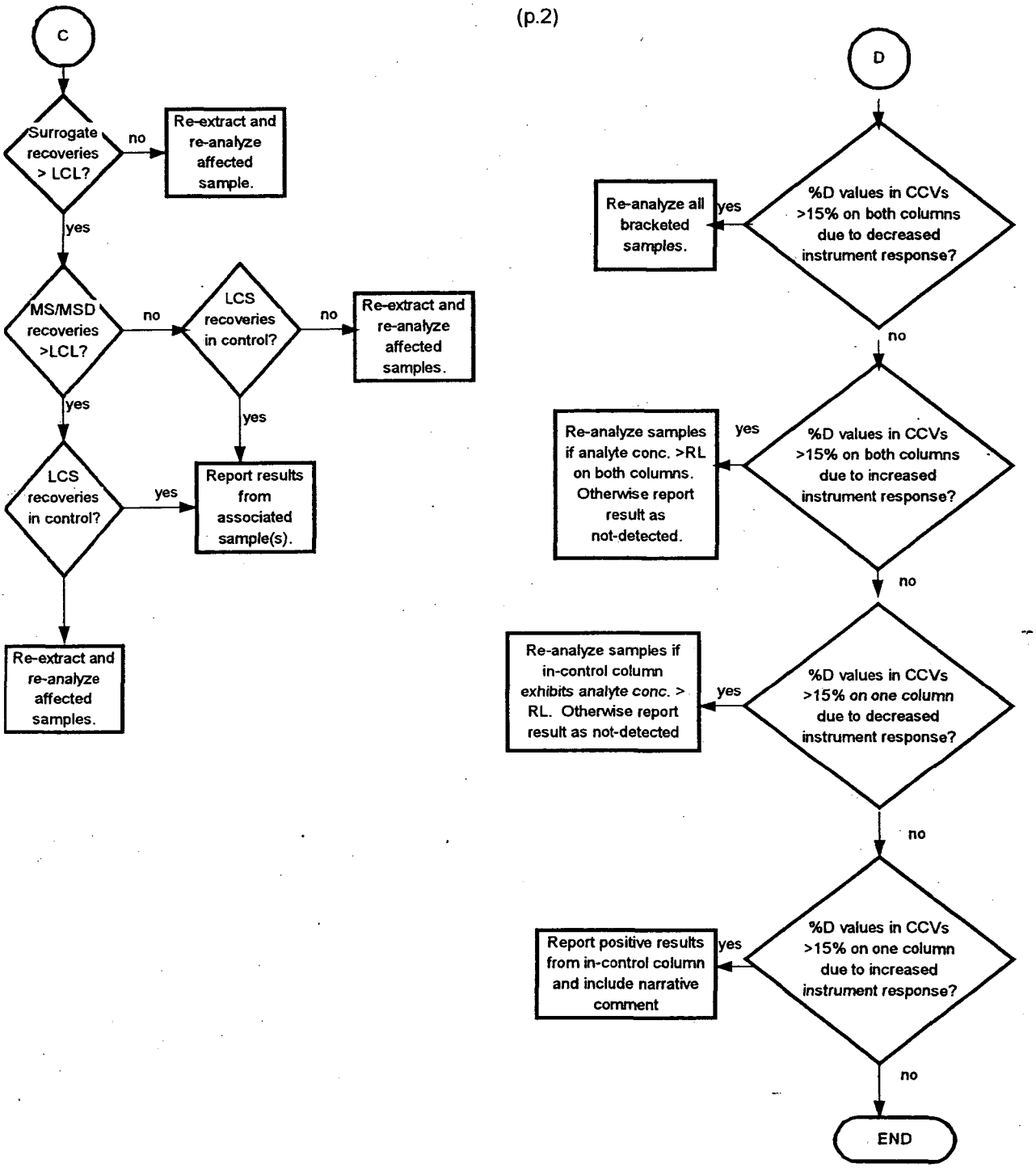
Column DB-5	Column DB-608
Dalapon	Dalapon
4-Nitrophenol	4-Nitrophenol
2,4-DCPAA (surr)	2,4-DCPAA (surr)
Dicamba	MCPP
MCPP	Dicamba
MCPA	MCPA
Dichloroprop (2,4-DP)	Dichloroprop (2,4-DP)
2,4-D	2,4-D
Pentachlorophenol	Pentachlorophenol
2,4,5-TP (Silvex)	2,4,5-TP (Silvex)
2,4,5-T	2,4,5-T
2,4-DB	Dinoseb
Dinoseb	2,4-DB
Picloram	Picloram
Hexachlorphene	Hexachlorphene

APPENDIX VI

Flow Chart



METHOD 8151 FLOW CHART
(p.2)



LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-8265

Title: **Determination of Volatile Organic Compounds by Method SW 8260B**

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1. Introduction and Scope

1.1 Method Description

Method 8260 is used in the determination of volatile organic compounds in soil, sediment, aqueous, and other matrices. This SOP addresses the determination of volatile organics in different matrices, which include medium level soils as well as low level water samples. A 25 mL sample volume is employed in order to achieve lower detection limits for the low level waters. In addition, the instrument acquisition parameters have been added for the analysis of vinyl chloride by Selected Ion Monitoring (SIM) in Appendix III, and Appendix IV contains a tabular list of the non-routine Appendix IX analytes and their respective calibration ranges.

1.1.1 Because this method employs sample introduction via a purge and trap sample concentrator, it is applicable to volatile compounds that have boiling points below 200°C and that are insoluble or only slightly soluble in water. Compounds that are more soluble in water have elevated detection limits due to their decreased purging efficiency. These include, but are not limited to ketones, nitriles, acetates, acrylates and ethers.

1.1.2 This method is restricted to use by, or under the supervision of analysts experienced in the use of purge and trap systems, gas chromatography/mass spectroscopy and in the interpretation of chromatograms and mass spectral data. Each analyst performing this method must have demonstrated the ability to perform the described chromatographic analysis and data interpretation.

1.2 Method Deviations

1.2.1 Detailed below are any deviations from the published version of method SW 8260B. All deviations are followed as the standard operation procedure by Laucks Testing Labs.

1) Laucks uses 1/2 the reporting limit (low level standard) for method blank criteria instead of method detection limits as referenced in SW 846. Common laboratory solvents, such as methylene chloride and acetone, are allowed to be present in the method blanks up to the RL as well as bromomethane in medium soil analyses. Refer to Section 6.4 for detailed method blank criteria.

2) The retention time window used for internal standards in all analyses is +/- 0.50 minutes relative to the daily CCV standard.

3) The BFB tuning criteria used is taken from CLP SOW OLM04.2, which is not a deviation from the method since SW 8260B allows the use of alternative tuning criteria, e.g., CLP and/or 524.2 The tuning criteria are tabulated in section 4.4.5.

1.3 Interferences

1.3.1 Problems have been associated with the following compounds analyzed by this method.

1.3.1.1 Chloromethane is the most likely compound to be lost if the purge flow is too fast.

1.3.1.2 Bromoform is one of the compounds to most likely to be purged very poorly if the purge flow is too slow. Cold spots and/or active sites in the transfer lines may adversely affect response. Response of the quantitation ion (m/z 173) is directly affected by the tuning of BFB at ions m/z 174/176. Increasing the m/z 174/176 ratio relative to m/z 95 may improve bromoform response.

1.3.1.3 Tetrachloroethane and 1,1-dichloroethane are degraded by contaminated transfer lines in the purge-and-trap system and/or active sites in trapping materials.

1.4 Sample Collection, Sample Storage, Holding Times

1.4.1 Waters

1.4.1.1 Samples are collected with zero headspace in 40 mL glass containers containing preservative (either HCl, H_2SO_4 or solid $NaHSO_4$) and sealed with Teflon-lined caps.

1.4.1.2 The water samples are preserved to a pH of ≤2, and all samples are stored at 4°C.

1.4.1.3 The holding time to analysis is 14 days from date of collection. The pH values for the water samples are measured subsequent to sample analysis. The pH values, when not preserved to a pH ≤2 are noted in the instrument logbook and the client report.

1.4.2 Soils

1.4.2.1 At the time of this writing, the 3rd update of the 3rd edition to SW 846 requires that low level soils be collected in duplicate using 5 gram and/or 1 gram aliquots which are to be weighed out in the field. The soil samples are to be collected in a 40 mL vial containing water, sodium bisulfate, and a stir bar. 0.2 grams of sodium bisulfate are added for each 1 gram of soil (see section 1.4.2.2 for issues associated with this method). Therefore, when collecting 5 grams of sample, the VOA vial should contain 1 gram of sodium bisulfate. The sodium bisulfate is added in order to ensure a sample pH of ≤2. The vials

used for low level soils should have the tared weight recorded on the label and sealed with septum-lined screw caps.

1.4.2.2 An in-depth study of the different sampling methods used for Method SW 846 5035 was performed by the IT Corporation and presented to the EPA at it's annual conference in May 2001.

1.4.2.3 Problems associated with sodium bisulfate were confirmed, including styrene degradation, acetone formation, and effervescence in some samples. Dangerous pressure and high methyl acetate results were also noted with sodium bisulfate.

1.4.2.4 IT is recommending removal of the sodium bisulfate preservation option from the next CLP SOW and EPA is planning to follow this recommendation

1.4.2.5 Another option is the use of the EnCore™ sampler, the Purge-and-Trap Sampler™, and a cut plastic syringe to transfer the sample to the soil vial. If the EnCore™ sampler is used in the field, the samples may be stored for up to 48 hours. However, samples collected in this device should be transferred to the soil sample vials (and preserved) as soon as possible, or analyzed within 48 hours. The holding time for soils is 14 days from the date of collection.

1.4.2.6 At the time of this writing, the 3rd update of the 3rd edition to SW 846 requires that high level soils be collected in using one of the following options:

1.4.2.6.1 Option 1: Samples will be collected in duplicate using 5 gram and/or 1 gram aliquots which are to be weighed out in the field. The soil samples are to be collected in a 40 mL vial containing methanol. The vials used for high level soils should have the tared weight recorded on the label and sealed with septum-lined screw caps.

1.4.2.6.2 Option 2: Samples will be collected using an EnCore type sampler or equivalent, and preserved at the laboratory by freezing.

1.4.2.6.3 Option 3: Samples will be collected in vials with zero headspace.

1.4.2.7 Per client request Laucks will continue to accept unpreserved soil samples for low or high level analysis. The samples must be collected in 2- or 4-oz glass containers and sealed with teflon-lined caps. These samples will be introduced by method 5030A and analyzed according to this SOP. Please note that for South Carolina samples, Method 5035 must be followed.

1.4.2.8 The holding time to analysis is 14 days from date of 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 or target analytes and surrogates are added each time samples are analyzed. Blank spikes are required on all NFESC work. In the context of this SOP, a blank spike is the same as a QC check standard. See also QC check standard.
CCC	Calibration check compound. There are 6 analytes which must not exceed the maximum %RSD of 30% in the initial calibration and a %D of 20% in the continuing calibration standard to validate linearity. These analytes are 1,1-dichloroethane, chloroform, 1,2-dichloropropane, toluene, ethylbenzene and vinyl chloride.
CCV	Continuing calibration verification. This is a standard analyzed at some prescribed frequency during the analysis sequence to determine whether the instrument has remained in calibration.
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.
IBLK	Instrument blank. An instrument blank is PFW containing the method surrogates and is introduced into the instrument to monitor for carry over between sample analyses.
ICV	Initial continuing verification. A calibration standard obtained from a different manufacturer than the standards used for the initial and continuing calibrations that is analyzed after a compliant 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.
PFW	Purge-free water. Laboratory deionized water that is boiled for 30 minutes prior to use. The systems used to provide deionized water at Laucks all contain carbon polishing filters which are capable of providing purge-free water for use as reagent water.
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 injection of BFB, followed by the standard. A QC period is terminated after 12 hours from the injection of BFB.
Reporting Limit (RL)	The reporting limit is defined by the low level standard, also referred to as the practical quantiation limit (PQL).
RF	Response factor. A measure of the response of an analyte compared to its internal standard response. Response factors are determined by standard analysis and are used in the calculation of concentrations of analytes in samples.
RRT	Relative retention time. A measure of the retention time of an analyte compared to the retention time of its internal standard.
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. 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 the GC column.
Sequence	A set of samples and standard solutions introduced into an instrument in a chronologically continuous group. See also QC period.
SPCC	System performance check compound. Specified compounds in which the minimum RFs must be met in order to demonstrate that the initial and continuing calibration standards are in control. These compounds are chloromethane, 1,1-dichloroethane, bromoform, chlorobenzene, and 1,1,2,2-tetrachloroethane.

2. Equipment List and Standards

2.1 Chromatographic System

2.1.1 Gas Chromatograph: Hewlett Packard 5890 I or II or 6890 employing a low-dead-volume interface from the sample concentrator to the GC injection port.

2.1.2 Carrier Gas: Helium 99.995% (high purity grade) or better.

2.1.3 Column: 60m x 0.25mm x 1.4 µm film thickness, or 30 m x 0.53 mm x 3.0 µm film thickness or 75 m x 0.45 x 2.55 µm film thickness, fused silica capillary column (J&W DB-624 or Restek RTx-624 or equivalent).

2.1.4 Purge and Trap: OI Analytical 4460A and 4560 sample concentrators or equivalent.

2.1.5 Autosampler: Dynatech Precision Sampling PTA-30W/S, Varian Archon or equivalent.

2.1.6 GC/MS Interface: Hewlett Packard 59913A jet separator assembly, split/splitless or equivalent.

2.1.7 Mass Spectrometer: Hewlett Packard 5970B, 5973 or equivalent.

2.1.8 Data System: PC based Teknivent with ENVIROLINK data acquisition and processing software or HP Chemstation.

2.1.9 Trap: OI Corporation, Supelco, or equivalent. Examples are listed below:

1) 1 cm 3% SP-2100/Chromosorb W AW, 7.7 cm Tenax TA, 7.7 cm silica gel 15, 7.7 cm activated charcoal. Supelco Pt No.:2-1139.

2) VOCARB 3000. 10 cm Carbopack C, 6 cm Carboxen 1000, 1 cm Carboxen 1001. Supelco Pt No.: 2-1131.

3) VOCARB 4000. 8.5 cm Carbopack C, 10 cm Carbopack B, 6 cm Carboxen 1000, 1 cm Carboxen 1001. Supelco Pt. No.: 2-1143.

2.1.10 Miscellaneous: Assorted gas-tight calibrated syringes, pipettes, 40 mL vials, caps, septa, sea sand, purge and trap grade methanol, ferrules, pH strips, purge-free DIW, volumetrics, laboratory oven capable of heating glassware up to 100°C, and assorted supplies.

2.2 Standards

2.2.1 Overview of Volatile Standards Preparation

2.2.1.1 All standards are made using a high purity purge and trap grade methanol. Every lot number of methanol is analyzed prior to use to ensure that it is free of volatile organic contaminants. A record of analysis of an aliquot from each batch is stored for a minimum of one year.

2.2.1.2 Two standard logbooks are employed to document all volatile standards. One standard logbook is maintained for stock solutions prepared from neat materials and to record the login of certified standards. The other standard logbook is maintained for working solutions which include solutions procured from commercial sources, as well as those solutions made in the laboratory. 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.

2.2.1.3 All standards must be identified and quantitated prior to use in the laboratory. This is performed by purchasing certified standard solutions from a commercial supplier that is recognized by the EPA and which are traceable to NIST. In addition, standards for the permanent gases and non-gases are monitored frequently by comparison to the initial calibration curve. Fresh standards should be prepared if the calibration standard(s) fail to meet the criteria specified in SW 846. Standards for gases need to be replaced after one week, or as recommended by the standard manufacturer, unless the acceptability of the standard can be documented. Standards for the non-gases need to be replaced after six months or as recommended by the standard manufacturer, unless the acceptability of the

standard can be documented. If the standards meet the criteria for the calibration standard(s) as specified in SW 846, they are considered acceptable.

2.2.1.4 All standard solutions are stored in the VOA freezer at -10°C to -20°C. The stock and secondary dilution standards are stored in flame-sealed amber ampules (with the exception of the internal and surrogate standards). The secondary dilution standards are checked for degradation or evaporation prior to preparing calibration standards. Secondary dilution standards should be replaced after one week, unless the acceptability of the standard can be documented. Pre-mixed certified solutions are stored according to the manufacturers' documented holding time and storage temperature recommendations. Prior to daily and initial calibration standard preparation, the standard solutions are removed from the freezer and allowed to warm to room temperature.

2.2.1.5 Refer to Appendix I for a tabular listing of all standard solutions and their concentrations. The additional appendix IX compounds (which are only analyzed upon request) and their standard concentrations are tabulated in Appendix IV.

2.2.2 Preparation of Internal Standards and Surrogate Standards

2.2.2.1 If starting with a neat material, a measured amount of the neat chemical is placed in a glass volumetric and diluted to volume with methanol, then stoppered. 125 mg of neat material is diluted into 25 mL of methanol. This yields an intermediate solution of 5000 µg/mL.

2.2.2.2 Aliquots of the intermediate solutions are taken from the individual internal and surrogate standards and then combined in a volumetric flask and diluted with methanol to yield a working standard which contains all compounds at a concentration of 250 µg/mL each. This is accomplished by using a gas-tight syringe to transfer each aliquot of 1.25 mL into 25 mL of methanol. A 1 µL aliquot of this solution is injected via the autosampler into 5 mL for waters, low and medium level soils (and 25 mL for low level waters) of sample, resulting in an internal and surrogate standard concentration of 50 µg/L (or 10 µg/L for low level waters).

Internal Standards	Surrogate Standards
Fluorobenzene	1,2-Dichloroethane-d4
Chlorobenzene-d5	Toluene-d8
1,4-Dichlorobenzene-d4	p-Bromofluorobenzene
	Dibromofluoromethane

2.2.3 Preparation of Matrix Spike Solution

2.2.3.1 At a minimum, five volatile analytes are used for spiking. Upon request by the client additional analytes may be used if they are of interest at the site. A certified matrix spiking solution which contains the five spiking analytes is purchased pre-mixed from a commercial supplier at a concentration of 2500 µg/mL each. This solution is then diluted in methanol to a concentration of 200 µg/mL.

Matrix Spike Solution	Source*	Stock Number*
1,1-Dichloroethene	Restek	30005
Benzene		
Trichloroethene		
Toluene		
Chlorobenzene		
* or equivalent		

2.2.3.2 A 12.5 µL (2.5 µL for low level waters) aliquot of this solution is spiked into 50 mL of sample, resulting in a spiked concentration of 50 µg/L (or 10 µg/L for low level waters) for each analyte.

Working Concentration	Aliquot	Final Volume	Concentration
Soils, 5 mL Water			
200 µg/mL	12.5 µL	50 mL PFW	50 µg/L
Medium Level Soils			
200 µg/mL	12.5 µL	50 mL PFW	(50 µg/L extract) 5000 µg/L sample
25 mL Water			
200 µg/mL	2.5 µL	50 mL PFW	10 µg/L

2.2.4 Preparation of p-Bromofluorobenzene (BFB) Solution

2.2.4.1 The preparation of BFB is similar to that of the internal standards and surrogate standards. Refer to Section 2.2.2 for details.

2.2.4.2 A solution of 25 ng/mL is prepared and stored in flame-sealed amber ampules.

2.2.5 Preparation of Initial Calibration Standards

2.2.5.1 Certified sets of stock solutions which contain all target analytes are purchased pre-mixed from a commercial supplier at a concentration of 2000 µg/mL each. If additional target analytes are requested, these analytes may be ordered separately, either in solution or as a neat material.

2.2.5.2 These solutions are then diluted in methanol to generate standards at concentrations of 200 µg/mL. This solution is stored in flame-sealed amber ampules.

2.2.5.3 Standards are stored in the VOA freezer at -10°C to -20°C. They are removed prior to making up the initial calibration standards and are allowed to warm to room temperature.

2.2.5.4 The initial calibration standards range from 1 µg/L to 50 µg/L for low level waters and 3 µg/L to 200 µg/L for soils, and 5 mL water samples for all target analytes with the exception of the ketones and m,p-xylenes. Please refer to Appendix I for a tabular listing of all analytes and calibration concentrations. The 5 mL water calibration standards are also employed in the analysis of medium or high level soils, since the aqueous calibration standards are purged at ambient temperature. Analysis of the solid matrices in the low level format requires a purge temperature of 40° C.

2.2.5.5 The standards are prepared by taking aliquots of the solutions and diluting them into a volumetric flask containing PFW. A 40 mL aliquot is immediately poured into a VOA vial (or a 5 mL aliquot for the low level soils is placed in a soil vessel) and placed on the autosampler. Each standard concentration is prepared just prior to analysis and any remaining standard solution is disposed of once the analytical run is initiated.

Solution	Source*	Stock Number*
VOC Mix 1	Supelco	4-8775
VOC Mix 2	Supelco	4-8777
VOC Mix 3	Supelco	4-8779
VOC Mix 4	Supelco	4-8786
VOC Mix 5	Supelco	4-8797
VOC Mix 6	Supelco	4-8799
TCL Mix 1	Supelco	4-8949
Carbon Disulfide	Supelco	4-0363

* or equivalent

Low Level Water (25 mL)

Working Solution	Aliquot non-ketones	Aliquot ketones	Final Volume	Concentrations non-ketones	Concentrations ketones
200 µg/mL	1.0 µL	-	200 mL	1 µg/L	
200 µg/mL	2.5 µL	2.5 µL	100 mL	5 µg/L	5 µg/L
200 µg/mL	5.0 µL	5 µL	100 mL	10 µg/L	10 µg/L
200 µg/mL	12.5 µL	12.5 µL	100 mL	25 µg/L	25 µg/L
200 µg/mL	12.5 µL	12.5 µL	50 mL	50 µg/L	50 µg/L
200 µg/mL	-	25 µL	50 mL	-	100 µg/L

Low Level Soil

Working Solution	Aliquot non-ketones	Aliquot ketones	Final Volume	Concentrations non-ketones	Concentrations ketones
200 µg/mL	1.5 µL	2.5 µL	100 mL/50 mL	3 µg/L	10 µg/L
200 µg/mL	2.5 µL	5 µL	50 mL	10 µg/L	20 µg/L
200 µg/mL	12.5 µL	12.5 µL	50 mL	50 µg/L	50 µg/L
200 µg/mL	5.0 µL	5.0 µL	10 mL	100 µg/L	100 µg/L
200 µg/mL	10.0 µL	10.0 µL	10 mL	200 µg/L	200 µg/L

5 mL Water And Medium Level Soil

Working Solution	Aliquot non-ketones	Aliquot ketones	Final Volume	Concentrations non-ketones	Concentrations ketones
200 µg/mL	1.5 µL	2.5 µL	100 mL/50 mL	3 µg/L	10 µg/L
200 µg/mL	2.5 µL	5 µL	50 mL	10 µg/L	20 µg/L
200 µg/mL	12.5 µL	12.5 µL	50 mL	50 µg/L	50 µg/L
200 µg/mL	25 µL	25 µL	50 mL	100 µg/L	100 µg/L
200 µg/mL	50 µL	50 µL	50 mL	200 µg/L	200 µg/L

2.2.6 Preparation of a Daily Calibration Standard

2.2.6.1 The concentration of the continuing calibration standard at a level of 10 µg/L for low level waters, 50 µg/L for low and medium level soils and 5 mL waters, is also the mid-point of the initial calibration curve. This standard is always prepared just prior to analysis by transferring an aliquot of each of the 200 µg/mL multi-component working solutions into a volumetric containing PFW.

3. Safety precautions & Waste disposal

3.1 Routine Safety Precautions

3.1.1 All standards and samples should be handled as if they are 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 Flammable solvents such as methanol are stored in the appropriate solvent locker located outside the volatile laboratory.

3.1.6 Many analytes are known or suspected carcinogens. 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.

3.2 Waste disposal

3.2.1 Waste solvents and expired standards are disposed of in the appropriate waste solvent container located in the prep area under the hood.

3.2.2 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.

4. Operation procedures

4.1 Analytical Conditions

GC Parameters	5970	5973
Injection Port Temperature	: 200°C	250°C
GC/MS Interface Temperature	: 250°C	250°C
Initial GC Temperature	: 35°C	40 °C
Initial Hold Time	: 4 min	4 min
Ramp Rate	: 4°C/min	10°C/min
Final Temperature	: 140°C	200°C
Final Time	: 4 min	8 min
Carrier Gas Flow	: 15 mL/min	
Column Head Pressure	: 9 psi	

Purge and Trap Parameters

Purge Time	: 11 min	11 min
Desorb Time	: 1 min	2 min
Bake Time	: 16 min	8 min
Desorb Preheat Temperature	: 20°C	180°C
Desorb Temperature	: 180°C	250 °C
Purge Flow	: 40 mL/min	40 mL/min
Purge Temperature	: Ambient (40°C for soils)	Ambient (40°C for soils)
Desorb Flow Rate	: 15 mL/min	15 mL/min

Mass Spectrometer Parameters

Electron Energy	: 70 volts
Mass Range	: 35 to 300 amu
Scan Time	: 1.4 sec/scan
Scan Start Time	: 0.1 min

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 for the determination of method detection limits. 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.

4.2.2 MDL studies will continue to be performed. This procedure is fully described in LTL-1011, *Procedure for the Determination and Reporting of Detection Limits, Reporting Limits, Precision and Accuracy Studies, and Control Limits.*

4.2.3 MDLs for this method typically are in the range of 0.2-3µg/L for 5 mL waters, 0.3-3.0µg/kg for low level soils and 0.06-1.0 µg/L for 25 mL waters.

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 10-50 times the MDL. In the absence of criteria for the initial demonstration of proficiency, the limits of 70%- 130% can be used.

4.4 Instrument Tuning

4.4.1 Prior to the analysis of any samples, blanks, or calibration standards, the instrument must demonstrate mass calibration and resolution by meeting the established tuning criteria for BFB.

4.4.2 FC-43 (PFTBA) is used as a mass calibrant. The following ratios are suggested in order to meet the tuning criteria for BFB:

Ion	% of ion 69	Isotope	Isotope Abundances
69	100%	70	0.5-1.5%
131	25-40%	132	2.0-4.0%
219	25-40%	220	2.5-5.0%
414	1-3%		

4.4.3 In addition to the tabulated abundances listed above, other criteria should be reviewed at this time.

1) Ion peak widths: The appropriate range is between 0.5 and 0.6 amu. Amu widths beyond this range can lead to loss of minor isotopes, while insufficient peak widths will result in decreased sensitivity.

2) Leak check: The abundances of ions 18, 28, and 32 (water, nitrogen and oxygen, respectively) should be less than 5 percent relative to 69. A level greater than 5 percent is indicative of a leak in the system.

4.4.4 Following the system tuning using FC-43, the GC/MS is then calibrated with BFB. A 2 µL aliquot (1 µL for low level waters) of 25 ng/µL of BFB is injected directly into the GC resulting in a concentration of 50 ng (25 ng for low level waters).

4.4.5 The ion abundances and ratios are checked against the criteria detailed below **or** alternatively, other criteria may be used (e.g., CLP, 524.2). If BFB meets the tuning criteria, then the system is determined to be calibrated. If BFB does not meet the tuning criteria, the GC/MS is re-tuned with FC-43 as described above.

4.4.6 SW 846 allows for the use of 5 - 50 ng of BFB. In the absence of specific recommendations on how to acquire the mass spectrum of BFB from the instrument manufacturer, SW 846 states that the following approach has been shown to be useful: the mass spectrum of BFB may be acquired in the following manner. 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 BFB. Do not background subtract part of the BFB peak. Alternatively, the analyst may use other documented approaches suggested by the instrument manufacturer.

4.4.7 CLP requires that the 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 BFB. Do not background subtract part of the BFB peak.

SW 846 Tuning Criteria

Mass	Abundance %
50	8 - 40% of mass 95
75	30 - 60% of mass 95
95	base peak, 100% relative abundance
96	5 - 9% of mass 95
173	< 2% of mass 174
174	> 50% of mass 95
175	5 - 9% of mass 174
176	>95%, < 101% of mass 174
177	5 - 9% of mass 176

CLP Tuning Criteria

Mass	Abundance %
50	8 - 40% of mass 95
75	30 - 66% of mass 95
95	base peak, 100% relative abundance
96	5 - 9% of mass 95
173	< 2% of mass 174
174	50-120% of mass 95
175	4 - 9% of mass 174
176	93 - 101% of mass 174
177	5 - 9% of mass 176

4.5 Initial Multi-Point Calibration

4.5.1 The first option is to begin with the simplest approach, the linear model through the origin using RSDs, as described in section 7.5 of 8000B. In methods where this method is not appropriate, because the calibration acceptance criteria cannot be met, the next option of calibration (linear regression) is used. This calibration option is typically used in fuels because of the elevated response obtained in these analyses. The requirements for the linear regression model is that R^2 be greater than or equal to 0.99. The more complex calibration option is use of the quadratic curve. This calibration option requires a minimum of 6 points and is used in cases where the detector doesn't meet calibration criteria over a wide range. The difficulty with the quadratic is that the intercept may be

greater than the detection limit. This calibration option exhibits a greater accuracy in the mid-range, and may demonstrate more extreme responses at the low and high end of the calibration, and therefore, it is important to dilute samples and extracts so that they are in the mid-range of the calibration.

4.5.2 For linear calibrations using the RSD, analyze standard solutions using a minimum of 5 different concentration levels. The lowest concentration should establish the reporting limit. The highest concentration should define the upper usable working range of the detector. Criteria for evaluating these standards are detailed in Section 6.

4.5.3 After completion of a compliant initial calibration curve, an initial calibration verification (ICV) may be analyzed. This second source independent calibration verification may be performed by analyzing a LCS as long as it meets the same acceptance criteria as a CCV detailed in Section 6.

4.6 Continuing Calibration Verification

4.6.1 A CCV is analyzed once the BFB tuning criteria have been met and the instrument has been calibrated. Criteria for evaluating a CCV standard are detailed in Section 6.

4.7 Instrument Blank

4.7.1 The analysis of an instrument blank (IBLK) is performed prior to the injection of BFB. This analysis ensures that there are no volatile organic contaminants in either the purge and trap sample concentrator or in the autosampler.

4.7.2 Any sample that demonstrates concentrations of target analytes high enough to saturate the detector must be followed by at least one IBLK, also known as a saturation blank. This IBLK analysis is performed to prevent any possible carry-over into the subsequent sample analysis. Evaluation criteria follow the same guidelines set forth for the analysis of a method blank.

4.8 Method Blank

4.8.1 Immediately following the analysis of the CCV and prior to sample analysis, a method blank must be analyzed. The analysis of the method blank demonstrates that the instrument is free of volatile organic contaminants and ensures that the reagent water is also free of contaminants. Refer to Section 6 for method blank acceptance criteria.

4.9 Sample Analysis

4.9.1 Samples (and associated QC) may be analyzed for up to 12 hours from the injection of BFB. The samples are analyzed subsequent to the calibration standard and method blank analyses. However, no more than twenty sample analyses are performed in a 12 hour period. Once all criteria for BFB, the calibration standard, and method blank have been met, the sample analyses are performed. The aqueous and medium level soil samples are analyzed against an aqueous (non-heated purge) calibration curve. The low level soils are analyzed against a calibration curve employing a heated purge temperature of 40°C.

4.10 Analysis sequence

IBLK (optional)
BFB
CCV
Method blank
Samples and QC

4.11 Sample Preparation

4.11.1 The samples are removed from the VOA refrigerator and are allowed to warm to room temperature. Aqueous samples which are received in 40 mL vials and low level soil samples containing the pre-weighed sample aliquot in sodium bisulfate are placed onto the autosampler carousel. See section 4.11.5 for the preparation of medium soils. The autosampler transfers a 5 mL or 25 mL aliquot of sample (or an aliquot of PFW for the soils) into the autosampler syringe, where it injects 1 µL of the internal standard/ surrogate standard solution.

4.11.2 The pH of all water and low level soil samples is measured subsequent to analysis in order to determine if they were preserved adequately without disturbing the integrity of the sample. The pH values when not preserved to a pH ≤ 2 are noted in the instrument logbook.

4.11.3 If the concentration of any target analyte exceeds the initial calibration range, the sample must be diluted and reanalyzed.

4.11.4 If aqueous samples require dilutions, they are diluted by one of two methods listed:

1) the samples are diluted with PFW in a volumetric where they are transferred to 40 mL vials and placed onto the autosampler, or

2) the undiluted samples are placed on the autosampler, where they are diluted with PFW by the autosampler. Refer to the instrumentation manuals for the complete operation of the autosampler.

4.11.5 Medium Soils

4.11.6 The soil sample is gently mixed (no supernatant liquid is removed) and a 5 gram aliquot (weighed out to the nearest 0.1 g) is transferred to a tared 15 mL vial. 10.0 mL of methanol is added to the vial. The vial is sealed, then shaken for two minutes. A 1 mL aliquot is transferred to a GC vial for storage in the dark at 4°C (±2°C). A 100 µL sample aliquot per 5 mL of PFW is placed onto the autosampler carousel. The autosampler transfers a volume of 5 mL of this sample into the autosampler syringe, where it injects 1 µL of the internal standard/ surrogate solution.

4.12 Qualitative Identification

4.12.1 Two criteria must be satisfied to verify the identification of target compounds:

1) elution of the sample component within 0.50 minutes of the standard component and,

2) appropriate correspondence between the sample mass spectrum and the standard mass spectra.

a) The three ions of greatest relative intensity, or any ions over 30% relative intensity which are present in the standard mass spectrum must be present in the sample spectrum.

b) The relative intensities of ions must be within 30% between the standard and sample spectra.

d) The emphasis of spectral review is on the three major ions. However, if a target compound cannot be verified by all the criteria listed above, but if, in the technical judgment of the analyst, the identification is correct, then the analyte will be quantitated, and reported. Compounds meeting the identification criteria must be reported with their spectra.

4.12.2 A library search may be performed for the purpose of identifying up to 10 largest non-target analytes also referred to as Tentatively Identified Compounds (TICs) if requested by the client. The criteria for confirming TICs are listed below.

1) Relative intensities of ions in the reference spectrum > 10% of the most abundant ion should be present in the sample spectrum.

2) Molecular ions in the reference spectrum should be present in the sample spectrum.

3) The relative intensities for the major ions should agree within 20%.

4) Ions in the sample spectrum but not present in the standard spectrum should be reviewed for possible background contamination or coelution.

6) If, after careful review and in the technical judgment of the analyst, no valid tentative identification can be made, the compound should be reported as follows:

A) If the library search produces a match at or above 85%, report that compound.
B) If the library search produces more than one compound at or above 85%, report the first compound.
C)If the library search produces no matches at or above 85%, report the compound as unknown. The analyst should give additional classification of the unknown compound, if possible (i.e., unknown hydrocarbon, unknown acid type, unknown chlorinated compound).

4.13 Manual Peak Integrations

4.13.1 Manual peak integrations should be used only when necessary to correct for matrix interference, tangent peaks, split peaks, overloaded peaks and rising baselines. Manual integrations are not to be used in an attempt to meet calibration, surrogate recovery, or spike recovery criteria. Refer to LTL-1020, *The Integration of IC, GC, HPLC, and GC/MS Peaks* for more detail.

4.13.2 If a manual integration is necessary, follow the following guidelines:

1) Integrate only the peak. Start where the peak lifts from the baseline and end as soon as it returns to the baseline. Do not integrate extra baseline in an attempt to increase peak area.

2) Do not "peak shave". Do not cut off legitimate parts of the peak in order to reduce peak area.

3) In cases of tangent skims, do not increase or decrease peak areas or heights by skimming extra long baselines or drawing the baseline too low.

4) Always initial and date your manual integrations.

4.14 Compound Quantification

4.14.1 Target compound concentrations are calculated using the following equations:

Aqueous samples:

$$\text{Conc } (\mu g / L) = \frac{A_x \times I_s \times Df}{A_{is} \times ARF \times V_o}$$

where:

A_x = Area of the characteristic ion (EICP) of the analyte.
A_{is} = Area of the characteristic ion (EICP) of the internal standard.
I_s = Amount of the internal standard (ng).
ARF = Average RF from the ambient temperature purge of the initial calibration.
V_o = Volume of water purged (mL).
Df = Dilution factor. Assume 1.0 for no dilution.

Low soil (on a dry-weight basis)

$$\text{Conc } (\mu g / kg) = \frac{A_x \times I_s}{A_{is} \times ARF \times W_s \times D}$$

where:

A_x = Area of the characteristic ion (EICP) of the analyte.
A_{is} = Area of the characteristic ion (EICP) of the internal standard.
I_s = Amount of the internal standard (ng).
ARF = Average response factor from the heated purge of the initial calibration.
W_s = Weight of sample added to purge vessel (g).

$$D = \frac{100 - \%\text{Moisture}}{100}$$

Medium soil (on a dry weight basis)

$$\text{Conc } (\mu g / kg) = \frac{A_x \times I_s \times V_t \times 1000 \times Df}{A_{is} \times ARF \times V_a \times W_s \times D}$$

where:

A_x = Area of the characteristic ion (EICP) of the analyte.
A_{is} = Area of the characteristic ion (EICP) of the internal standard.
I_s = Amount of the internal standard (ng).
ARF = Average RF from the ambient temperature purge of the calibration standard.
V_t = Total volume of the methanol extract in milliliters (10 mL).
V_a = Volume of the methanol extract in microliters added to the reagent water for purging.
W_s = Weight of sample added to purge vessel (g).
Df = Dilution factor. Assume 1.0 for no dilution.

5. Reports

5.1 Data Packet Organization

5.1.1 See Appendix II for a check list detailing data packet organization.

5.2 Quality Control Reports

5.2.1 All results for quality control tests are entered into the lab database. Printouts of all data entered must be included in the data packet. The routine minimum is a method blank report, a blank spike report, and a MS/MSD report.

5.3 Control Limits

5.3.1 The laboratory has a computerized database which is used to generate control limits for various analyses, matrices, and analytes. The control limits define the range in which 99% of all values produced by a system should lie. Because the control limits are updated periodically, the current control limits for QC analyses have not been defined in this SOP. A copy of all current control limits are located in Laucks' Control Limits Database.

5.4 Data Qualifying Flags

5.4.1 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.
J	The analyte of interest was detected below the practical quantitation 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.
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.
N	Used to denoted the presumptive evidence of a target analyte. This flag is used when it is not possible to confirm the presence of a compound by the strict guidelines for mass spectral interpretation, but in the technical judgment of the analyst, this compound is present.

6. Quality Control

6.1 Initial Calibration

6.1.1 Criteria

6.1.1.1 Initial calibration data are evaluated using %RSD and the relative response factors.

RFs are calculated using the equation:

$$RF = \frac{Ax}{Ais} \times \frac{Cis}{Cs}$$

where:

A_x = Response of target analyte
A_{is} = Response of internal standard
C_x = Amount of target analyte (ng/mL).
C_{is} = Amount of internal standard (ng/mL).

%RSDs are calculated using the equation:

$$\%RSD = \frac{SD_i}{RF_i} \times 100$$

where:

Sd_i = Standard deviation of the initial calibration points
RF_i = Average RF from initial calibration

6.1.2 The System Performance Check Compounds (SPCCs) are checked to determine that the minimum average relative response factors tabulated below are met, and that the maximum RSD for each Calibration Check Compound (CCC) is ≤ 30%. The RSD for all other target analytes *should* be ≤ 15%. If the RSD of any target analyte is greater than or equal to 15%, but ≤ 30%, additional calibration options may be used. Alternatively, if the mean of the RSD values for all analytes in the calibration is ≤ 15%, the initial calibration is considered acceptable. Laucks uses 40% percent as the upper limit for all compounds as an internal guideline although it is not a requirement of SW 846.

6.1.2.1 The mean RSD criterion applies to all analytes in the standards, regardless of whether or not they are of interest for a specific project.

6.1.2.2 The data used must be supplied with either a summary of the initial calibration data or a specific list of those compounds for which the RSD exceeded 15% and the results of the mean RSD calculation.

SPCC Compounds	Minimum RF Limit
Chloromethane	0.100
1,1-Dichloroethane	0.100
Bromoform	0.100
Chlorobenzene	0.300
1,1,2,2-Tetrachloroethane	0.300

CCC Compounds	%RSD Limit
Vinyl chloride	≤30%
1,1-Dichloroethene	≤30%
Chloroform	≤30%
1,2-Dichloropropane	≤30%
Toluene	≤30%
Ethylbenzene	≤30%

6.1.3 Corrective action

6.1.3.1 If the criteria are not met, additional standards may be analyzed or appropriate instrument maintenance and analysis of new standards should be performed.

6.1.4 Documentation

6.1.4.1 Copies of the initial calibration standards and the calculated RRFs and RSDs are stored with the raw data. If criteria are not met, reanalysis of additional standard(s) are noted in the instrument run log.

6.2 Continuing Calibration Verification

6.2.1 Criteria

6.2.1.1 At the beginning of each 12 hour QC period, a CCV standard is analyzed. The RRF for each compound is calculated and the percent difference is calculated as follows:

$$\%D = \frac{RF_i - RF_c}{RF_i} \times 100$$

where:

RF_i = Average RF from Initial Calibration
RF_c = RF from CCV standard

6.2.1.2 The minimum RRFs for the SPCCs must meet the criteria applied in the initial calibration detailed above. The %D for the CCCs cannot exceed the 20% CCV criteria as tabulated below.

CCC Compounds	% D Limit
1,1-Dichloroethene	≤20%
Chloroform	≤20%
1,2-Dichloropropane	≤20%
Toluene	≤20%
Ethylbenzene	≤20%
Vinyl chloride	≤20%

6.2.1.3 Laucks uses a maximum %D of 40% for all other reported analytes as an internal guideline, although it is not a requirement of SW 846.

6.2.2 Corrective action

6.2.2.1 Check calculations, check standard solutions or perform instrument maintenance. Reanalyze the standard, if this fails, re-do initial calibration.

6.2.3 Documentation

6.2.3.1 Copies of the continuing calibration standards and the calculated RFs and %Ds are stored with the raw data. If criteria are not met, reanalysis of additional standard(s) are noted in the instrument run log.

6.3 Instrument Blank

6.3.1 Criteria

6.3.1.1 The criteria used are the same as those used for the method blank control limits.

6.3.2 Corrective action

6.3.2.1 If the initial IBLK contains measurable levels of target analytes above one-half the reporting limit, except where noted below, the system is out of control. The source of contamination must be identified and corrected. If analysis of an additional IBLK does not demonstrate that the analytical system is free of contaminants, then instrument maintenance such as cleaning the transfer lines or replacing the trap may be required.

6.3.3 Documentation

6.3.3.1 Copies of instrument blank analyses are stored with the sample analyses raw data. Re-analysis of the method blank and/or maintenance performed is documented in the instrument run log.

6.4 Method Blanks

6.4.1 Criteria

6.4.1.1 A method blank is used to verify contamination free reagents and apparatus. A method blank is analyzed following every CCV and prior to sample analysis. Method blank criteria are listed below.

6.4.1.2 Laucks criteria for a method blank is less than one-half the RL for each analyte.

6.4.2 Corrective action

6.4.2.1 When these criteria are exceeded, corrective action should be taken to find/reduce/eliminate the source of this contamination in the method blank. Sample corrective action may be limited to qualification for blank contamination. When the concentrations of any target analytes within the method blank are above one-half of the reporting limit, the effect this may have had on the samples will be assessed as detailed below:

1) If any analyte is found only in the method blank, but not in any batch samples, no further corrective action may be necessary. Steps shall be taken to

find/reduce/eliminate the source of this contamination in the method blank. The case narrative should also discuss the situation.

2) If an analyte is found in the method blank and some, or all, of the other batch samples, additional corrective action is required to reanalyze the method blank, and any samples containing the same contaminant(s) which exceeded the corrective action limit(s). If the contamination remains, the contaminated samples of the batch would be reprepared and reanalyzed with a new method blank and batch specific QC samples.

3) Sporadic cases of contamination may be difficult to control however, daily contamination would not be acceptable.

4) Out-of-control surrogate recoveries in the method blank require reanalysis of the method blank.

5) If common common lab contaminates; such as acetone and methylene chloride are present, up to the reporting limit, the assoicated sample results for these compounds are flagged appropriately. Analytes may be present as long as they are less than 10 percent of the regulatory limit associated with that analyte, or less than 10 percent of the sample result for the same analyte, whichever is greater for the method blank to be acceptable. In addition, bromomethane may be present up to the RL in a medium soil method blank. This is due to the foaming action of the methanol with the sparging frit and is very difficult to control.

6.4.3 Documentation

6.4.3.1 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. Outliers are discussed in the case narrative.

6.5 Blank Spikes

6.5.1 Criteria

6.5.1.1 A blank spike follows the same protocol as a matrix spike analysis except that the spiking solution is added to an aliquot of PFW (or sand for soil samples) 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. It is recommended that all target analytes of concern be 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 per the USACOE Shell document, or if the target list contains more than 50 components per the DOD Quality Systems Manual- Final Version 1.

6.5.1.2 A blank spike may be used to fill the requirements for the performance of an initial calibration and continuing calibration verification standard. In addition, the level spiked will periodically be varied within the established calibration range.

6.5.2 Corrective action

6.5.2.1 The blank spike is used to determine whether a method is in control during sample preparation and analysis. Sample reanalysis 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.

6.5.3 Documentation

6.5.3.1 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.

6.6 Matrix Spike

6.6.1 Criteria

6.6.1.1 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 prior to analysis. A matrix spike analysis is performed with each analytical 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. The recovery of spike analytes is calculated as follows:

$$Recovery = \frac{SS - S}{SpikedAmount} \times 100$$

where:

SS = concentration in spiked sample
S = native concentration in unspiked sample

6.6.2 Corrective action

6.6.2.1 Samples with spike recoveries outside control limits will be reviewed for possible corrective action. Corrective action may involve recalculation and/or reanalysis. This process should also include evaluation of the recovery of surrogate compounds in the MS sample and recovery of matrix spiking compounds from the blank spike analysis. In all cases a narrative explanation of the condition is required to detail the corrective actions taken.

6.6.3 Documentation

6.6.3.1 The raw data for the matrix spike analyses are stored with the sample analyses raw data. The results for the matrix spike analyses are reported electronically via the laboratory's LIMS database.

6.7 Matrix Spike Duplicate

6.7.1 Criteria

6.7.1.1 A matrix spike duplicate analysis is performed with each analytical 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 relative percent difference (RPD) between the matrix spike and matrix spike duplicate recovery values. 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

6.7.2 Corrective action

6.7.2.1 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.

6.7.3 Documentation

6.7.3.1 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.

6.8 Surrogate Recovery

6.8.1 Criteria

6.8.1.1 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. 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

6.8.2 Corrective Action

6.8.2.1 Check calculations for possible error. Reanalysis is required for all surrogate recoveries which exceed the established control limits.

6.8.2.2 Out-of-control surrogate recoveries in the method blank require that the method blank be reanalyzed. Sample analyses are not performed until all criteria are met in the method blank analysis. Sample and QC analyses require reanalysis for out-of-control surrogate recoveries. If the sample reanalyses also demonstrate out-of-control surrogate recoveries due to matrix interference, this corrective action is discussed in the narrative.

6.8.3 Documentation

6.8.3.1 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 for out-of-control surrogate recoveries are designated by an "RE" in the instrument run log.

7. References

1) Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, (SW-846), US EPA Office of Solid Waste and Emergency Response, - Method 8260B, 3rd edition, 2nd revision, December 1996.

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 5000B, 3rd edition, revision 0, December 1996.

4) Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, (SW-846), US EPA Office of Solid Waste and Emergency Response, - Method 5030B, 3rd edition. 2nd revision, December 1996.

5) Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, (SW-846), US EPA Office of Solid Waste and Emergency Response, - Method 5035, 3rd edition, revision 0, December 1996.

APPENDIX I

Initial Calibration Concentrations For Low Level (25 mL) Waters (µg/L)

Compound	STD1	STD2	STD3	STD4	STD5
Dichlorodifluoromethane	1	5	10	25	50
Chloromethane	1	5	10	25	50
Vinyl Chloride	1	5	10	25	50
Bromomethane	1	5	10	25	50
Chloroethane	1	5	10	25	50
Trichlorofluoromethane	1	5	10	25	50
1,1-Dichloroethene	1	5	10	25	50
Acetone	5	10	20	50	100
Carbon disulfide	1	5	10	25	50
Methylene chloride	1	5	10	25	50
trans-1,2-Dichloroethene	1	5	10	25	50
1,1-Dichloroethane	1	5	10	25	50
Vinyl acetate	1	5	10	25	50
2,2-Dichloropropane	1	5	10	25	50
cis-1,2-Dichloroethene	1	5	10	25	50
2-Butanone	5	10	20	50	100
Bromochloromethane	1	5	10	25	50
Chloroform	1	5	10	25	50
1,1,1-Trichloroethane	1	5	10	25	50
Carbon tetrachloride	1	5	10	25	50
1,1-Dichloropropene	1	5	10	25	50
Benzene	1	5	10	25	50
1,2-Dichloroethane	1	5	10	25	50
Trichloroethene	1	5	10	25	50
1,2-Dichloropropane	1	5	10	25	50
Dibromomethane	1	5	10	25	50
Bromodichloromethane	1	5	10	25	50
cis-1,3-Dichloropropene	1	5	10	25	50
4-Methyl-2-pentanone	5	10	20	50	100
Toluene	1	5	10	25	50
trans-1,3-Dichloropropene	1	5	10	25	50

Compound	STD1	STD2	STD3	STD4	STD5
1,1,2-Trichloroethane	1	5	10	25	50
Tetrachloroethene	1	5	10	25	50
1,3-Dichloropropane	1	5	10	25	50
2-Hexanone	5	10	20	50	100
Chlorodibromomethane	1	5	10	25	50
1,2-Dibromoethane	1	5	10	25	50
Chlorobenzene	1	5	10	25	50
1,1,1,2-Tetrachloroethane	1	5	10	25	50
Ethylbenzene	1	5	10	25	50
m,p-Xylene	2	10	20	50	100
o-Xylene	1	5	10	25	50
Styrene	1	5	10	25	50
Bromoform	1	5	10	25	50
Isopropylbenzene	1	5	10	25	50
Bromobenzene	1	5	10	25	50
1,2,3-Trichloropropane	1	5	10	25	50
1,1,2,2-Tetrachloroethane	1	5	10	25	50
n-Propylbenzene	1	5	10	25	50
2-Chlorotoluene	1	5	10	25	50
4-Chlorotoluene	1	5	10	25	50
1,3,5-Trimethylbenzene	1	5	10	25	50
tert-Butylbenzene	1	5	10	25	50
1,2,4-Trimethylbenzene	1	5	10	25	50
sec-Butylbenzene	1	5	10	25	50
1,3-Dichlorobenzene	1	5	10	25	50
1,4-Dichlorobenzene	1	5	10	25	50
p-Isopropyltoluene	1	5	10	25	50
1,2-Dichlorobenzene	1	5	10	25	50
n-Butylbenzene	1	5	10	25	50
1,2-Dibromo-3-chloropropane	1	5	10	25	50
1,2,4-Trichlorobenzene	1	5	10	25	50
Naphthalene	1	5	10	25	50
Hexachlorobutadiene	1	5	10	25	50
1,2,3-Trichlorobenzene	1	5	10	25	50
Methyl tert-butyl ether	1	5	10	25	50

Initial Calibration Concentrations Of Routine Target Analytes For Low And Medium Level Soils & 5 mL Waters

Compound (µg/L)	STD1	STD2	STD3	STD4	STD5
Dichlorodifluoromethane	3	10	50	100	200
Chloromethane	3	10	50	100	200
Vinyl Chloride	3	10	50	100	200
Bromomethane	3	10	50	100	200
Chloroethane	3	10	50	100	200
Trichlorofluoromethane	3	10	50	100	200
1,1-Dichloroethene	3	10	50	100	200
Acetone	10	20	50	100	200
Carbon disulfide	3	10	50	100	200
Methylene chloride	3	10	50	100	200
trans-1,2-Dichloroethene	3	10	50	100	200
1,1-Dichloroethane	3	10	50	100	200
cis-1,2-Dichloroethene	3	10	50	100	200
2-Butanone	10	20	50	100	200
Chloroform	3	10	50	100	200
1,1,1-Trichloroethane	3	10	50	100	200
Carbon tetrachloride	3	10	50	100	200
Benzene	3	10	50	100	200
1,2-Dichloroethane	3	10	50	100	200
Trichloroethene	3	10	50	100	200
1,2-Dichloropropane	3	10	50	100	200
Bromodichloromethane	3	10	50	100	200
cis-1,3-Dichloropropene	3	10	50	100	200
4-Methyl-2-pentanone	10	20	50	100	200
Toluene	3	10	50	100	200
trans-1,3-Dichloropropene	3	10	50	100	200
1,1,2-Trichloroethane	3	10	50	100	200
Tetrachloroethene	3	10	50	100	200
2-Hexanone	10	20	50	100	200
Chlorodibromomethane	3	10	50	100	200
Chlorobenzene	3	10	50	100	200
Ethylbenzene	3	10	50	100	200
m,p-Xylene	6	20	100	200	400
o-Xylene	3	10	50	100	200
Styrene	3	10	50	100	200
Bromoform	3	10	50	100	200

Compound (µg/L)	STD1	STD2	STD3	STD4	STD5
1,1,2,2-Tetrachloroethane	3	10	50	100	200

Initial Calibration Concentrations Of Additional Analytes For Low And Medium Level Soils & 5 mL Waters

Compound (µg/L)	STD1	STD2	STD3	STD4	STD5
1,1,1,2-Tetrachloroethane	3	10	50	100	200
2,2-Dichloropropane	3	10	50	100	200
Bromochloromethane	3	10	50	100	200
1,1-Dichloropropene	3	10	50	100	200
1,2-Dibromoethane	3	10	50	100	200
Dibromomethane	3	10	50	100	200
1,3-Dichloropropane	3	10	50	100	200
Isopropylbenzene	3	10	50	100	200
Bromobenzene	3	10	50	100	200
1,2,3-Trichloropropane	3	10	50	100	200
n-Propylbenzene	3	10	50	100	200
2-Chlorotoluene	3	10	50	100	200
4-Chlorotoluene	3	10	50	100	200
1,3,5-Trimethylbenzene	3	10	50	100	200
tert-Butylbenzene	3	10	50	100	200
1,2,4-Trimethylbenzene	3	10	50	100	200
sec-Butylbenzene	3	10	50	100	200
1,3-Dichlorobenzene	3	10	50	100	200
1,4-Dichlorobenzene	3	10	50	100	200
p-Isopropyltoluene	3	10	50	100	200
1,2-Dichlorobenzene	3	10	50	100	200
n-Butylbenzene	3	10	50	100	200
1,2-Dibromo-3-chloropropane	3	10	50	100	200
1,2,4-Trichlorobenzene	3	10	50	100	200
Naphthalene	3	10	50	100	200
Hexachlorobutadiene	3	10	50	100	200
1,2,3-Trichlorobenzene	3	10	50	100	200
Iodomethane	3	10	50	100	200
trans-1,4-Dichloro-2-butene	3	10	50	100	200
Methyl tert-butyl ether	3	10	50	100	200

APPENDIX II

Data Packet Sequence

1. QC Summary
   - Surrogate recoveries
   - MS/MSD summary
   - Method blank summary
   - Instrument performance check (tuning)
   - Internal standard areas and RT summary

2. Sample Data
   - Target compound results
   - TICs (if requested)
   - Chromatogram normalized to nonsolvent peak
   - Quantitation report
   - Spectra

3. Standards Data
   - Initial calibration form
   - Chromatograms
   - Quantitation reports

   - CCV form
   - Chromatograms
   - Quantitation reports

4. Raw QC
   - BFB tune spectrum, chromatogram, and tabular listing
   - Method blank results, TICs, chromatogram, quantitation report, and spectra
   - MS/MSD results, chromatogram, quantitation report, spectra and control charts

5. Bench Sheets
   - Copy of instrument logbook, copy of COC, copy of holding blank analysis

6. Narrative.

7. Electronic Disk Deliverables (EDD) when requested

8. Control charts

APPENDIX III

Determination of Vinyl Chloride by Selected Ion Monitoring (SIM)

Analytical Conditions:

GC Parameters

Injection Port Temperature	: 200°C
GC/MS Interface Temperature	: 250°C
Initial GC Temperature	: 30°C
Initial Hold Time	: 0 min
Ramp Rate	: 6°C/min
Final Temperature	: 105°C
Final Time	: 0 min
Carrier Gas Flow	: 15 mL/min
Column Head Pressure	: 9 psi

Purge and Trap Parameters

Purge Time	: 11 min
Desorb Time	: 1 min
Bake Time	: 16 min
Desorb Preheat Temperature	: 20°C
Desorb Temperature	: 180°C
Purge Flow	: 40 mL/min
Purge Temperature	: Ambient
Desorb Flow Rate	: 15 mL/min

Mass Spectrometer Parameters

Electron Energy	: 70 volts
Acquisition Start Time	: 0.1 min

Group 1:

M/Z	Dwell Time (milliseconds)
61	50
62	400
63	50
64	50

Group 2:

M/Z	Dwell Time (milliseconds)
49	50
51	50
128	100
129	50

Group 3:

M/Z	Dwell Time (milliseconds)
65	50
67	50
102	50
104	50

Standards:

Internal Standard: Bromochloromethane
Surrogate: 1,2-Dichloroethane-d4

APPENDIX IV

Additional Appendix IX Compounds And Their Initial Concentrations For Low Level (25mL) Waters

Compound* (µg/L)	STD1	STD2	STD3	STD4	STD5
Acrolein	10	20	50	100	200
Bromoethane	10	20	50	100	200
Allyl chloride	10	20	50	100	200
Acrylonitrile	10	20	50	100	200
Chloroprene	10	20	50	100	200
Methacrylonitrile	10	20	50	100	200
Ethyl methacrylate	10	20	50	100	200
trans-1,4-Dichloro-2-butene	10	20	50	100	200
2-Chloroethylvinyl ether[1]	10	20	50	100	200

* The calibration range defines the reporting range for these compounds. However, the reporting limits may change for individual projects, based on MDLs, mass spectral confirmation, or project-specific requirements.

1 This analyte is not recommended because it decomposes in water, and does not recover in acidified samples.

APPENDIX V

Method 8260 Requirements and Corrective Actions

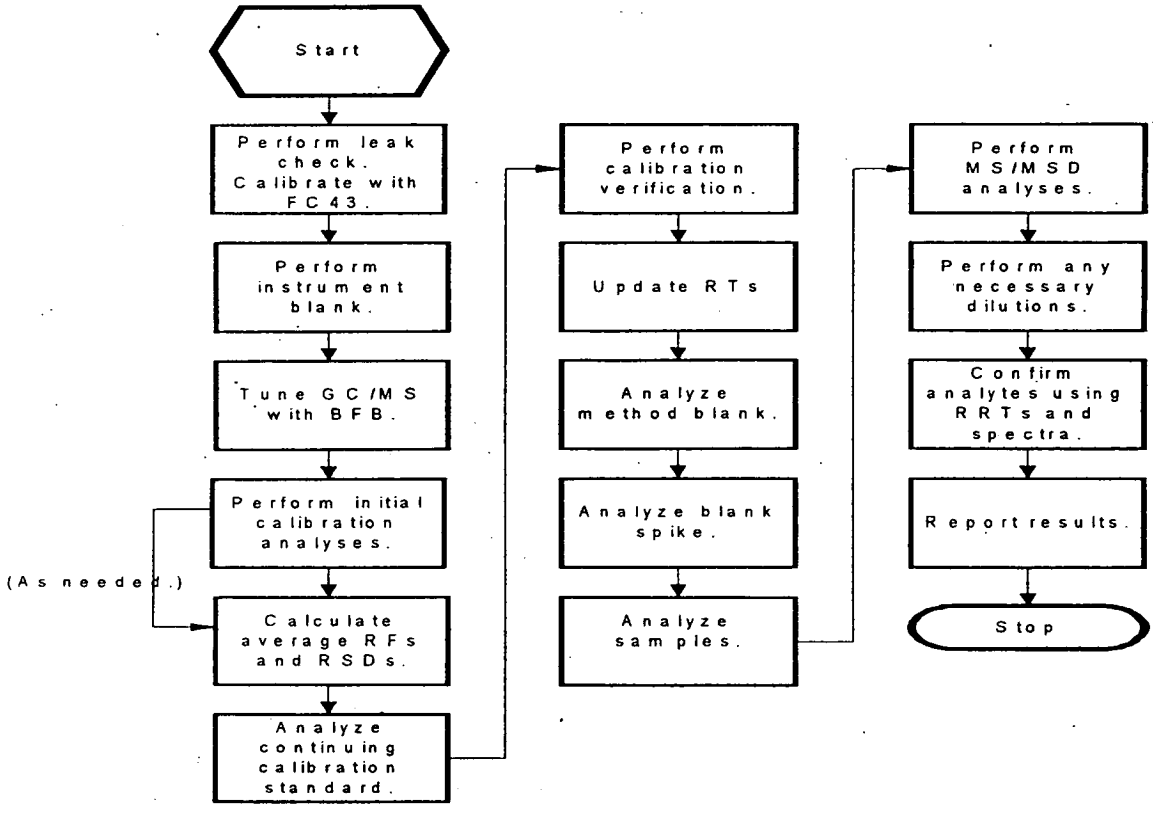
QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
Holding Time	14 days from collection.	14 days from collection.	N/A	N/A	HTVR (holding time violation report).
Tuning Verification 5 - 50 ng BFB	Mass Abundance 50 15-40% of 95 75 30-60% of 95 95 100% 96 5-9% of 95 173 < 2% of 174 174 > 50% of 95 175 5-9% of 174 176 95-101% of 174 177 5-9% of 176 *Alternate tuning criteria may be used (e.g.,CLP,524.2).	Mass Abundance 50 8-40% of 95 75 30-66% of 95 95 100% 96 5-9% of 95 173 < 2% of 174 174 50-120% of 95 175 4-9% of 174 176 93-101% of 174 177 5-9% of 176 * Alternate tuning criteria may be used.	Every 12 hours.	Re-tune instrument to meet criteria.	Copy of BFB raw data and tune criteria with file.
Initial Calibration	Minimum of 5 levels with lowest near RL. %RSD for CCCs ≤30% RF for SPCCs: chloromethane 0.10 1,1-dichloroethane 0.10 bromoform 0.10 chlorobenzene 0.30 1,1,2,2-tetrachloroethane 0.30 Non-CCCs: all analytes or average of all analytes = ≤15%.	5 levels 1, 5, 10, 20, 50 µg/L. (Ketones 5,10,20,50,100 µg/L) %RSD for CCCs ≤30% RFs for SPCCs: chloromethane 0.10 1,1-dichloroethane 0.10 bromoform 0.10 chlorobenzene 0.30 1,1,2,2-tetrachloroethane 0.30 Non-CCCs: all analytes or average of all analytes ≤15%. 40%RSD for each analyte as guideline.	Initially.	Reanalysis of out of control standards.	Copies of all raw data, tune file, and Form VI.
Initial Calibration Verification		Typically mid-range standard. Must meet limits applicable to CCV.	Once after initial calibration.	Re-analysis of initial calibration.	
Continuing Calibration Verification	Mid-level calibration standard every 12 hours. RF for SPCCs same as initial. RF for CCCs must be ≤20% D.	%D for CCC ≤20% %D for all other compounds < 40% as laboratory guideline.	Every 12 hours.	Reanalyze for analytes that exceed the control limits.	Copies of raw data and Form VII.
Internal Standards	Fluorobenzene, chlorobenzene-d5, 1,4-dichlorobenzene-d4, recommended.	Fluorobenzene, chlorobenzene-d5 and 1,4-dichlorobenzene-d4. RT must be ± 30 seconds from last calibration; area must be 50 to 100%.	Every sample.	Reanalyze all samples that do not meet these criteria.	IS areas and RTs are submitted on Form 8, and included in data package.

QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
Method Blank/ Instrument Blank	One method blank per extraction batch (up to 20 samples) or when there is a change in reagents, whichever is more frequent.	< 1/2 Reporting limit.	One method blank per QC period, following the CCV, prior to sample analysis. Typically, an instrument blank is analyzed prior to tuning the instrument.	Evaluate, qualify.	Copies of raw data filed, and reported electronically. Daily control charts for all method blanks are recorded. Narrate any analytes >1/2 RL
Surrogate Standards	4-bromofluorobenzene, dibromofluoromethane 1,2-dichloroethane-d4 or toluene-d8 recommended. Compare %R to laboratory established limits.	1,2-dichloroethane-d4, toluene-d8, 4-bromofluorobenzene, and dibromofluoromethane. Percent recoveries must meet established laboratory control limits. See QC database for control limits.	Every sample.	Reanalysis if surrogate recoveries exceed the established control limits.	Surrogates that exceed the control limits are documented in associated file.
Quality Control	One MS/MSD per 20 samples or each batch of samples, whichever is more frequent. Compare % recovery to laboratory established limits.	Blank spike recoveries and RPDs must meet control limits established by laboratory. MS/MSD recoveries are allowed to be out if due to matrix effect. See QC database for control limits.	One MS/MSD per 20 samples. A blank spike is analyzed every QC period.	Reanalysis of MS/MSD unless matrix effect has already been demonstrated. This can be determined by comparing with the blank spike recoveries.	Blank spike and MS/MSD recoveries are stored electronically. Raw data is stored with file. Out of control events are notated in file.
Qualitative Identification	All ions > 10% intensity must be ± 20% of standard; ± 0.06 RRT units of standard RRT.	All ions > 10% intensity must be ± 20% of standard; ± 0.50 min. of standard RT.	For identifying all target analytes in each sample.		Copies of all mass spectra stored with data.

QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
Sample Preservation and Storage	pH ≤2 with HCL for waters. pH ≤ 2 with sodium bisulfate for low level soils. Medium soils: zero headspace, methanol, or EnCore™ sampler. Store at 4 ° C.	pH ≤2 with HCL for waters. pH ≤2 with sodium bisulfate for low level soils. Medium soils: zero headspace, methanol, or EnCore™ sampler. Store at 4° C.	All water and low level soil samples.	If the water and low level soil samples are not acid-preserved, this is narrated in final report.	pH of all water samples and low level soils, where not preserved to a pH of ≤2, noted in instrument logbook.
Standard Solution Expiration	Stock standards (except gases): 6 months. Store between -10 to -20° C in teflon-sealed liners and amber bottles with minimal headspace, protect from light. Stock gas standards: 2 months. Storage conditions same as stock standards. Calibration standards: daily.	Stock standards (except gases): 6 months. Gas stock standards: 2 months. Stored at -10° to -20° C. Calibration standards: daily. All standards sealed in flame-sealed ampules: 2 years (not to exceed parent expiration date).			All standard data recorded in standard logbook.
Field Sample Amount	2 40 mL vials with zero headspace. Soils: vials, with zero headspace, or a sample aliquot in 40 mL vial. Glass container, septum-sealed screw-caps.	Waters:4 40 mL vials with zero headspace. Soils: 2 oz vials, with zero headspace, or a sample aliquot in 4 -40 mL vial. Glass container, septum-sealed screw-caps.			Bottles received by laboratory docume electronically.
Applicability	Groundwaters, soils, sediments, sludges, non-water miscible wastes and others.				

APPENDIX VI

Method 8260B Flow Chart



Refer to corrective action chart for out of control events.

APPENDIX VII

Method 8260 Target Analytes

Dichlorodifluoromethane	Chloromethane
Vinyl Chloride	Bromomethane
Chloroethane	Trichlorofluoromethane
1,1-Dichloroethene	Acetone
Carbon disulfide	Methylene chloride
trans-1,2-Dichloroethene	1,1-Dichloroethane
1,1,2,2-Tetrachloroethane	2,2-Dichloropropane
cis-1,2-Dichloroethene	2-Butanone
Bromochloromethane	Chloroform
1,1,1-Trichloroethane	Carbon tetrachloride
1,1-Dichloropropene	Benzene
1,2-Dichloroethane	Trichloroethene
1,2-Dichloropropane	Dibromomethane
Bromodichloromethane	cis-1,3-Dichloropropene
4-Methyl-2-pentanone	Toluene
trans-1,3-Dichloropropene	1,1,2-Trichloroethane
Tetrachloroethene	1,3-Dichloropropane
2-Hexanone	Chlorodibromomethane
1,2-Dibromoethane	Chlorobenzene
1,1,1,2-Tetrachloroethane	Ethylbenzene
m,p-Xylene	o-Xylene
Styrene	Bromoform
Methyl tert-butyl ether	

APPENDIX VIII

Method 8260 Optional Analytes for Low Level (25 mL) Water Analyses

Isopropylbenzene	Bromobenzene
1,2,3-Trichloropropane	2-Chlorotoluene
n-Propylbenzene	1,3,5-Trimethylbenzene
4-Chlorotoluene	1,2,4-Trimethylbenzene
tert-Butylbenzene	1,3-Dichlorobenzene
sec-Butylbenzene	p-Isopropyltoluene

Method 8260 Optional Analytes for Low Level (25 mL) Water Analyses

1,4-Dichlorobenzene	n-Butylbenzene
1,2-Dichlorobenzene	1,2,4-Trichlorobenzene
1,2-Dibromo-3-chloropropane	Hexachlorobutadiene
Naphthalene	1,2,3-Trichlorobenzene
Vinyl acetate	

Appendix IX

Additional Appendix IX Compounds (25 mL)

Acrolein	Bromoethane
Allyl chloride	Acrylonitrile
Chloroprene	Methacrylonitrile
Methyl methacrylate	trans-1,4-Dichloro-2-butene
2-Chloroethylvinyl ether	Ethyl methacrylate
Iodomethane	

APPENDIX X

Target Analytes And Their Associated Internal Standards

Fluorobenzene	**Chlorobenzene-d5**	**1,4-Dichlorobenzene-d4**
Dichlorodifluoromethane	Toluene	Isopropylbenzene
Chloromethane	trans-1,3-Dichloropropene	Bromobenzene
Vinyl Chloride	1,1,2-Trichloroethane	1,2,3-Trichloropropane
Bromomethane	Tetrachloroethene	1,1,2,2-Tetrachloroethane
Chloroethane	1,3-Dichloropropane	n-Propylbenzene
Trichlorofluoromethane	2-Hexanone	2-Chlorotoluene
1,1-Dichloroethene	Chlorodibromomethane	4-Chlorotoluene
Acetone	1,2-Dibromoethane	1,3,5-Trimethylbenzene
Carbon disulfide	Chlorobenzene	tert-Butylbenzene
Methylene chloride	1,1,1,2-Tetrachloroethane	1,2,4-Trimethylbenzene
trans-1,2-Dichloroethene	Ethylbenzene	sec-Butylbenzene
1,1-Dichloroethane	m,p-Xylene	1,3-Dichlorobenzene
Vinyl acetate	o-Xylene	1,4-Dichlorobenzene

Fluorobenzene	**Chlorobenzene-d5**	**1,4-Dichlorobenzene-d4**
2,2-Dichloropropane	Styrene	p-Isopropyltoluene
cis-1,2-Dichloroethene	Bromoform	1,2-Dichlorobenzene
2-Butanone		n-Butylbenzene
Bromochloromethane		1,2-Dibromo-3-chloropropane
Chloroform		1,2,4-Trichlorobenzene
1,1,1-Trichloroethane		Naphthalene
Carbon tetrachloride		Hexachlorobutadiene
1,1-Dichloropropene		1,2,3-Trichlorobenzene
Benzene		
1,2-Dichloroethane		
Trichloroethene		
1,2-Dichloropropane		
Dibromomethane		
Bromodichloromethane		
cis-1,3-Dichloropropene		
4-Methyl-2-pentanone		
Methyl tert-butyl ether		

Additional Appendix IX Compounds And Associated Internal Standard

Fluorobenzene (IS)	**Chlorobenzene-d5**
Acrolein	Ethyl methacrylate
Bromoethane	
Allyl chloride	
Acrylonitrile	
Chloroprene	
Methacrylonitrile	
Methyl methacrylate	
trans-1,4-Dichloro-2-butene	
Iodomethane	
2-Chloroethylvinyl ether	

APPENDIX XI

Target Analytes And Their Quantitation Ions

Compound	Primary Quant Ions*	Secondary Quant Ions*
Dichlorodifluoromethane	85	87
Chloromethane	50	52
Vinyl Chloride	62	64
Bromomethane	96	94
Chloroethane	64	66
Trichlorofluoromethane	101	103
1,1-Dichloroethene	96	61,63
Acetone	43	58
Carbon disulfide	76	78
Methylene chloride	84	86
trans-1,2-Dichloroethene	96	98,61
1,1-Dichloroethane	63	65,83
2,2-Dichloropropane	77	97
cis-1,2-Dichloroethene	96	98,61
2-Butanone	43	57
Bromochloromethane	128	49,130
Chloroform	83	85
1,1,1-Trichloroethane	97	99,61
Carbon tetrachloride	117	119
1,1-Dichloropropene	75	77,110
Benzene	78	-
1,2-Dichloroethane	62	98
Trichloroethene	95	97,130,132
1,2-Dichloropropane	63	112
Dibromomethane	93	95,174
Bromodichloromethane	83	85,127
cis-1,3-Dichloropropene	75	77
4-Methyl-2-pentanone	43	58,85
Toluene	92	91
trans-1,3-Dichloropropene	75	77

Compound	Primary Quant Ions*	Secondary Quant Ions*
1,1,2-Trichloroethane	83	97,85
Tetrachloroethene	166	164
1,3-Dichloropropane	76	78
2-Hexanone	43	58,100
Chlorodibromomethane	129	208,206
1,2-Dibromoethane	107	109
Chlorobenzene	112	114
1,1,1,2-Tetrachloroethane	131	133
Ethylbenzene	91	106
m,p-Xylene	106	91
o-Xylene	106	91
Styrene	104	78
Bromoform	173	175
Isopropylbenzene	105	120
Bromobenzene	156	158
1,2,3-Trichloropropane	75	77
1,1,2,2-Tetrachloroethane	83	85
n-Propylbenzene	120	91
2-Chlorotoluene	126	91
4-Chlorotoluene	91	126
1,3,5-Trimethylbenzene	105	120
tert-Butylbenzene	91	134,119
1,2,4-Trimethylbenzene	105	120
sec-Butylbenzene	105	134

Compound	Primary Quant Ions*	Secondary Quant Ions*
1,3-Dichlorobenzene	146	148,111
1,4-Dichlorobenzene	146	148,111
p-Isopropyltoluene	119	134,91
1,2-Dichlorobenzene	146	148,111
n-Butylbenzene	91	92
1,2-Dibromo-3-chloropropane	75	155,157
1,2,4-Trichlorobenzene	180	182
Naphthalene	128	-
Hexachlorobutadiene	225	223,227
1,2,3-Trichlorobenzene	180	182
Methyl tert-butyl ether	73	57,41

Additional Appendix IX Compounds And Their Quantitation Ions

Compound	Primary Quant Ions*	Secondary Quant Ions*
Acrolein	56	55,58
Bromoethane	108	-
Allyl chloride	41	78
Acrylonitrile	53	52,51
Chloroprene	53	51
Methacrylonitrile	41	39
Ethyl methacrylate	69	-
Methyl methacrylate	41	39
trans-1,4-Dichloro-2-butene	53	75
Vinyl acetate	43	86
Iodomethane	142	127
Vinyl acetate	43	86
2-Chloroethylvinyl ether	63	65

* Primary and secondary quantitation ions assigned by Laucks may be slightly different than those recommended in SW 846, in order to avoid interference.

APPENDIX XII

Target Analytes, Their Elution Order And Standard Mixes

Compound	Standard Mix
Dichlorodifluoromethane	6
Chloromethane	6
Vinyl Chloride	6
Bromomethane	6
Chloroethane	6
Trichlorofluoromethane	6
Acrolein	8
1,1-Dichloroethene	5
Acetone	7
Iodomethane	9
Bromoethane	10
Carbon disulfide	11
Allyl Chloride	12
Methylene chloride	5
trans-1,2-Dichloroethene	5
Acrylonitrile	13
1,1-Dichloroethane	4
Vinyl acetate	14
Chloroprene	15
2,2-Dichloropropane	4
cis-1,2-Dichloroethene	5
2-Butanone	7
Methacrylonitrile	12
Bromochloromethane	4
Chloroform	4
1,1,1-Trichloroethane	4
Carbon tetrachloride	4
1,1-Dichloropropene	3
1,2-Dichloroethane-d4 (surr)	18
Benzene	2
1,2-Dichloroethane	3
Trichloroethene	3
1,2-Dichloropropane	3
Dibromomethane	4
Methyl methacrylate	12

Compound	Standard Mix
Bromodichloromethane	5
2-Chloroethylvinyl ether	16
cis-1,3-Dichloropropene	3
Ethyl methacrylate	12
4-Methyl-2-pentanone	7
Toluene-d8 (surr)	18
Toluene	2
trans-1,3-Dichloropropene	3
1,1,2-Trichloroethane	3
Tetrachloroethene	4
1,3-Dichloropropane	3
2-Hexanone	7
Chlorodibromomethane	5
1,2-Dibromoethane	3
Chlorobenzene	1
1,1,1,2-Tetrachloroethane	3
Ethylbenzene	2
m,p-Xylene	1,2
o-Xylene	1
Styrene	2
Bromoform	4
Isopropylbenzene	1
4-Bromofluorobenzene (surr)	18
Bromobenzene	2
1,2,3-Trichloropropane	3
1,1,2,2-Tetrachloroethane	3
n-Propylbenzene	1
trans-1,4-Dichloro-2-butene	17
2-Chlorotoluene	1
4-Chlorotoluene	1
1,3,5-Trimethylbenzene	2
tert-Butylbenzene	1
1,2,4-Trimethylbenzene	2

Compound	Standard Mix
sec-Butylbenzene	1
1,3-Dichlorobenzene	1
1,4-Dichlorobenzene	1
p-Isopropyltoluene	2
1,2-Dichlorobenzene	1
n-Butylbenzene	2
1,2-Dibromo-3-chloropropane	3
1,2,4-Trichlorobenzene	2
Naphthalene	2
Hexachlorobutadiene	3
1,2,3-Trichlorobenzene	2
Methyl tert-butyl ether	19

Key:

1 = Supelco VOC Mix 1
2 = Supelco VOC Mix 2
3 = Supelco VOC Mix 3
4 = Supelco VOC Mix 4
5 = Supelco VOC Mix 5
6 = Supelco VOC Mix 6
7 = Supelco TCL Mix 1
8 = From neat
9 = Supelco Single std
10 = Chem Service Single Standard
11 = Supelco single standard
12 = Supelco 8240B Mix 7
13 = Supelco single std
14 = Supelco single standard
15 = Neat Material
16 = Supelco Single standard
17 = Supelco Single standard
18 = Neat material
19= Supelco Single standard

At the time of this writing, these are the current standard solutions used for the calibration standards. However, these standards may change due to Vendor supply or project-specific requirements.

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-8277

Determination of Polynuclear Aromatic Hydrocarbon Compounds by Selective Ion Monitoring (SIM) Method 8270C and 8270D

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1. Introduction and Scope

1.1 Method Description

1.1.1 This method is used for the determination of polynuclear aromatic hydrocarbon analytes in aqueous, soil, sediment, and other matrices by Selective Ion Monitoring (SIM) method. The SIM analysis scans for only a selected group of ions instead of the whole range of 35 to 500 m/z. The difference in scan time results in increased detector sensitivity, which allows us to report target analytes at very low levels.

1.1.2 This SOP follows SW-846 Method 8270D except for the specific deviations listed below or outlined in a project specific QAPP. This SOP is also applicable to SW-846 Method 8270C as all differences between the two revisions are clerical in nature. There are no technical differences.

1.1.3 This method is restricted to use by, or under the supervision of, analysts experienced in the use of gas/liquid/chromatography/mass spectroscopy and in the interpretation of chromatograms and mass spectra. Each analyst performing this method must have demonstrated the ability to perform the described chromatographic analysis and/or data interpretation.

1.2 Method Deviations & Comments

1.2.1 The following items represent deviations and comments on Method 8270D, as published, which are followed as standard operating procedure in the performance of this method at Laucks:

1.2.1.1 Method 3611B (Alumina Column Cleanup and Separation of Petroleum Wastes) is utilized routinely for all soil/sediment sample extracts. Alumina cleanup is performed on aqueous sample extracts as deemed necessary.

1.2.1.2 The 5 initial calibration levels have been established from 0.2 µg/mL to 8.0 µg/mL in order to demonstrate linearity for all target analytes and to provide a low-level standard that will act as the reporting limit as outlined in the method.

1.2.1.3 Neutral surrogate compounds 1-Fluoronaphthalene, Fluorene-d10, and Pyrene-d10 are used routinely. Current surrogate recoveries are maintained in Laucks' quality control database.

1.2.1.4 The following compounds are used as spiking analytes:

2-Methylnaphthalene	Benzo(a)anthracene
Acenaphthylene	Chrysene
Acenaphthene	Benzo(b)fluoranthene
Fluorene	Benzo(k)fluoranthene
Phenanthrene	Benzo(a)pyrene
Anthracene	Indeno(1,2,3-cd)pyrene
Fluoranthene	Dibenz(a,h)anthracene
Pyrene	Benzo(g,h,i)perylene

1.2.1.5 Surrogates and matrix spikes are added to the sample such that the final amount injected from normally concentrated samples is 2.5 ng for all spiking analytes.

1.2.1.6 The concentration of internal standards added to all sample extracts and calibration standards has been decreased from 40 ng/µL per compound to 1.0 ng/µL as allowed by the method.

1.2.1.7 A 2 µL injection of all calibration standards, method blank, LCS, MS/MSD and sample extracts is performed. A 2 µL injection provides more mass on-column than a 1 µL injection, which improves the ability to confirm the presence of target analytes at low concentrations.

1.2.1.8 Laucks uses ±0.50 minutes relative to the daily CCV standard as an acceptable retention time window for internal standards in all analyses.

1.2.1.9 Laucks uses a relative response factor for all analytes. The method specifies that if the average RSD of all analytes for the initial calibration is ≤15%, then the RRF may be used for individual analytes with RSDs >15%. This method option will be used if any analyte's RSD exceeds 15% in the initial calibration. However, Laucks uses an internal guideline of 40 percent as an upper limit.

1.2.1.10 CLP Statement of Work, OLM04.2, DFTPP tuning criteria have been substituted as allowed by the method. Tuning criteria are listed in Appendix II.

1.2.1.11 All standards are stored at less than -10°C or by the manufacturer's recommendation. Sample extracts are stored at 4°C (±2°C).

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 and soil samples must be extracted within 14 days from the date of collection. All sample extracts must be analyzed within 40 days from the date of extraction.

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.

Method Blank Spike	A background free matrix (DIW for water, clean sand for soils/sediments) to which known amounts or target analytes and surrogates are added each time sample extracts are prepared. Blank spikes are required on all NFESC work. In the context of this SOP, a blank spike is the same as a QC check standard.
CCC	Calibration Check Compound. A compound of analytical interest whose RRF in the CCV is compared to the average RRF from the initial calibration. The % difference must be less than the value specified in the method for the CCV to be considered valid. CCCs must also meet maximum %RSD criteria in an initial calibration.
CCV	Continuing calibration verification. This is the same acronym used in the CLP program. This is a standard injected at some prescribed frequency during the analysis sequence to determine whether the instrument has remained in calibration.
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.
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.

DFTPP	A solution containing DFTPP, pentachlorophenol, benzidine, and p,p'-DDT. An aliquot of this solution is analyzed at the start of a 12 hour QC period in order to verify DFTPP tuning criteria.
Internal Standard	A compound added to every standard, blank, matrix spike, matrix spike duplicate, and sample extract at a know concentration, prior to analysis. Internal standards are used as the basis for quantitation of target compounds.
ICV	Initial continuing verification. A calibration standard obtained from a different manufacturer than the standards used for the initial and continuing calibrations that is analyzed after a compliant initial calibration.
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.
QC Period	Quality control period. An analysis sequence initiated by the injection of one or more standards, followed by sample extracts. A QC period is 12 hours starting with the injection of the DFTPP solution.
RF	Response Factor. The measure of the mass spectral response of an analyte compared to its internal standard. Response factors are determined by analysis of standards and are used in the calculation of concentrations of analytes in samples. RF is determined by the following equation:

$$RF = \frac{A_x \times C_{is}}{A_{is} \times C_x}$$

where:

A_x - Area of target analyte primary ion
C_{is} - Concentration of internal standard
A_{is} - Area of internal standard primary ion
C_x - Concentration of target analyte

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. 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 the GC column.
Sequence	A set of sample extracts and standard solutions injected into an instrument in a chronologically continuous group. See also QC period.
SIM	Selective Ion Monitoring. This is a type of analysis when the MS detector is programmed to scan for only the selected ions.
Surrogate	Compounds added to every standard, blank, matrix spike, matrix spike duplicate, and sample at a known concentration; used to evaluate extraction and analytical efficiency by measuring recovery. Surrogates are brominated, fluorinated, or isotopically labeled compounds not expected to be detected in environmental samples.

2. Equipment List and Standards

2.1 Chromatographic System

Gas Chromatograph: Hewlett Packard 5890 I or II.

Carrier Gas: Helium 99.995% (high purity) or better.

Column: 30 m x 0.25 mm ID x 0.25 µm df capillary column (Restek RTX-5Sil MS or equivalent).

Automatic Sampler: Hewlett Packard 7673A with 19405A and 3396A controllers.

GC/MS Interface: Capillary direct to the ion source of the mass spectrometer, fixed temperature.

Mass Spectrometer: Hewlett Packard 5970B.

Data System: PC based Teknivent with ENVIROLINK data acquisition and processing software or HP Chemstation.

Miscellaneous: Assorted syringes, vials, caps, septa, injection port liners, ferrules, etc.

Note: All of the above equipment may be substituted with equivalent or better equipment.

2.2 Standards

2.2.1 All standards prepared from this operating procedure must be logged into one of two standards preparation logbooks. One is maintained for stock solutions prepared from neat chemicals or commercially prepared and certified standard solutions; the other is maintained for all working solutions. These logbooks are kept in the GC/MS semivolatile working area. When a standard is made, a solution number is assigned to it. This solution number is unique and will be used to track and identify the standard every time it is analyzed.

2.2.2 The following is an example of the solution nomenclature used for a working SIM PNA standard prepared on 11/13/91. The solution number assigned was MS2-77-2. This label represents the following:

MS	Solution was made and used as Mass Spec Standard
2	Solution was logged into standard book #2
77	Page number on which solution has been recorded
2	This denotes the second entry on page 77

2.2.3 All standards must also be verified both qualitatively and quantitatively in order to satisfy EPA requirements for traceability. This may be accomplished by purchasing solutions which have been fully documented by a commercial vendor.

2.2.4 Internal Standard Solution (SIM IS MIX @ 200 ug/mL).

Internal standards
Naphthalene-d8
Acenaphthene-d10
Phenanthrene-d10
Chrysene-d12
Perylene-d12
1,4-Dichlorobenzene-d4 (A)
(A) - this compound is present in the mix, but not appropriate to use for PNA analysis, and therefore, not reported.

2.2.4.1 Commercially prepared and certified internal standard solution is purchased at a concentration of 2000 µg/mL and is diluted 1:10. This standard is kept at -10°C until put into use. Once opened, the standard is kept at room temperature to avoid having the less soluble compounds fall out of solution. A new ampule of internal standard is opened on a weekly basis.

2.2.5 Preparation of DFTPP solution

2.2.5.1 Prepare a 25 µg/mL tuning solution which consists of DFTPP, pentachlorophenol, benzidine, and 4,4'DDT in methylene chloride. This solution is kept at -10°C.

2.2.6 Preparation of Calibration Standards

2.2.6.1 Calibration standards are prepared in methylene chloride from stock solutions that are purchased from a commercial source (e.g., Supelco or Restek). If an analyte required for calibration is not present in an available mixed solution, laboratory-prepared stock solutions that have been verified by GC/MS may be used. Laboratory prepared stock solutions should be tested against independent reference standards when they are available.

2.2.6.2 Calibration standards are prepared at five concentration levels. Standard concentrations at 0.2, 0.4, 1, 4 and 8 µg/mL are required. Each calibration standard contains all compounds of interest, surrogates, and internal standards.

2.2.7 Preparation of PNA stock solution at 200 µg/mL.

Stock Solution - PNA200
Total Volume 10ml

PNA Mix 2000 µg/ml	1ml	Supelco #47543-U
Carbazole 2000 µg/ml	1ml	Supelco #4-8076
PNA Surrogates 2000 µg/ml	1ml	Crescent Custom Mix #CCS-512
Methylene chloride	7ml	

2.2.7.1 Combine appropriate amounts of all solutions in a clean, 10 mL volumetric flask so that all analytes are present at 200 µg/mL. Dilute to volume with methylene chloride, stopper the flask and mix well. Record all information in the working standards logbook and transfer the contents of the volumetric flask into an amber screw-cap vial. Store this solution in the freezer when not in use. The vial must be marked with the logbook name, standard type, preparation date, solvent used, expiration date, and preparer initials.

2.2.7.2 The vendor and catalog numbers provided are for reference only. Other vendor's certified solutions may be substituted.

2.2.8 Preparation of working calibration standards

2.2.8.1 To prepare working calibration standards, add the amounts listed below in (µL) of PNA200, internal standard solution (SIM IS @ 200 µg/mL) and methylene chloride to clean vial inserts and use within one week.

SIM PNA Calibration Curve

	Amount of **PNA200**	Amount of Methylene Chloride
Working PNA 8	8µl	192µl
Working PNA 4	4µl	196µl
Working PNA 1	1µl	199µl

Intermediate PNA solution
1 µl **PNA200** in 199µl methylene chloride

	Amount of Intermediate Solution	Amount of Methylene Chloride
Working PNA 0.4	80µl	120µl
Working PNA 0.2	40µl	160µl

2.2.8.2 The working PNA 1 standard is the continuing calibration solution. The continuing calibration solution must be prepared on a weekly basis.

2.2.8.3 Calibration stock solutions which are received sealed in ampules from the manufacturer are useable up to their manufacturer's expiration date. The mixed PNA200 stock solution must be prepared once every twelve months, or sooner, if standards have degraded or concentrated such as evidenced by a significant increase in response for all analytes in the standard.

3. Safety precautions

3.1 Routine Safety Precautions

3.1.1 All standards and sample extracts should be handled as if they are 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 Almost all of the analytes under consideration are known or suspected carcinogens. Analysts should wash their hands after using any standard, solvent or sample extract. Additionally, a respirator should be worn or a fume hood utilized for extremely hazardous compounds or very dirty extracts.

3.2 Waste disposal

3.2.1 All waste solvents, expired standards and old extracts should be disposed of in the solvent waste can located in the prep area fume hood. Refer to LTL-2001, *Waste Segregation and Disposal* for more detail.

4. Operation procedures

4.1 Analytical Conditions

4.1.1 Chromatographic Conditions

Initial Temperature:	80°C.
Initial Time:	1 minutes.
Column Temperature Program:	80°-250°C at 40 °C /minute, 250-320 at 20 °C /minute
Final Temperature:	320°C for 5.5 minutes.
Injector Temperature:	275-300°C.
Transfer Line Temperature:	280-310°C.
Injector Purge Time Off:	1 minute.
Injection Volume:	2 µL.
Column Linear Velocity:	30-40 cm/sec (nominal 35 cm/sec measured at 30°C).

4.1.2 Mass Spectrometer Conditions

Electron Energy:	70 volts.
Scan Time:	Not to exceed 1 second per scan.
Scan Start Time:	3.5 minutes.
Scan Time Range:	from 3.5 to 6.5 minutes.
Scans in Mass Segment:	125 to 177 amu.
Scan Time Range:	from 6.5 to 10.8 minutes.
Scans in Mass Segment:	165 to 245 amu.
Scan Time Range:	from 10.8 to 15 minutes.
Scans in Mass Segment:	248 to 280 amu.

4.2 Method Detection Limit Study

4.2.1 MDL studies will continue to be performed. This procedure is fully described in Laucks SOP on Determination of MDL's.

4.2.2 MDLs for this method are in the range of 0.005 – 0.1 µg/L for waters and 0.4 – 2.6 µg/kg for soils.

4.3 Method Reporting Limits

4.3.1 The reporting limits for this method are determined by the low level standard. Reporting limits are listed in Appendix VII.

4.4 Method Validation

4.4.1 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. This procedure is fully described in Laucks SOP on Determination of Precision and Accuracy Studies.

4.5 Routine Instrument Maintenance

4.5.1 Instrument maintenance may be required for good chromatography and proper calibration. The following steps may be undertaken if needed before the analysis of any standard or sample:

A. Cool the GC oven to 30°C.
B. Check background for the instrument using manual tune to determine the operating status of the instrument.
C. Remove the injector septum and quartz liner.
D. Remove the column from the injector.
E. Install a new column ferrule.
F. Clip off 10 cm of the column. Check for a proper cut.
G. Reinstall the column and adjust the alignment.
H. Install a clean quartz liner.
I. Reinstall the O-ring or replace it if worn.
J. Install a new septum.
K. Clean and reinstall the autosampler syringe.

4.5.2 After any of these steps have been taken, recheck background, correct any leaks by tightening fitings, then ramp the GC oven twice from 50° to 310°C at 20° /minute for 10 minutes.

4.6 Instrument Tuning

4.6.1 The HP 5970B mass spectrometer uses FC-43 (PFTBA) as a mass calibration compound. Each instrument will require different ion ratios to pass the required DFTPP performance criteria. See Appendix II for the DFTPP tuning criteria. The following ratios are therefore approximate. Use manual tuning to tune the mass spectrometer.

Ion	% of ion 69
69	100%
131	25-35%
219	25-35%
414	1-3%

4.6.2 Ion peak widths should be in the 0.5 to 0.6 amu range. Excessive peak width can lead to loss of minor isotope peaks. Insufficient peak width can result in the loss of sensitivity. Ions for water, nitrogen, and oxygen should be <5% of ion 69.

4.6.3 Analyze an aliquot of the DFTPP tuning solution in order to verify DFTPP tuning criteria, degradation, and column tailing factors. The spectrum of the DFTPP must pass tuning criteria before any other standards are injected. Retuning of the instrument may be necessary to achieve this. Additionally, the DFTPP spectrum should be well within the performance criteria - i.e., no ion abundance should be borderline and the ratios should be routinely reproducible to insure a stable calibration.

4.6.4 The DFTPP tuning solution should also be used to assess GC column performance and injection port inertness. Degradation of DDT to DDE and DDD should not exceed 20%. Benzidine and pentachlorophenol should be present at their normal responses, with no visible peak tailing, as demonstrated by the peak tailing factor. The calculation of peak tailing factors is illustrated in Appendix XIII. The acceptance criteria for benzidine is <3.0 and pentachlorophenol is <5.0. If degradation is excessive and/or poor chromatography is noted, the injection port may require cleaning. It may also be necessary to break off the first 6-12 inches of the capillary column.

4.6.5 Analysis of the DFTPP must meet the ion abundance criteria listed in Appendix II before initiation of initial or continuing calibration standard analysis.

4.7 Initial and Continuing Calibration Standards and Initial Calibration Verification

4.7.1 After demonstrating compliance with the DFTPP tuning criteria, analyze the calibration standards within 12 hours.

4.7.2 Check the integrations and retention times of all compounds in each standard. Examine the peaks to ensure that peak saturation and/or chromatographic overload has not occurred in the upper calibration standard.

4.7.3 All compounds in the initial and continuing calibration standards must meet the criteria listed in Appendix IV and Appendix V, respectively.

4.7.4 After completion of a compliant initial calibration curve, an initial calibration verification (ICV) may be analyzed. This standard is from a source different than that of the calibration standards. All analyte recoveries should be within 70-130% of the expected value with up to 2 analytes exceeding this control limit due to sporadic marginal failures.

4.8 Sample Analysis

4.8.1 After completion of a compliant continuing calibration standard, sample analysis may be performed.

4.8.2 Remove the sample extracts from the refrigerator and allow to warm to room temperature.

4.8.3 Transfer 200 µL of extract to a vial insert.

4.8.4 Add 2 µL of IS solution (SIM IS MIX @ 200 ug/mL).

4.8.5 Cap the vial and mix well.

4.8.6 Place the vial onto the autosampler for analysis.

4.8.7 For dilutions, decide what dilution is necessary from previous data or analyst judgment. Make dilution and then add 2 µL of SIM IS solution prior to capping vial. Mix well prior to analysis.

4.8.8 In general, the method blank accompanying the samples is injected prior to the analysis of the samples. This is not a requirement, however. Samples are then injected until the end of the 12 hour clock.

4.8.9 Compound Identification

4.8.10 Compounds are tentatively identified if a peak elutes within 0.5 minute of that compound in the CCV standard. In addition, the internal standard for that compound should also be within 0.5 minute of its counterpart in the CCV standard. To confirm the presence of that compound in the sample extract, the mass spectrum of the peak must be evaluated. Spectra are compared against standard spectra of each compound generated on the instrument used for analysis.

4.8.10.1 The following criteria are used to evaluate mass spectra.

4.8.10.1.1 The intensities of the characteristic ions of a compound maximize within one scan of each other. Searches performed based on the presence of a target compound at a compound-specific retention time will be accepted as meeting this criterion.

4.8.10.1.2 All ions present in the standard mass spectra at a relative intensity greater than 30% (most abundant ion in the spectrum equals 100%) or the three ions of greatest intensity must be present in the sample spectrum.

4.8.10.1.3 The relative intensities of ions specified must agree within 30% between the standard and sample spectra. Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample ion abundance must be between 20 and 80 percent.

4.8.10.1.4 If a compound cannot be verified by all of these criteria, but in the technical judgment of the analyst, the identification is correct, then report that identification and proceed with quantification.

4.8.10.1.5 The experienced analyst's judgment weighs heavily in evaluating chromatograms and mass spectra for compound identification. For instance, the retention times of surrogate compounds may be outside their expected windows due to sample matrix effects. If this has occurred, it must be fully documented in the appropriate report notes.

4.8.11 Common Analytical Problems

4.8.11.1 An analyst's professional judgment plays a large role in how data is interpreted. The following guidelines should be followed in order to facilitate consistency between analysts. Any anomalies not addressed in this SOP must be discussed with the supervisor prior to implementation. All anomalies and corrective actions must be documented.

4.8.12 Carryover

4.8.12.1 In some cases, if analytes in a sample are very high, there may be carryover from one analysis to the next. If a sample is suspected of being high due to historical data or extract color, the sample should be diluted prior to analysis, or one or more blanks should be analyzed after the sample to insure that there is no carryover between analyses.

4.8.12.2 However, in the case where high levels were not expected, and do appear in a sample analysis, the analysis after it should be examined carefully for carryover.

4.9 Manual Peak Integrations

4.9.1 Manual peak integrations should be used only when necessary to correct for matrix interference, tangent peaks, and rising baselines. Manual integrations are not to be used in an attempt to meet calibration, surrogate recovery, or spike recovery criteria. Refer to LTL-1020, *The Integration of IC, GC, HPLC, and GC/MS Peaks* for more detail.

4.9.2 If the chromatogram shows degradation due to sample loading e.g. split peaks, lift off, or severe tailing, the sample should be diluted and reanalyzed if required detection limits permit.

4.9.3 If a manual integration is necessary, use the following guidelines:

- Integrate only the peak. Start where the peak lifts from the baseline and end as soon as it returns to the baseline. Do not integrate extra baseline in an attempt to increase peak area.
- Do not "peak shave". Do not cut off legitimate parts of the peak in order to reduce peak area.
- In cases of tangent skims, do not increase or decrease peak areas or heights by skimming extra long baselines or drawing the baseline too low.
- Always initial and date your manual integrations.

4.10 Compound Quantification

4.10.1 Target compound concentrations are calculated using the following equations:

$$\text{Sample Concentration (ng/}\mu\text{L)} = \frac{A_x \times C_{is}}{A_{is} \times RF_{average}}$$

where:

A_x = Response for the target analyte
A_{is} = Response for the internal standard
C_{is} = Concentration of internal standard, in ng/µL
$RF_{average}$ = Average Response Factor (calculated from the initial calibration)

4.10.2 If the %RSD of a compound's relative response factor is 15% or less, than the concentration may be determined using the average response factor from the initial calibration. Alternatively, the RF may be used as long as the average RSD of all calibration analytes is ≤15%. Laucks uses 40% percent as the upper limit for all compounds as an internal guideline although it is not a requirement of SW 846.

4.10.3 The above equation is used directly by the HP computer to yield the extract concentration.

4.10.4 To calculate the actual sample concentration, the following calculation must be used.

Aqueous samples:

$$\text{Extract Concentration (}\mu\text{g/L)} = \frac{F \times D \times V_f \times GPC}{V_i}$$

where:

F = Amount found from HP quantitation report (ng/µL)
D = Dilution factor of extract
V_f = Final extract volume (µL)
GPC = GPC dilution factor. Use 1 if GPC was not performed, 2 if GPC was used
V_i = Initial sample volume (mL)

Non-aqueous samples:

$$\text{Sample Concentration}(\mu g/kg) = \frac{F \times D \times V_f \times GPC}{W_s \times T_s}$$

where:

W_s = Sample size extracted in grams.
T_s = Total Solids in decimal format (i.e. 0.76 not 76).

4.10.5 Normally, these calculations are automatically performed by the LIM system.

4.10.6 Any sample extracts which exceed the upper calibration range for any analyte of interest must be diluted and reanalyzed to bring the analyte into the working range of the calibration.

5. Quality Control

5.1 General Issues

5.1.1 See Appendix VIII and IX for QA/QC limit and corrective action tables.

5.2 Initial Calibration

5.2.1 Criteria

5.2.1.1 Initial calibration data are evaluated using %RSD of the relative response factors as well as minimum average RRFs. The %RSD must be ≤ 30% for each individual Calibration Check Compound (CCC). All other RRFs must be ≤ 15%. Alternatively, RRFs may be used as long as the average RRFs for all compounds in the method are ≤ 15%. Laucks uses an internal guideline of 40% as an upper control limit for each compound.

5.2.1.2 Calculate the %RSD for all compounds. CCC criteria are listed in Appendix V.

5.2.1.3 Calculate the individual and average RFs for each compound.

5.2.1.4 RFs are calculated using the equation

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

where:

A_s = Response of target analyte
A_{is} = Response of internal standard
C_s = Amount of target analyte (ng/µL)
C_{is} = Amount of internal standard (ng/µL)

5.2.1.5 The minimum acceptable average RF for all analytes is 0.010.

5.3 *Continuing Calibration Verification*

5.3.1 Criteria

5.3.1.1 At the beginning of each 12 hour QC period, a CCV standard is analyzed. The RF for each compound is calculated and the percent difference is calculated as follows:

$$\%\,Difference = \frac{RF_c - RF_i}{RF_i} \times 100$$

where:

RF_i = Average RF from Initial Calibration.
RF_c = RRF from CCV standard.

5.3.1.2 The %D results for all CCCs must be ≤20%. There are no guidelines for the %D for all other compounds, however Laucks uses 40% as an internal guideline.

5.3.1.3 In addition, all compounds must have a minimum RRF of at least 0.010. See Appendix V for all CCV criteria.

5.3.2 Corrective action

5.3.2.1 Check that all peaks have been properly integrated. Check the calculations. If the %D criteria are still not met, perform corrective instrument maintenance or re-tuning, and reanalyze the standard. If the %D or minimum RF criteria are still not met, a new CCV standard may need to be prepared, a new initial calibration performed, a new column installed, or other instrument maintenance performed in order to meet the CCV criteria.

5.4 Method Blank

5.4.1 Criteria

5.4.1.1 A method blank is used to verify contamination-free reagents and apparatus. A method blank is prepared with every set of samples extracted at the same time, at a frequency of at least one blank per 20 samples.

5.4.1.2 Laucks criteria for a method blank is less than one-half the RL for each analyte, or less than 10 percent of the regulatory limit associated with that analyte, or less than 10 percent of the sample result for the same analyte, whichever is greater for the method blank to be acceptable. Method blank control limits are detailed in Appendix VI.

5.4.2 Corrective action

5.4.2.1 If an analyte is found in the blank but not in any of the associated samples, the sample batch may not require re-extraction unless this is required by contractual obligations. Consult the QC officer to determine if re-extraction and reanalysis are required.

5.4.2.2 If any analyte exceeds the control limit in the blank and is also found in the associated sample extracts, the samples must be re-extracted and reanalyzed.

5.4.2.3 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.

5.5 QC Check Sample (LCS)

5.5.1 Criteria

5.5.1.1 The LCS is used to determine whether a method is in control during sample preparation and analysis. A LCS follows the same protocol as the matrix spike analysis except that the spiking solution is added to a blank matrix (deionized water for water or sea sand for soil/sediments) instead of an actual sample. A Lab Control Sample is prepared with every set of samples extracted at the same time, at a frequency of at least one LCS per 20 samples. At the time of the writing of this SOP, the established control limits are 20-160% for all spiking compounds.

5.5.2 Corrective action

5.5.2.1 Check all peak integrations and sample calculations.

5.5.2.2 If the analyte recoveries still exceed the control limits, the blank spike extract may be reanalyzed.

5.5.2.3 If the analyte recoveries are still out of control, re-extraction of the associated samples is required.

5.5.3 Matrix Spike

5.5.3.1 Criteria

5.5.3.2 A sample is chosen from the samples to be analyzed, and an aliquot of spiking solution is added to this sample prior to extraction. It is not required that a matrix spike analysis be performed with each extraction batch unless the project QAPP requires it. However, 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 selected target analytes. Analyte recovery is calculated as follows:

$$\%Recovery = \frac{SSR - SR}{SA} \times 100$$

where:

SSR = Concentration in spiked sample.
SR = Native concentration in unspiked sample.
SA = Concentration of spike added.

5.5.3.3 At the time of the writing of this SOP, the established control limits are 20-160% for all spiking compounds.

5.5.4 Corrective action

5.5.4.1 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.

5.6 Matrix Spike Duplicate

5.6.1 Criteria

5.6.1.1 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.

5.6.1.2 This calculation is as follows:

$$RPD = \frac{S1 - S2}{(S1 + S2)/2} \times 100$$

where:

S1 = Measured concentration for MS sample.
S2 = Measured concentration for MSD sample.

5.6.1.3 At the time of the writing of this SOP, the established control limits for MS/MSD recoveries are 20-160% and 30 for the RPD values.

5.7 Surrogate Recovery

5.7.1 Criteria

5.7.1.1 Surrogates are chemically similar compounds added to every sample, method blank and QC sample prior to sample processing. They are used to monitor for potential sample processing errors and matrix effects. Surrogate compound recoveries are calculated as follow:

$$\%Recovery = \frac{S_m}{S_a} \times 100$$

where:

S_m = Concentration of surrogate measured in extract.
S_a = Concentration of surrogate added.

5.7.1.2 At the time of the writng of this SOP, the established control limits for surrogate recoveries are 20-160%.

5.7.2 Corrective Action

5.7.2.1 Check calculations for possible error.

5.7.2.2 Check instrument performance, if necessary correct the problem and re-analyze the extract.

5.7.2.3 Some samples may require dilution in order to bring one or more target analytes within the calibration range or to overcome significant matrix interference. This may result in the dilution of the surrogate response to the point that the recoveries can not 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. For all data package work both the diluted and undiluted analyses will be provided.

5.7.2.4 Re-extraction is not necessary in the case where a sample is chosen for MS/MSD analyses and the same recovery pattern is present in all three analyses. In this case, matrix effects may be assumed and re-extraction is not required for this sample.

5.7.2.5 All other circumstances require re-extraction and reanalysis of the affected sample(s).

5.7.2.6 Out of control surrogate recoveries in the method blank require that all the samples in the associated batch be re-extracted and reanalyzed. 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.

6. Reports

6.1 Data Packet Organization

6.1.1 See Appendix I for a check list detailing data packet organization.

6.2 Quality Control Reports

6.2.1 All results for quality control tests are entered into the lab 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

6.3.1.1 Sample report results are qualified with data qualifying flags. These flags have the following definitions:

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.

J: The analyte of interest was detected below the practical quantitation 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.

X: Indicates an unresolvable isomeric pair. This flag indicates that calculated results are the sum of the two isomers.

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.

7. References

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 4th Edition, Method 8270D, "Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS): Capillary Column Technique," Revision 4, January 1998, U.S. EPA.

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 4th Edition, 2nd Update, Method 3611B, "Alumina Cleanup," Revision 4, January 1998, US EPA.

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 4th Edition, 2nd Update, "Method 8000B, Determinative Chromatographic Separations", Revision 2, December 1996, U.S.EPA.

US EPA. Contract Laboratory Program, Statement of Work for Organic Analysis, Multi-Media, Multi-Concentration, Document Number OLM04.2, May 1999.

APPENDIX I

Data Packet Check List

QC Summary
Surrogate Recovery Summary Report
Blank Spike Recovery Report
MS/MSD Recovery Report
Method Blank Summary
GC/MS Instrument Performance Check
Internal Standard Area and RT Summary Report

Sample Data
Target Compound Results (Organics Analysis Data Sheet)
Sample Chromatograms, quantitation reports and spectra for all samples

Standards Data
Initial Calibration Summary Report
Chromatograms and quantitation reports for all initial calibration standards
Continuing Calibration Summary Reports
Chromatograms and quantitation reports for all CCV Standards

Raw QC Data
Bar Graph Spectrum, mass listing and chromatogram for every DFTPP injection
Method Blank Data
Target Compound Results (Organics Analysis Data Sheet)
Chromatograms, quantitation reports and spectra for all method blanks
Blank Spike Data
Target Compound Results (Organics Analysis Data Sheet)
Chromatograms, quantitation reports and spectra for all blank spikes
Matrix Spike/Matrix Spike Duplicate Data
Target Compound Results (Organics Analysis Data Sheet)
Chromatograms, quantitation reports and spectra for all MS analyses

Bench Sheets
All extraction bench sheets, analysis log book pages, chains of custody, and any other pertinent information.

APPENDIX II

DFTPP Tuning Criteria

Mass	Relative Abundance
51	30-80% of mass 198
68	less than 2% of 69
69	present
70	less than 2% of 69
127	25-75% of mass 198
197	less than 1% of 198
198	100%
199	5-9% of mass 198
275	10-30% of mass 198
365	greater than 0.75% of mass 198
441	0-100 % of mass 443
442	40-110% of mass 198
443	15-24% of mass 442

CLP requires that the 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.

SW 846 states that the following approach has been shown to be useful: the mass spectrum of DFTPP may be acquired in the following manner. 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. Alternatively, the analyst may use other documented approaches suggested by the instrument manufacturer.

APPENDIX III

Calibration Standard Solution Concentrations, ng/µL

Compound	STD1	STD2	STD3	STD4	STD5
1-Fluoronaphthalene	0.2	0.4	1.0	4.0	8.0
Naphthalene	0.2	0.4	1.0	4.0	8.0
2-Methylnaphthalene	0.2	0.4	1.0	4.0	8.0
Acenaphthylene	0.2	0.4	1.0	4.0	8.0
Acenaphthene	0.2	0.4	1.0	4.0	8.0
Fluorene-d10	0.2	0.4	1.0	4.0	8.0
Fluorene	0.2	0.4	1.0	4.0	8.0
Phenanthrene	0.2	0.4	1.0	4.0	8.0
Anthracene	0.2	0.4	1.0	4.0	8.0
Carbazole	0.2	0.4	1.0	4.0	8.0
Fluoranthene	0.2	0.4	1.0	4.0	8.0
Pyrene-d10	0.2	0.4	1.0	4.0	8.0
Pyrene	0.2	0.4	1.0	4.0	8.0
Benzo(a)anthracene	0.2	0.4	1.0	4.0	8.0
Chrysene	0.2	0.4	1.0	4.0	8.0
Benzo(b)fluoranthene	0.2	0.4	1.0	4.0	8.0
Benzo(k)fluoranthene	0.2	0.4	1.0	4.0	8.0
Benzo(a)pyrene	0.2	0.4	1.0	4.0	8.0
Indeno(1,2,3-cd)pyrene	0.2	0.4	1.0	4.0	8.0
Dibenz(a,h)anthracene	0.2	0.4	1.0	4.0	8.0
Benzo(g,h,i)perylene	0.2	0.4	1.0	4.0	8.0

APPENDIX IV

Initial Calibration Criteria

Calibration Check Compound	%RSD Limit
Acenaphthene	≤30%
Fluoranthene	≤30%
Benzo(a)pyrene	≤30%

$RRF_{average}$ for all compounds must be < 15%.

APPENDIX V

Continuing Calibration Verification Criteria

Calibration Check Compound	%D Limit
Acenaphthene	≤20%
Fluoranthene	≤20%
Benzo(a)pyrene	≤20%

%D for all other analytes should be within 40%.

APPENDIX VI

Method Blank Control Limits

Compound	Control Limits Water	Soil
All compounds	<1/2RL*	<1/2RL*

* See Appendix VII

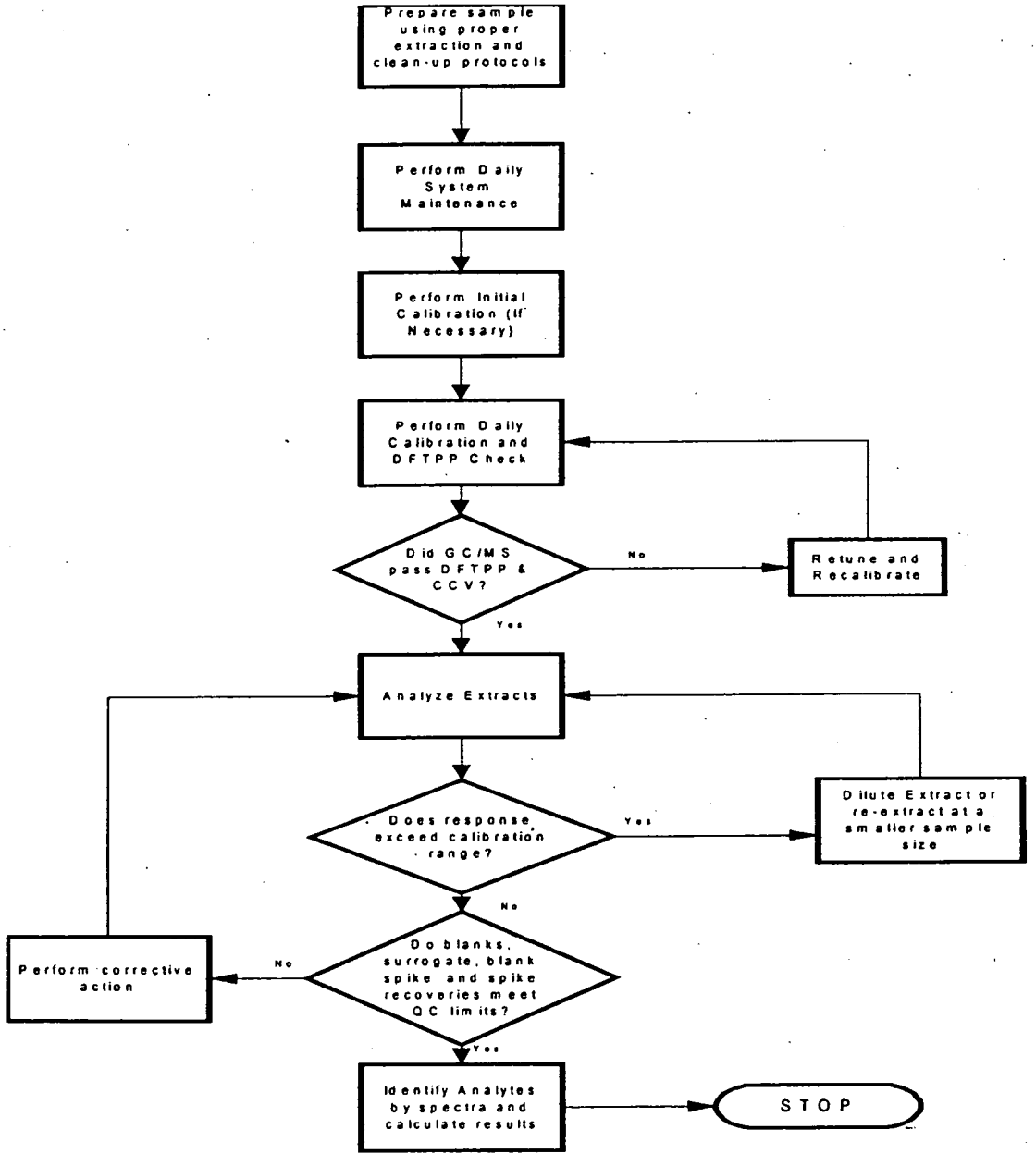
APPENDIX VII

Reporting Limits

Compound	Water µg/L	Soil µg/kg
2-Methylnaphthalene	0.1	7
Acenaphthylene	0.1	7
Acenaphthene	0.1	7
Fluorene	0.1	7
Phenanthrene	0.1	7
Anthracene	0.1	7
Carbazole	0.1	7
Fluoranthene	0.1	7
Pyrene	0.1	7
Benzo(a)anthracene	0.1	7
Chrysene	0.1	7
Benzo(b)fluoranthene	0.1	7
Benzo(k)fluoranthene	0.1	7
Benzo(a)pyrene	0.1	7
Indeno(1,2,3-cd)pyrene	0.1	7
Dibenz(a,h)anthracene	0.1	7
Benzo(g,h,i)perylene	0.1	7

APPENDIX VIII

Method 8270D Flow Chart



APPENDIX IX

Method 8270D QC Requirements and Corrective Actions

QC Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
Initial Calibration	Minimum of 5 levels, lowest near but above MDL, %RSD for CCC ≤30, All others should be ≤15%.	5 levels, %RSD for CCC ≤30%, all others ≤15%, All RFs >0.01 Alternatively, average RSD must be <15%.	As necessary due to major instrument maintenance or continuing difficulties meeting the CCV requirements.	Re-analysis of out of control standards.	Copies of all raw data, mass calibration, tune, and Form VI.
Internal Standards	Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10, Chrysene-d12, Perylene-d12, all @ 40 ng/uL ea. Area must be -50% to +100% of the IS in the CCV. RT must be within ±0.06 RT units of the RT of the IS in the CCV.	Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10, Chrysene-d12, Perylene-d12, all @ 2.0 ng/ul ea. Area must be -50% to + 100% of the area of the IS in the CCV. RT must be within 0.5 minutes of RT in CCV.	All standards, blanks, matrix spikes, matrix spike duplicates, blank spikes, SRMs, and sample re-extracts.	Re-analyze any sample which IS areas or RTs are out of range.	Notation in case narrative if applicable.
DFTPP Tuning Verification (50 ng)	Mass Abundance 51 30-60% of 198 68 <2% of 69 69 present 70 <2% of 69 127 40-60% of 198 197 <1% of 198 198 100% 199 5-9% of 198 275 10-30% of 198 365 >.1% of 198 441 present but < 443 442 >40% of 198 443 17-23% of 442	Mass Abundance 51 30-80% of 198 68 <2% of 69 69 present 70 <2% of 69 127 25-75% of 198 197 <1% of 198 198 100% 199 5-9% of 198 275 10-30% of 198 365 >.75% of 198 441 present but < 443 442 40-110% of 198 443 15-24% of 442	Every 12 hours; CLP Criteria is used as allowed by the method.	Retune instrument to pass criteria.	Copy of DFTPP check with the file.
Continuing Calibration Verification	Mid-level standard every 12 hours. %D ≤20% for CCCs, all others ≤30.	1.0 ng/ul standard every 12 hours. %D for CCC≤20, all others ≤40.	Every 12 hours.	Perform system maintenance, re-analyze CCV standard.	Copies of raw data, mass calibration, tune, and Form VII.
Method Blank	Analytes must be <MDL	All analytes <1/2RL.	One method blank per 20 samples or each extraction batch of samples, whichever is more frequent.	Re-analyze blank. If still out of control, re-extract the entire batch of samples.	Notation in case narrative if applicable.
Surrogate Recovery	Upper and lower recovery limits determined by 3X standard deviation of at least twenty samples. To be performed at least semi-annually.	1-Fluoronaphthalene, Fluorene-d10, Pyrene-d10 surrogates are used. Limits are updated annually.	All samples, method blanks, blank spike, MS/MSD.	Re-extraction of the sample is required if any surrogate is out. All surrogates must be in control in the method blank otherwise all associated samples must be re-extracted..	Any out of control surrogates are to be documented in the job comments section or case narrative.

QC Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
Blank Spike Recovery	Empirically derived from 20 or more BS. QC interval equals 3X standard deviation.	Empirically derived from 20 BS. QC interval equals 3X standard deviation.	One per batch of twenty.	Re-extract batch unless MS/MSD is perfect.	Narrate in case narrative.
MS/MSD Recovery & RPD	Empirically derived from 10 or more MS/MSD pairs. QC interval equals 3X standard deviation.	Empirically derived from 10 or more MS/MSD pairs. QC interval equals 3X standard deviation. Control limits: 20-160%	One per batch of twenty.	Re-extract batch unless blanks spike is perfect or documentable matrix effect is present.	Narrate problems in case narrative.

APPENDIX X

Analytes Ammenable to Analysis by Method 8270D SIM

Current 8270 SIM PNA Target Analytes:

Compound	Primary Ion	Secondary Ion(s)
Naphthalene	128	129,127
2-Methylnaphthalene	142	141
Acenaphthylene	152	151,153
Acenaphthene	153	154,152
Fluorene	166	165,167
Phenanthrene	178	179,176
Anthracene	178	176,179
Carbazole	167	166
Fluoranthene	202	200
Pyrene	202	200,203
Benzo(a)anthracene	228	229,226
Chrysene	228	226,229
Benzo(b)fluoranthene	252	253
Benzo(k)fluoranthene	252	253
Benzo(a)pyrene	252	253
Indeno(1,2,3-cd)pyrene	276	274
Dibenzo(a,h)anthracene	278	279
Benzo(g,h,i)perylene	276	274,277
1-Fluoronaphthalene	146	147,145
Fluorene-d10	176	174,177
Pyrene-d10	212	

APPENDIX XI

Elution Order of the Compounds

Compound	Retention Time (min)
Naphthalene	4.38
2-Methylnaphthalene	4.88
Acenaphthylene	5.56
Acenaphthene	5.69
Fluorene	6.08
Phenanthrene	6.90
Anthracene	6.94
Carbazole	7.08
Fluoranthene	8.07
Pyrene	8.34
Benzo(a)anthracene	9.77
Chrysene	9.83
Benzo(b)fluoranthene	11.27
Benzo(k)fluoranthene	11.30
Benzo(a)pyrene	11.78
Indeno(1,2,3-cd)pyrene	13.78
Dibenzo(a,h)anthracene	13.79
Benzo(g,h,i)perylene	14.36
1-Fluoronaphthalene	4.36
Fluorene-d10	6.06
Pyrene-d10	8.31

APPENDIX XII

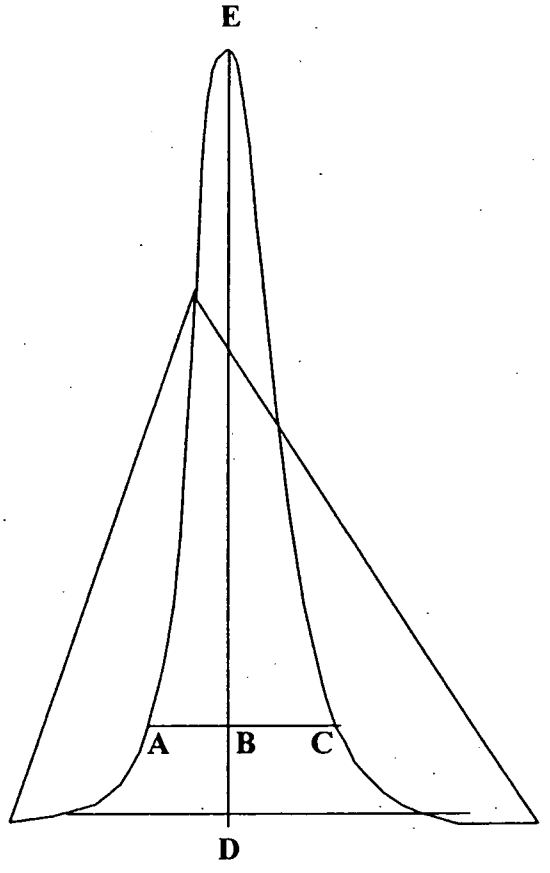
Semivolatile Internal Standards With Corresponding Analytes Assigned For Quantitation

Naphthalene-d8	**Acenaphthene-d10**
Naphthalene	Acenaphthylene
2-Methylnaphthalene	Acenaphthene
1-Fluoronaphthalene	Fluorene
	Fluorene-d10

Phenanthrene-d10	**Chrysene-d12**	**Perylene-d12**
Phenanthrene	Pyrene	Benzo(b)fluoranthene
Anthracene	Benzo(a)anthracene	Benzo(k)fluoranthene
Carbazole	Chrysene	Benzo(a)pyrene
Fluoranthene	Pyrene-d10	Indeno(1,2,3-cd)pyrene
		Dibenzo(a,h)anthracene
		Benzo(g,h,i)perylene

Appendix XIII

Calculation of Peak Tailing Factors



Peak Tailing Factor = BC/AB

Sample calculation: Peak Height = DE =100mm
10% Peak Height = BD = 10mm
Peak Width at 10% Peak Height = AC = 23mm
AB = 11mm
BC = 12mm
Tailing Factor = 12/11 = 1.1

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-8279

Determination of Semivolatile Organic Compounds by SW-846 Methods 8270C and 8270D

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Revised by: Julia B. Ryl — Date: 3/20/02
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Harry Romberg, QA Officer

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1. Introduction and Scope

1.1 Method Description

1.1.1 This method is used for the determination of semivolatile organic analytes in aqueous, soil, sediment, and other matrices. This SOP follows SW-846 Method 8270D except for the specific deviations listed below or outlined in a project's specific QAPP. This SOP is also applicable to SW-846 Method 8270C as all differences between the two revisions are clerical in nature. There are no technical differences.

1.1.2 This method is restricted to use by, or under the supervision of, analysts experienced in the use of gas/liquid/chromatography/mass spectroscopy and in the interpretation of chromatograms and mass spectra. Each analyst performing this method must have demonstrated the ability to perform the described chromatographic analysis and/or data interpretation.

1.2 Method Deviations & Comments

1.2.1 The following items represent deviations and comments of Method 8270D, as published, which are followed as standard operating procedure in the performance of this method at Laucks:

1.2.1.1 Method 3640A (Gel Permeation Chromatography cleanup) is utilized routinely for all soil/sediment sample extracts. GPC cleanup is performed on aqueous sample extracts as deemed necessary.

1.2.1.2 The initial calibration has been increased from five to six concentration levels in order to demonstrate linearity for all target analytes and to provide a low-level standard that will act as the reporting limit as outlined in the method.

1.2.1.3 The concentration of internal standards added to all sample extracts and calibration standards has been decreased from 40 ng/µL per compound to 20 ng/µL in order to accommodate 2 µL injection volumes as allowed by the method. This adjustment keeps the total nanograms injected the same and prevents overloading the analytical column.

1.2.1.4 Lauck's uses a relative response factor for all analytes. The method specifies that if the average RSD of all analytes for the initial calibration is ≤15%, then the RRF may be used for individual analytes with RSDs >15%. This method option will be used if any analyte's RSD exceeds 15% in the initial calibration. However, Laucks uses an internal guideline of 40 percent as an upper limit.

1.2.1.5 For Appendix IX and TCLP analyses, the compound 3-methylphenol (m-Cresol) coelutes with 4-methylphenol (p-Cresol). Since the spectrum and retention time for these two compounds are the same, these two compounds will be reported together as

the sum of these two compounds and with the assumption that 3-methylphenol has the same response factor as the 4-methylphenol present in the standards.

1.2.1.6 CLP Statement of Work, OLM04.1, DFTPP tuning criteria has been substituted as allowed by the method. Typical tuning criteria are listed in Appendix II.

1.2.1.7 All standards are stored at less than -10°C or by the manufacturer's recommendation. Sample extracts are stored at 4°C ±2°C.

1.2.1.8 The surrogate and matrix spikes will be added to the sample such that the final amount injected from normally concentrated samples is 100 ng for the base/neutral compounds and 150 ng for the acids. Acids will not be injected at 200 ng per injection to prevent exceeding the highest calibration standard of 160 ng.

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 collection. Soil samples must be extracted within 14 days of collection. All sample extracts must be analyzed within 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.

Method Blank Spike	A background free matrix (DIW for water, clean sand for soils/sediments) to which known amounts or target analytes and surrogates are added each time sample extracts are prepared. Blank spikes are required on NFESC work. In the context of this SOP, a blank spike is the same as a QC check standard.
CCC	Calibration Check Compound. A compound of analytical interest whose RRF in the CCV is compared to the average RRF from the initial calibration. The % difference must be less than the value specified in the method for the CCV to be considered valid. CCCs must also meet maximum %RSD criteria in an initial calibration.
CCV	Continuing calibration verification. This is the same acronym used in the CLP program. This is a standard injected at some prescribed frequency during the analysis sequence to determine whether the instrument has remained in calibration.
ICV	Initial continuing verification. A calibration standard obtained from a different manufacturer than the standards used for the initial and continuing calibrations that is analyzed after a compliant initial calibration.
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.
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.
DFTPP	A solution containing DFTPP, pentachlorophenol, benzidine, and p,p'-DDT. An aliquot of this solution is analyzed at the start of a 12 hour QC period in order to verify DFTPP tuning criteria.
Internal Standard	A compound added to every standard, blank, matrix spike, matrix spike duplicate, and sample extract at a know concentration, prior to analysis. Internal standards are used as the basis for quantitation of target compounds.

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 approximately 4x the empirically determined MDLs on an extract basis. This standard is used to verify that the instrument is capable of detecting the target analytes on an ongoing basis.
QC Period	Quality control period. An analysis sequence initiated by the injection of one or more standards, followed by sample extracts. A QC period is 12 hours starting with the injection of the CCV standard or DFTPP performance evaluation.
RF	Response Factor. The measure of the mass spectral response of an analyte compared to its internal standard. Response factors are determined by analysis of standards and are used in the calculation of concentrations of analytes in samples. RF is determined by the following equation: $RF = \frac{A_x \times C_{is}}{A_{is} \times C_x}$ where: A_x - Area of target analyte primary ion; C_{is} - Concentration of internal standard; A_{is} - Area of internal standard primary ion; C_x - Concentration of target analyte
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. 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 the GC column.
Sequence	A set of sample extracts and standard solutions injected into an instrument in a chronologically continuous group. See also QC period.

SPCC	System Performance Check Compound. A compound of analytical interest whose relative response factor (RRF) is monitored in the CCV for signs of chromatographic degradation. SPCCs generally have low RRFs and tend to decrease in response as the chromatographic system begins to deteriorate. They must meet a minimum RRF for initial and continuing calibrations.
EICP	Extracted ion current profile-a plot of ion abundance versus time (or scan number) for ion(s) of specified mass(es).
Surrogate	Compounds added to every standard, blank, matrix spike, matrix spike duplicate, and sample extract at a known concentration; used to evaluate extraction and analytical efficiency by measuring recovery. Surrogates are brominated, fluorinated, or isotopically labeled compounds not expected to be detected in environmental samples.

2. Equipment List and Standards

2.1 Chromatographic System

Gas Chromatograph:	Hewlett Packard 5890 I or II
Carrier Gas:	Helium 99.999% (ultra purity) or better
Column:	30 m x 0.25 mm x 0.25 μ capillary column (Restek RTX5SIL-MS or equivalent)
Automatic Sampler:	Hewlett Packard 7673A or 7673 with 19405A and 3396A controllers
GC/MS Interface:	Capillary direct to the ion source of the mass spectrometer, fixed temperature
Mass Spectrometer:	Hewlett Packard 5970B
Data System:	PC based Teknivent with ENVIROLINK data acquisition and processing software or HP Chemstation.
Miscellaneous:	Assorted syringes, vials, caps, septa, injection port liners, ferrules, etc.
Note:	All of the above equipment may be substituted with equivalent or better equipment

2.2 Standards

2.2.1 Preparation of Semivolatile Standards

2.2.1.1 All standards prepared from this operating procedure must be logged into one of two standards preparation logbooks. One is maintained for stock solutions prepared from

neat chemicals; the other is maintained for all working solutions. These logbooks are kept in the GC/MS semivolatile working area. When a standard is made, a solution number is assigned to it. This solution number is unique and will be used to track and identify the standard every time it is analyzed.

2.2.1.2 An example of the solution nomenclature used in a working ABN standard prepared on 11/13/91. The solution number assigned was MS 2-77-2. This label represents the following:

MS	Solution was made and used as a Mass Spec standard.
2	Solution was logged into standard book #2.
77	Page number on which solution has been recorded.
2	This denotes the second entry on page 77.

2.2.1.3 All standards must also be verified both qualitatively and quantitatively in order to satisfy EPA requirements for traceability. This may be accomplished by purchasing solutions which have been fully documented by a commercial vendor.

2.2.2 Preparation of Internal Standard Solution (ABN IS MIX @ 2000 ug/mL).

Internal Standards
1,4-Dichlorobenzene-d4
Naphthalene-d8
Acenaphthene-d10
Phenanthrene-d10
Chrysene-d12
Perylene-d12

2.2.2.1 Commercially prepared and certified internal standard solution is purchased at a concentration of 2000 µg/mL and is used undiluted. This standard is kept at -10°C until put into use. Once opened, the standard is kept at room temperature to avoid having the less soluble compounds fall out of solution. A new ampule of internal standard is opened on a weekly basis.

2.2.3 Preparation of DFTPP solution:

2.2.3.1 Prepare a 25 µg/mL tuning solution which consists of DFTPP, pentachlorophenol, benzidine, and 4,4'DDT in methylene chloride. This solution is kept at -10°C.

2.2.4 Prepartion of Calibration Standards

2.2.4.1 Calibration standards are prepared in methylene chloride from stock solutions which are purchased from a commercial source (e.g., Supelco or Crescent). If an analyte required for calibration is not present in an available mixed solution, laboratory-prepared stock

solutions which have been verified by GC/MS may be used. Laboratory prepared stock solutions should be tested against independent reference standards when they are available.

2.2.4.2 Calibration standards are prepared at six concentration levels (5, 10, 25, 40, 60 and 80 ng/µL). Each calibration standard contains all compounds of interest, surrogates, and internal standards. The internal standards are added so that they are present in all calibration standards at a concentration of 20 ng/µL each.

2.2.5 Preparation of ABN200 stock solution

2.2.5.1 Assemble the following solutions in order to prepare a combined stock solution which will contain all analytes of interest at a concentration of 200 µg/mL each:

Analyte Mix	**Vendor**	**Stock #**
Benzidines Mix 2	Crescent	CC2410
Base/Neutrals Mix 1	Crescent	CC2458
Acids Mix 3	Crescent	CC2471R
SV Mix w/ Pyridine& Carbazole	Crescent	CC2473
Acid Surrogate Mix	Supelco	4-7261
B/N Surrogate Mix	Supelco	4-7262

Note: 1,2-diphenylhydrazine is detected as azobenzene. Azobenzene may be substituted for 1,2-diphenylhydrazine as it is in many commercially purchased calibration mixes.

2.2.6 Preparation of APPEND200 stock solution

2.2.6.1 Assemble the following solutions in order to prepare a combined stock solution which will contain all analytes of interest at a concentration of 200 µg/mL each:

Analyte Mix	**Vendor**	**Stock #**
Appendix IX Semivolatiles (15)	Crescent	CC2289
Appendix IX Semivolatiles (9)	Crescent	CC2289A
Appendix IX Semivolatiles (10)	Crescent	CC2289B
Appendix IX 1,3,5-TNB	Crescent	CC2289C
Semivolatiles Mix 5	Crescent	8SM-008A
Pentachlorethane	Crescent	3347D.20

2.2.6.2 The vendor and catalog numbers provided are for reference only. Other vendor's certified solutions may be substituted.

2.2.6.3 Combine appropriate amounts of all solutions in a clean, 10 mL volumetric flask so that all analytes are present at 200 µg/mL. Dilute to volume with methylene chloride, stopper the flask and mix well. Record all information in the working standards logbook

and transfer the contents of the volumetric flask into an amber screw-cap vial. Store this solution in the freezer when not in use. The vial must be marked with the logbook name, standard type, preparation date, solvent used, expiration date, and preparer initials.

2.2.7 Preparation of working calibration standards

2.2.7.1 To prepare working calibration standards, add the amounts listed below (in µL) of ABN200 stock solution, internal standard solution (ABN IS MIX @ 2000 ug/mL) and methylene chloride to clean vial inserts and use within one week.

	Amount of Standard ABN200 in µl	Amount of Standard APPEND200 in µl	Amount of Internal Standard in µl	Amount of CH_2Cl_2 in µl
Working ABN 5	5	5	2	190
Working ABN 10	10	10	2	180
Working ABN 25	25	25	2	150
Working ABN 40	40	40	2	120
Working ABN 60	60	60	2	80
Working ABN 80	80	80	2	40

2.2.7.2 Log into the working solutions logbook all of the above information as the standards are made. Store all standards at less than -10°C for up to one week when not in use.

2.2.7.3 The ABN 25 standard is the continuing calibration standard and it will need to be prepared on a weekly basis.

2.2.7.4 Calibration stock solutions which are received sealed in ampules from the manufacturer are useable up to their manufacturer's expiration date. The mixed ABN200 and APPEND200 stock solution must be prepared once every twelve months, or sooner, if standards have degraded or concentrated.

3. Safety precautions

3.1 Routine Safety Precautions

3.1.1 All standards and sample extracts should be handled as if they are 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 Almost all of the analytes under consideration are known or suspected carcinogens. Analysts should wash their hands after using any standard, solvent or sample extract. Additionally, a respirator should be worn or a fume hood utilized for extremely hazardous compounds or very dirty extracts.

3.2 Waste disposal

3.2.1 All waste solvents, expired standards and old extracts should be disposed of in the solvent waste can located in the prep area fume hood. Consult the laboratory SOP for more detail on waste disposal.

4. Operation procedures

4.1 Analytical Conditions

4.1.1 Chromatographic Conditions

Initial Temperature:	45°C
Initial Time:	4 minutes
Column Temperature Program:	8°C/minute
Final Temperature:	320°C
Final Time:	8 minutes
Injector Temperature:	250-300°C (instrument dependent)
Transfer Line Temperature:	280-310°C (instrument dependent)
Injector Purge Time Off:	0.15 minutes
Injection Volume:	2 µL
Column Linear Velocity:	30-40 cm/sec (nominal 35 cm/sec measured at 30°C)

4.1.2 Mass Spectrometer Conditions

Electron Energy:	70 volts
Mass Range:	35 to 500 amu
Scan Time:	Not to exceed 1 second per scan

4.2 Method Detection Limit Study

4.2.1 MDL studies are performed on an annual basis. This procedure is fully described in Laucks SOP on Determination of MDL's.

4.2.2 MDLs for this method are in the range of 0.27 – 2.5 µg/L for waters and 29.0 – 201 µg/kg for soils.

4.3 Method Reporting Limits

4.3.1 The method reporting limit for this method shall be set as described by method 8000B by using the lowest calibration standard as the method report limit. Values detected below this level will be reported but will be "J" flagged as outlined in Section 5.2 of this SOP.

4.3.2 Reporting limits for aqueous samples are 5 µg/L with the exception of benzoic acid and 2,4-dinitrophenol which are 10 µg/L. Reporting limits for non-aqueous samples are 330 µg/kg with the exception of benzoic acid and 2,4-dinitrophenol which are 670 µg/kg.

4.3.3 For the additional AppendIX analytes, the reporting limit for aqueous samples is 5 µg/L with the exception of a,a-dimethylphenylethylamine and famphur where the reporting limit is 10 µg/L. Reporting limits for non-aqueous samples are 330 µg/kg and 670 µg/kg respectively.

4.4 Method Validation

4.4.1 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. This procedure is fully described in Laucks SOP on Determination of QC limits.

4.5 Daily Instrument Maintenance

4.5.1 Instrument maintenance may be required for good chromatography and proper calibration. The following steps may be undertaken if needed before the analysis of any standard or sample:

A. Cool the GC oven to 30°C.
B. Check the background for the instrument using manual tune to determine the operating status of the instrument.
C. Remove the injector septum and quartz liner.
D. Remove the column from the injector.
E. Install a new column ferrule.
F. Clip off 10 cm of the column. Check for a proper cut.
G. Reinstall the column and adjust the alignment.
H. Install a clean quartz liner.
I. Reinstall the O-ring or replace it if worn.
J. Install a new septum.
K. Clean and reinstall the autosampler syringe.

4.5.2 After any of these steps have been taken, recheck background, correct any leaks by tightening fitings, then ramp the GC oven twice from 50° to 310°C at 20° /minute for 10 minutes

4.6 Instrument Tuning

4.6.1 The HP 5970B mass spectrometer uses FC-43 (PFTBA) as a mass calibration compound. Each instrument will require different ion ratios to pass the required DFTPP performance criteria. See Appendix II for the DFTPP tuning criteria. The following ratios are therefore approximate. Use manual tuning to tune the mass spectrometer.

Ion	% of ion 69
69	100%
131	25-35%
219	25-35%
414	1-3%

4.6.2 Ion peak widths should be in the 0.5 to 0.6 amu range. Excessive peak width can lead to loss of minor isotope peaks. Insufficient peak width can result in the loss of sensitivity. Ions for water, nitrogen, and oxygen should be <5% of ion 69. A copy of the PFTBA spectrum and tabular listing should be kept with the instrument historical file.

4.6.3 The DFTPP tuning solution should also be used to assess GC column performance and injection port inertness. Degradation of DDT to DDE and DDD should not exceed 20%. Benzidine and pentachlorophenol should be present at their normal responses, with no visible peak tailing, as demonstrated by the peak tailing factor. The calculation of peak tailing factors is illustrated in Appendix XII. The acceptance criteria for benzidine is <3.0 and pentachlorophenol is <5.0. If degradation is excessive and/or poor chromatography is noted, the injection port may require cleaning. It may also be necessary to break off the first 6-12 inches of the capillary column.

4.6.4 Analysis of the DFTPP must meet the ion abundance criteria listed in Appendix II before initiation of initial or continuing calibration standard analysis.

4.7 Initial and Continuing Calibration Standards and Initial Calibration Verification

4.7.1 After demonstrating compliance with the DFTPP tuning criteria, analyze the calibration standards within 12 hours.

4.7.2 Check the integrations and retention times of all compounds in each standard. Examine the peaks to ensure that peak saturation and/or chromatographic overload has not occurred in the upper calibration standard.

4.7.3 All compounds in the initial and continuing calibration standards must meet the criteria

listed in Appendix IV and Appendix V, respectively.

4.7.4 After completion of a compliant initial calibration curve, an initial calibration verification (ICV) may be analyzed. This standard is from a source different than that of the calibration standards. At the time of the writing of this SOP, Laucks uses a commercially prepared and certified standard solution purchased from Radian International (Catalog # ERS072). This ICV standard is analyzed at a concentration range of 32-64 ug/mL which is higher than the CCV analyzed on a routine basis. All analyte recoveries should be within 70-130% of the expected value with up to ten analytes exceeding this control limit due to sporadic marginal failures.

4.8 Sample Analysis

4.8.1 After completion of a compliant continuing calibration standard, sample analysis may be performed.

4.8.2 Remove the sample extracts from the refrigerator and allow to warm to room temperature.

4.8.3 Transfer 200 µL of extract to a vial insert.

4.8.4 Add 2 µL of IS solution (ABN IS MIX @ 2000 µg/mL).

4.8.5 Cap the vial and mix well.

4.8.6 Place the vial onto the autosampler for analysis.

4.8.7 For dilutions, decide what dilution is necessary from previous data or analyst judgment. Make dilution and then add 2 µL of ABN IS solution prior to capping vial. Mix well prior to analysis.

4.8.8 In general, the method blank accompanying the samples is injected prior to the analysis of the samples. This is not a requirement, however. Samples are then injected until the end of the 12 hour clock.

4.9 Compound Identification

4.9.1 Compounds are tentatively identified if a peak elutes within 0.5 minute of that compound in the CCV standard. In addition, the internal standard for that compound should also be within 0.5 minute of its counterpart in the CCV standard. To confirm the presence of that compound in the sample extract, the mass spectrum of the peak must be evaluated. Spectra are compared against standard spectra of each compound generated on the instrument used for analysis.

4.9.2 The following criteria are used to evaluate mass spectra.

4.9.2.1 The intensities of the characteristic ions of a compound maximize within one scan of each other. Searches performed based on the presence of a target compound at a compound-specific retention time will be accepted as meeting this criterion.

4.9.2.2 All ions present in the standard mass spectra at a relative intensity greater than 30% (most abundant ion in the spectrum equals 100%) or the three ions of greatest intensity must be present in the sample spectrum.

4.9.2.3 The relative intensities of ions specified must agree within 30% between the standard and sample spectra. Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample ion abundance must be between 20 and 80 percent.

4.9.2.4 If a compound cannot be verified by all of these criteria, but in the technical judgment of the analyst, the identification is correct, then report that identification and proceed with quantification.

4.9.2.5 The experienced analyst's judgment weighs heavily in evaluating chromatograms and mass spectra for compound identification. For instance, the retention times of surrogate compounds may be outside their expected windows due to sample matrix effects. If this has occurred, it must be fully documented in the appropriate report notes.

4.10 Common Analytical Problems

4.10.1 An analyst's professional judgment plays a large role in how data are interpreted. The following guidelines should be followed in order to facilitate consistency between analysts. Any anomalies not addressed in this SOP must be discussed with the supervisor prior to implementation. All anomalies and corrective actions must be documented.

4.10.2 Interferences

4.10.2.1 Problems have been associated with the following compounds analyzed by this method.

4.10.2.2 Dichlorobenzidine and 4-chloroaniline can be subject to oxidative losses during solvent concentration.

4.10.2.3 Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reactions in acetone solution, and photochemical decomposition.

4.10.2.4 N-nitrosodiphenylamine decomposes in the gas chromatograph inlet forming diphenylamine and, consequently, may be detected as diphenylamine.

4.10.3 Carryover

4.10.3.1 In some cases, if analytes in a sample are very high, there may be carryover from one analysis to the next. If a sample is suspected of being high due to historical data or extract color, the sample should be diluted prior to analysis, or one or more blanks should be analyzed after the sample to insure that there is no carryover between analyses.

4.10.3.2 However, in the case where high levels were not expected, and do appear in a sample analysis, the analysis after it should be examined carefully for carryover. Any sample analyte whose concentration exceeds 250 ng/µL in the extract may be considered a candidate for carryover.

4.10.4 Manual Peak Integrations

4.10.4.1 Manual peak integrations should be used only when necessary to correct for matrix interference, tangent peaks, and rising baselines. Manual integrations are not to be used in an attempt to meet calibration, surrogate recovery, or spike recovery criteria. Refer to LTL-1020, *The Integration of IC, GC, HPLC, and GC/MS Peaks* for more detail.

4.10.4.2 If the chromatogram shows degradation due to sample loading e.g. split peaks, lift off, or severe tailing, the sample should be diluted and reanalyzed if required detection limits permit.

4.10.4.3 If a manual integration is necessary, use the following guidelines:

- Integrate only the peak. Start where the peak lifts from the baseline and end as soon as it returns to the baseline. Do not integrate extra baseline in an attempt to increase peak area.
- Do not "peak shave". Do not cut off legitimate parts of the peak in order to reduce peak area.
- In cases of tangent skims, do not increase or decrease peak areas or heights by skimming extra long baselines or drawing the baseline too low.
- Always initial and date your manual integrations.

4.11 Compound Quantification

4.11.1 Target compound concentrations are calculated using the following equations:

4.11.2 The equation for internal standard calculations is

$$Extract\ Concentration(ng / \mu L) = \frac{A_x \times C_{is}}{A_{is} \times RF_{average}}$$

where:

A_x = Response for the target analyte
A_{is} = Response for the internal standard
C_{is} = Concentration of internal standard, in ng/µL
$RF_{average}$ = Average Response Factor (calculated from the initial calibration)

4.11.3 If the %RSD of a compound's relative response factor is 15% or less, than the concentration may be determined using the average response factor from the initial calibration. Alternatively, the RF may be used as long as the average RSD of all calibration analytes is ≤15%. Laucks uses 40% percent as the upper limit for all compounds as an internal guideline although it is not a requirement of SW 846.

4.11.4 The above equation is used directly by the HP computer to yield the extract concentration.

4.11.5 Aqueous samples

4.11.5.1 To calculate the actual sample concentration, the following calculation must be used.

$$\text{Extract Concentration } (\mu g/L) = \frac{F \times D \times V_f \times GPC}{V_i}$$

where:

F = Amount found from HP quantitation report (ng/µL)
D = Dilution factor of extract
V_f = Final extract volume (µL)
GPC = GPC dilution factor. Use 1 if GPC was not performed, 2 if GPC was used
V_i = Initial sample volume (mL)

4.11.5.2 Any sample extracts which exceed the upper calibration range for any analyte of interest must be diluted and reanalyzed to bring the analyte into the working range of the calibration.

4.11.6 Non-aqueous samples

4.11.6.1 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.

$$\text{Sample Concentration}(\mu g/kg) = \frac{F \times D \times Vf \times GPC}{W_s \times T_s}$$

where:

W_s = Sample size extracted in grams.
T_s = Total Solids in decimal format (i.e. 0.76 not 76).

4.11.6.2 Any sample extracts which exceed the upper calibration range for any analyte of interest must be diluted and reanalyzed to bring the analyte into the working range of the calibration.

5. Reports

5.1 Data Packet Organization

5.1.1 See Appendix III for a check list detailing data packet organization.

5.2 Quality Control Reports

5.2.1 All results for quality control tests are entered into the lab 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.

5.3 Sample Result Reports

5.3.1 Data Qualifying Flags

5.3.1.1 Sample report results are qualified with data qualifying flags. These flags have the following definitions:

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.

J: The analyte of interest was detected below the practical quantitation 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.

X: Indicates an unresolvable isomeric pair. This flag indicates that calculated results

are the sum of the two isomers.

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.

6. Quality Control

6.1 General Issues

6.1.1 See Appendices VII and VIII for flow chart and QA/QC limit and corrective action tables.

6.2 Initial Calibration

6.2.1 Criteria

6.2.1.1 Initial calibration data are evaluated using %RSD of the relative response factors as well as minimum average RRFs. The %RSD must be ≤ 30% for each individual Calibration Check Compound (CCC). All other RRFs must be ≤15%. Alternatively, RRFs may be used as long as the average RRFs for all compounds in the method are ≤15% and the CCCs are ≤30%. Laucks uses an internal guideline of 40% as an upper control limit for each compound.

6.2.1.2 Calculate the %RSD for all compounds. CCC criteria are listed in Appendix IV.

6.2.1.3 Calculate the individual and average RFs for each compound.

6.2.1.4 RFs are calculated using the equation

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

where:

A_s = Response of target analyte
A_{is} = Response of internal standard
C_s = Amount of target analyte (ng/µL)
C_{is} = Amount of internal standard (ng/µL)

6.2.1.5 Laucks has established additional criterion by requiring a minimum acceptable average RRF for all non SPCC analytes of 0.010. At this time the Appendix IX compounds have no minimum RRF. See Appendix IV for a listing of all SPCCs.

6.2.2 Corrective action

6.2.2.1 If the criteria are not met, other standards may be analyzed or appropriate instrument maintenance and analysis of new standards must be performed. Failure to achieve the required minimum average RRF for the SPCC compounds may indicate the need to perform instrument maintenance or prepare fresh calibration standards.

6.2.2.2 Some compounds, including but not limited to the nitroanilines, the nitrophenols and some additional Appendix IX analytes, tend to show poor or erratic response at the lower calibration levels.

6.2.2.3 For routine analyte lists the lowest standard may be omitted from the initial calibration as long as the %RSD does not exceed 30% for any which are CCCs. Additionally, those compounds which are omitted from the lower calibration levels will also have an elevated reporting level equivalent to that of the lowest standard.

6.3 Continuing Calibration Verification

6.3.1 Criteria

6.3.1.1 At the beginning of each 12 hour QC period, a CCV standard at a concentration level of 25 µg/mL is analyzed. The RF for each compound is calculated and the percent difference is calculated as follows:

$$\%Difference = \frac{RF_c - RF_i}{RF_i} \times 100$$

where:

RF_i = Average RF from Initial Calibration.
RF_c = RRF from CCV standard.

6.3.2 The %D results for all CCCs must be less than or equal to 20%. Laucks uses 40% percent as the upper limit for all compounds as an internal guideline although it is not a requirement of SW 846.

6.3.2.1 In addition, all compounds (with the exception of the Appendix IX analytes) must have a minimum RRF of at least 0.010 compounds. See Appendix V for all CCV criteria.

6.3.3 Corrective action

6.3.3.1 Check that all peaks have been properly integrated. Check the calculations. If the %D criteria are still not met, perform corrective instrument maintenance or re-tuning, and reanalyze the standard. If the %D or minimum RF criteria are still not met, a new CCV

standard may need to be prepared, a new initial calibration performed, a new column installed, or other instrument maintenance performed in order to meet the CCV criteria.

6.4 Method Blank

6.4.1 Criteria

6.4.1.1 A method blank is used to verify contamination-free reagents and apparatus. A method blank is prepared with every set of samples extracted at the same time, at a frequency of at least one blank per 20 samples.

6.4.1.2 Laucks criteria for a method blank is less than one-half the RL for each analyte or less than 10 percent of the regulatory limit associated with that analyte, or less than 10 percent of the sample result for the same analyte.

6.4.1.3 Method blank corrective action limits are detailed in Appendix VI.

6.4.2 Corrective action

6.4.2.1 When these criteria are exceeded, corrective action should be taken to find/reduce/eliminate the source of this contamination in the method blank. Sample corrective action may be limited to qualification for blank contamination. When the concentrations of any target analytes within the method blank are above one-half of the reporting limit, the effect this may have had on the samples will be assessed.

1) If any analyte is found only in the method blank, but not in any batch samples, no further corrective action may be necessary. Steps shall be taken to find/reduce/eliminate the source of this contamination in the method blank. The case narrative should also discuss the situation.

2) Re-analysis of the method blank and any samples containing the same contaminant(s) which exceeded the corrective action limit(s) is performed if an analyte is found in the method blank and some, or all, of the other batch samples. If the contamination remains, the contaminated samples of the batch would be reprepared and reanalyzed with a new method blank and batch specific QC samples.

3) Sporadic cases of contamination may be difficult to control however, daily contamination would not be acceptable.

4) Out-of-control surrogate recoveries in the method blank require reanalysis of the method blank.

6.4.3 Documentation

6.4.3.1 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. Outliers are discussed in the case narrative.

6.5 QC Check Sample (LCS)

6.5.1 The LCS is used to determine whether a method is in control during sample preparation and analysis. A LCS follows the same protocol as the matrix spike analysis except that the spiking solution is added to a blank matrix (deionized water for water or sea sand for soil/sediments) instead of an actual sample. A Lab Control Sample is prepared with every set of samples extracted at the same time, at a frequency of at least one LCS per 20 samples. It is recommended that all target analytes of concern be 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 per the USACOE Shell document and DoD Quality Systems Manual – Final Version 1, October 2000.

6.5.2 The LCS may fill the requirements for the performance of an initial calibration and continuing calibration verification standard as specified in Sections 9.4.2.1 and 9.4.2.2 in the DoD Quality Systems Manual – Final Version 1, October 2000. The spiking levels vary from 20µg/mL to 30µg/mL.

6.5.3 Criteria

6.5.3.1 At the time of the writing of this SOP, the established control limits are as follows:

TABLE 1
Blank Spike Recovery Limits

Compound	%Recovery Water	%Recovery Soil/Sediment
Phenol	10-101	24-121
2-Chlorophenol	11-117	29-116
1,4-Dichlorobenzene	20-97	27-111
N-Nitroso-di-n-propylamine	40-123	23-123
1,2,4-Trichlorobenzene	22-102	29-114
4-Chloro-3-methylphenol	40-114	32-120
Acenaphthene	49-112	35-118

Compound	%Recovery Water	%Recovery Soil/Sediment
4-Nitrophenol	10-119	10-147
2,4-Dinitrotoluene	41-120	24-121
Pentachlorophenol	10-160	10-158
Pyrene	48-132	27-127

6.5.4 Corrective action

6.5.4.1 Check all peak integrations and sample calculations.

6.5.4.2 If the analyte recoveries still exceed the control limits, the blank spike extract may be reanalyzed.

6.5.4.3 If the analyte recoveries are still out of control, re-extraction of the associated samples is required.

6.6 Matrix Spike/Matrix Spike Duplicate Sample

6.6.1 A sample is chosen from the samples to be analyzed, and an aliquot of spiking solution is added to this sample prior to extraction. It is not required that a matrix spike analysis be performed with each extraction batch unless the project QAPP requires it. However, 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 Calculate the recovery of each matrix spike compound using the equation below.

$$\%\text{Recovery} = \frac{Spiked\ \ sample\ result - sample\ result}{Spike\ \ added} \times 100$$

6.6.2 Calculate the relative percent difference (RPD) of the recoveries of each compound in the matrix spike and matrix spike duplicate as follows:

$$RPD = \frac{|Matrix\ spike\ recovery - Matrix\ spike\ duplicate\ recovery|}{1/2(Matrix\ spike\ recovery + Matrix\ spike\ duplicate\ recovery)} \times 100$$

The vertical bars in the formula above indicate the absolute value of the difference, therefore RPD is always expressed as a positive value.

6.6.3 Criteria

6.6.3.1 At the time of the writing of this SOP, the established control limits are as follows:

TABLE 2
Matrix Spike Recovery and Relative Percent Difference Limits

Compound	%Recovery Water	RPD Water	%Recovery Soil/Sediment	RPD Soil/Sediment
Phenol	33-112	35	41-109	28
2-Chlorophenol	41-115	35	40-106	30
1,4-Dichlorobenzene	33-96	39	34-107	36
N-Nitroso-di-n-propylamine	53-128	38	48-118	28
1,2,4-Trichlorobenzene	43-103	37	40-121	30
4-Chloro-3-methylphenol	49-121	35	55-120	22
Acenaphthene	47-121	39	41-122	42
4-Nitrophenol	38-134	43	23-143	37
2,4-Dinitrotoluene	52-122	38	32-127	25
Pentachlorophenol	60-131	39	20-159	43
Pyrene	52-116	36	25-141	50

6.6.4 Corrective action

6.6.4.1 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.

6.6.4.2 If any analyte recovery exceeds the control limits the following action must be taken:

6.6.4.2.1 If the blank spike analysis yielded recoveries outside the control limits then re-extract and reanalyze all samples extracted with the MS/MSD.

6.6.4.2.2 If the blank spike analysis was in control then recoveries outside the control limits can be attributed to matrix effect and sample results are processed as normal. The report comments or narrative section must include comments about the out-of-control recoveries.

6.6.4.3 Corrective action for RPD values which exceed the control limits follows the corrective action for MS/MSD recoveries. If more than one RPD exceeds the control limit, re-extraction may not be required if it can be demonstrated that the sample is non-homogeneous and all MS/MSD recoveries are within the control limits.

6.7 Surrogate Recovery

6.7.1 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.

6.7.2 Surrogate compound recoveries are calculated as follow:

$$\%Recovery = \frac{S_m}{S_a} \times 100$$

where:
S_m = Concentration of surrogate measured in extract.
S_a = Concentration of surrogate added.

6.7.3 Criteria

6.7.4 The semivolatile surrogates can be divided into two groups: base/neutral compounds (nitrobenzene-d5, 2-fluorobiphenyl, 1,2-dichlorobenzene-d4, and terphenyl-d14); acid compounds (phenol-d5, 2-fluorophenol, 2,4,6-tribromophenol, and 2-chlorophenol-d4). At the time of the writing of this SOP, the established control limits are follows:

TABLE 3
SURROGATE RECOVERY LIMITS

Compound	%Recovery Water	%Recovery Soil
Nitrobenzene-d5	35-105	35-140
2-Fluorobiphenyl	30-88	35-140
Terphenyl-d14	33-129	35-140
Phenol-d5	10-94	35-140
2-Fluorophenol	10-100	35-140
2,4,6-Tribromophenol	10-123	35-140
2-Chlorophenol-d4	10-120 (advisory)	35-140 (advisory)
1,2-Dichlorobenzene-d4	28-94 (advisory)	35-140 (advisory)

6.7.5 Corrective Action

6.7.5.1 Check calculations for possible error.

6.7.5.2 Check instrument performance, if necessary correct the problem and re-analyze the extract.

6.7.5.3 Some samples may require dilution in order to bring one or more target analytes within the calibration range or to overcome significant matrix interference. This may result in the dilution of the surrogate response to the point that the recoveries can not 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. For all package work both the diluted and undiluted analyses will be provided.

6.7.5.4 Re-extraction is not necessary in the case where a sample is chosen for MS/MSD analyses and the same recovery pattern is present in all three analyses. In this case, matrix effects may be assumed and re-extraction is not required for this sample.

6.7.5.5 If only one fraction is being analyzed and surrogates that relate to the other fraction are out-of-control, then re-extraction and reanalysis for the target fraction is not required.

6.7.5.6 All other circumstances require re-extraction and reanalysis of the affected sample(s).

6.7.5.7 Out of control surrogate recoveries in the method blank require that all the samples in the associated batch be re-extracted and reanalyzed. 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.

7. References

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 4th Edition, Method 8270D, "Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS): Capillary Column Technique," Revision 4, January 1998, U.S. EPA.

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, 2nd Update, Method 3640A, "Gel-Permeation Cleanup," Revision 1, November 1992, US EPA.

US EPA. Contract Laboratory Program, Statement of Work for Organic Analysis, Multi-Media, Multi-Concentration, Document Number OLM04.2, May 1999.

APPENDIX I

Calibration Standard Solution Concentrations, ng/µL

Compound	STD1	STD2	STD3	STD4	STD5	STD6
Phenol	5	10	25	40	60	80
bis(2-Chloroethyl)ether	5	10	25	40	60	80
2-Chlorophenol	5	10	25	40	60	80
1,3-Dichlorobenzene	5	10	25	40	60	80
1,4-Dichlorobenzene	5	10	25	40	60	80
Benzyl Alcohol	5	10	25	40	60	80
1,2-Dichlorobenzene	5	10	25	40	60	80
2-Methylphenol	5	10	25	40	60	80
Bis(2-chloroisopropyl)ether	5	10	25	40	60	80
4-Methylphenol	5	10	25	40	60	80
N-Nitroso-di-n-propylamine	5	10	25	40	60	80
Hexachloroethane	5	10	25	40	60	80
Nitrobenzene	5	10	25	40	60	80
Isophorone	5	10	25	40	60	80
2-Nitrophenol	5	10	25	40	60	80
2,4-Dimethylphenol	5	10	25	40	60	80
Benzoic Acid	5	10	25	40	60	80
bis(2-Chloroethoxy)methane	5	10	25	40	60	80
2,4-Dichlorophenol	5	10	25	40	60	80
1,2,4-Trichlorobenzene	5	10	25	40	60	80
Naphthalene	5	10	25	40	60	80
4-Chloroaniline	5	10	25	40	60	80
Hexachlorobutadiene	5	10	25	40	60	80
4-Chloro-3-methylphenol	5	10	25	40	60	80
2-Methylnaphthalene	5	10	25	40	60	80
Hexachlorocyclopentadiene	5	10	25	40	60	80
2,4,6-Trichlorophenol	5	10	25	40	60	80
2,4,5-Trichlorophenol	5	10	25	40	60	80
2-Chloronaphthalene	5	10	25	40	60	80
2-Nitroaniline	5	10	25	40	60	80
Dimethylphthalate	5	10	25	40	60	80
Acenaphthylene	5	10	25	40	60	80
2,6-Dinitrotoluene	5	10	25	40	60	80
3-Nitroaniline	5	10	25	40	60	80
Acenaphthene	5	10	25	40	60	80
2,4-Dinitrophenol	5	10	25	40	60	80

Compound	STD1	STD2	STD3	STD4	STD5	STD6
4-Nitrophenol	5	10	25	40	60	80
Dibenzofuran	5	10	25	40	60	80
2,4-Dinitrotoluene	5	10	25	40	60	80
Diethylphthalate	5	10	25	40	60	80
4-Chlorophenyl-phenylether	5	10	25	40	60	80
Fluorene	5	10	25	40	60	80
4-Nitroaniline	5	10	25	40	60	80
4,6-Dinitro-2-methylphenol	5	10	25	40	60	80
N-Nitrosodiphenylamine	5	10	25	40	60	80
4-Bromophenyl-phenylether	5	10	25	40	60	80
Hexachlorobenzene	5	10	25	40	60	80
Pentachlorophenol	5	10	25	40	60	80
Phenanthrene	5	10	25	40	60	80
Anthracene	5	10	25	40	60	80
Carbazole	5	10	25	40	60	80
Di-n-butylphthalate	5	10	25	40	60	80
Fluoranthene	5	10	25	40	60	80
Pyrene	5	10	25	40	60	80
Butylbenzylphthalate	5	10	25	40	60	80
3,3'-Dichlorobenzidine	5	10	25	40	60	80
Benzo(a)anthracene	5	10	25	40	60	80
Chrysene	5	10	25	40	60	80
bis(2-Ethylhexyl)phthalate	5	10	25	40	60	80
Di-n-octylphthalate	5	10	25	40	60	80
Benzo(b)fluoranthene	5	10	25	40	60	80
Benzo(k)fluoranthene	5	10	25	40	60	80
Benzo(a)pyrene	5	10	25	40	60	80
Indeno(1,2,3-cd)pyrene	5	10	25	40	60	80
Dibenzo(a,h)anthracene	5	10	25	40	60	80
Benzo(g,h,i)perylene	5	10	25	40	60	80
N-Nitrosodimethylamine	5	10	25	40	60	80
2-Fluorophenol	5	10	25	40	60	80
Aniline	5	10	25	40	60	80
Phenol-d5	5	10	25	40	60	80
2-Chlorophenol-d4	5	10	25	40	60	80
1,2-Dichlorobenzene-d4	5	10	25	40	60	80
Nitrobenzene-d5	5	10	25	40	60	80
2-Fluorobiphenyl	5	10	25	40	60	80
2,4,6-Tribromophenol	5	10	25	40	60	80
1,2-Diphenylhydrazine	5	10	25	40	60	80
Benzidine	5	10	25	40	60	80
Terphenyl-d14	5	10	25	40	60	80

APPENDIX II

DFTPP Tuning Criteria

Mass	Relative Abundance
51	30-80% of mass 198
68	less than 2% of 69
69	present
70	less than 2% of 69
127	25-75% of mass 198
197	less than 1% of 198
198	100%
199	5-9% of mass 198
275	10-30% of mass 198
365	greater than 0.75% of mass 198
441	0-100 % of mass 443
442	40-110% of mass 198
443	15-24% of mass 442

CLP requires that the 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.

SW 846 states that the following approach has been shown to be useful: the mass spectrum of DFTPP may be acquired in the following manner. 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. Alternatively, the analyst may use other published tuning criteria.

APPENDIX III

Data Packet Order List

QC Summary
Surrogate Recovery Summary Report
Blank Spike Recovery Report
MS/MSD Recovery Report
Method Blank Summary
GC/MS Instrument Performance Check
Internal Standard Area and RT Summary Report

Sample Data
Target Compound Results (Organics Analysis Data Sheet)
Tentatively Identified Compound (TIC) Results (if required)
Sample Chromatograms, quantitation reports and spectra for all samples

Standards Data
Initial Calibration Summary Report
Chromatograms and quantitation reports for all initial calibration standards
Continuing Calibration Summary Reports
Chromatograms and quantitation reports for all CCV Standards

Raw QC Data
Bar Graph Spectrum, mass listing and chromatogram for every DFTPP injection
Method Blank Data
Target Compound Results (Organics Analysis Data Sheet)
Tentatively Identified Compound (TIC) Results (if required)
Chromatograms, quantitation reports and spectra for all method blanks
Blank Spike Data
Target Compound Results (Organics Analysis Data Sheet)
Chromatograms, quantitation reports and spectra for all blank spikes
Matrix Spike/Matrix Spike Duplicate Data
Target Compound Results (Organics Analysis Data Sheet)
Chromatograms, quantitation reports and spectra for all MS analyses
Control Charts

Bench Sheets
All extraction bench sheets, analysis log book pages, chains of custody, and any other pertinent information

APPENDIX IV

Initial Calibration Criteria

Calibration Check Compound	%RSD Limit
Phenol	≤30%
1,4-Dichlorobenzene	≤30%
2-Nitrophenol	≤30%
2,4-Dichlorophenol	≤30%
Hexachlorobutadiene	≤30%
4-Chloro-3-methylphenol	≤30%
2,4,6-Trichlorophenol	≤30%
Acenaphthene	≤30%
N-Nitrosodiphenylamine	≤30%
Pentachlorophenol	≤30%
Fluoranthene	≤30%
Di-n-octylphthalate	≤30%
Benzo(a)pyrene	≤30%

System Performance Check Compound	Minimum Average RF
N-Nitroso-di-n-propylamine	0.050
Hexachlorocyclopentadiene	0.050
2,4-Dinitrophenol	0.050
4-Nitrophenol	0.050

APPENDIX V

Continuing Calibration Verification Criteria

Calibration Check Compound	%D Limit
Phenol	≤20%
1,4-Dichlorobenzene	≤20%
2-Nitrophenol	≤20%
2,4-Dichlorophenol	≤20%
Hexachlorobutadiene	≤20%
4-Chloro-3-methylphenol	≤20%
2,4,6-Trichlorophenol	≤20%
Acenaphthene	≤20%
N-Nitrosodiphenylamine	≤20%
Pentachlorophenol	≤20%
Fluoranthene	≤20%
Di-n-octylphthalate	≤20%
Benzo(a)pyrene	≤20%

System Performance Check Compound	Minimum RF
N-Nitroso-di-n-propylamine	0.050
Hexachlorocyclopentadiene	0.050
2,4-Dinitrophenol	0.050
4-Nitrophenol	0.050

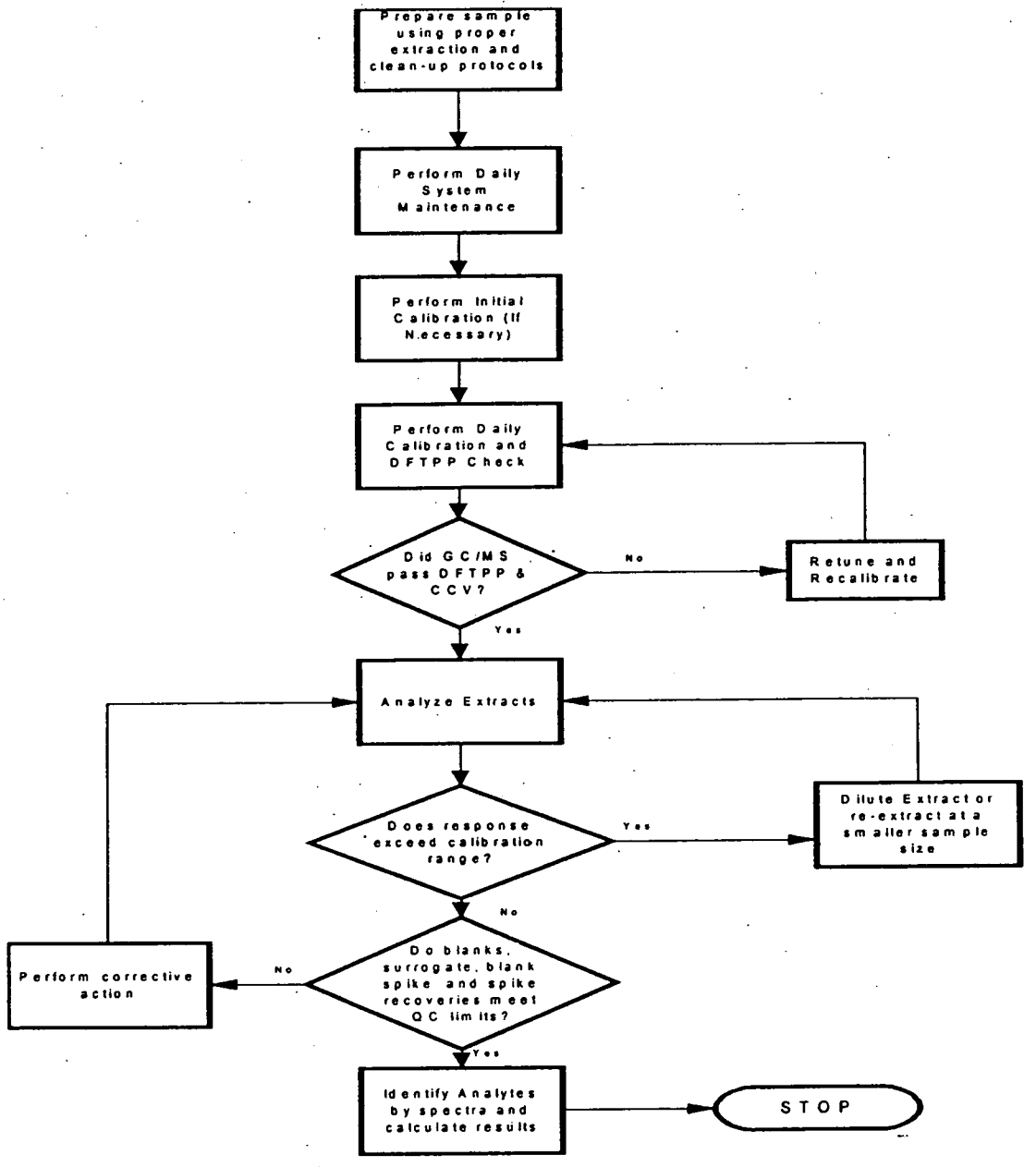
APPENDIX VI

Method Blank Corrective Action Limits

Compound	Control Limits Water	Soil
Phthalates	RL	RL
All other compounds	1/2 RL	1/2 RL

APPENDIX VII

Method 8270D Flow Chart



APPENDIX VIII

Method 8270D QC Requirements and Corrective Actions

QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
DFTPP Tuning Verification (50 ng)	Mass Abundance 51 30-80% of 198 68 <2% of 69 69 present 70 <2% of 69 127 25-75% of 198 197 <1% of 198 198 100% 199 5-9% of 198 275 10-30% of 198 365 >.75% of 198 441 present but < 443 442 40-110% of 198 443 15-24% of 442	Mass Abundance 51 30-80% of 198 68 <2% of 69 69 present 70 <2% of 69 127 25-75% of 198 197 <1% of 198 198 100% 199 5-9% of 198 275 10-30% of 198 365 >.75% of 198 441 present but < 443 442 40-110% of 198 443 15-24% of 442 Alternatively, any published tuning criteria may be used.	Every 12 hours; CLP Criteria is used as allowed by the method.	Retune instrument to pass criteria.	
Initial Calibration	Minimum of 5 levels, lowest near but above MDL, %RSD for CCC ≤30, All others should be ≤15%. RF for SPCC >0.05.	6 levels, %RSD for CCC ≤30, All others <15%, All RFs >0.010 Alternatively, average RSD must be ≤15%, 40% as an upper limit.	As necessary due to major instrument maintenance or continuing difficulties meeting the CCV requirements.	Re-analysis of out of control standards.	Copies of all raw data, mass calibration, tune, and Form VI.
Initial Calibration Verification		Mid-range standard; concentrations range from 32-64µg/mL. Rec= 70-130% with up to 10 sporadic marginal failures.	Once after initial calibration.	Re-analysis of initial calibration.	
Continuing Calibration Verification	Mid-level standard every 12 hours. %D ≤20% for CCCs SPCCs >0.05. IS Area must be -50% to +100% of the IS in the ICV. RT of IS must be within ±30 seconds of the RT of the IS in the IC.	25 ng/µl standard every 12 hours. %D for CCC ≤20. All RFs >0.010. Average %D must be ≤15%. 40% as an upper limit. IS Area must be -50% to +100% of the IS in the IC. No RT limits for IS in the CCV.	Every 12 hours.	Perform system maintenance, re-analyze CCV standard.	

QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
Internal Standards	1,4-Dichlorobenzene-d4, Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10, Chrysene-d12, Perylene-d12, all @ 40 ng/uL ea..	1,4-Dichlorobenzene-d4, Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10, Chrysene-d12, Perylene-d12, all @ 20 ng/µl ea. Area must be -50% to +100% of the area of the IS in the CCV. RT must be within 0.5 minutes of RT in CCV.	All standards, blanks, matrix spikes, matrix spike duplicates, blank spikes, SRMs, and sample re-extracts.	Re-analyze any sample which IS areas or RTs are out of range.	Notation in case narrative if applicable.
Method Blank	Analytes must be <MDL except phthalates which must be <5X the MDL.	All analytes <1/2 RL, except phthalates up to RL.	One method blank per 20 samples or each extraction batch of samples, whichever is more frequent.	Re-analyze blank. If still out of control, re-extract the entire batch of samples unless the offending analyte(s) are not detected in the associated samples.	Notation in case narrative if any analytes >1/2 reporting limit are present.
Surrogate Recovery	Nitrobenzene-d5, 2-Fluorobiphenyl, Terphenyl-d14, Phenol-d6, 2-Fluorophenol, & 2,4,6-Tribromophenol. Upper and lower recovery limits determined by 3X standard deviation of at least twenty samples. To be performed at least semi-annually.	Nitrobenzene-d5, 2-Fluorobiphenyl, Terphenyl-d14, Phenol-d6, 2-Fluorophenol, & 2,4,6-Tribromophenol. Upper and lower recovery limits determined by 3X standard deviation of at least twenty samples. To be performed at least semi-annually.	All samples, method blanks, LCSs, LESs.	Re-extraction of the sample is required if any surrogate is out. All surrogates must be in control in the method blank, otherwise all associated samples must be re-extracted.	Notation in case narrative if applicable.
Blank Spike Recovery	MS/MSD Recovery criteria	Empirically derived from five or more blank spikes. QC limit equals 3X standard deviation. See QC database.	One per batch of twenty.	Re-extract batch unless MS/MSD is perfect.	Narrate in case narrative.
MS/MSD Recovery & RPD	Empirically derived from five or more MS/MSD pairs. QC interval equals 3X standard deviation.	Empirically derived from five or more MS/MSD pairs. QC interval equals 3X standard deviation. See QC database.	One per batch of twenty.	Re-extract batch unless blanks spike is perfect or documentable matrix effect is present.	Narrate problems in case narrative.

APPENDIX IX

Appendix IX Calibration Standard Solution Concentrations, ng/µL

Compound	STD1	STD2	STD3	STD4	STD5	STD6
2,6-Dichlorophenol	5	10	25	40	60	80
1,2,4,5-Tetrachlorobenzene	5	10	25	40	60	80
2,3,4,6-Tetrachlorophenol	5	10	25	40	60	80
Dinoseb	5	10	25	40	60	80
Methanesulfonate, methyl	5	10	25	40	60	80
Methanesulfonate, ethyl	5	10	25	40	60	80
Phosphorothiotic Acid	5	10	25	40	60	80
Safrole	5	10	25	40	60	80
Isosafrole, cis & trans	5	10	25	40	60	80
1,4-Naphthoquinone	5	10	25	40	60	80
1,3-Dinitrobenzene	5	10	25	40	60	80
Thionazin	5	10	25	40	60	80
2,4-D, methyl ester	5	10	25	40	60	80
Diallate	5	10	25	40	60	80
Phorate	5	10	25	40	60	80
Dimethoate	5	10	25	40	60	80
Silvex, methyl ester	5	10	25	40	60	80
2,4,5-T, methyl ester	5	10	25	40	60	80
Pronamide	5	10	25	40	60	80
Disulfoton	5	10	25	40	60	80
Methyl parathion	5	10	25	40	60	80
Ethyl parathion	5	10	25	40	60	80
Isodrin	5	10	25	40	60	80
Chlorobenzilate	5	10	25	40	60	80
Kepone	5	10	25	40	60	80
Famphur	5	10	25	40	60	80
3-Methylcholanthrene	5	10	25	40	60	80
Ethanamine,N-methyl-N-nitroso	5	10	25	40	60	80
N-nitrosomorpholine	5	10	25	40	60	80
Butanamine, N-butyl-N-nitroso	5	10	25	40	60	80
2-Naphthalenamine	5	10	25	40	60	80
Diphenylamine	5	10	25	40	60	80
1,3,5-Trinitrobenzene	5	10	25	40	60	80
4-Aminobiphenyl	5	10	25	40	60	80
Methyapyrilene, HCL	5	10	25	40	60	80

Compound	STD1	STD2	STD3	STD4	STD5	STD6
p-Dimethylaminoazobenzene	5	10	25	40	60	80
2-Acetylaminofluorene	5	10	25	40	60	80
7,12-Dimethylbenz(a)anthracene	5	10	25	40	60	80
2-Picoline	5	10	25	40	60	80
Pentachloroethane	5	10	25	40	60	80
Acetophenone	5	10	25	40	60	80
N-Nitrosopyrrolidine	5	10	25	40	60	80
N-Nitrosopiperidine	5	10	25	40	60	80
Hexachloropropene	5	10	25	40	60	80
1,4-Phenylenediamine	5	10	25	40	60	80
Pentachlorobenzene	5	10	25	40	60	80
1-Naphthylamine	5	10	25	40	60	80
5-Nitro-o-toluidine	5	10	25	40	60	80
Pentachloronitrobenzene	5	10	25	40	60	80
N-Nitroquinoline-N-oxide	5	10	25	40	60	80
3,3-Dimethylbenzidine	5	10	25	40	60	80
Hexachlorophene	5	10	25	40	60	80
N-Nitrosodiethylamine	5	10	25	40	60	80
o-Toluidine	5	10	25	40	60	80
Phentermine	5	10	25	40	60	80
Sulfotep	5	10	25	40	60	80
Aramite	5	10	25	40	60	80
Phenacetin	5	10	25	40	60	80

Appendix X

Analytes Amenable to Analysis by Method 8270D

Current 8270D Target Analytes:

Compound	Primary Ion	Secondary Ion(s)
Phenol	94	65, 66
bis(2-Chloroethyl)ether	93	63, 95
2-Chlorophenol	128	64, 130
1,3-Dichlorobenzene	146	148, 111
1,4-Dichlorobenzene	146	148, 111
Benzyl Alcohol	108	79, 77
1,2-Dichlorobenzene	146	148, 111
2-Methylphenol	107	108, 77
Bis(2-chloroisopropyl)ether	45	77, 121
4-Methylphenol	107	108, 77
N-Nitroso-di-n-propylamine	70	42, 101
Hexachloroethane	117	201, 199
Nitrobenzene	77	123, 65
Isophorone	82	195, 138
2-Nitrophenol	139	109, 65
2,4-Dimethylphenol	122	107, 121
Benzoic Acid	122	105, 77
bis(2-Chloroethoxy)methane	93	95, 123
2,4-Dichlorophenol	162	164, 98
1,2,4-Trichlorobenzene	180	182, 145
Naphthalene	128	129, 127
4-Chloroaniline	127	129, 65
Hexachlorobutadiene	225	223, 227
4-Chloro-3-methylphenol	107	144, 142
2-Methylnaphthalene	142	141
Hexachlorocyclopentadiene	237	235, 272
2,4,6-Trichlorophenol	196	198, 200
2,4,5-Trichlorophenol	196	198, 97
2-Chloronaphthalene	162	127, 164
2-Nitroaniline	65	92, 138
Dimethylphthalate	163	194, 164
Acenaphthylene	152	151, 153
2,6-Dinitrotoluene	165	63, 89

Current 8270D Target Analytes:

Compound	Primary Ion	Secondary Ion(s)
3-Nitroaniline	138	108, 92
Acenaphthene	154	153, 152
2,4-Dinitrophenol	184	63, 154
4-Nitrophenol	139	109, 65
Dibenzofuran	168	139
2,4-Dinitrotoluene	167	
4-Nitroaniline	138	65, 108
4,6-Dinitro-2-methylphenol	198	51, 105
N-Nitrosodiphenylamine	169	168, 167
4-Bromophenyl-phenylether	248	250, 141
4-Chlorophenyl-phenylether	204	206, 141
Fluorene	166	165, 167
Diethylphthalate	149	177, 150
Hexachlorobenzene	284	142, 249
Pentachlorophenol	266	264, 268
Phenanthrene	178	179, 176
Anthracene	178	176, 179
Carbazole	167	84
Di-n-butylphthalate	149	150
Fluoranthene	202	101
Pyrene	202	200, 203
Butylbenzylphthalate	149	91
3,3'-Dichlorobenzidine	252	254, 126
Benzo(a)anthracene	228	229, 226
Chrysene	228	226, 229
bis(2-Ethylhexyl)phthalate	149	167, 279
Di-n-octylphthalate	149	167, 43
Benzo(b)fluoranthene	252	253, 125
Benzo(k)fluoranthene	252	253, 125
Benzo(a)pyrene	252	253, 125
Indeno(1,2,3-cd)pyrene	276	138, 227
Dibenzo(a,h)anthracene	278	139, 279
Benzo(g,h,i)perylene	276	138, 277
N-Nitrosodimethylamine	74	42
2-Fluorophenol	112	64
Aniline	93	66, 65

Current 8270D Target Analytes:

Compound	Primary Ion	Secondary Ion(s)
Phenol-d5	99	42, 71
2-Chlorophenol-d4	132	68
1,2-Dichlorobenzene-d4	152	115
Nitrobenzene-d5	82	128, 54
2-Fluorobiphenyl	172	171
2,4,6-Tribromophenol	330	332, 141
1,2-Diphenylhydrazine	77	182, 105
Benzidine	184	92, 185
Terphenyl-d14	244	122, 212

Current Appendix IX Analytes:

Compound	Primary Ion	Secondary Ion(s)
2,6-Dichlorophenol	162	164, 63
1,2,4,5-Tetrachlorobenzene	216	214, 218
2,3,4,6-Tetrachlorophenol	230	232, 234
Dinoseb	211	163, 117
Methanesulfonate, methyl	80	79, 95
Methanesulfonate, ethyl	109	97
Phosphorothiotic Acid	97	121, 198
Safrole	162	104, 131
Isosafrole, cis & trans	162	104, 131
1,4-Naphthoquinone	158	102, 104
1,3-Dinitrobenzene	168	76, 122
Thionazin	97	96, 107
2,4-D, methyl ester	199	175, 234
Diallate	86	234, 236
Phorate	260	231, 121
Dimethoate	87	93, 125
Silvex, methyl ester	196	225, 282
2,4,5-T, methyl ester	233	235, 268
Pronamide	173	175, 255
Disulfoton	88	274, 142
Methyl parathion	263	125, 109
Ethyl parathion	291	235, 186
Isodrin	193	195, 230

Current Appendix IX Analytes:

Compound	Primary Ion	Secondary Ion(s)
Chlorobenzilate	139	251, 253
Kepone	272	274, 355
Famphur	218	125, 217
3-Methylcholanthrene	268	252, 253
Ethanamine,N-methyl-N-nitroso	42	88, 43
N-nitrosomorpholine	56	86, 116
Butanamine, N-butyl-N-nitroso	84	41, 57
2-Naphthalenamine	143	144, 115
Diphenylamine	169	168, 167
1,3,5-Trinitrobenzene	213	75, 74
4-Aminobiphenyl	169	168, 170
Methyapyrilene, HCL	58	97, 191
p-Dimethylaminoazobenzene	120	225, 226
2-Acetylaminofluorene	181	180, 223
7,12-Dimethylbenz(a)anthracene	256	241, 239
2-Picoline	93	92, 78
Pentachloroethane	167	165, 119
Acetophenone	105	77, 51
N-Nitrosopyrrolidine	100	41, 42
N-Nitrosopiperidine	42	114, 55
Hexachloropropene	213	215, 211
1,4-Phenylenediamine	108	80, 81
Pentachlorobenzene	250	252, 248
1-Naphthylamine	143	144, 115
5-Nitro-o-toluidine	152	77, 106
Pentachloronitrobenzene	237	214, 295
N-Nitroquinoline-N-oxide	190	160, 89
3,3-Dimethylbenzidine	212	213, 211
Hexachlorophene	196	198, 209
N-Nitrosodiethylamine	74	42
o-Toluidine	106	107
Phentermine	58	91, 134
Sulfotep	97	322, 202
Aramite	135	193, 208
Phenacetin	108	109, 179

APPENDIX XI

Semivolatile Internal Standards With Corresponding Analytes Assigned For Quantitation

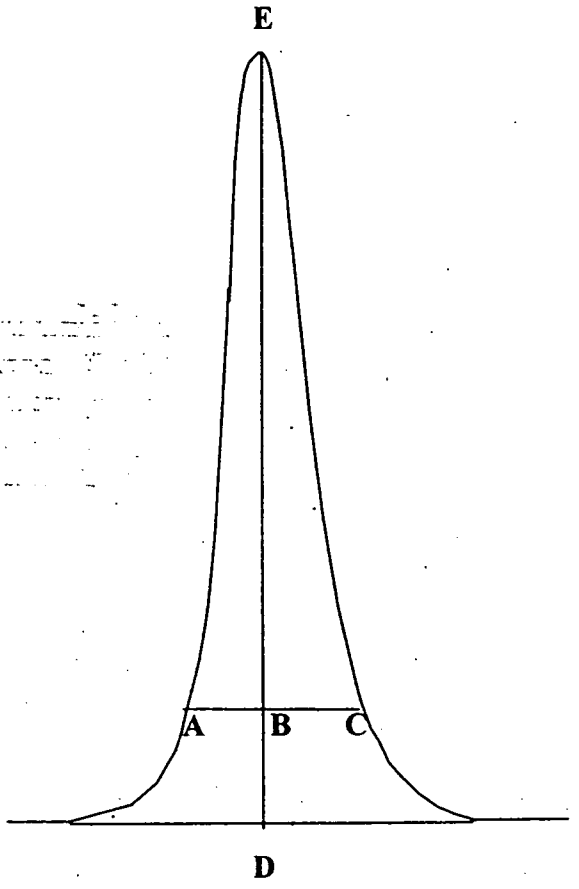
1,4-Dichlorobenzene-d4	Naphthalene-d8	Acenaphthene-d10
Phenol	Nitrobenzene	Hexachlorocyclopentadiene
Bis(2-Chloroethyl)ether	Isophorone	2,4,6-Trichlorophenol
2-Chlorophenol	2-Nitrophenol	2,4,5-Trichlorophenol
1,3-Dichlorobenzene	2,4-Dimethylphenol	2-Chloronaphthalene
1,4-Dichlorobenzene	Benzoic Acid	2-Nitroaniline
Benzyl Alcohol	bis(2-Chloroethoxy)methane	Dimethylphthalate
1,2-Dichlorobenzene	2,4-Dichlorophenol	Acenaphthylene
2-Methylphenol	1,2,4-Trichlorobenzene	2,6-Dinitrotoluene
Bis(2-chloroisopropyl)ether	Naphthalene	3-Nitroaniline
4-Methylphenol	4-Chloroaniline	Acenaphthene
N-Nitroso-di-n-propylamine	Hexachlorobutadiene	2,4-Dinitrophenol
Hexachloroethane	4-Chloro-3-methylphenol	4-Nitrophenol
Aniline	2-Methylnaphthalene	Dibenzofuran
Pyridine	Nitrobenzene-d5	2,4-Dinitrotoluene
Phenol-d5	2,6-Dichlorophenol	4-Nitroaniline
2-Chlorophenol-d4	Safrole	Fluorene
1,2-Dichlorobenzene-d4	Isosafrole, cis & trans	4-Chlorophenyl-phenylether
N-Nitrosodimethylamine	1,4-Naphthoquinone	Diethylphthalate
2-Fluorophenol	Butanamine, N-methyl-N-nitroso	1,2,4,5-Tetrachlorobenzene
Methanesulfonate methyl	Hexachloropropene	2,3,4,6-Tetrachlorophenol
Methanesulfonate ethyl	1,4-phenylenediamine	1,3-Dinitrobenzene
Phosphorothiotic acid	Phentermine	Thionazin
Ethanamine, N-methyl-N-nitroso		2,4-D methyl ester
N-Nitrosomorpholine		Diallate
2-Picoline		Phorate
Pentachloroethane		Dimethoate
Acetophenone		Silvex methyl ester
N-Nitrosopyrrolidine		2,4,5-T methyl ester
N-Nitrosopiperidine		2-Naphthaleneamine

1,4-Dichlorobenzene-d4	Naphthalene-d8	Acenaphthene-d10
N-Nitrosodiethylamine O-Toluidine		Pentachlorobenzene 1-Naphthylamine 5-Nitro-o-toluidine Pentachloronitrobenzene Sulfotep Aramite

Phenanthrene-d10	Chrysene-d12	Perylene-d12
4,6-Dinitro-2-methylphenol N-Nitrosodiphenylamine 4-Bromophenyl-phenylether Hexachlorobenzene Pentachlorophenol Phenanthrene Anthracene Carbazole Di-n-butylphthalate Fluoranthene 2,4,6-Tribromophenol 1,2-Diphenylhydrazine Dinoseb Pronamide Disulfoton Methyl parathion Ethyl parathion Isodrin Diphenylamine 1,3,5-Trinitrobenzene 4-Aminobiphenyl Methapyrilene, HCL N-Nitroquinoline-n-oxide 3,3-Dimethylbenzidine Phenacetin	Pyrene Butylbenzylphthalate 3,3'-Dichlorobenzidine Benzo(a)anthracene Chrysene bis(2-Ethylhexyl)phthalate Benzidine Terphenyl-d14 Chlorobenzilate Kepone Famphur P-Dimethylaminoazobenzene 2-Acetylaminofluorene 7,12- Dimethylbenz(a)anthracene Hexachlorophene	Di-n-octylphthalate Benzo(b)fluoranthene Benzo(k)fluoranthene Benzo(a)pyrene Indeno(1,2,3-cd)pyrene Dibenzo(a,h)anthracene Benzo(g,h,i)perylene 3-Methylcholanthrene

Appendix XII

Calculation of Peak Tailing Factors



Peak Tailing Factor = BC/AB

Sample calculation: Peak Height = DE =100mm
10% Peak Height = BD = 10mm
Peak Width at 10% Peak Height = AC = 23mm
AB = 11mm
BC = 12mm
Tailing Factor = 12/11 = 1.1

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-8303

Determination of Picric and Picramic Acids

Revision history:

Number	Date
1	10/11/90
2	10/11/93
3	01/28/98
4	10/27/98
5	05/09/02

Revised by: _____ Date: 5/10/02
Chad Christianson, Organic Chemist

Approved by: Harry Romberg Date: 5-13-02
Harry Romberg, QA Officer

Approved by: Kathy Kreps Date: 5-13-02
Kathy Kreps, Laboratory Director

Controlled Document

No. 20 Assigned to: Tetr

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1. Introduction and Scope

1.1 Method Description

1.1.1 This method is used for the analysis of ordnance degradation products by high performance liquid chromatography. This method employs the use of a CN (cyano) reverse phase column for the primary column, and a C18 (octadecyl) reverse phase column for confirmation. Target analyte concentrations are measured at 254 nm using a UV detector. The separation employed utilizes an ion-pairing technique.

Compound	Acronym
2,4,6-Trinitrophenol	Picric Acid
2-Amino-4,6-dinitrophenol	Picramic Acid

1.1.2 This method is restricted to use by, or under the supervision of, analysts experienced in the use of high pressure liquid 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 order to attain lab-wide consistency among staff members for decision-making processes with regard to laboratory anomalies, several common items have been addressed in this SOP. Any occurrences which are not covered in this SOP should be discussed with the supervisor, prior to implementing a solution.

1.1.4 One example is the determination of potential carry-over in sample analyses. Any samples analyzed subsequent to a high level sample (which is defined by yielding one or more target analytes above the calibration range) should be thoroughly examined for potential carry-over of the same target analyte(s). Corrective action in the form of reanalysis for possible carry-over should be performed and documented in the narrative.

1.1.5 Another example is the review of all sample chromatograms for analytes which may not appear on the sample quantitation report due to data system error or retention time shift. All peaks should be examined and evaluated based on the retention times and sample concentration in order to prevent reporting false negatives.

1.2 Sample Collection, Sample Storage, Holding Times

1.2.1 Samples are collected in amber glass containers with Teflon-lined caps. All samples and sample extracts are stored at 4°C ±2°C. According to guidelines listed in SW-846 for the extraction of semivolatile compounds, water samples must be extracted within 7 days of

collection, and soil samples must be extracted within 14 days of collection. All extracts must be analyzed within 40 days of sample preparation.

1.3 Definition of Terms

1.3.1 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.

Method 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 injected at some prescribed frequency during the analysis sequence to determine whether the instrument has remained in calibration.
CF	Calibration factor. The ratio of peak response to nanograms injected. This term is defined in the same way in both the CLP contract and SW-846.
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	An instrument blank is solvent containing the method surrogates and is injected into the instrument to monitor for carryover between sample extract injections.
ICV	Initial calibration verification. It is a standard which 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 at Laucks.
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 injection of one or more standards, followed by sample extracts, and terminated with a standard injection. 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. 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 the 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 and standard solutions injected into an instrument in a chronologically continuous group. See also QC period.

2. Equipment List and Standards

2.1 Chromatographic System

Primary Column:	PAH C18 (octadecyl) reverse phase HPLC column, 25 cm x 4.6 mm, 5 µm particle size, (Supelcosil PAH-C18 or equivalent).
Secondary Column:	CN (cyano) reverse phase HPLC column, 25 cm x 4.6 mm, 5 µm particle size, (Supelcosil LC-CN or equivalent).
Mobile Phase:	PIC A Reagent for the PAH (or C18) column - (tetrabutylammonium phosphate ion-pairing agent purchased from Waters, part # WAT085101.) Methanol - (EM Science brand high purity solvent or equivalent) Acetonitrile with 0.1% phosphoric acid in water for the CN column Reagent water - (Modulab Polisher HPLC grade water or equivalent).
UV Detector:	254 nm
HPLC System:	Rainin HPLC system - HPXL solvent delivery system capable of achieving 4000 psi or equivalent. 50 µL sample loop. Knauer variable wavelength UV detector or equivalent. Dynamax automatic sample injector or equivalent. Digital integrator: EZChrom or equivalent. Waters System - Waters 712 WISP Sample Processor or equivalent. 50 µL sample loop or equivalent. Waters 486 tunable absorbance detector or equivalent. Waters 600E Multisolvent delivery system or equivalent. Digital Integrator: EZChrom.

2.1.1 Column Temperature Control:

2.1.2 Column temperature can be controlled through the use of a column heater surrounding the column that is maintained at a temperature of 25°C. However, this is not required, and is currently not used.

2.2 Standards

2.2.1 Ion-Pairing Agent (confirmation only)

2.2.1.1 Prepare 1000 mL 1:1 methanol/HPLC grade DIW. Add contents of 1 bottle PIC A Reagent (tetrabutylammonium phosphate). Stir 5 minutes, then filter using a solvent resistant 0.22 micron filter (Millipore GVWP-04700 filters or equivalent).

2.2.2 Individual Target Analyte Stock Solution

2.2.2.1 The picramic acid, picric acid and 4,6-dinitro-o-cresol (surrogate) standards are purchased individually from AccuStandard, Inc. (25 Science Park, New Haven, CT 06511). The standard solutions come in 1 mL ampules at 1000 µg/mL in 1:1 methanol/acetonitrile.

2.2.3 IBLK Working Solution

2.2.3.1 The working instrument blank solution contains the surrogate at a concentration of 4.0 µg/mL. Prepare this solution by adding 100 µL of the 1000 µg/mL surrogate stock solution to a 25 mL volumetric flask. Dilute to volume with 1:1 methanol/reagent grade water.

2.2.4 Working Calibration Standards

2.2.4.1 Prepare the working calibration standards in the following manner. All solutions are prepared in a 1:1 methanol/water mixture.

Standard	Source Solution	Amount Added	Final Volume (mL)	Final Conc. (µg/mL)
Standard #5	A,B,C	250 µL	10	25
Standard #4	D	5 mL	10	12.5
Standard #3	D	2 mL	10	5
Standard #2	F	2 mL	10	1
Standard #1	F	1 mL	10	0.5

Source Solutions	Concentration (µg/mL)
A = Picramic Acid	1000
B = Picric Acid	1000
C = 4,6-Dinitro-o-cresol	1000
D = Standard 5	25
E = Standard 4	12.5
F = Standard 3	5

2.2.4.2 Note: Store all standard and surrogate solutions in amber glass vials with screw caps and Teflon-lined septa. Minimize headspace in these vials and store them in a refrigerator kept at 4°C ±2°C. Allow standards to come to room temperature prior to use.

2.2.4.3 Stock solutions may be used for up to one year, and working solutions are good for at least six months, or the expiration date of the parent standard, whichever is sooner.

2.2.4.4 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 standards.

3. Safety precautions

3.1.1 Routine Safety Precautions
All standards and sample extracts should be handled as if they are 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 All compounds analyzed by this method are the degradation products of explosives. When making stock solutions for calibration, treat each explosive compound with caution.

3.2 Waste disposal

3.2.1 Out of date standards and sample extracts are disposed of in the designated organic waste container located in the organic preparation area.

3.2.2 HPLC eluent waste is disposed of by pouring down the drain of a sink with the tap flowing for several minutes.

4. Operation procedures

4.1 Analytical Conditions

4.1.1 PAH-C18 Column Conditions:

Solvent:	0.005 M PIC A in 1:1 methanol/water
Flow:	1.0 mL/minute:
Run Time:	15 minutes
Acquisition Time:	15 minutes
Injection Volume:	50 µL inj.

4.1.2 CN Column Conditions:

Solvent:	0.1 percent phosphoric acid
Flow:	1.6 mL/minute:
Run Time:	15 minutes
Acquisition Time:	15 minutes
Injection Volume:	50 µL inj.

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 determination of detection limits. 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. At the time this SOP was written the MDL for picric acid and picramic acid was 0.074 µg/L and 0.094 µg/L for water and 2.1 µg/kg and 10 µg/kg for soils respectively.

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.

4.4 Retention Time Windows

4.4.1 Prior to the analysis of any samples, it is necessary to establish retention time windows for the method by analyzing standards for all target analytes over at least a 24-hour period. A 24-hour time period is deemed appropriate for this analysis because the instrument is never operated for longer periods when analyzing sample extracts. In addition, the ion pairing method is not sufficiently robust to allow operation for a 72-hour period, as in many other methods. At least 5 standards must be injected during the 24-hour time period, at about equal time intervals. These standards should be interspersed with real sample extracts in order to mimic actual instrument operating conditions. Tabulate the retention times for all standard compounds and compute the sample (n-1) standard deviations of all the retention times.

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 (e.g. new column) or whenever the chromatographic method is modified.

4.4.3 In some cases, the retention time window may be modified in order to take into account any pattern shifting. This shift is acknowledged by observation of the surrogate peak behavior and the surrounding CCV standards. If retention time shift has occurred and the possibility of mis-identifying peaks exists, then the sample is reanalyzed bracketed by in-control CCV standards.

4.4.4 See the Laucks SOP on determination of retention time windows for more specifics on their determination and use.

4.5 Initial Multi-Point Calibration

4.5.1 Analyze standard solutions (including the surrogate solution) using at least 5 different concentration levels. The lowest concentration standard will determine 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. Laucks routinely uses standard concentrations of 0.5, 1.0, 5.0, 12.5, and 25.0 µg/mL. Criteria for evaluating these standards are detailed in Section 6.

4.6 Initial Calibration Verification

4.6.1 At the beginning of an analysis sequence, analyze the mid-point calibration standard. The computed calibration factor (CF) or concentration measurement must meet the criteria detailed in Section 6.

4.6.2 The retention time windows for compound identification are updated using the retention times for each target analyte in the ICV standard 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.

4.6.3 The retention time windows for compound identification are updated every 24 hours of acquisition time from the ICV standard as the center of the window to a neighboring CCV. This neighboring CCV is determined to be a more accurate representation of peak behavior based on the surrogate, spiked extracts and surrounding standards.

4.7 Instrument Blank

4.7.1 After the analysis of Standard 5, an instrument blank (IBLK) is analyzed. This is to verify that there is no carryover between sample injections. Evaluation criteria are detailed in Section 6.

4.7.2 Any sample that is suspected of containing high concentrations of target analytes should be followed by an IBLK. This IBLK analysis is used only to make a judgment as to the possibility of carryover into the sample analysis immediately following the IBLK. Evaluation criteria are detailed in Section 6.

4.8 Continuing Calibration Verification

4.8.1 A mid-range calibration is analyzed after every ten injections. In addition, this standard must be the last injection made in the analysis sequence. Evaluation criteria are detailed in Section 6.

4.9 Sample Analysis

4.9.1 Analysis sequence

See Appendix II for a detailed analysis injection sequence.

4.9.2 Compound Identification

4.9.2.1 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 retention time window on a second column. Retention time windows are established as previously described and are updated each QC period. Compounds can only be identified if the ICV and CCV criteria detailed in Section VI are strictly adhered to.

4.9.2.2 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.

4.9.3 Compound Quantification

4.9.3.1 Target compound concentrations are calculated using the following equations:

4.9.3.1.1 Aqueous samples

The external standard equation, as expressed in SW-846 is

$$Concentration(\mu g / L) = \frac{As \times Vt \times D}{\overline{CFs} \times Vi \times Vs}$$

where:

As	= 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 an extract is diluted 10 µL to 1000 µL and subsequently diluted an additional 10 µL to 1000 µL, the expression is: (1000/10) * (1000/10) = 100 * 100 = 10,000. If no dilution was made, D = 1.
$\overline{CFs}$	= Mean calibration factor from the initial calibration.
V_t	= Volume of total extract, µL.
V_s	= Volume of aqueous sample extracted or purged in mL. If units of liters are used for this term, multiply the results by 1000.

4.9.3.1.2 To report concentrations in alternate units, apply an appropriate factor:

mg/L = µg/L * 0.001

4.9.3.2 Non-aqueous samples

4.9.3.2.1 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.

$$Concentration(\mu g / kg) = \frac{Vt \times As \times D}{\overline{CF} \times Vi \times (Ws)}$$

where:

W_s = Weight of sample extracted. Either the wet weight or dry weight may by used, depending upon the specific application of the data.

4.9.3.2.2 One or more analytes may require manual integration on the data system quantitation reports. The manual integrations are flagged, initialed and dated by the analyst. A list of the manual integration flags are detailed below.

M = Manual integration due to irregular peak shape.
MS = Manual integration due to split peak.
MR = Manual integration due to retention time shift.
MI = Manual integration of correct isomer or peak.
MT = Manual integration due to peak tailing.
MB = Manual integration due to irregular baseline.

4.9.3.3 If the concentration of any target analyte exceeds the calibration range, the sample extract must be diluted and reanalyzed.

5. Reports

5.1 Data Packet Organization

See Appendix III for a list detailing data packet organization.

5.2 Quality Control Reports

5.2.1 All results for quality control tests are entered into the lab 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.

5.3 Sample Result Reports

5.4 Data Qualifying Flags

5.4.1 Sample report results are qualified with data qualifying flags. These flags have the following definitions:

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.

J:	The analyte of interest was detected below the practical quantitation 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.
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.
X:	The sample has been analyzed at several dilutions. The value reported has been determined to be the most appropriate quantitative value.

6. Quality Control

See the Requirements and Corrective Actions table in Appendix IV for additional information.

6.1 Initial Calibration

6.1.1 Criteria

6.1.1.1 The initial calibration is evaluated by calculating the %RSD of the calibration factors from the five linearity standards.

6.1.1.2 CFs are calculated using the equation:

$$CF = \frac{\text{response}}{\text{ng injected}}$$

6.1.1.3 This %RSD method assumes a linear response with the calibration curve passing through the origin.

6.1.1.4 The calculated CFs are tabulated and the %RSDs calculated. All compounds must have a %RSD of 20% to meet the method criteria.

6.1.2 Corrective action

6.1.2.1 If the %RSD criteria of 20% are not met, the out of control standard should be reanalyzed. If the curve is still out of control, determine the cause of failure and correct.

Recalibrate the instrument and reanalyze any samples associated with the out of control curve.

6.2 Initial Calibration Verification

6.2.1 Criteria

6.2.1.1 Using the average CF calculation technique, compute the CFs for each compound. The calibration factors for the ICV standard are compared to the mean CFs for the initial multi-point calibration. The percent difference for these calibration factors is calculated as follows:

$$\%Difference = \frac{CFi - CFa}{CFa} \times 100$$

where:

CF_a = Mean CF from the initial multi-point calibration
CF_i = Calibration Factor from the calibration verification standard.

6.2.1.2 The %D cannot exceed 15% for any target analytes or surrogates.

6.2.1.3 The mid-point for the RT window of each compound is updated using the ICV RTs.

6.2.2 Corrective action

6.2.2.1 If the ICV criteria are not met, no sample extracts can be analyzed. Determine the cause of the ICV failure and correct. Reanalyze the ICV and if it is still out of control, a new calibration curve must be analyzed.

6.3 Continuing Calibration Verification

6.3.1 Criteria

6.3.1.1 A CCV standard is analyzed singly for every 10 injections, and after the last sample of the sequence. The CF for each compound is calculated and the percent difference is calculated as shown above.

6.3.1.2 The %D results cannot exceed 15% for any target analytes or surrogates.

6.3.1.3 The retention times for all target analytes must fall within the RT windows established by the ICV.

6.3.2 Corrective action

6.3.2.1 Determine the cause of failure and correct. Reanalyze the calibration curve. All samples bracketed by an out of control CCV must be reanalyzed unless the CCV demonstrates an increase in response and no analytes are detected above the RL in the associated samples.

6.4 Instrument Blank

6.4.1 Criteria

6.4.1.1 There must be no target analyte levels above ½ the reporting limit in the initial IBLK.

6.4.2 Corrective action

6.4.2.1 If the initial IBLK contains measurable levels of target analytes, the system is out of control. The source of contamination must be identified and corrected.

6.4.2.2 IBLKs are 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 reanalyzed if there is a detectable amount of the analyte found in the IBLK.

6.5 Method Blank

6.5.1 Criteria

6.5.1.1 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 at least one blank for every 20 samples, whichever is more frequent. Analytes of interest should not be detected at levels greater than ½ the current reporting limit in the method blank sample. If any analytes are detected above the reporting limit, corrective action must be taken.

6.5.2 Corrective action

6.5.2.1 Reanalyze the blank and check calculations. If it is still out of control, re-extract the entire batch of samples unless the analyte(s) present in the method blank are not present

in the associated samples. 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.

6.6 Blank Spike or QC Check Sample (LCS)

6.6.1 Criteria

6.6.1.1 A blank spike follows the same protocol as 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. At the time this SOP was written the blank spike percent recovery control limits were between 40 and 160 for both compounds. These control limits are updated periodically.

6.6.2 Corrective action

6.6.2.1 The blank spike is used to determine whether a method is in control during sample preparation and analysis. Sample re-extraction and reanalysis would be triggered by any analytes falling outside of control limits in the blank spike sample unless all sample surrogate recoveries and MS/MSD spike recoveries are in control.

6.7 Matrix Spike

6.7.1 Criteria

6.7.1.1 A sample is either chosen at random or is designated by the client 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. However, the minimum frequency for MS analysis is 1 each per 20 samples per matrix. This frequency may be changed on a project specific basis. 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:

$$\%Recovery = \frac{SSR - SR}{SA} \times 100$$

where:

SSR = Concentration in spiked sample.
SR = Native concentration in unspiked sample.
SA = Concentration of spike added.

6.7.1.2 At the time this SOP was written the matrix spike percent recovery control limits were between 48 and 152 for picric acid, and between 60 and 128 for picramic acid. These control limits are updated periodically.

6.7.2 Corrective action

6.7.2.1 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.

6.8 Matrix Spike Duplicate

6.8.1 Criteria

6.8.1.1 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:

$$RPD = \frac{|S1 - S2|}{(S1 + S2)/2} \times 100$$

where:

S1 = Measured concentration for MS sample.
S2 = Measured concentration for MSD sample.

6.8.1.2 At the time this SOP was written the matrix spike duplicate percent recovery control limits were between 48 and 152 for picric acid, and between 60 and 128 for picramic acid. These control limits are updated periodically.

6.8.2 Corrective action

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. At the time this SOP was written the RPD percent control limits were 50. These control limits are updated periodically.

6.9 Surrogate Recovery

6.9.1 Criteria

6.9.1.1 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:

$$\%Recovery = \frac{S_m}{S_a} \times 100$$

where:

S_m = Concentration of surrogate measured in sample.
S_a = Concentration of surrogate added.

6.9.1.2 At the time this SOP was written the surrogate percent recovery control limits were between 48 and 152 for picric acid, and between 50 and 150.

6.9.2 Corrective Action

6.9.2.1 Reanalyze the sample. Low surrogate recoveries are greater potential indicators of poor method performance than high surrogate recoveries since non-GC/MS methods cannot separate co-eluting interferents. In instances where high surrogate recoveries are attributable to matrix effects, no corrective action is taken. However, if elevated surrogate recoveries are attributable to preparation error, re-extraction and reanalysis is performed.

6.9.2.2 Check calculations for possible error. Re-extract the sample if surrogate recovery is less than the lower control limit. If a poor injection is suspected, reanalyze the sample. A low surrogate recovery in the re-extract is evidence of matrix interference.

6.9.2.3 Low surrogate recoveries in the method blank may require that all the samples in the associated batch be re-extracted and reanalyzed. 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.

7. References

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Method 8000B, "Gas Chromatography," Revision 2, December 1996, U.S.E.P.A.

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, 3rd Update, Method 8330, "Nitroaromatics and Nitramines by High Performance Liquid Chromatography (HPLC)," Revision 0, September 1994, U.S.E.P.A.

40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984, U.S.E.P.A.

APPENDIX I

Calibration Standard Solution Concentrations, µg/mL

Compound	STD1	STD2	STD3	STD4	STD5
Picric Acid	0.5	1.0	5.0	12.5	25.0
Picramic Acid	0.5	1.0	5.0	12.5	25.0
Surrogate					
4,6-Dinitro-o-cresol	0.5	1.0	5.0	12.5	25.0

Surrogate Stock Solution

Compound	Concentration
4,6-Dinitro-o-cresol	1000 µg/mL

IBLK Solution

Compound	Concentration
4,6-Dinitro-o-cresol	4.0 µg/mL

APPENDIX II

Analysis Sequence

Injection	Sample
1	Standard #1
2	Standard #2
3	Standard #3 (CCV Standard)
4	Standard #4
5	Standard #5
6	IBLK
7	ICV
	injections (8-16)
17	IBLK
18	CCV Standard
19	injections (19-27)
28	BLK
29	CCV Standard
	Sample injections (total of 10 injections between CCVs)
last	IBLK
last	CCV Standard

APPENDIX III

Data Packet Organization List

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
Quantitation Report

III. STANDARD DATA:

Linearity Report
ICAL Data
ICAL Response, ICAL std concentrations
ICV reports
CCV reports
Other Standards Used to Support Sample Data and Instrument Blanks

V. Raw QC Data:

Method Blank
Chromatograms
Quantitation Report

Blank Spike
Chromatograms
Quantitation Report

Matrix Spike
Chromatograms
Quantitation Report

Matrix Spike Duplicate
Chromatograms
Quantitation Report

V. Bench Sheets

SDG Report
Extraction Bench Sheets
Injection Sequence (logbook copy)
Miscellaneous Work Sheets. (%TS, calcs, HTVRs)
Standards Logs

VI. Reject Data:

Data not used to support reported 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

Picric/Picramic Requirements and Corrective Actions

QA Element	Laucks Criterion	Frequency	Corrective Action	Documentation
Initial Calibration	Minimum of 5 levels. Must demonstrate an RSD of <20%.	As necessary due to major instrument maintenance or difficulties meeting the CCV requirements.	Reanalyze out of control standard. If still out, determine cause of curve failure and correct. Reanalyze curve and any samples analyzed against curve.	Target forms and raw data.
Initial Calibration Verification	+/- 15% of the initial calibration response factor.	Every 24 hrs. or at the beginning of an analytical sequence, which ever is more frequent, or as necessary.	Determine cause of ICV failure and correct. Reanalyze ICV and if out of control a new calibration curve must be analyzed.	Target form and raw data.
Continuing Calibration Verification	+/- 15% of the initial calibration response factor.	Every 10 injections and at the end of an analytical sequence.	Determine cause of failure and correct. Re-analyze calibration curve. All samples bracketed by an out of control CCV must be reanalyzed unless the CCV demonstrates an increase in response and no analytes are detected above the reporting limit.	Target form and raw data.
Instrument Blank	Analyze instrument blank after samples when high levels of matrix are suspected. Analyze instrument blank before the CCV standard. No target analytes present in the blank > ½ the RL. Surrogate must be within control limit.	Analyze instrument blank after samples when high levels of matrix are suspected. Analyze instrument blank before the CCV standard.	Reanalyze any samples with suspected carryover.	Raw data
Method Blank	All analytes must be less than ½ the reporting limit	One method blank per 20 samples or each extraction batch, whichever is more frequent.	Reanalyze blank. If still out of control, re-extract the entire batch of samples unless the detected analyte(s) are not present in the associated samples.	Method Blank Summary and raw data. Narrative comment when necessary.

QA Element	Laucks Criterion	Frequency	Corrective Action	Documentation
Surrogate Recovery	Current control limits are stored in QC database. All surrogate recoveries must fall within the generated limits. If laboratory limits are not established due to the implementation of a new surrogate , the default limits of 70% - 130% are used until enough data points are collected to generate new limits.	All samples, method blanks, and QC samples.	Re-extract if surrogate recovery is < the lower control limit. If a poor injection is suspected re-analyze the sample.	Target Surrogate Summary form or special test results. Narrative comment when necessary.
MS/MSD	Current control limits are stored in the QC database.	1 MS/MSD pair per 20 samples or every extraction batch which ever is more frequent.	If MS/MSD recoveries are out of control, no further action is taken if blank spike recoveries are in control.	MS/MSD report and raw data. Narrative comment when necessary.
Blank Spike	Current control limits are stored in QC database. All recoveries and RPDs must fall within the generated limits.	1 per 20 samples or every extraction batch which ever is more frequent.	Re-extract if analyte recoveries are outside of control limits.	Blank Spike report and raw data. Narrative comment when necessary.

APPENDIX V

Elution Order of Target Analytes

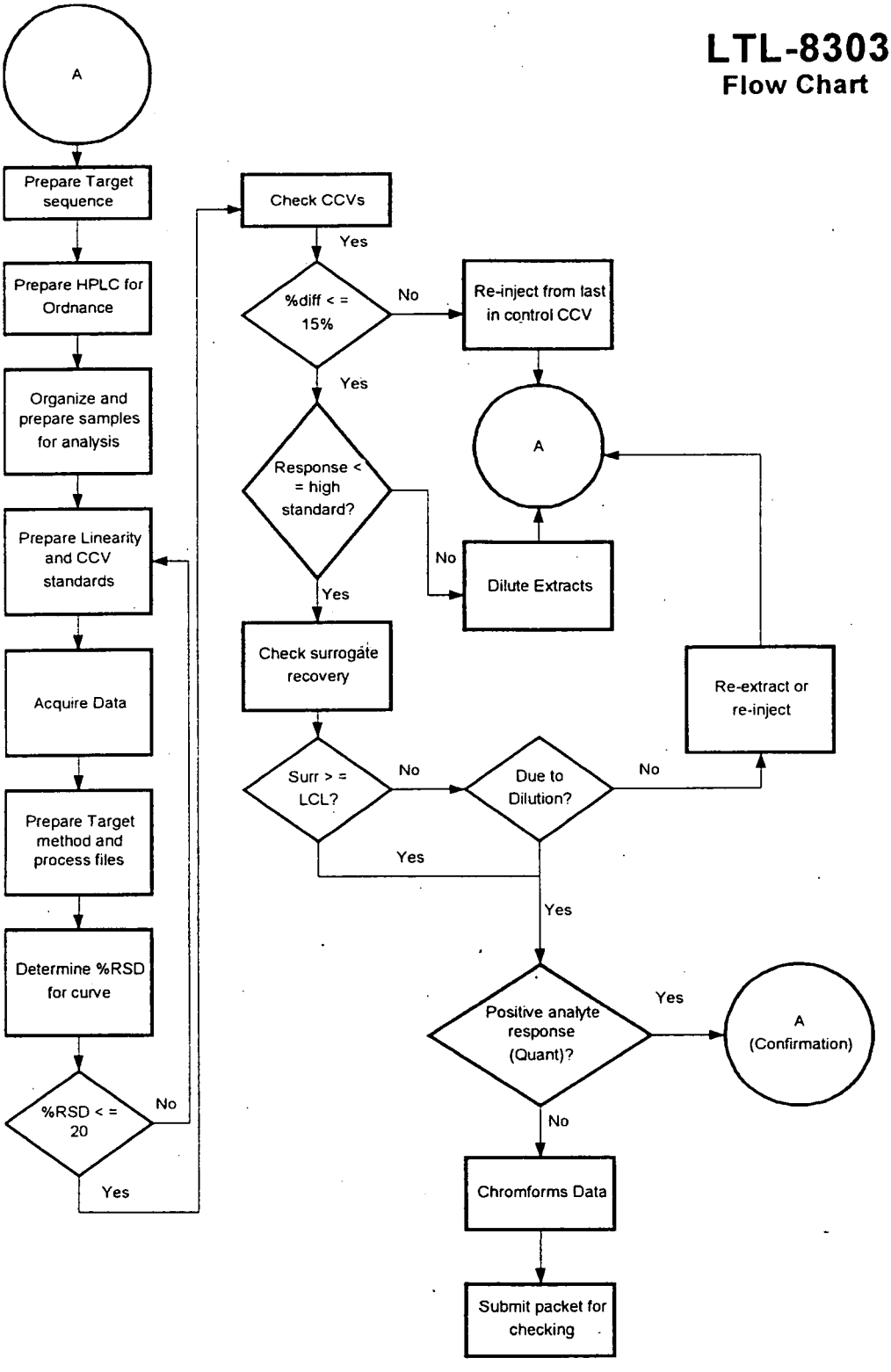
Compound	PAH - C18 Column
Picric Acid	3
Picramic Acid	1
Surrogate	
4,6-Dinitro-o-cresol	2

Compound	CN Column
Picric Acid	1
Picramic Acid	3
Surrogate	
4,6-Dinitro-o-cresol	2

APPENDIX VI

LTL 8303 Flow Chart

LTL-8303
Flow Chart



LAUCKS TESTING LABORATORIES INC.

Seattle, Washington

SOP #:LTL-8330

Determination of Nitroaromatics and Nitramines by SW-846 Method 8330A & 8332

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1. Introduction and Scope

1.1 Method Description

1.1.1 This method is used for the trace analysis of ordnance compounds in water, soil, and sediment samples by high performance liquid chromatography. The concentrated water sample extracts are diluted 1:1 (v/v) with reagent grade water prior to analysis. The sample extracts are analyzed using a C18 (octadecyl) reverse phase column, and target analyte concentrations are measured at either 254 nm or 210 nm using a UV detector. All positive measurements observed on the C18 column are confirmed by a second analysis which uses a CN (cyano) column (with a C8 column in series for the 6 additional compounds).

1.1.2 The C18 column is considered the primary column and is used for quantitation of all target analytes.

1.1.3 This method is used to determine part per billion levels of the ordnance analytes listed below:

Compound	Acronym
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine	HMX
Hexahydro-1,3,5-trinitro-1,3,5-triazine	RDX
1,3,5-Trinitrobenzene	1,3,5-TNB
1,3-Dinitrobenzene	1,3-DNB
Methyl-2,4,6-trinitrophenylnitramine	Tetryl
Nitrobenzene	NB
2,4,6-Trinitrotoluene	2,4,6-TNT
4-Amino-2,6-dinitrotoluene	4-Am-DNT
2-Amino-4,6-dinitrotoluene	2-Am-DNT
2,4-Dinitrotoluene	2,4-DNT
2,6-Dinitrotoluene	2,6-DNT
2-Nitrotoluene	2-NT
3-Nitrotoluene	3-NT
4-Nitrotoluene	4-NT

6 Additional Compounds
(Separate Analysis at 254 nm)

Compound	Acronym
2,4-Diamino-6-nitrotoluene	2,4-DA-6-NT
2,6-Diamino-4-nitrotoluene	2,6-DA-4-NT
3,5-Dinitroaniline	3,5-DNA
1-Nitroso-3,5-dinitro-1,3,5-hexahydrotriazine	MNX
1,3,5-Trinitroso-1,3,5-hexahydrotriazine	TNX
2,2',6,6'-Tetranitro-4,4'-azoxytoluene	4,4'-TN-AZOXY

PETN/NG Compounds
(Separate Analysis at 210 nm)

Compound	Acronym
Nitroglycerin	NG
Pentaerythritoltetranitrate	PETN

1.1.4 Aqueous samples of higher concentration can be directly analyzed by diluting 1:1 (v/v) with methanol or acetonitrile, filtering, separating on a C18 reverse phase column, and determined at either 254 nm or 210 nm, and confirmed on a CN column.

1.1.5 This method is restricted to use by, or under the supervision of, analysts experienced in the use of high pressure liquid 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.

1.2 Method Deviations & Comments

1.2.1 The following items represent deviations from the published version of method SW 8330 and SW 8332 which are followed as standard operating procedure in the performance of this method at Laucks.

1. Single injections of calibration standards are analyzed rather than triplicate injections in a random order. It has been determined at Laucks that single injections of these standards yield acceptable calibration and linearity data as evidenced by the calculated percent RSDs used to evaluate the initial calibration data.

2. Method SW 8330 and SW 8332 specifies that all analyses are to be performed using a mobile phase which consists of a 50:50 mixture of

methanol/water under isocratic conditions. Laucks employs a gradient elution program (detailed in Section IV) in order to improve the separation of the target analytes on the CN-C8 columns.

3. According to Method 8330 and 8332, all working standards are to be prepared daily in a methanol/calcium chloride solution. The practice at Laucks for 8330/8332 and the 6 additional compounds is to prepare working standards using acetonitrile and diluting 50/50 with water just prior to analysis. NG/PETN are prepared in a 50/50 mixture of acetonitrile and water. These working solutions have been demonstrated to be stable for at least 6 months. The stability of target analyte responses in the working solutions in use (especially that of tetryl) is used to determine whether new solutions should be prepared.

4. Tetryl decomposes rapidly in methanol/water solutions, as well as with heat. Laucks has experienced erratic recovery of tetryl from spiked sample extracts.

5. Currently, the confirmation column will not demonstrate full separation for the ordnance compounds. The following target analytes will co-elute: 2-Nitrotoluene, 3-Nitrotoluene, and 4-Nitrotoluene. As well as 4-Amino-2,6-dinitrotoluene and 2-Amino-4,6-dinitrotoluene. Therefore, positive confirmation can not be made when these peaks have been tentatively identified on the primary column.

6. At the time of this writing, analysis of the 6 additional compounds (not including PETN/NG) combined with the 14 ordnance compounds results in the separation of all compounds on the primary column (C18).

7. Although the compounds NG and PETN are not listed in SW 846 Method 8330/8332, Laucks has found that adequate recovery of these compounds can be achieved using this method by modifying the wavelength from 254 nm to 210 nm.

1.2.2 In order to attain lab-wide consistency among staff members for decision-making processes with regard to laboratory anomalies, several common items have been addressed in this SOP. Any occurrences which are not covered in this SOP should be discussed with the supervisor, prior to implementing a solution.

1.2.3 One example is the determination of potential carry-over in sample analyses. Any samples analyzed subsequent to a high level sample (which is defined by yielding one or more target analytes above the calibration range) should be thoroughly examined for potential carry-over of

the same target analyte(s). Corrective action in the form of reanalysis for possible carry-over should be performed and documented in the narrative, if required.

1.2.4 Another example is the review of all sample chromatograms for analytes which may not show up on the sample quantitation report due to data system error or retention time shift. All peaks should be examined and evaluated based on the retention times and sample concentration in order to prevent reporting false negatives.

1.3 Sample Collection, Sample Storage, Holding Times

1.3.1 Samples are collected in amber glass containers with Teflon-lined caps. All samples and sample extracts are stored at 4°C ±2°C. According to guidelines listed in SW-846 for the extraction of semivolatile compounds, water samples must be extracted within 7 days of collection, and soil samples must be extracted within 14 days of collection. All extracts must be analyzed within 40 days of sample preparation.

1.3.2 Although not a routine sampling practice, a soil holding time study performed by the U.S. Army Cold Regions Research and Engineering Laboratory recommends a maximum holding time of eight weeks when samples are frozen.

1.3.3 A similar study performed for water samples recommends a maximum holding time of 50 days for relatively sterile samples which are refrigerated. Surface waters, or samples likely to have significant microbial activity, may suffer significant losses of nitroaromatic compounds (particularly trinitrobenzene and trinitrotoluene) within 1-2 days, even under refrigeration. If microbial activity is suspected, water samples should be extracted as soon after collection as is practical.

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.

Method 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 injected at some prescribed frequency during the analysis sequence to determine whether the instrument has remained in calibration.
CF	Calibration factor. The ratio of peak response to nanograms injected. This term is defined in the same way in both the CLP contract and SW-846.
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	An instrument blank is solvent containing the method surrogates and is injected into the instrument to monitor for carryover between sample extract injections.
ICV	Initial calibration verification. It is a standard which 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 at Laucks.
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 injection of one or more standards, followed by sample extracts, and terminated with a standard injection. A QC period can be open-ended chronologically, but calibration verification must be documented using the procedures in this SOP.
Reporting Limit	Also known as PQL, or Practical Quantitation Limit. This is determined the by low level standard concentration.
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. 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 the LC 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 and standard solutions injected into an instrument in a chronologically continuous group. See also QC period.

2. Equipment List and Standards

2.1 Chromatographic System

Primary Column:	C18 (octadecyl) reverse phase HPLC column, 15 cm x 4.6 mm, 5 µm particle size, (Rainin Microsorb or equivalent).
Secondary Column:	CN (cyano) reverse phase HPLC column, 25 cm x 4.6 mm, 5 µm particle size, (Supelcosil LC-CN or equivalent).
	C8 and CN reverse phase HPLC columns in series, 10cm x 3.9mm, 4µm particle size, (Waters Nova- Pak or equivalent). These are used for the analysis of the 6 additional attenuation compounds.

Mobile Phase:	Methanol (EM Science brand high purity solvent or equivalent). Reagent water (Modulab Polisher HPLC grade water or equivalent).
UV Detector:	254 nm (210 nm for NG and PETN)
HPLC System:	Rainin HPLC system - HPXL solvent delivery system capable of achieving 4000 psi. 50 µL sample loop. Knauer variable wavelength UV detector. Dynamax automatic sample injector. Digital integrator: EZChrom.
Waters System:	Waters 712 WISP Sample Processor or equivalent. 50 µL sample loop or equivalent. Waters 486 tunable absorbance detector or equivalent. Waters 600E Multisolvent delivery system or equivalent. Digital Integrator: EZChrom.
Hewlett Packard System:	HP 1313A Autosampler. HP G1311A QuatPump. HP G1322A On-line degasser. HP G1316A Thermostat column compartment. HP 1314A Variable wavelength detector. Digital Integrator: EZChrom.

2.1.1 Column Temperature Control:

2.1.2 Column temperature is controlled through the use of a column heater which is maintained at a temperature of 25°C.

2.2 Standards

2.2.1 Target Analyte Stock Solution

2.2.1.1 The stock solution used contains the 14 standard compounds in the mix at a concentration of 1000 µg/mL and is generally purchased from AccuStandard Inc. (25 Science Park, New Haven CT 06511). Equivalent solutions from this or other vendors are also acceptable.

2.2.1.2 The NG and PETN stock solutions are purchased individually from AccuStandard, Inc. (25 Science Park, New Haven, CT 06511). The NG solution comes in 1 mL ampules at 4000

µg/mL in ethanol. The PETN solution comes in 1 mL ampules at 1000 µg/mL in methanol. Equivalent solutions from this or other vendors are also acceptable.

2.2.1.3 The 3,5-Dinitroaniline and 1,3,5-Trinitroso-1,3,5-hexahydrotriazine standards are made from standard analytical reference materials obtained from the U.S. Army Environmental Center (Aberdeen Proving Ground, MD 21010). The 2,4-Diamino-6-nitrotoluene, 2,6-Diamino-4-nitrotoluene and 2,2',6,6'-Tetranitro-4,4'-azoxytoluene standards are made from standard analytical reference materials obtained from AccuStandard, Inc. (25 Science Park, New Haven, CT 06511). The 1-Nitroso-3,5-dinitro-1,3,5-hexahydrotriazine standards are made from standard analytical reference materials obtained from Stanford Research.

2.2.1.4 Calibration standard, surrogate stock and IBLK surrogate solutions are detailed in Appendix I.

2.2.2 Surrogate Stock Solution

2.2.2.1 The surrogate stock solution is received in a methanolic solution at a concentration of 1000 µg/mL. The surrogate can also be prepared by weighing 100 mg of 1,2-dinitrobenzene into a 100 mL volumetric flask and diluting to volume with methanol to yield a concentration of 1000 µg/mL.

2.2.3 IBLK Working Solution

2.2.3.1 The working instrument blank solution contains the surrogate compound only at a concentration of 2.0 µg/mL. Prepare this solution by adding 100 µL of the 1000 µg/mL surrogate stock solution to a 50 mL volumetric flask. Dilute to volume so that the final solvent concentration is methanol/water at a ratio of 1:1.

2.2.4 Working Calibration Standards

2.2.4.1 Prepare the working calibration standards for the 14 standard analytes in the following manner. All solutions are prepared in acetonitrile and diluted 1:1 with water just prior to analysis. These 14 analytes are combined into one working solution, since they do not co-elute on the primary column.

Standard	Source Solution	Amount Added (mL)	Final Volume (mL)	Final Concentration (µg /mL)
Standard #6	A	0.2	10	20.0
	B	0.2		
Standard #5	C	2.5	10	5.0
Standard #4	C	0.1	2	1.0
Standard #3	C	0.05	2	0.5
Standard #2	C	0.01	2	0.1
Standard #1	C	0.005	2	0.05

Source Solution	Concentration (µg /mL)
A = 14 Component Mix	1000
B = Surrogate Stock Solution	1000
C = Standard #6	20.0

2.2.4.2 Prepare the working calibration standards for the 6 additional analytes in the following manner. All solutions are prepared in acetonitrile and diluted 1:1 with water just prior to analysis.

Standard	Source Solution	Amount Added (mL)	Final Volume (mL)	Final Concentrations (µg /mL)
Standard #6	A	2.0	10	20.0
	B	0.2		
	C	0.2		
	D	0.2		
	E	0.2		
	F	2.0		
Standard #5	H	2.5	10	5.0
Standard #4	H	0.5	10	1.0
Standard #3	I	1.0	10	0.5
Standard #2	J	1.0	10	0.1
Standard #1	K	1.0	10	0.05

Source Solution	Concentration (µg/mL)
A = MNX	100
B = TNX	1000
C = 3,5-DNA	1000
D = 2,6-DA-4-NT	1000
E = 2,4-DA-6-NT	1000
F = 4,4'-TN-AZOXY	100
H = Standard 6	20.0
I = Standard 5	5.0
J = Standard 4	1.0
K = Standard 3	0.5

2.2.4.3 Prepare the working calibration standards for PETN/NG in the following manner. All solutions are prepared in a 1:1 acetonitrile/water mixture.

Standard	Source Solution	Amount Added (mL)	Final Volume (mL)	Final Concentrations NG:PETN:1,2-DNB (µg /mL)
Standard #5	A	0.20	10	20.0
	B	0.10	10	10.0
	C	0.10	10	10.0
Standard #4	D	0.25	0.5	10.0, 5.0, 5.0
Standard #3	D	0.125	0.5	5.0, 2.5, 2.5
Standard #2	D	0.025	0.5	1.0, 0.5, 0.5
Standard #1	D	0.025	1.0	0.5, 0.25, 0.25

Source Solution	Concentration (µg/mL)
A = Nitroglycerin	1000
B = PETN Solution	1000
C = Surrogate Stock Solution	1000
D = Standard 5	As Above

2.2.4.4 Note: Store all standard and surrogate solutions in amber glass vials with screw caps and Teflon-lined septa. Minimize headspace in these vials and store them in a refrigerator kept at 4°C ±2°C. Allow standards to come to room temperature prior to use.

2.2.4.5 Stock solutions may be used for up to one year, and working solutions are good for at least six months, or the expiration date of the parent standard, whichever is sooner.

2.2.4.6 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 standards.

3. Safety precautions

3.1 Routine Safety Precautions

3.1.1 All standards and sample extracts should be handled as if they are hazardous substances.

3.1.2 All compounds analyzed by this method are used either in the manufacture of explosives or are the degradation products of these compounds. When making stock solutions for calibration, treat each explosive compound with caution.

3.1.3 Refer to the instrument manufacturer's manual for routine instrument precautions.

3.1.4 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.

3.1.5 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.

3.1.6 Almost all of the analytes under consideration are known or suspected carcinogens. Analysts should wash their hands after using any standard, solvent or sample extract. Additionally, a respirator should be worn or a fume hood utilized for extremely hazardous compounds or very dirty extracts.

3.2 Waste disposal

3.2.1 Out of date standards and sample extracts are disposed of in the designated organic waste container located in the organic preparation area.

3.2.2 HPLC liquid waste is disposed of by pouring into the designated organic waste container located in the solvent storage area.

4. Operation procedures

4.1 Analytical Conditions

4.1.1 Current C18 Column Conditions for the 14 Compounds:

HPLC3		HPLC4	
Pump A Solvent:	Methanol	Solvent:	Methanol/Water
Pump B Solvent:	Water	Flow:	0-31 min = 0.75 mL/min
Flow:	0.65 mL/minute:		31-48 min = 1.80 mL/min
Gradient:	Linear		48-50 min = 0.75 mL/min
Run Time:	30 minutes	Run Time:	50 minutes
Acquisition Time:	30 minutes	Acq. Time:	50 minutes
Injection Volume:	50 µL inj.	Time:	50 µL

4.1.2 Current CN/Column Conditions for the 14 Compounds:

HPLC4 File #12:

Pump B Solvent:	Water/0.05% H_3PO_4 buffer
Pump C Solvent:	Acetonitrile
Pump D Solvent:	Methanol
Flow:	0.75 mL/minute
Gradient:	Linear
Run Time:	50 minutes
Acquisition Time:	50 minutes

Initial %B	80
Initial %C	10
Initial %D	10

Ramp Time 1:	17 minutes	31 - 48 minutes
Ramp Time 2:	2 minutes	48 - 50 minutes

4.1.3 Current C18 Column Conditions for the 6 Additional Compounds:

Gradient Profile (HPLC3)		**Run Time Profile**
HPLC3 File:	EXTRAS	
Pump A Solvent:	Water	
Pump B Solvent:	Methanol	
Flow:	1.0 mL/minute	
Gradient:	Linear	
Run Time:	53 minutes	
Acquisition Time:	30 minutes	
Initial %A	90	
Initial %B	10	
Gradient 1 %A:	70	
Gradient 1 %B:	30	
Ramp Time 1:	5 minutes	0 - 5 minutes
Hold Time 1 :	0 minutes	
Gradient 2 %A:	50	
Gradient 2 %B:	50	
Ramp Time 2:	3 minutes	5 - 8 minutes
Hold Time 2 :	7 minutes	8 - 15 minutes
Gradient 3 %A:	26	
Gradient 3 %B:	74	
Ramp Time 3:	2 minutes	15 - 17 minutes
Hold Time 3:	13 minutes	17 - 30 minutes
Gradient 4 %A:	90	
Gradient 4 %B:	10	
Ramp Time 4:	2 minutes	30 - 32 minutes
Hold Time 4:	21 minutes	32 - 53 minutes (Column Equilibration)

4.1.4 Current CN/C8 Column Conditions for the 6 Additional Compounds:

Time (minutes)	Flow (mL/min)	% Methanol	% Water
0	1.0	15	85
2.4	1.0	15	85
7.0	1.0	40	60
10.0	1.0	50	50
17.0	1.0	50	50
20.0	1.0	80	20
21.0	0	15	85

4.1.5 Current Column Conditions for NG/PETN:

C18		CN	
Pump A Solvent:	Methanol	Pump A Solvent:	Methanol
Pump B Solvent:	Water	Pump B Solvent	Water
Flow:	0.7 mL/minute:	Flow: 0.7 mL/min	1.2 mL/minute
Gradient:	Linear (1:1)	Gradient:	Linear (1:1)
Run Time:	30 minutes	Run Time:	15 minutes
Acquisition Time:	15 minutes	Acq. Time:	15 minutes
Injection Volume:	50 µL inj.	Time:	50 µL

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 determination of detection limits. 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. MDL studies are performed on both columns. At the time this SOP was written the MDL for the 14 Compounds were between 0.057 mg/kg and 0.64 mg/kg for soils and between 0.071 µg/L and 0.82 µg/L for water. The MDL for the 6 Additional Compounds were between 0.19 mg/Kg and 0.26 mg/kg for soils and between 0.14 µg/L and 0.48 µg/L for water. The MDL for NG/PETN were 0.58 mg/kg and 0.31 mg/kg for soils and 0.16 µg/L and 0.18 µg/L for water respectively.

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.

4.4 Retention Time Windows

4.4.1 It is necessary to establish retention time windows for the method by analyzing standards for all target analytes over at least a 24-hour period. A 24-hour time period may be deemed more appropriate for this analysis because the instrument is not always operated for longer periods when analyzing sample extracts. At least 5 standards must be injected during the 24-hour time period, at about equal time intervals. These standards should be interspersed with real sample extracts in order to mimic actual instrument operating conditions. Tabulate the retention times for all standard compounds and compute the sample (n-1) standard deviations of all the retention times.

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 or whenever the chromatographic method is modified.

4.4.3 In some cases, the retention time window may be modified in order to take into account any pattern shifting. This shift is acknowledged by observation of the surrogate peak behavior and the surrounding CCV standards. If retention time shift has occurred and the possibility of misidentifying peaks exists, then the sample is reanalyzed bracketed by in-control CCV standards.

4.4.4 See the Laucks SOP on determination of retention time windows for more specifics on their determination and use.

4.5 Initial Multi-Point Calibration

4.5.1 Analyze standard solutions (including the surrogate solution) using at least 5 different concentration levels. The lowest concentration defines 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. Criteria for evaluating these standards are detailed in Section 6.

4.6 Initial Calibration Verification

4.6.1 At the beginning of an analysis sequence, analyze the mid-point calibration standard (STD 3). The computed calibration factor (CF) or concentration measurement must meet the criteria detailed in Section 6.

4.6.2 Since the retention time windows which were established by the retention time study are relative and not absolute, the windows are anchored by the ICV. This allows the retention times from the ICV to become the mid-point of the retention time windows.

4.7 Instrument Blank

4.7.1 After the analysis of Standard 5, an instrument blank (IBLK) is analyzed. This is to verify that there is no carryover between sample injections. Evaluation criteria are detailed in Section 6.

4.7.2 Any sample that is suspected of containing high concentrations of target analytes should be followed by an IBLK. This IBLK analysis is used only to make a judgment as to the possibility of carryover into the sample analysis immediately following the IBLK. Evaluation criteria are detailed in Section 6.

4.8 Continuing Calibration Verification

4.8.1 A mid-range calibration standard (STD 3) is analyzed after every ten sample injections. In addition, this standard must be the last injection made in the analysis sequence. Evaluation criteria are detailed in Section 6.

4.9 Sample Analysis

4.9.1 Analysis sequence

See Appendix II for a detailed analysis injection sequence.

4.9.2 Sample Preperation

4.9.2.1 Prior to injection on the instrument water sample extracts are diluted 1:1 with water. Any extract that exceeds the instrument calibration range is diluted with 1:1 acetonitrile and water with a dilution factor necessary to quantitate the analytes within the instruments calibration range.

4.9.3 Compound Identification

4.9.3.1 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 retention time window on a second column. Currently, separation of the ordnance compounds is achievable. However, when there are analyte co-elutions on the secondary column, the responses are no longer summed. Instead, separate individual standards are analyzed and the sample results are still flagged appropriately. All analyte quantitations come from the C18 column. The CN/C8 columns in

series are typically not used for quantitation purposes. Retention time windows are established as previously described and are updated each QC period. Compounds can only be identified if the ICV and CCV criteria detailed in Section VI are strictly adhered to. Due to constraints of the software, the RT of the co-eluting compounds is determined by assigning the RT to the highest point within a give window. For the co-eluting compounds that may have a slight but not complete separation, such as: 2-nitrotoluene, 3-nitrotoluene and 4-nitrotoluene, this determination of RT can result in RT windows which exceed those identified by the standard (due to the changes in peak heights with concentration values). In order to avoid potential exceedance of RT windows, and in order to accurately identify these co-eluting target analytes, the retention time windows may be administratively set for the co-eluting compounds.

4.9.3.2 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.

4.9.4 Compound Quantification

4.9.4.1 Target compound concentrations are calculated using the following equations:

4.9.4.2 Aqueous samples

The external standard equation, as expressed in SW-846 is

$$Concentration(\mu g / L) = \frac{A_x \times A \times V_t \times D}{A_s \times V_i \times V_s}$$

where:

A_x = Response for the analyte in the extract, in area or height units.
A = Amount of standard injected (in nanograms).
A_s = Response for the external standard, same units as A_x.
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 an extract is diluted 10 µL to 1000 µL and subsequently diluted an additional 10 µL to 1000 µL, the expression is: (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.

4.9.4.3 In routine use at Laucks, the equation reduces as follows.

4.9.4.4 First, CF is used directly in the equation. Since $Cf = A_s/A$, this substitution is made. Next, since Laucks routinely measures all final extract volumes in mL, a conversion factor for µL to mL must be made in the numerator of the expression - i.e., $V_t = 1000 * mL$. Finally, the sample preparation process is represented as the algebraic ratio of initial sample size to final extract volume.

4.9.4.5 The equation then becomes

$$Concentration(\mu g / L) = \frac{1000 \times Ax \times D}{CF \times Vi \times (Vs / Vt)}$$

4.9.4.6 This expression is completely equivalent to the SW-846 equation, yielding the same final result. To report concentrations in alternate units, apply an appropriate factor:

mg/L = µg/L * 0.001

4.9.4.7 Non-aqueous samples

4.9.4.8 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.

$$Concentration(\mu g / kg) = \frac{1000 \times A_x \times D}{CF \times V_i \times (W / V_t) \times T_s}$$

where:

W_s = Sample size extracted in grams.
T_s = Total Solids in decimal format (i.e. 0.76 not 76).

5. Reports

5.1 Data Packet Organization

See Appendix III for a check list detailing data packet organization.

5.2 Quality Control Reports

5.2.1 All results for quality control tests are entered into the lab 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.

5.3 Data Qualifying Flags/

5.3.1 Sample report results are qualified with data qualifying flags. These flags have the following definitions:

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.
J:	The analyte of interest was detected below the practical quantitation 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 technique is employed, this flag indicates that calculated results from the two columns differ by more than 25 percent.
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.
X:	The sample has been analyzed at several dilutions. The value reported has been determined to be the most appropriate quantitative value.
Z:	The value reported is from the C18 column and there is coelution with another target analyte on the CN or CN/C8 columns in series.

6. Quality Control

See the Requirements and Corrective Actions table in Appendix IV for additional information.

6.1 Initial Calibration

6.1.1 Criteria

6.1.1.1 The initial calibration is evaluated by calculating the %RSD of the calibration factors from the five linearity standards.

6.1.1.2 CFs are calculated using the equation:

$$CF = \frac{\text{response}}{\text{ng injected}}$$

6.1.1.3 This %RSD method assumes a linear response with the calibration curve passing through the origin.

6.1.1.4 The calculated CFs are tabulated and the %RSDs calculated. All compounds must have a %RSD less then or equal to 20% to meet the method criteria.

6.1.2 Corrective action

6.1.2.1 If the %RSD criteria of less then or equal to 20% are not met, the out of control standard should be reanalyzed. If the curve is still out of control, determine the cause of failure and correct. Recalibrate the instrument and reanalyze any samples associated with the out of control curve.

6.2 Initial Calibration Verification

6.2.1 Criteria

6.2.1.1 Using the average CF calculation technique, compute the CFs for each compound. The calibration factors for the ICV standard are compared to the mean CFs for the initial multi-point calibration. The percent difference for these calibration factors is calculated as follows:

$$\%\,Difference = \frac{CF_a - CF_i}{CF_a} \times 100$$

where:
CF_a = .Average CF from the initial multi-point calibration
CF_i = Calibration Factor of the calibration verification standard.

6.2.1.2 The %D cannot exceed 15% for any target analytes or surrogates.

6.2.1.3 The mid-point for the RT window of each compound is updated using the ICV RTs.

6.2.2 Corrective action

6.2.2.1 If the ICV criteria are not met, no sample extracts can be analyzed. Determine the cause of the ICV failure and correct. Reanalyze the ICV and if it is still out of control, a new calibration curve must be analyzed.

6.3 Continuing Calibration Verification

6.3.1 Criteria

6.3.1.1 A CCV standard is analyzed singly for every 10 injections, and after the last sample of the sequence. The CF for each compound is calculated and the percent difference is calculated as shown above.

6.3.1.2 The %D results cannot exceed 15% for any target analytes or surrogates.

6.3.1.3 The retention times for all target analytes must fall within the RT windows established by the ICV.

6.3.2 Corrective action

6.3.2.1 Determine the cause of failure and correct. Reanalyze the calibration curve. All samples bracketed by an out of control CCV must be reanalyzed unless the CCV demonstrates an increase in response and no analytes are detected above the reporting limit in the associated samples.

6.4 Instrument Blank

6.4.1 Criteria

6.4.1.1 There must be no target analyte levels above half the reporting limit in the initial IBLK.

6.4.2 Corrective action

6.4.2.1 If the initial IBLK contains measurable levels of target analytes, the system is out of control. The source of contamination must be identified and corrected.

6.4.2.2 IBLKs are 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 reanalyzed if there is a detectable amount of the analyte found in the IBLK.

6.5 Method Blank

6.5.1 Criteria

6.5.1.1 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 at least one blank for every 20 samples, whichever is more frequent. Analytes of interest should not be detected at levels greater than half the current reporting limit, or less than 5% the regulatory limit, or less than 5% of the sample result for the same analyte. If any analytes are detected above half the reporting limit, corrective action must be taken.

6.5.2 Corrective action

6.5.2.1 Steps shall be taken to find/reduce/eliminate the source of the contamination. Sample corrective action may be limited to qualification for blank contamination. When the concentrations of any target analytes in the method blank are above 1/2 the reporting limit for the majority of target analytes or above the reporting limit for target analytes known to be common laboratory contaminants, the effect this may have had on the samples will be assessed. If any analyte is found only in the method blank, but not in any batch samples, no further corrective action may be necessary. Steps shall be taken to find/reduce/eliminate the source in the method blank. The case narrative should aso discuss the situation. If an analyte is found in the method blank and some, or all, of the other batch samples, additional corrective action is required to reanalyze the method blank and any samples containing the same contaminant. If the contamination remains, the contaminated samples of the batch would be reprepared and

reanalyzed with a new method blank and batch specific QC samples. Sporadic cases of contamination may be difficult to control, however, daily contamination would not be acceptable.

6.6 Blank Spike or QC Check Sample (LCS)

6.6.1 Criteria

6.6.1.1 A blank spike follows the same protocol as the matrix spike analysis except that the spiking solution is added to a method blank solution instead of an actual sample. In addition, this spiking solution is supplied from a source other than the calibration standards. The use of a second source for the spiking standards is employed in order to verify the calibration standards. A method blank with added analytes is a blank spike. At the time this SOP was written the blank spike percent recovery control limits were between 30 and 150. These control limits are updated periodically.

6.6.1.2 These control limits are updated periodically.

6.6.2 Corrective action

6.6.2.1 The blank spike is used to determine whether a method is in control during sample preparation and analysis. Sample re-extraction and reanalysis would be triggered by any analytes falling outside of control limits in the blank spike sample unless all sample surrogate recoveries and MS/MSD spike recoveries are in control.

6.7 Matrix Spike

6.7.1 Criteria

6.7.1.1 A sample is chosen at random (unless designated by project-specific requirements) 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. However, the minimum frequency for MS analysis is 1 each per 20 samples per matrix. This frequency may be changed on a project specific basis. This matrix spike sample is used to evaluate the matrix effect of the sample upon recovery of the analytes. This spiking solution is supplied from a source other than the calibration standards. The use of a second source for the spiking standards is employed in order to verify the calibration standards. The recovery of spike analytes is calculated as follows:

$$\%Recovery = \frac{SSR - SR}{SA} \times 100$$

where:

SSR = Concentration in spiked sample.
SR = Native concentration in unspiked sample.
SA = Concentration of spike added.

6.7.1.2 At the time this SOP was written the matrix spike percent recovery control limits were between 30 and 150. These control limits are updated periodically.

6.7.2 Corrective action

6.7.2.1 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.

6.8 Matrix Spike Duplicate

6.8.1 Criteria

6.8.1.1 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:

$$RPD = \frac{S1 - S2}{(S1 + S2)/2} \times 100$$

where:
S1 = Measured concentration for MS sample.
S2 = Measured concentration for MSD sample.

6.8.1.2 At the time this SOP was written the matrix spike duplicate percent recovery control limits were between 30 and 150. These control limits are updated periodically.

6.8.2 Corrective action

6.8.2.1 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. At the time this SOP was written the RPD control limits was 50 percent. These control limits are updated periodically.

6.9 Surrogate Recovery

6.9.1 Criteria

6.9.1.1 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:

$$\%Recovery = \frac{S_m}{S_a} \times 100$$

where:
S_m = Concentration of surrogate measured in sample.
S_a = Concentration of surrogate added.

6.9.1.2 At the time this SOP was written the surrogate recovery control limits were between 50 and 150 percent. These control limits are updated periodically.

6.9.1.3

6.9.2 Corrective Action

6.9.2.1 Reanalyze the sample. Low surrogate recoveries are greater potential indicators of poor method performance than high surrogate recoveries since non-GC/MS methods cannot separate co-eluting interferents. In instances where high surrogate recoveries are attributable to matrix effects, no corrective action is taken. However, if elevated surrogate recoveries are attributable to preparation error, re-extraction and reanalysis is performed.

6.9.2.2 Check calculations for possible error. Re-extract the sample if surrogate recovery is less than the lower control limit. If a poor injection is suspected, reanalyze the sample.

6.9.2.3 Low surrogate recoveries in the method blank may require that all the samples in the associated batch be re-extracted and reanalyzed. 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.

7. References

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Method 8000B, "Gas Chromatography," Revision 1, July 1992, U.S.E.P.A.

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40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984, U.S.E.P.A.

Special Report 93-11, "Experimental Assessment of Analytical Holding Times for Nitroaromatic and Nitroamine Explosives in Soil," Clarence L. Grant et al, June 1993, U.S. Army Cold Regions Research and Engineering Laboratory.

Special Report 93-24, "Evaluation of Pre-extraction Analytical Holding Times for Nitroaromatic and Nitroamine Explosives in Water," Clarence L. Grant et al, August 1993, U.S. Army Cold Regions Research and Engineering Laboratory.

APPENDIX I

Calibration Standard Solution Concentrations, µg/mL

Compound	STD1	STD2	STD3	STD4	STD5	STD6
HMX	0.05	0.1	0.5	1.0	5.0	20.0
RDX	0.05	0.1	0.5	1.0	5.0	20.0
1,3,5-TNB	0.05	0.1	0.5	1.0	5.0	20.0
1,3-DNB	0.05	0.1	0.5	1.0	5.0	20.0
Tetryl	0.05	0.1	0.5	1.0	5.0	20.0
NB	0.05	0.1	0.5	1.0	5.0	20.0
2,4,6-TNT	0.05	0.1	0.5	1.0	5.0	20.0
4-Am-DNT	0.05	0.1	0.5	1.0	5.0	20.0
2-Am-DNT	0.05	0.1	0.5	1.0	5.0	20.0
2,4-DNT	0.05	0.1	0.5	1.0	5.0	20.0
2,6-DNT	0.05	0.1	0.5	1.0	5.0	20.0
2-NT	0.05	0.1	0.5	1.0	5.0	20.0
3-NT	0.05	0.1	0.5	1.0	5.0	20.0
4-NT	0.05	0.1	0.5	1.0	5.0	20.0
Surrogate						
1,2-Dinitrobenzene	0.05	0.1	0.5	1.0	5.0	20.0

Calibration Standard Solution Concentrations, µg/mL

Compound	STD1	STD2	STD3	STD4	STD5	STD6
TNX	0.05	0.1	0.5	1.0	5.0	20.0
2,6-DA-4-NT	0.05	0.1	0.5	1.0	5.0	20.0
2,4-DA-4-NT	0.05	0.1	0.5	1.0	5.0	20.0
MNX	0.05	0.1	0.5	1.0	5.0	20.0
3,5-DNA	0.05	0.1	0.5	1.0	5.0	20.0
4,4'-TN-AZOXY	0.05	0.1	0.5	1.0	5.0	20.0
Surrogate						
1,2-Dinitrobenzene	0.05	0.1	0.5	1.0	5.0	20.0

Calibration Standard Solution Concentrations, µg/mL

Compound	STD1	STD2	STD3	STD4	STD5
NG	0.5	1.0	5.0	10.0	20.0
PETN	0.25	0.5	2.5	5.0	10.0
Surrogate					
1,2-Dinitrobenzene	0.25	0.5	2.5	5.0	10.0

Surrogate Stock Solution

Compound	Concentration
1,2-Dinitrobenzene	1000 µg/mL

IBLK Solution

Compound	Concentration
1,2-Dinitrobenzene	2.0 µg/mL

APPENDIX II

Analysis Sequence

Injection	Sample
1	Standard #1
2	Standard #2
3	Standard #3
4	Standard #4(ICV Standard)
5	Standard #5
6	Standard #6
7	IBLK
8	ICV
	injections (9-16)
17	IBLK
18	CCV Standard
	injections (19-27)
28	IBLK
29	CCV Standard
	injections (total of 10 injections between CCVs)
last	IBLK
last	CCV Standard

APPENDIX III

Data Packet Order List

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
Chromatogram, primary column
Quantitation Report, primary column
Chromatogram, secondary column
Quantitation Report, secondary column

III. STANDARD DATA:

Linearity Report
ICAL Data
ICAL Response, ICAL std concentrations
ICV reports
CCV reports
Other Standards Used to Support Sample Data and Instrument Blanks

V. Raw QC Data:

Method Blank
Chromatograms
Quantitation Report

Blank Spike
Chromatograms,
Quantitation Report

Matrix Spike
Chromatograms
Quantitation Report

Matrix Spike Duplicate
Chromatograms
Quantitation Report

V. Bench Sheets

SDG Report
Extraction Bench Sheets
Injection Sequence (logbook copy)
Miscellaneous Work Sheets. (%TS, calcs, HTVRs)
Standards Logs

VI. Reject Data:

Data not used to support reported 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 8330 Requirements and Corrective Actions					
QA Element	**Method Criterion**	**Laucks Criterion**	**Frequency**	**Corrective Action**	**Documentation**
Initial Calibration	Minimum of 5 levels.	Minimum of 5 levels. Must demonstrate an RSD of <20%.	As necessary due to major instrument maintenance or difficulties meeting the CCV requirements.	Reanalyze out of control standard. If still out, determine cause of curve failure and correct. Re-analyze curve and any samples analyzed against curve.	Target forms and raw data.
Initial Calibration Verification	+/- 15% of the initial calibration response factor.	+/- 15% of the initial calibration response factor.	Every 24 hr. or at the beginning of an analytical sequence, which ever is more frequent, or as necessary.	Determine cause of ICV failure and correct. Reanalyze ICV and if out of control a new calibration curve must be analyzed.	Target form and raw data.
Continuing Calibration Verification	+/- 15% of the initial calibration response factor. Analyze singly every 10 injections and after the final sample.	+/- 15% of the initial calibration response factor.	Every 10 injections and at the end of an analytical sequence.	Determine cause of failure and correct. Reanalyze calibration curve. All samples bracketed by an out of control CCV must be reanalyzed unless the CCV demonstrates an increase in response and no analytes are detected above the reporting limit.	Target form and raw data.
Instrument Blank	Analyze after analysis of a sample with analyte levels which exceed the upper calibration level.	Analyze instrument blank after samples when high levels of matrix are suspected. Analyze instrument blank before the CCV standard. No target analytes present in the blank > the RL. Surrogate must be within control limit.	Analyze instrument blank after samples when high levels of matrix are suspected. Analyze instrument blank before the CCV standard.	Reanalyze any samples with suspected carryover.	Raw data
Method Blank	All analytes must be < MDL	All analytes must be less than half the Reporting Limit, or <5% regulatory limit, or <5% of the sample result, whichever is greater.	One method blank per 20 samples or each extraction batch, whichever is more frequent.	Reanalyze blank. If still out of control, re-extract the entire batch of samples unless the detected analyte(s) are not present in the associated samples.	Method Blank Summary and raw data. Narrative comment when necessary.

Method 8330 Requirements and Corrective Actions					
QA Element	**Method Criterion**	**Laucks Criterion**	**Frequency**	**Corrective Action**	**Documentation**
Surrogate Recovery	Minimum of 1 surrogate. Recoveries must fall within the labs established windows.	See latest version of Laucks Testing Labs control limits database. All surrogate recoveries must fall within the generated limits. If laboratory limits are not established due to the implementation of a new surrogate , the default limits of 70% - 130% are used until enough data points are collected to generate new limits.	All samples, method blanks, and QC samples.	Re-extract if surrogate recovery is < the lower control limit. If a poor injection is suspected reanalyze the sample.	Target Surrogate Summary form or special test results. Narrative comment when necessary.
MS/MSD	One per 20 samples or extraction batch which ever is more frequent. Must be per matrix.	See latest version of Laucks control limits located in the QC database.	1 MS/MSD pair per 20 samples or every extraction batch which ever is more frequent.	Per SW 846, if analyte recoveries are out of control in the MS/MSD but are in control in the associated blank spike, no further action is required.	MS/MSD report and raw data. Narrative comment when necessary.
Blank Spike	N/A	See latest version of Laucks Testing Labs control limits in the QC database. All recoveries must fall within the generated limits.	1 per 20 samples or every extraction batch which ever is more frequent.	Re-extract if analyte recoveries are outside of control limits.	Blank Spike report and raw data. Narrative comment when necessary.

APPENDIX V

Elution Order of Target Analytes

Compound	Order of Elution on Primary (C18) Column	Order of Elution on Confirmation (CN/C8) Column
HMX	1	15
RDX	2	11
1,3,5-TNB	3	2
1,3-DNB	5	3
Tetryl	6	14
NB	7	1
2,4,6-TNT	8	9
4-Am-DNT*	9	12
2-Am-DNT*	10	13
2,4-DNT	12	7
2,6-DNT	11	8
2-NT*	13	4
3-NT*	15	5
4-NT*	14	6
Surrogate		
1,2-Dinitrobenzene	4	10

Elution Order of 6 Additional Analytes

Compound	Order of Elution on Primary (C18) Column	Order of Elution on Confirmation (C8/CN) Column
TNX	3	1
2,6-DA-4-NT	2	2
2,4-DA-6-NT	1	3
MNX	4	4
3,5-DNA	5	5
4,4'-TN-AZOXY	7	6
Surrogate		
1,2-Dinitrobenzene	6	5

Elution Order of PETN/NG

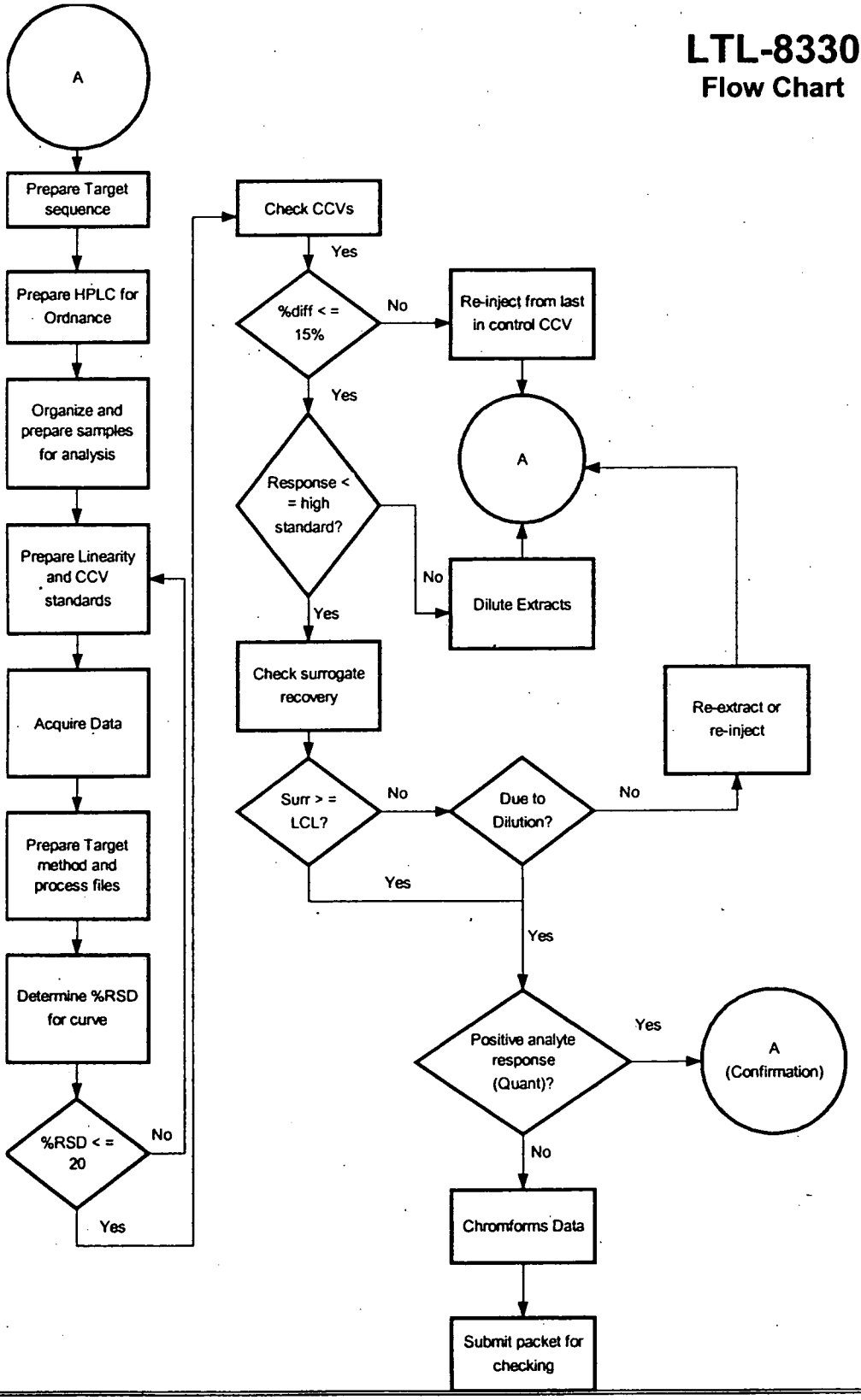
Compound	Order of Elution on Primary (C18) Column	Order of Elution on Confirmation (CN) Column
NG	2	2
PETN	3	3
Surrogate		
1,2-Dinitrobenzene	1	1

*Indicates the compound co-elutes on the confirmation (CN) column.

APPENDIX VI

Method 8330 Flow Chart

LTL-8330
Flow Chart



LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP : LTL-9104

Title: **Preparation and Analysis of Total and Amenable Cyanide according to EPA Methods 335.1, 335.3, and SW 846 Method 9012A.**

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AUTOANALYZER FLOW DIAGRAM 25

1. Introduction and Scope

1.1 Method Description

1.1.1 Cyanide in samples is determined by a preparation with manual (SW846 Method 9012A) or online distillation (Method 335.3) followed by an automated spectrophotometric analysis on an auto analyzer with a UV digester. The routine reporting limit is 10 µg/L in waters, and 0.50 mg/kg DB in soils and sediments. Pretreatment for the determination of cyanides amenable to chlorination (Method 335.1) in waters is also included in this SOP.

1.1.2 This SOP is applicable to the sample preparation and analysis of cyanide in drinking waters, surface and saline waters, domestic and industrial wastes according to EPA methods 335.1, 335.3 and SW846 Method 9012A with the main difference being the use of the in-line still and UV digestion in EPA 335.3. Also, MIDI distillation with a 50 mL water sample instead of the normal distillation of a 500 mL sample is used in this SOP. Other differences from 9012A are listed on the QA chart at the end of this SOP. Soils and sediments are MIDI distilled as a 1 g sample.

1.1.3 This method is restricted to use by, or under the supervision of analysts experienced in the technique described and in SW846 methodology. Each analyst performing this method must have demonstrated the ability to perform the described analysis.

1.2 Method Deviations and Comments

1.2.1 The following items represent deviations of Method 9012A, as published, which are followed as standard operating procedures in the performance of this method at Laucks:

1.2.1.1 The MIDI distillation procedure is used, exactly as written in the CLP statement of work. This distillation uses a 50 mL aliquot of sample and a final distillation volume of 50 mls. This procedure allows the lab to use less sample, and dispose of smaller volumes of waste material. All molar ratios in this distillation are identical to the method as written.

1.2.1.2 The calibration curve specified in 9012A is reduced by 2 to compensate for the lack of sample concentration in the distillation step.

1.3 Method Summary

1.3.1 **Sample Preparation:** The MIDI distillation procedure applies to relatively solid samples such as soils, sediments and sludges, or, if requested, to water samples. Cyanide determined by this method is defined as cyanide ion and complex cyanides converted to hydrocyanic acid by reaction in a reflux system with mineral acid in the presence of magnesium ion. The cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by means of a MIDI reflux-

distillation operation and absorbed in a scrubber containing sodium hydroxide solution. The cyanide in the distillate is then determined in a spectrophotometric analysis.

1.3.2 Water samples analyzed under EPA 335.3 are not externally distilled and are directly analyzed unless otherwise requested.

1.3.3 **Spectrophotometric Analysis:** On a Technicon auto analyzer, the samples are acidified and passed through a UV digester and then distilled in-line. The cyanide released is converted to cyanogen chloride, CNCl, by reaction with chloramine-T at pH less than 8 without hydrolysis to the cyanate. After the reaction is complete, color is formed on the addition of pyridine-barbituric acid reagent. The absorbance is read at 570 nm. To obtain colors of comparable intensity, it is essential to have the same salt content in both the samples and the standards.

1.4 Sample Handling, Sample Storage, Holding Times

1.4.1 Samples are preserved with 8 pellets of sodium hydroxide per liter of sample (pH > 12) at the time of collection. Samples must be stored at 4°C ± 2°C and must be analyzed within the specified holding time of 14 days from date of collection. The samples can be submitted in either plastic or glass containers. The pH is checked at the time of sample receipt and at the time of analysis and the client should be notified if the pH is less than 12.

1.4.2 Samples are to be checked for chlorine interference at the time of collection and the appropriate action should be taken.

1.5 Interferences

1.5.1 Sulfide interference: Some sulfides convert CN^- to SCN^-. Add cadmium carbonate to sample until lead acetate test paper no longer darkens (treat 25 mL more than is necessary for the distillation). Yellow cadmium sulfide precipitates if the sample contains sulfide. Avoid a large excess of cadmium carbonate and a long contact time in order to minimize a loss by complexation or occlusion of cyanide on the precipitated material. Filter sample through a dry filter paper into a dry container then proceed with the distillation procedure. A narration is included in the final report. Run a standard treated in the same manner with the treated samples.

1.5.2 Chlorine interference: Chlorine decomposes most cyanides. Add ascorbic acid to the 50 mL sample ~0.02 g at a time until KI-starch test paper no longer turns bluish then add an additional 0.02 g of ascorbic acid. Proceed with the distillation procedure. A narration is included in the final report.

1.5.3 NO_3 / NO_2 interference: Nitrates and/or nitrites can form oximes with organic compounds which can decompose under test conditions to form HCN. If high levels are suspected (e.g. fertilizers) then sulfamic acid is added to the sample to remove the interference.

1.5.4 Surfactants. For manual distillation, the presence of surfactants, detergents or fatty acids may cause the sample to foam during refluxing. If this occurs, add an antifoam agent such as Baker Antifoam B Silicone Emulsion.

1.5.5 Interferences are eliminated or reduced by the distillation procedure

1.5.6 Thiocyanates are a positive interference. During the UV Digestion thiocyanates are decomposed to cyanide.

1.6 Definition of Terms

1.6.1 This section defines terms and acronyms as they are used in this SOP. Other terms 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 only preceded by an "A" rather than a "B" for inorganic batches. The preparation batch IDs are discussed in other documentation. The batch identifier for the second set of water samples analyzed on Feb 6, 1998 would be A020698AA1W02.

CCB - Continuing Calibration Blank - This is the same acronym used in the CLP program. This is a blank which is analyzed immediately after the CCV (almost always after every 10 samples and at the end of the analytical run) during the analysis sequence to determine whether the instrument or system has maintained a stable baseline.

CCV - Continuing Calibration Verification. - This is the same acronym used in the CLP program. This is a standard analyzed at some prescribed frequency (almost always after every 10 samples and at the end of the analytical run) during the analysis sequence to determine whether the instrument or system has remained in calibration.

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 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, r - 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. This water should be free of virtually all analytes.

ICB - Initial calibration blank - This term is borrowed from CLP. An instrument blank is made up in the same way as calibration standards, without target analytes.

ICV - Initial calibration verification - This term is borrowed from the CLP protocol. It is a standard which is analyzed at the start of each analytical run and compared to the initial calibration to determine whether the instrument calibration is accurate.

MDL - Method detection limit - The lowest concentration a sample which will yield a positive result that is greater zero at a known level of confidence. MDLs are empirically determined by Laucks.

SRM or LCS - Standard Reference Material or Laboratory Control Sample. This is a material of approximately the same matrix as the samples, containing a known and usually certified amount of target analyte and which is prepared and analyzed in the same manner as a typical sample. This sample is used to demonstrate that the analytical system is in control.

QC period - Quality control period - An analysis sequence initiated by the analysis of one or more standards, followed by samples, and terminated with a standard and blank analysis. A QC period can be open-ended chronologically, but calibration verification must be documented using the procedures in this SOP

Sequence - A set of sample extracts and standard solutions injected into an instrument in a chronologically continuous group. See also QC period.

2. Equipment, Reagents, and Standards

2.1 Equipment

2.1.1 Required instrumentation includes the following:

2.1.1.1 Midi reflux distillation system with heating block capable of maintaining 125°C ± 5°C. We use the MIDI-VAP model MC-100 ("CYN-TEN").

2.1.1.2 Technicon Auto-Analyzer with in-line distillation unit and UV digester.

2.1.1.3 Any laboratory PC equipped with Excel and the Cyanide template may be used for calculation of data.

2.2 Reagents

2.2.1 0.25 N NaOH: dissolve 10.0 g NaOH pellets in 1 L DIW. CAUTION: this reagent will get hot upon mixing!

2.2.2 $MgCl_2$ solution: dissolve 510 g $MgCl_2 \cdot 6H_2O$ and dilute to 1 L with DIW.

2.2.3 1:1 H_2SO_4: carefully and slowly add with mixing 500 mL of conc. H_2SO_4 to 500 mL of DIW. CAUTION: this reagent will get **EXTREMELY** hot upon mixing! Mix in a Pyrex or equivalent container! **DO NOT ADD WATER TO ACID!**

2.2.4 Phosphate buffer: dissolve 13.6 g monobasic potassium phosphate (KH_2PO_4) and 0.28 g anhydrous dibasic sodium phosphate (Na_2HPO_4) and dilute to 1 L with DIW.

2.2.5 Chloramine -T solution: dissolve 1.0 g in 250 mL of DIW. Prepare this reagent fresh daily.

2.2.6 Color reagent: place 15 g of barbituric acid in the bottom of a container, and rinse down the sides of the container with DIW. Add 100 mL of DIW and swirl gently. Add 75 mL of pyridine and mix. Add 15 mL of conc. HCl, mix, and cool. Dilute to 1 L with DIW. This reagent should be stored at 4°C. This reagent should be made under a hood.

2.2.7 Distillation reagent: to 500 mL of DIW add 250 mL conc. H_3PO_4 and 50 mL 50% H_3PO_2 and then dilute to 1 L with DIW.

2.2.8 Sodium Hypochlorite solution: Commercial bleach such as Clorox (5.5%).

2.3 Standards

2.3.1 KCN stock cyanide solution for standards and spiking, 100 mg/L CN. Place 0.2510 g of KCN and approx. 1.5 g NaOH in a 1.0 L volumetric flask and dissolve. Dilute up to the mark with DIW. Record this standard in a standards logbook. The stock standard is good for one year.

2.3.2 Intermediate cyanide standard solution, 1.00 mg/L CN. Dilute 1.0 mL of stock standard solution 2.3.1 to 100 mL with 0.25 N NaOH. Prepare fresh solution at least weekly and record in a standards logbook.

2.3.3 Blank solution for zero standard, blanks and diluting samples and standards: Dilute 200 µL 10 N NaOH to 100 mL with DIW. Prepare fresh solution at least weekly and as needed.

2.3.4 Calibration standards:

2.3.4.1 Method 9012A

Concentration (mg/L)	µLs of 2.3.2	Final volume (mL)
0.200	1000	5.0
0.150	750	5.0
0.100	500.	5.0
0.050	250.	5.0
0.020	100	5.0
0.010	50.	5.0
0	0	5.0

All standards should be diluted up to final volume with 2.3.3 Blank solution. Standards are consumed during analysis so prepare fresh standards for each analytical run.

2.3.4.2 Method 335.3

Concentration (mg/L)	µLs of 2.3.2	Final volume (mL)
0.250	1250	5.0
0.100	500	5.0
0.050	250	5.0
0.010	50	5.0
0	0	5.0

All standards should be diluted up to final volume with 2.3.3 Blank solution. Standards are consumed during analysis so prepare fresh standards for each analytical run.

2.3.5 SRM/ICV stock solution: dissolve 0.2115 mg potassium ferricyanide ($K_3Fe(CN)_6$) and approximately 1.5 g NaOH in DIW and dilute to 1 L in a volumetric flask. This stock standard has a cyanide concentration of 100 mg/L and should be stored at 4°C ± 2°C. This standard expires after one year.

3. Safety Precautions

3.1 Refer to the Laucks SOP on lab safety practices and the instrument manufacturer's manual for routine instrument precautions.

3.2 All standards, samples and sample solutions should be handled as if they are hazardous substances. Some forms of cyanide can be released as a gaseous form upon acidification. Treat all samples as if they definitely contain cyanide.

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.

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.

3.5 Sodium hydroxide and sulfuric and phosphoric acid are extreme irritants if they come in contact with skin or eyes. When using these chemicals, the analyst should wear gloves and safety glasses.

3.6 The color reagent (containing pyridine) should be prepared under a hood.

4. Calibration and Quality Control

4.1 Method Detection Limit Study

4.1.1 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 determining detection limits. Briefly, it involves the analysis of 7 replicate samples spiked at a concentration 1-5 times the anticipated method detection limit. A Student's T-test is then applied to these measured values to calculate the MDL. The LTL estimated water MDLs are 0.002 mg/L for EPA method 335.3 and SW846 method 9012A and 0.3 mg/Kg for SW846 method 9012A for soils.

4.2 Initial Multi-Point Calibration

4.2.1 The calibration standards listed in section 2.3.4 should be analyzed in order. This calibration MUST IMMEDIATELY PRECEDE sample analysis.

4.2.2 The highest standard used in the linear regression calculation defines the upper usable working range of the instrument. Any sample concentration value that exceeds the concentration of this high standard must be diluted with blank solution and reanalyzed.

4.2.3 Criteria

4.2.3.1 Initial calibration data is evaluated using the correlation coefficient of a linear regression analysis. The linear correlation coefficient must be 0.995 or greater. All CCVs and sample concentrations must be computed using the regression equation.

4.2.4 Corrective action

4.2.4.1 If the criteria are not met the instrument must be recalibrated. No data may be reported for an analyte that does not have a valid calibration.

4.2.5 Calibration for samples containing sulfide

4.2.5.1 Five standards of similar concentration to those in section 2.3.4 should be distilled in the same manner as samples, adding similar amounts of cadmium carbonate to all standards.

4.3 Initial Calibration Verification

4.3.1 At the start of each analytical run, analyze a standard from a source other than that from which the calibration material was obtained.

4.3.2 For method 335.3, the ICV/SRM is prepared by diluting 0.010 mL of Potassium Ferricyanide stock solution to 10 mL with blank solution.

4.3.3 For SW846 Method 9012A, the ICV/SRM is prepared by spiking 250uL of Potassium Ferricyanide stock solution to 50 mL of DIW and distilling along with the samples. The distillate is diluted by a factor of 10 at the instrument.

4.3.4 This standard must be prepared with every 20 samples or with every batch, whichever is more frequent. Only the first ICV/SRM is considered an ICV for the analysis.

4.3.5 Criteria

4.3.5.1 The calculated concentration of the ICV/SRM must be within the limits supplied by the manufacturer or not to exceed ±15% of the true value.

4.3.6 Corrective action

4.3.6.1 If the ICV criteria are not met, no samples can be analyzed. Perform system maintenance and re-check the ICV. If the criteria still cannot be met, the system must be recalibrated. No data can be reported for an analyte that does not have a valid ICV.

4.4 Initial Calibration Blank

4.4.1 After the analysis of the ICV standard an instrument blank (ICB) is analyzed. The levels of target analytes in the ICB should not exceed ½ of the reporting limit.

4.4.2 Corrective action

4.4.2.1 If the ICB contains target analyte levels above ½ of the reporting the system is considered to be out of control. The source of contamination must be identified and corrected

before proceeding with the analysis. No data can be reported for an analyte that does not have a valid ICB.

4.5 Blank Spikes

4.5.1 For Method 9012A, standards spiked with 10µL and 50µL of the 100mg/L KCN stock standard are distilled with every batch. These standards are analyzed immediately following the ICB. These standards must agree within ± 10% of the undistilled standard before continuing analysis. If the standards do not meet this criteria, the cause of the error should be found before proceeding.

4.6 Method Detection Limit Standard

4.6.1 After the analysis of the ICV and the ICB, but before the analysis of any sample extracts, an MDL standard is to be analyzed. The MDL standard is used to provide on-going verification of the ability of the system to detect analytes at a concentration near the method detection limit. The MDL standard should read between 67% and 220% of the true value. This limit may be overlooked if the recovery of this check standard is high. It must, however, be detected for the system to be considered in control.

4.6.2 Corrective Action

4.6.2.1 If target analytes are not detected, the analysis must be terminated until the problem has been solved. Alternatively, if the affected samples are well above the detection limit (i.e. bracketed by appropriate standards), they may be reported. No undetected values should be reported if the MDL standard for that analyte(s) is undetected.

4.7 Continuing Calibration Verification (CCV) and Blank (CCB)

4.7.1 A mid-range calibration standard is analyzed at a minimum of once every 10 sample injections. Immediately following the CCV, a blank solution is analyzed. In addition, at the end of the run, this standard should be run at a different level than preceding CCVs to verify that the curve has remained linear throughout the analysis. A CCB should follow this final CCV.

4.7.2 Criteria

4.7.2.1 The CCV must fall within ± 15% of the true value.

4.7.2.2 The levels of target analytes in the CCB should not exceed ½ of the reporting limit.

4.7.3 Corrective action

4.7.3.1 If CCV limits are exceeded, check calculations or perform instrument maintenance. Recalibrate and reanalyze. No sample results may be reported that are not bracketed by a

successful ICV and a CCV which is in control or by preceding and following CCVs which are within limits.

4.7.3.2 If the CCB contains target analyte levels above ½ of the reporting limit, the system is out of control. The source of contamination must be identified and corrected and the affected samples re-analyzed. As with the CCVs, no sample results may be reported that are not bracketed by a successful initial and continuing calibration blank that are in control or by preceding and following CCBs that are within limits.

4.8 Method Blanks

4.8.1 Method blanks are used to verify contamination free reagents and apparatus. They are prepared with every set of samples prepared at the same time, or at least one blank every 20 samples, whichever is more frequent. Any analyte response above the reporting limit is reported. Method blank control limits are that contamination should not exceed ½ of the reporting limit for waters.

4.8.2 For manual distillation preparation (Method 9012A), the method blank consists of a 50 mL sample of DIW and is used to verify contamination free reagents and apparatus. A Method Blank is distilled every 20 samples or with every batch whichever is more frequent.

4.8.3 For autoanalyzed water samples (Method 335.3), a method blank is analyzed for every 20 samples analyzed. The method blank consists of a sample of blank solution.

4.8.4 Corrective action

4.8.4.1 Corrective action may necessitate re-preparation and re-analysis of the sample set. For example if an analyte were found in the blank but not in any of the associated samples then sample group may not require re-analysis. In addition, if sample levels exceed 10 times the blank, the level of contamination may be considered insignificant. In any case, if re-preparation and re-analysis is not being undertaken, the analyst must first discuss the issue with the Quality Control Officer. It is the laboratory's responsibility to ensure that method interferences caused by contaminants in acids, solvents, reagents, glassware, and other sample processing hardware leading to discrete artifacts and/or elevated baselines in the analytical run 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.

4.9 Matrix Spike/Matrix Spike Duplicate

4.9.1 Project-specific criteria will determine whether MS/MSD or MS/Duplicate analysis is to be performed. MS/MSD Duplicate precision is calculated as in Section 4.9 – precision usually is project-specific.

4.9.2 For manual distillation preparation 10 µL of 100 mg/L CN standard solution is added to the 50 mL of sample prior to distillation, for a spike value of 0.100 mg/L in the 50 mL of distillate.

4.9.3 For autoanalyzed water samples the 10 µL of the 100 mg/L CN standard is added to 10 mL of sample prior to analysis for a spike value of 0.100 mg/L.

4.9.4 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 preparation. The analyst should attempt to avoid selecting samples which are identified by the client as blanks. As the purpose of the matrix spike is to test the system under "typical" conditions, the analyst may also avoid selecting the most difficult sample of the batch for spiking. It is not always required that a matrix spike analysis be performed with each preparation/analysis batch, however, the minimum frequency for MS analysis is 1 each per 20 samples per matrix. This will be best accomplished by running one with every batch for many analyses. 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:

$$\% \text{ recovery} = \frac{(SS - S) * 100}{SA}$$

where: SS = concentration in spiked sample
S = native concentration in unspiked sample
SA = spiked added, the amount of spiking material actually added to the sample calculated on the sample basis

The recovery criteria are detailed in the current in the Quality Control Database and will change from time to time. The current water control limits are 64-135% recovery; the current soil control limits are 50-150% recovery.

4.9.5 Corrective action

4.9.5.1 Samples with spike recoveries outside control limits will be reviewed for possible corrective action. Corrective action will first involve recalculation, followed by possible re-preparation, and/or reanalysis. This process should also look at the recovery of matrix spiking compounds from the SRM and/or blank spike analysis. In all cases a narrative explanation of the condition is required to detail the corrective actions taken.

4.10 Sample Duplicate

4.10.1 Criteria

4.10.1.1 Sample duplicates are required when running CLP practices are employed.. At least one duplicate sample per 20 samples per matrix is required. RPD values are calculated in the following manner:

$$RPD = \frac{|S1 - S2| * 100}{(S1 + S2)/2}$$

where: S1 = measured concentration in the initial analysis
S2 = measured concentration in the duplicate analysis

The RPD control limits are detailed in the Quality Control Database and will change from time to time. The current water control limits are 11% RPD; The current soil control limits are 30% RPD.

4.10.2 Corrective action

4.10.2.1 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. Generally, if recoveries are in control and no analyte of interest was detected in any of the samples, no immediate action will be taken on that sample set. If integrity of reported sample values is in doubt, re-analysis may be called for. Corrective actions should be discussed with the Quality Control Officer.

5. Operation procedures

5.1 Pre-distillation Sample Screen for Waters

5.1.1 Water samples are screened for sulfide and chlorine interferences prior to distillation as follows:

5.1.1.1 Pour a small amount of pH 4 buffer into a 1oz. plastic cup.

5.1.1.2 Check for the presence of sulfide with lead acetate test paper. Wet the paper with pH 4 buffer and then drop ~10 µL of sample onto it. A darkening of the paper indicates the presence of S^{2-}. If present then see Section 1.4 Interferences before proceeding with the distillation.

5.1.1.3 Check for the presence of chlorine with potassium iodide-starch test paper. Wet the paper with pH 4 buffer and then drop ~10 µL of sample onto it. A bluish discoloration indicates the presence of chlorine. If present then see Section 1.4 Interferences before proceeding with the distillation.

5.1.2 Any interferences are noted on the bench sheet.

5.2 Pretreatment for Cyanides Amenable to Chlorination

5.2.1 Two sample aliquots are required for chlorine amenable cyanide determination. One is pretreated, the other is not pretreated. Both are prepped and analyzed and the difference between the two is the cyanide amenable to chlorination.

5.2.1.1 To the sample aliquot designated for pretreatment add bleach solution dropwise until an excess of chlorine is maintained. Test for residual chlorine with KI-starch paper. Paper will turn blue.

5.2.1.2 Maintain excess for one hour with continued agitation using a Teflon stir bar and a stir plate.

5.2.1.3 After one hour, add ascorbic acid in small increments (~0.01 g) until KI-starch paper shows no residual chlorine and analyze.

5.3 Manual Distillation

5.3.1 Samples are distilled using the MIDI distillation method. The distillation procedure is as follows:

5.3.1.1 Remove fritted tubes from absorbers, rinse, and set aside.

5.3.1.2 Rinse out absorbers, and invert to drain.

5.3.1.3 Add 50.0 mL of a liquid sample (or 1.0 g of a solid sample) to a sample tube. For solid samples, dilute with DIW to the 50 mL mark on the tube.

5.3.1.4 Set up sample tubes for the appropriate QC (SRM, Method Blank, MS/MSD), but do not spike the SRM or the MS/MSD samples yet.

5.3.1.5 Add 3-4 boiling stones to each tube.

5.3.1.6 Insert reflux impingers into the sample tubes.

5.3.1.7 Fill the absorber tubes with 50.0 mL of 0.25 N NaOH, and insert the fritted tubes.

5.3.1.8 Place sample tubes in the back row of the heating block, and the absorbers into the front row.

5.3.1.9 Insert the cold-finger condensers into the top of the sample tubes.

5.3.1.10 Hook up all vacuum hoses.

5.3.2 Turn on water flow, and adjust flow meter to approx. the same number of samples that are being distilled (about 9-10 for 10 samples).

5.3.2.1 Plug in the vacuum pump.

5.3.2.2 Stabilize the flow rate at about 3 bubbles per second and wait for about 5 minutes.

5.3.2.3 Spike the SRM and the MS/MSD with the appropriate spiking material.

5.3.2.4 Add 5 mL of 1:1 H_2SO_4 to each tube, and let mix for about 3 minutes.

5.3.2.5 Add 2 mL $MgCl_2$ to each tube, and rinse tubes with DIW.

5.3.2.6 Turn power on, and turn knob to mark.

5.3.2.7 When distillation is complete (10 minutes to heat to reflux, 60 mins of reflux, and 15 minutes of cooling) the heating block will automatically shut itself off. Replace tubes in tube rack, removing the fritted tubes before turning the vacuum pump off.

5.3.2.8 Pour off the liquid from the absorbers into a clean container, label, and store at 4°C if the distillates will not be analyzed immediately.

5.3.2.9 Rinse all glassware with DIW, and store fritted tubes in DIW.

6. Sample Analysis Using a Technicon Auto Analyzer

6.1 Instrument start-up and operation

6.1.1 The auto-analyzer should be set up for cyanide analysis according to the Laucks SOP on configuring the Technicon Autoanalyzer. Turn on power and allow heating bath to reach 150 degrees C while flushing reagent tubes with DIW. After the temperature is reached, place the reagent tubes into their proper reagents. Turn on chart drive motor and allow reagents to flow through completely. When baseline has settled, set baseline at about 90%T.

6.2 Analysis procedure

6.2.1 Prepare the 1.0 ppm working standard and the blank solution

6.2.2 From these solutions make the standard curve in 1 oz plastic cups, swirl and transfer to sampler cups, and load onto sampler.

6.2.3 Immediately after the calibration standards, load an EPA approved LCSW as the ICV. Immediately after the ICV, load the blank solution for the ICB.

6.2.4 Load standards, water samples, and distillates from manual distillation (distillates are analyzed the same as water samples) as in the following example and press the reset button on the autosampler to begin the analysis:

Method 9012A

cup#	cup contains
1	STD 1 0 ppb
2	STD 2 10 ppb
3	STD 3 20 ppb
4	STD 4 50 ppb
5	STD 5 100 ppb
6	STD 6 150 ppb
7	STD 7 200 ppb
8	ICV/LCSW1
9	ICB/PBW1
10	Blank spike low
11	Blank spike high
12	Sample 1
13	Sample 1MS
14	Sample 1MSD
15	Next Sample
16	...
17	CCVx
18	CCBx

Method 335.3

cup#	cup contains
1	Std 1 0.250 mg/L
2	Std 2 0.100 mg/L
3	Std 3 0.050 mg/L
4	Std 4 0.010 mg/L
5	Std 5 0 mg/L
6	ICV/LCSW1
7	ICB/PBW1
8	MDL
9	Sample 1
10	Sample 1MS
11	Sample 1MSD
12	Next Sample
13	...
14	CCVx
15	CCBx

6.2.5 After sampling is finished and the last sample peak has been recorded, turn off the chart drive motor, put reagent tubes into wash and turn off the oil bath heater. Once the oil bath has cooled below 100 degrees C, the instrument can be entirely shut down.

6.3 Compound Quantification

6.3.1 The data for each sample is recorded in strip-chart form. On a bench sheet is recorded the information for each sample such as Sample ID, Cup #, and Dilution. Then the value for the Peak Ht and Baseline, as read from the strip-chart (to the nearest 0.25 units), is recorded for each sample. This data is then entered into a standard spreadsheet (Excel or equivalent) for the calculation of all other values. (An example of the spreadsheet is included in appendix II.)

6.3.1.1 Percent transmittance is calculated from the formula:

$$\%T = \text{Peak Ht}/(\text{Baseline}/100)$$

where the ratio Baseline/100 accounts for baseline drift.

6.3.1.2 Absorbance is calculated from %T by the formula:

$$\text{Abs} = 2\text{-log}(\%T)$$

6.3.1.3 The spreadsheet performs a linear regression including the calibration standards 0 mg/L up to 0.200 mg/L with x being the true value of the standards, and y being their corresponding absorbances.

6.3.1.4 Concentration of CN^- in the samples is calculated from the linear regression curve using the formula y=mx+b. Substituting the sample absorbance as the y value and solving for x (conc. of CN^- in mg/L) and multiplying by the dilution factor, the formula becomes:

conc. of CN^- mg/L = [(Abs. - y intercept) / slope] * dilution

6.3.2 For soil/sludge samples, the mg/L integrator value is converted to mg/Kg DB by the following equation

Soil: $$Cs = \frac{Ci * Vs * 100}{Ws\ TS}$$

Cs = Sample concentration (mg/kg DB)
Ci = Concentration in sample injected (mg/L)
Vs = Volume of extract (mL)
Ws = Weight of sample extracted (gm)
TS = Total solids (represented as decimal)

7. Reports

7.1 Sample Results and Quality Control Reports

7.1.1 Data packages shall consist of the sample results summary, the chromatograms for samples in the workorder, a copy of the calibration curve and standard log book, and a copy of the QC summary report form. These include the method blank analysis, matrix spike results, duplicate results, and the Standard Reference Material (SRM) reports. A copy of the QC summary report form must be included in order to indicate that the QC was evaluated for analytical consistency.

7.2 Data Qualifying Flags

7.2.1 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.
*	: QC limits were exceeded.

Appendix I
Laucks Testing Laboratories
Method 335.1, 335.3 and SW846 9012A QA Requirements and Corrective Actions

QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
Initial Calibration	9012 A: 7 standards plus a blank. r ≥0.995 335.3: No criteria	6 stds plus a blank r ≥0.995 (standards must be distilled if sulfide is found in samples) 4 standards plus a blank r ≥0.995	Beginning of run	Recalibrate if r < 0.995	In raw data.
Initial Calibration Verification / LCSW	Verify calibration every 15 samples with an independently prepared check standard.±15%.	Independent source ±15%.	1 per batch or 1 per 20 samples including one immediately after calibration.	Reanalyze, if reanalysis fails recalibrate and or perform instrument maintenance. No data can be reported if ICV fails.	In the raw data package, and in the quality control data base.
Initial Calibration Blank	No criteria.	less than ½ the reporting limit	1 per run immediately after ICV.	Reanalyze. No data can be reported if ICB fails.	In the raw data package.
Continuing Calibration Verification	Verify calibration with the mid-range standard. Must agree within 15% of true value.	Verify calibration with the mid-range standard. Must agree within 15% of true value.	1 after every 10 samples, and at the end of the run.	Samples which are not bracketed by in control CCVs must be reanalyzed.	In the raw data package.
Continuing Calibration Blank	No criteria.	less than ½ the reporting limit	1 after every 10 samples, and at the end of the run.	Samples which are not bracketed by in control CCBs must be reanalyzed.	In the raw data package.

QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
Method Blank Soil: Water:	 No criteria. No criteria.	less than ½ the reporting limit	1 per batch or 1 per 20 samples.	If sample concentration exceed 10x the contamination level, no action required. Samples with contaminated Method Blanks must be re-prepared and reanalyzed.	In the raw data package, and in the quality control data base.
Matrix Spike (%Rec) Soil: Water:	Run one spike duplicate every 10 samples. No recovery criteria .	Water 64-135% Soil 50-150%	1 per batch or 1 per 20 samples.	Review data, consult QC officer, some conditions may require reanalysis.	In the raw data package, and in the quality control data base.
Matrix Spike Dup. (RPD) Soil: Water:	See MS.	Water 11% Soil 30%	1 per batch or 1 per 20 samples.	Review data, consult QC officer, some conditions may require reanalysis.	In the raw data package, and in the quality control data base.
Distilled SRM (%Rec) (Manually distilled soils and waters only.)	Independent check sample	+/- 15% of true value.	1 per batch or 1 per 20 samples.	Reprep and reanalyze.	In the raw data package, and in the quality control data base.
Distilled Blank Spikes	9012A: two standards, one low, one high 335.3: No criteria	+/- 10% of undistilled standards	2 standards, one high, one low, per batch.	Reprep and reanalyze.	In the raw data package, and in the quality control data base.

Appendix II

Excel spreadsheet used for cyanide calculations.
(example)

Cyanide Analysis	ITEM	DATE	METHOD	ANALYST	CHECKER	
JOB#:	prep.		Man. Distill	PL		
MATRIX: water	analysis	02/14/00	EPA 335.3	PL		

STANDARD CURVE LCSW: WP586 (tv=0.100 ppm)

standard stock:
TE4-67-17

	T.V. (mg/L CN)	Peak Ht.	Baseline	%T	Absorbance
1	0.250	16.00	92.00	17.39	0.760
2	0.100	42.50	89.00	47.75	0.321
3	0.050	61.00	89.50	68.16	0.166
4	0.010	82.50	90.00	91.67	0.038
5	0.000	89.00	89.50	99.44	0.002
6	--x value--				--y value--

r= 0.9997 m= 3.0173 y(0)= 0.0101 x(0)= -0.003

ms/msd=0.100ppm

	Sample I.D.	Dilution	Peak Ht.	Baseline	%T	Absorbance	CN (mg/L)	
7	ICV / LCSW1	5	41.00	95.00	57.11	0.337	0.1082	108% Rec.
8	ICB	1	87.5	95.00	99.21	0.002	-0.0025	0.005 U
9	MDL tv=0.005 mg/L	1	84.00	95.00	96.05	0.020	0.0034	68% Rec.
0	b021400cnw01	1	86.50	95.00	99.47	0.003	0.0116	0.005 U
1	0005555-2	1	78.00	95.00	99.47	0.045	-0.0025	0.005 U
2	0005555-1	1	85.00	95.00	50.53	0.003	0.1395	140% Rec.
3	0005555-1ms	1	31.50	95.00	50.79	0.431	0.1325	132% Rec.
4	0005555-1msd	1	32.50	95.00	99.21	0.410	0.0004	0.005 U
5		1						
6		1						
7		1						
8		1						
9	CCV1 tv=0.100 mg/L	1	28.50	82.50	47.89	0.243	0.1082	108% Rec.
0	CCB1	1	83.00	83.00	98.95	0.005	0.0008	0.005 U

Appendix III

Sample Bench Sheet

Laucks Testing Labs, Inc.

Cyanide Analysis Run Log

Date	Method	Analyst
3/5/02	EPA 335.3	NS

Intermediate Std: TE6-45-4 tv=1.00 mg/L

LCSW: APG 26602 tv=0.630 mg/L

Cup #	Sample ID	Peak Ht.	Baseline	Dilution (mL/mL)	pH	Cl_2	S^{2-}
1	Sys. Rinse	92.00	92.50				
2	0.250 mg/L	16.00	92.00				
3	0.100 mg/L	42.50	89.00				
4	0.050 mg/L	61.00	89.50				
5	0.010 mg/L	82.50	~~89.50~~ 86.00				
6	0.000 mg/L	89.00	~~89.50~~ 89.50				
7	ICV/LCSW1	41.00	89.00				
8	ICB	87.50	88.00				
9	MDL	84.00	88.00				
10	PBW1	86.50	87.00				
11	0203024-1	78.00	86.50		?!!	-	-
12	0203029-1	~~85.50~~ 85.50	85.50				
13	IMS	31.50	85.00				
14	IMSD	32.50	83.50				
15							
16							
17							
18							
19	CCV1	33.00	82.50				
20	CCB1	83.00	83.00				
21							
22							
23							
24							
25							
26							
27							
28							
29							
30							
31	CCV2						
32	CCB2						

Cup #	Sample ID	Peak Ht.	Baseline	Dilution (mL/mL)	pH	C[illegible]
33	–					
34						
35						
36						
37						
38						
39						
40						
41						
42						
43	CCV3					
44	CCB3					
45						
46						
47						
48						
49						
50						
51					–	
52						
53						
54						
55	CCV4					
56	CCB4					
57						
58						
59						
60						
61						
62						
63						
64						
65						
66						
67	CCV5					
68	CCB5					

ck for interferences from sulfides and chlorine

P (Pass): test paper did not change color

F (Fail): test paper changed color

Appendix III

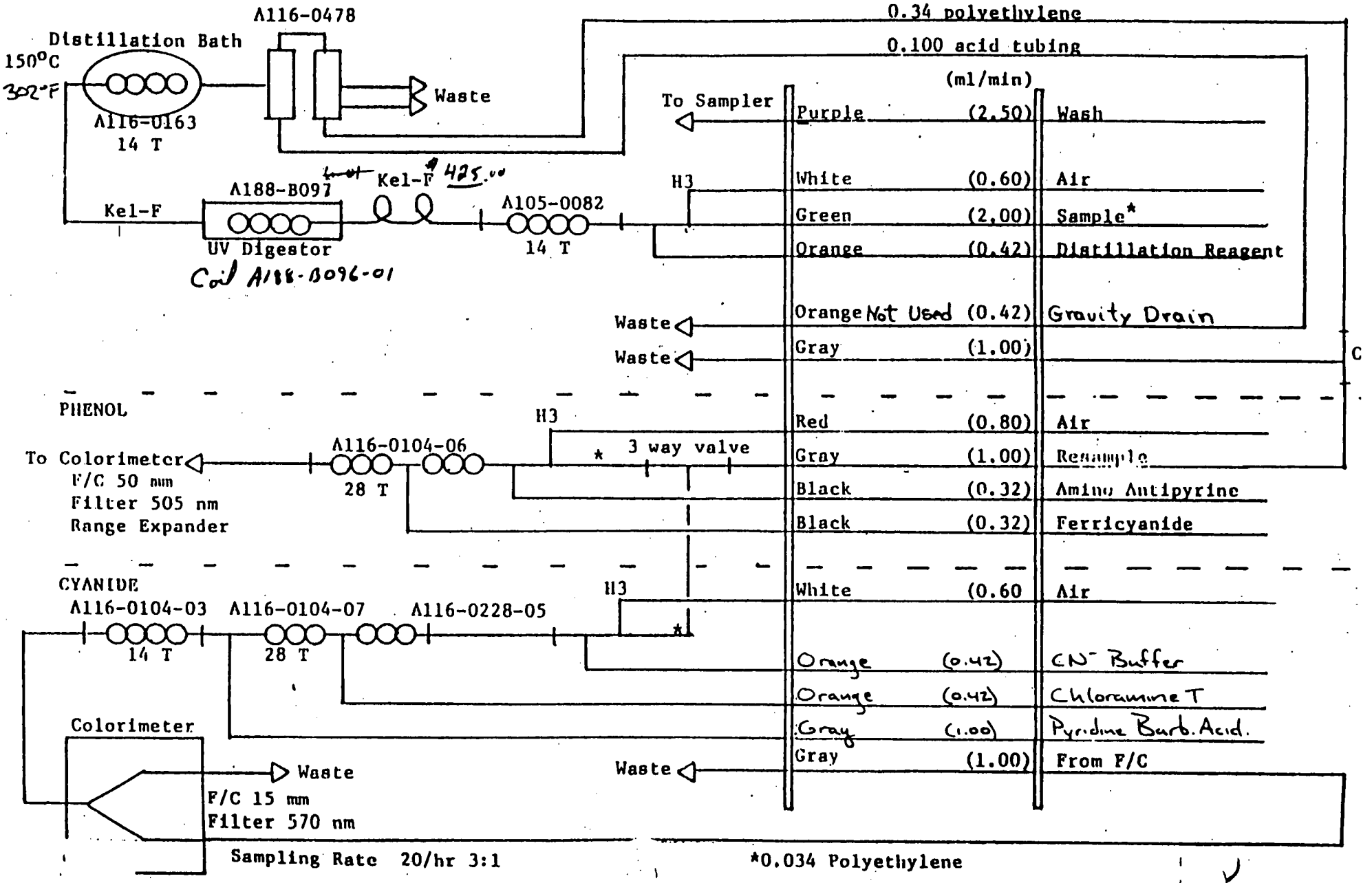
Autoanalyzer Flow Diagram

Manual chemistry
currently in use.
Jan 29, 1991 MS

CYANIDE-PHENOL
Combin[illegible] Manifold
AAI

ALPKEM Co[illegible]ation
1981
RRP

DISTILLATION



LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-9110

Determination of Anions by Ion Chromatography by EPA Method 300.0A or SW846 Method 9056

Revision history:

Number	Date
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5	1/12/98
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Joan Phillips, Inorganics Manager

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Kathy Kreps, Laboratory Director

Controlled Document

No. 20 **Assigned to:** Tetr

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1. Introduction and Scope

1.1 Method Description

1.1.1 This method describes the technique used to determine anions in water using Ion Chromatography. The method is capable of being extended to the analysis of anions in soil matrices if a preliminary leaching step is performed to solubilize the anions. Also, anion determinations may also be performed on the solution resulting from the oxygen bomb decomposition of fuels, solids, oils, and total/organic halogen extracts. The ions that may be quantified by this method are fluoride, chloride, nitrite, nitrate, sulfate, bromide and phosphate. **However, this is a trace-level method and, in many cases, it may be preferable to use a colorimetric/turbidimetric method.**

1.1.2 The anions in an aqueous solution are introduced via an autosampler into a flowing eluant stream. This stream is passed through a cation exchange column, which strips the metallic elements from the solution. It then passes through an anion exchange column where the chromatographic separation occurs. The separation column effluent is then passed through an anion micromembrane suppresser where counter ions are exchanged for hydronium ions. This serves to suppress the conductance of the eluant and enhances the conductance of the anionic analytes of interest by forming their complementary acids. Following this exchange the stream is passed through a conductivity detector. The detector output is collected by a data acquisition system, which stores the chromatograms for later calculation and interpretation.

1.1.3 The method is based on EPA 300.0 A, or SW-846 9056. Method choice is based on client request or environmental program. The following table summarizes the differences between the two methods.

Method 300.0 Criteria	Method 9056
CCV must be ±10%	CCV must be ±5%
Duplicate frequency is 1/20	Duplicate frequency is 1/10

1.1.4 This method is restricted to use by, or under the supervision of analysts experienced in the technique described. Each analyst performing this method must have demonstrated the ability to perform the described analysis.

1.2 Sample Collection, Sample Storage, Holding Times

1.2.1 Samples are collected in 500 or 1000 mL unpreserved polyethylene bottles. Upon receipt, samples are stored 4° ± 2° C.

1.2.2 Analysis holding time is dependent upon the anion of interest. Holding time for Nitrate, Nitrite, and Ortho phosphate analysis is 48 hrs. Holding time for Bromide, Chloride, Fluoride, and Sulfate is 28 days.

1.3 Interferences

1.3.1 Interferences can be caused by substances with retention times that are similar to and overlap those of the anion of interest. Large amounts of an anion can interfere with the peak resolution of an adjacent anion. Sample dilution and/or spiking can be used to solve most interference problems.

1.3.2 The water dip or negative peak that elutes near and can interfere with the fluoride peak. Care should be taken so that integration is being done properly.

1.3.3 Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baseline in IC.

1.3.4 Samples that contain particles larger than 0.45 microns and reagent solutions that contain particles larger than 0.20 microns require filtration to prevent damage to instrument columns and flow systems.

1.3.5 Any anion that is not retained by the column or only slightly retained will elute in the area of fluoride and interfere. Known coelution is caused by carbonate and other small organic anions. At concentrations of fluoride above 1.5 mg/L this interference may not be significant. The analytical column AS14 now in use, minimizes this problem.

1.3.6 The acetate anion elutes early during the chromatographic run. The retention times of the anions seem to differ when large amounts of acetate are present. Therefore this method is not recommended for leachates of solid samples when acetic acid is used for pH adjustment.

1.4 Definition of Terms

CCB - Continuing Calibration Blank - This is the same acronym used in the CLP program. This is a blank which is analyzed immediately after the CCV (almost always after every 10 samples and at the end of the analytical run) during the analysis sequence to determine whether the instrument or system has maintained a stable baseline and to estimate carry-over from a mid-level standard (CCV).

CCV - Continuing calibration verification. - This is the same acronym used in the CLP program. This is a standard analyzed at some prescribed frequency (almost always after every 10 samples and at the end of the analytical run) during the analysis sequence to determine whether the instrument or system has remained in calibration.

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 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, r - Correlation coefficient (r)- 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. This water should be free of virtually all analytes.

ICB - Initial calibration blank - This term is borrowed from CLP. An instrument blank is made up in the same way as calibration standards, without target analytes.

ICV - Initial calibration verification - This term is borrowed from the CLP protocol. It is a standard which is analyzed at the start of each analytical run that is compared to the initial multi-point calibration to determine whether the instrument calibration is within control.

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 determined empirically by Laucks. See section 4.1 for a more detailed discussion of MDL determination.

SRM or LCS - Standard Reference Material or Laboratory Control Sample. This is a material of approximately the same matrix as the samples, containing a known and usually certified amount of target analyte and which is prepared and analyzed in the same manner as a typical sample. This sample is used to demonstrate that the analytical system is in control.

QC period - Quality control period - An analysis sequence initiated by the analysis of one or more standards, followed by samples, and terminated with a standard and blank 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. 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 the IC (or other) column.

RT window - Retention time window - The +/- value which is applied to the individual analyte peaks to establish the time range used to make tentative target analyte identifications.

Sequence - A set of sample extracts and standard solutions injected into an instrument in a chronologically continuous group. See also QC period.

2. Equipment List and Standards

2.1 Equipment

2.1.1 Ion chromatograph, Dionex model DX100 or equivalent consisting of a single piston pump, autosampler, either manual or automated injector, guard column, separator column, anion micromembrane suppresser, and a conductivity detector.

2.1.2 Guard column, Dionex AG14 or equivalent

2.1.3 Chromatographic column, Dionex AS14 or equivalent

2.1.4 Anion Micro Membrane Suppresser, Dionex ASRS-1 or equivalent

2.1.5 Electronic data collection device, AI-450 Chromotography Software or equivalent, or other applicable data collection system.

2.2 Standards and Solutions

2.2.1 Calibration Standard/Spiking Solution.

2.2.1.1 A 100 mL calibration standard/spiking solution is prepared as stated in the following table from vendor supplied primary standards or prepared in-house standards. The primary standards are stored in the standards refrigerator at 4° C. They are replaced annually. Upon receipt the bottles are logged into the standard logbook and are QC'd.

Analyte	Stock Conc. (mg/L)	Volume of Stock (µl)	Final Conc. (mg/L)
F	1000	500	4
Cl	1000	1000	10
NO_2 as N	1000	125	2
Br	1000	100	5
NO_3 as N	1000	100	4
PO_4 as P	1000	100	5
SO_4	1000	100	20

2.2.1.2 The above solution expires after three months. It is stored at room temperature. The routine calibration solution does not contain Br and PO_4. These analytes are added when required.

2.2.1.3 A 1000 mg/L bromide stock solution is prepared by diluting 0.149 g of desiccated NaBr to a final volume of 100 mL. This solution is prepared annually. Desiccated NaBr is prepared by first drying the salt in a 105°C ± 5°C drying oven for four hours. The salt is then cooled to room temperature in a desiccator.

2.2.1.4 A 1000 mg/L phosphate stock solution is prepared by diluting 0.439 g of desiccated KH_2PO_4 to a final volume of 100 mL. This solution is prepared annually. Desiccated KH_2PO_4 is prepared by first drying the salt in a 105°C ± 5°C drying oven for four hours. The salt is then cooled to room temperature in a desiccator.

2.2.1.5 Spiking - Samples are spiked by adding 100µl of solution prepared in 2.2.1.1 to an aliquot of sample and diluting to 500 µl. The dilution of sample and spike are recorded in the dilution column of the batch schedule. The reference number of the spike is recorded in the sample name field of the batch schedule.

2.2.2 ICV Solution

2.2.2.1 An ICV mix for fluoride, chloride, nitrite, bromide, nitrate, phosphate and sulfate is vendor purchased.

2.2.3 Eluant Solution

2.2.3.1 The eluant is 1.7 mM sodium carbonate and 1.8 mM sodium bicarbonate. The eluant is prepared by dissolving 0.170 g sodium bicarbonate and 0.740 g sodium carbonate in DIW and diluting to a final volume of 2 L.

3. Safety precautions and Waste Disposal

3.1 Safety Precautions

3.1.1 All standards, samples and sample solutions should be handled as if they are 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.

3.2 Waste Disposal

3.2.1 There is no significant waste generated from this procedure. Any remaining liquids are disposed of by flushing down the sink. Solid material may be disposed of in the garbage.

4. Calibration and Quality Control

4.1 Method Detection Limit Study

4.1.1 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 the determination of method detection limits (LTL-1011). This SOP can be found in the SOP manual. Briefly, it involves the analysis of 7 replicate samples spiked at a concentration 1-5 times the anticipated method detection limit. A Student's t-test is then applied to these measured values to calculate the MDL.

4.1.2 MDL studies for the ion chromatograph must be determined at a minimum of every year months, with each new analyst, or whenever there is a significant change in system response.

4.1.3 Approximate MDLs

Analyte	Estimated MDL
Fluoride	0.02 mg/L
Chloride	0.04 mg/L
Nitrite	0.01 mg/L
Bromide	0.08 mg/L
Nitrate	0.01 mg/L
Phosphate	0.06 mg/L
Sulfate	0.08 mg/L

4.2 Determination of Retention Time Windows

4.2.1 Every six months, or any time there is a significant change in the system (such as analytical column replacement), the retention time windows need to be determined.

4.2.2 The RW is determined by taking the retention times of three CCVs (mid range standards) on any one day, and computing the standard deviation. The standard deviation multiplied by three is the retention time window. This procedure is similar to that described in the Laucks SOP on Determination of Retention Time Windows (LTL-8000) except one run is used rather than a 72-hour period. This value is then entered into the AI-450 method. The retention time windows are stored in the method.

4.2.3 This data is generated on an Excel spreadsheet and is archived on the laboratory data base.

4.3 Initial Multi-Point Calibration

4.3.1 A calibration curve consists of four points and a blank. All calibration standards are diluted in sample vials at the instrument just prior to analysis as stated in the following table:

Standard Number	Volume Standard	Volume DIW	Total Volume
1	25 µl	475 µl	500 µl
2	100 µl	400 µl	500 µl
3	250 µl	250 µl	500 µl
4	500 µl	0 µl	500 µl

Analyte	STD 1 (mg/L)	STD 2 (mg/L)	STD 3 (mg/L)	STD 4 (mg/L)
Fluoride	0.2	0.8	2	4
Chloride	0.5	2	5	10
Nitrite	0.1	0.4	1	2
Bromide	0.25	1	2.5	5
Nitrate	0.2	0.8	2	4
Phosphate	1	4	10	20
Sulfate	1	4	10	20

4.3.2 The elution order for this system is fluoride, chloride, nitrite, bromide, nitrate, phosphate, sulfate.

4.3.3 Samples whose responses exceed the high standard must be diluted.

4.3.4 A multi-point calibration of the system is not required with every analytical run.

4.3.4.1 If the previous calibration is verified by an ICV, the calibration is considered valid and the instrument does not require re-calibration.

4.3.4.2 A curve is not valid for a period of greater than six months.

4.3.5 Criteria

4.3.5.1 Initial calibration data is evaluated using the correlation coefficient of a linear regression analysis. The linear correlation coefficient (r) must be 0.995 or greater. All CCVs and sample concentrations must be computed using the regression equation.

4.3.6 Corrective action

4.3.6.1 If the criteria are not met the instrument must be recalibrated. No data may be reported for an analyte that does not have a valid calibration.

4.4 Initial Calibration Verification

4.4.1 At the start of each analytical run, analyze a standard from a source other than that from which the calibration material was obtained.

4.4.2 Criteria

4.4.2.1 The calculated concentration of the must be within the limits supplied by the manufacturer or not to exceed ±10% of the true value.

4.4.3 Corrective action

4.4.3.1 If the ICV criteria are not met, no samples can be analyzed. Perform system maintenance and re-check the ICV. If the criteria still cannot be met, the system must be recalibrated. No data can be reported for an analyte that does not have a valid ICV.

4.5 Initial Calibration Blank

4.5.1 After the analysis of the ICV standard an instrument blank (ICB) is analyzed. The levels of target analytes in the ICB should not exceed the reporting limit.

4.5.2 Corrective action

4.5.2.1 If the ICB contains target analyte levels above ½ of the reporting the system is considered to be out of control. The source of contamination must be identified and corrected before proceeding with the analysis. No data can be reported for an analyte that does not have a valid ICB.

4.6 Continuing Calibration Verification (CCV) and Blank (CCB)

4.6.1 A mid-range calibration standard is analyzed at a minimum of once every 10 sample injections. Immediately following the CCV, a blank solution is analyzed. In addition, at the end of the run, this standard should be run at a different level than preceding CCVs to verify that the curve has remained linear throughout the analysis. A CCB should follow this final CCV.

4.6.2 Criteria

4.6.2.1 The CCV must fall within ± 10% of the true value for Method 300.0, and within ± 5% for Method 9056.

4.6.2.2 The levels of target analytes in the CCB should not exceed ½ of the reporting limit.

4.6.3 Corrective action

4.6.3.1 If CCV limits are exceeded, check calculations or perform instrument maintenance. Recalibrate and reanalyze. No sample results may be reported that are not bracketed by a successful ICV and a CCV which is in control or by preceding and following CCVs which are within limits.

4.6.3.2 If the CCB contains target analyte levels above ½ of the reporting limit, the system is out of control. The source of contamination must be identified and corrected and the affected samples re-analyzed. As with the CCVs, no sample results may be reported that are not bracketed by a successful initial and continuing calibration blank that are in control or by preceding and following CCBs that are within limits.

4.7 Method Blanks

4.7.1 Method blanks are used to verify contamination free reagents and apparatus. They are prepared with every set of samples prepared at the same time, or at least one blank every 20 samples, whichever is more frequent. Any analyte response above the reporting limit is reported. For the purpose of water analyses, the ICB, CCBs, and the method blank are the same. Method blank control limits are that contamination should not exceed ½ of the reporting limit for waters.

4.7.2 Corrective action

4.7.2.1 Corrective action may necessitate re-preparation and re-analysis of the sample set. For example if an analyte were found in the blank but not in any of the associated samples then sample group may not require re-analysis. In addition, if sample levels exceed 10 times the blank, the level of contamination may be considered insignificant. In any case, if re-preparation and re-analysis is not being undertaken, the analyst must first discuss the issue with the Quality Control Officer. It is the laboratory's responsibility to ensure that method interferences caused by contaminants in acids, solvents, reagents, glassware, and other sample processing hardware leading to discrete artifacts and/or elevated baselines in the analytical run 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.

4.8 Matrix Spike/Matrix Spike Duplicate

4.8.1 Project-specific criteria will determine whether MS/MSD or MS/Duplicate analysis is to be performed. MS/MSD Duplicate precision is calculated as in Section 4.9 – precision usually is project-specific.

4.8.2 Samples are spiked by adding 100µl of calibration/spiking solution to an aliquot of sample and diluting to 500 µl. The dilution factor of the sample and the spike are

recorded in the dilution field of the batch schedule. The reference number for the spike is recorded on the bench sheet.

4.8.3 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 preparation. The analyst should attempt to avoid selecting samples which are identified by the client as blanks. As the purpose of the matrix spike is to test the system under "typical" conditions, the analyst may also avoid selecting the most difficult sample of the batch for spiking. It is not always required that a matrix spike analysis be performed with each preparation/analysis batch, however, the minimum frequency for MS analysis is 1 each per 20 samples per matrix. This will be best accomplished by running one with every batch for many analyses. 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:

$$\% \text{ recovery} = \frac{(SS - S) * 100}{SA}$$

where: SS = concentration in spiked sample
S = native concentration in unspiked sample
SA = spiked added, the amount of spiking material actually added to the sample calculated on the sample basis

4.8.4 The recovery criteria are detailed in the Quality Control Database and will change from time to time. The current control limits are:

Analyte	Lower Control Limit (%)	Upper Control Limit (%)	RPD Limit (%)
Fluoride	66	121	11
Chloride	73	121	11
Nitrite	50	150	30
Bromide	50	150	30
Nitrate	79	117	10
Phosphate	80	110	10
Sulfate	81	115	10

4.8.5 Corrective action

4.8.5.1 Samples with spike recoveries outside control limits will be reviewed for possible corrective action. Corrective action will first involve recalculation, followed by possible re-preparation, and/or reanalysis. This process should also

look at the recovery of matrix spiking compounds from the SRM and/or blank spike analysis. In all cases a narrative explanation of the condition is required to detail the corrective actions taken.

4.9 Sample Duplicate

4.9.1 Criteria

4.9.1.1 Sample duplicates are required when running Method 300.0 or 9056. At least one duplicate sample per 10 samples per matrix is required when method 9056 is being performed. At least one duplicate sample per 20 is required for Method 300.0. CLP protocols do not specify duplicate frequency and so the less-stringent criterion is used. RPD values are calculated in the following manner:

$$RPD = \frac{|S1 - S2| * 100}{(S1 + S2)/2}$$

where: S1 = measured concentration in the initial analysis
S2 = measured concentration in the duplicate analysis

4.9.1.2 The RPD control limits are detailed in the Quality Control Database and will change from time to time. The current control limits are detailed in 4.8.4.

4.9.2 Corrective action

4.9.2.1 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. Generally, if recoveries are in control and no analyte of interest was detected in any of the samples, no immediate action will be taken on that sample set. If integrity of reported sample values is in doubt, re-analysis may be called for. Corrective actions should be discussed with the Quality Control Officer.

5. Operation Procedures

5.1 Initial Multi-Point Calibration

5.1.1 Creating a method

5.1.1.1 To start the Method Editor program double-click on the Method icon in the AI-450 MainMenu.

5.1.1.2 Method Settings:

System: Dionex DX-100
Number of Detectors: 1
Detector 1: Other-COND conductivity detector
1000mV=30.000uS
Run Time: 6-13 min. depending on retention time of sulfate peak
Plot Min.: -1
Plot Max: 30
Sampling Rate: 2 Hz
Timed Events: Init-Pump on
0.1:Offset on, Sampler on, Pump on, Begin Sampling on
Detector 1: Integration- Threshold-10.0, Width-10.0 sec, Reject-1000.0, Reference Peak area reject-2000.0
Data Events- void volume treatment for this peak at Fluoride retention time
Calibration- 4 levels, linear, calibration update- replace, standardization- external, Resp. for unknowns-area. The rest is set with the default settings.
Components- Enter each component that will be analyzed and their respective retention times, retention time windows. Calibrate by area. Reference component #1.
Enter amount of analyte at each calibration level.
Save new method as icMMDDYY.met where M=month, D=day, Y=year.

5.1.2 Creating a Calibration Curve Schedule

5.1.2.1 To start the Schedule Editor Program, double-click on the [Schedule] icon in the AI-450 MainMenu.

5.1.2.2 Enter sample name. For calibration purposes *autocal1r* is the name for the level 1 standard, *autocal2r* is the name for the level 2 standard, etc.

5.1.2.3 Enter the name of the method saved in 5.1.1.2

5.1.2.4 Enter a file name cMMDDYY, where M=month, D=day, Y=year. The program will number the filenames during analysis.

5.1.2.5 Save Schedule as cMMDDYY.sch., where M=month, D=day, Y=year.

5.1.3 Starting a run

5.1.3.1 Double-click on the [run] icon in the AI-450 MainMenu.

5.1.3.2 Load the schedule into the run program.

5.1.3.3 Load autosampler with cartridge containing the 4 levels of standards. Set autosampler to Run.

5.1.3.4 Set DX-100 to relay control.

5.1.3.5 Choose the run menu and start in the Run Program of AI-450.

5.2 Sample Analysis

5.2.1 Analysis tools and observations

5.2.1.1 If a discrete bottle number is referenced on the sample container, this information must be recorded in the sample name field of the batch schedule.

5.2.1.2 Samples that appear overly turbid or that have suspended or floating particles must be filtered through a 0.45 µm syringe filter prior to analysis. If this procedure is followed it should be documented.

5.2.1.3 If available, conductivity or TDS data can be used as a tool in determining appropriate dilutions.

5.2.1.4 Poor resolution between chloride and nitrite, phosphate and sulfate, and nitrate and bromide in standards or CCVs is an indication that column should be cleaned. If after cleaning the CCV does not resolve back to baseline between the two peaks of interest, the column has lost enough theoretical plates to render it unsuitable for analysis of those ions.

5.2.1.5 An abnormally shaped sulfate peak may indicate a sample with a high phosphate concentration. The chromatogram should be compared to one run at a greater dilution to see if acceptable peak resolution can be obtained.

5.2.1.6 The expected baseline conductivity for the system is 13.0 to 15.0 µS.

5.2.1.7 The expected back pressure of the system is 750 to 1600 psi. When the upper limit is approached the analyst should replace the eluant filter, replace the bed supports, clean the column, or reduce the flow rate. It is acceptable to reduce the flow down to 1.2 mL/min.

5.2.1.8 Other anomalies should be discussed with the departmental supervisor in order to determine appropriate corrective action.

5.3 Analysis sequence

Calibration standards (from low to high concentration)
ICV Solutions necessary for that analytical run
ICB
10 or fewer injections
midrange standard (CCV)
DIW (CCB)
additional samples (not more than 10 injections)
additional CCVs and CCBs
...
...
must close with CCV and CCB

5.4 Instrumental Conditions

5.4.1 System Conditions

- Eluant flow is between 0.5 and 2.5 mL/min.
- Injection volume is 500 µL.
- Temperature correction factor is 1.7.
- Detector range is 30 µS.
- Analysis time is between 10 and 20 minutes.
- Background conductivity is between 13-18 µS.

5.5 Analytical Operation

5.5.1 Analytical procedure for liquid matrixes

5.5.1.1 A set of samples is chosen to be analyzed. Consideration should be given to holding times, due dates, and analytes of interest when choosing the sample set for a run.

5.5.1.2 A schedule is constructed for the sample set. This includes the appropriate dilutions for the given samples, the method name that corresponds to the curve that is in effect, and the filename where data for the sample will be saved. The file name extension is updated during analysis, therefore the analyst will not need to type in an extension.

5.5.1.3 The schedule is loaded into the run program of AI-450 Chromatography Software.

5.5.1.4 An appropriate number of 500 µL sample vials are placed into the auto sampler trays.

5.5.1.5 500 µL of standards, samples and QC events are placed into the sample vials.

5.5.1.6 Dilutions up to 50x can be done directly in the sample vials, greater dilutions will require an external dilution in a Solo cup or a combination of external and sample cup dilutions.

5.5.1.7 Samples that appear turbid or that have suspended particles should be filtered through a 0.45 µm syringe filter prior placing in sample vials and/or dilution. If a sample is pre-filtered, it must be documented.

5.5.1.8 Sample vials are capped with filter caps and placed in the auto sampler.

5.5.1.9 The "Control" button on the DX-100 is set on relay and the autosampler is set on local control and run.

5.5.1.10 Choose the run menu and start in the Run Program of AI-450.

5.5.2 Analytical procedure for soil or sludge matrixes.

5.5.2.1 The soil/sludge is leached with DIW by transferring 10 g to a tared, 250 mL digest bottle, adding 100 mL DIW and placing on the shaker for 15 minutes or more at a shaking rate sufficient to suspend the majority of the solids. The solids are then allowed to settle and an aliquot of the supernatant is filtered through a 0.45 µm syringe filter prior to use. The leaching and filtration of the sample must be recorded in the pretreatment field of the batch summary and a prep sheet completed.

5.5.2.2 A 100 mL aliquot of DIW is shaken in a 250 mL digest bottle and used as a method blank.

5.5.2.3 The resulting supernatant is treated as a water sample.

5.5.2.4 A total solids determination is made on all soil/sludge samples and the results are reported on a dry weight basis.

5.6 Compound Quantification

5.6.1 The data acquisition system (AI-450 Chromatography Software, or equivalent) generates a report with the chromatogram of the sample, the date analyzed, the sample identification, the method used to quantify the sample, the sample dilution, and the calculated concentration of the sample corrected for dilution.

5.6.2 For soil/sludge samples, the mg/L integrator value is converted to mg/kg DB by the following equation

Soil:

$$Cs = \frac{Ci * Vs * 100}{Ws \ Ts}$$

Cs = Sample concentration (mg/kg DB)
Ci = Concentration in sample injected (mg/L)
Vs = Volume of extract (mL)
Ws = Weight of sample extracted (gm)
TS = Total solids (%)

5.6.3 The data is exported into a spreadsheet program (Excel or equivalent) to produce a sample results summary.

6. Reports

6.1 Sample Results and Quality Control Reports

6.1.1 Data packages shall consist of the sample results summary, the chromatograms for samples in the workorder, a copy of the calibration curve and standard log book, and a copy of the QC summary report form. These include the method blank analysis, matrix spike results, duplicate results, and the Standard Reference Material (SRM) reports. A copy of the QC summary report form must be included in order to indicate that the QC was evaluated for analytical consistency.

6.2 Data Qualifying Flags

6.2.1 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.

Appendix I

Method 300.0A, 9056 QA Requirements and Corrective Actions

QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
Initial Calibration	A minimum three point curve that brackets the sample concentrations and a blank.	A four point curve that brackets the sample concentrations Corr coef r≥ 0.995	As instrument performance dictates, or when any change is made in the analytical system.	Fix the problem and recalibrate.	In the raw data package for all validatable packages and referenced in all other data.
Initial Calibration Verification / SRM	Not to exceed ±10% of the true value.	Limits are vendor supplied but must not exceed ±10% of the true value.	Once per analytical run, or 1/20.	Reanalyze, if reanalysis fails recalibrate and or perform instrument maintenance. No data can be reported if ICV fails.	In the raw data package, and in the quality control data base.
Initial Calibration Blank	Value not to exceed the MDL.	Value not to exceed ½ of the Reporting Limit.	Immediately following the ICV.	Reanalyze. No data can be reported if ICB fails.	In the raw data package, and in the quality control data base.
Continuing Calibration Verification	Not to exceed ±10% of the true value.	Method 300.0: Not to exceed ±10% of the true value. ---------- - Method 9056 not to exceed ± 5% of the true value.	At a minimum, after every 10 samples and as the final injection.	Samples which are not bracketed by in control CCVs must be reanalyzed.	In the raw data package.
Continuing Calibration Blank	Value not to exceed the MDL.	Value not to exceed ½ of the Reporting Limit.	Immediately following a CCVs.	Samples which are not bracketed by in control CCBs must be reanalyzed.	In the raw data package.
Method Blank	Value not to exceed the MDL.	ICB and method blank are the same QA event for waters and must not exceed ½ of the reporting	Run at a minimum of 1 per 20 samples and as dictated	If sample concentration exceed 10x the contamination level, no action required.	In the raw data package, and in the quality control data base.

QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
		limit. Soil method blanks must not exceed ½ of the reporting limit.	by non-water matrixes.	Samples with contaminated Method Blanks must be re-prepared and reanalyzed.	
Matrix Spike /Matrix Spike Duplicate Recovery	Not to exceed ±20% of the true value or x ± 3S. Once every 10 samples.	To meet or exceed criteria in the quality control data base. Current limits are detailed in section 4.8.4.	Once every 20 samples, or per client request, whichever is more frequent.	Review data, consult QC officer, some conditions may require reanalysis.	Narrative comment in report in quality control data base, and in raw data package.
Duplicate/ Relative % Difference (RPD)	NA	To meet or exceed criteria in the quality control data base. Current limits are detailed in section 4.8.4.	Method 300.0: Once every 20 samples, or per client request, whichever is more frequent. --- ---------- Method 9056: Once every 10 samples.	Review data, consult QC officer, some conditions may require reanalysis.	Narrative comment in report in quality control data base, and in raw data package.

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #: LTL-9113

Title: **pH in Soil and Waste Samples Using SW846 Method 9045C**

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Written by: Bill Lundberg — Date: 1/16/97
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Approved by: Karen J Kotz — Date: 1/16/97
Karen Kotz, Lab Director

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1. Introduction and Scope

1.1 Method Description

1.1.1 This method is an electrometric procedure for the determination of pH in soils and waste samples.

1.1.2 The sample is mixed with deionized water (DIW). The pH of the solution is then measured with a pH meter.

1.1.3 This method is restricted to use by, or under the supervision of analysts experienced in the technique described. Each analyst performing this method must have demonstrated the ability to perform the described analysis.

1.2 Interferences:

1.2.1 Samples with very low or very high pH may give incorrect readings on the meter. For samples with a true pH of >10, which is not uncommon for some ash and other waste materials, the measured pH may be incorrectly low. This error can be minimized by using a low-sodium-error electrode. Strong acid solutions, with a true value of <1, an uncommon condition, may give incorrectly high measurements.

1.2.2 Temperature fluctuations will cause measurement errors. Most pH electrodes are calibrated to 25°C. Whereas Laucks does use a temperature correction probe with the pH meter, significant differences in pH can affect the solubility and apparent pH characteristics of the solution itself. Therefore, measurements should be made near the appropriate temperature by allowing the sample and diluent (DIW) to warm to room temperature prior to analysis.

1.2.3 Errors can occur when the pH electrode becomes coated. If this occurs, the electrode must be thoroughly clean and re-buffered prior to measuring the pH of subsequent samples.

1.3 Sample Collection, Sample Storage, Holding Times

1.3.1 There is no official holding time for the analysis of soil pH. The holding time for aqueous samples is to analyze immediately. Soil should not demonstrate significant pH fluctuations if refrigerated and analyzed within a reasonable time but Laucks has chosen to analyze soils samples as soon as is reasonable after collection, not to exceed 7 days from collection.

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.

1.4.1.1 **DIW** - Deionized water - Lab reagent water. This water should be free of virtually all analytes.

1.4.1.2 **Sequence** - A set of sample extracts and standard solutions presented to an instrument in a chronologically continuous group.

2. Equipment List, Reagents and Standards

2.1 Apparatus

pH meter with means for temperature correction (temperature correction probe)
Glass electrode
50 ml. beaker
Analytical balance capable of weighing to 0.1 g.

2.2 Standards

pH 4 buffer
pH 7 buffer
pH 10 buffer

2.3 Reagents

Deionized water (DIW)

3. Safety precautions and Waste Disposal

3.1 Safety Precautions

3.1.1 All standards, samples and sample solutions should be handled as if they are hazardous substances.

3.1.2 Refer to the instrument manufacturer's manual for routine instrument precautions.

3.1.3 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.

3.2 Waste Disposal

3.2.1 There should be no significant waste associated with this procedure which cannot be disposed of in the laboratory sink and/or garbage.

4. Calibration and Quality Control

4.1 Calibration

4.1.1 The pH meter must be calibrated with at least two pH buffers. One is the pH 7 buffer and the other depends upon the samples. If high pH is expected, the second buffer should be at pH 10 or higher. If low pH is expected, the second buffer should be the pH 4 buffer. High pH samples should not be analyzed from a low pH calibration and visa versa.

4.2 Sample Duplicate

4.2.1 Criteria

4.2.1.1 At least one duplicate sample per 10 samples per matrix is required. RPD values are not currently calculated for this analysis. The control limit is considered to be 0.5 pH units.

4.2.2 Corrective action

4.2.2.1 If an out-of-control duplicate pair 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. If integrity of reported sample values is in doubt, re-analysis may be called for. Corrective actions should be discussed with the Quality Control Officer.

5. Operation procedures

5.1 Sample preparation and pH measurement of soils

5.1.1 To 20 grams of soil in a 50 ml beaker, add 20 mls of DIW and stir the suspension for 5 minutes. This may also be done with a magnetic stirring bar.

5.1.2 Allow the suspension to stand for about 1 additional hour with no agitation in order to allow most of the suspended particulates to settle out.

5.1.3 Immerse the electrode (including the temperature correction probe) just far enough into the solution to establish good electrical contact. It should not come into contact with the soil itself.

5.1.4 The electrodes should be thoroughly rinsed between samples.

5.1.5 Report the results as "soil pH measured in water @ ____ °C."

5.2 Sample preparation and pH measurement of waste material:

5.2.1 To 20 grams of waste material in a 50 ml beaker, add 20 mls of DIW and stir the suspension for 5 minutes. This may also be done with a magnetic stirring bar.

5.2.2 Allow the suspension to stand for about 15 additional minutes with no agitation in order to allow most of the suspended particulates to settle out.

> Note: If the waste is hygroscopic and absorbs all the DIW, begin the test again using 20 g of waste and 40 ml of DIW.
>
> Note: If the supernatant is multiphasic, decant the oily phase and measure the pH of the aqueous phase.

5.2.3 Immerse the electrode (including the temperature correction probe) just far enough into the solution to establish good electrical contact. It should not come into contact with the waste material itself.

5.2.4 The electrodes should be thoroughly rinsed between samples.

5.2.5 Report the results as "waste pH measured in water @ _____ °C.

6. Reports

6.1 Data Packet Organization

6.1.1 The data package for this analysis consists of the data sheet and a quality control database (QC_DB) report form.

6.2 Quality Control Reports

6.2.1 All results for quality control tests are entered into the lab data base using the QC_DB program. The report form must be filled out in order to indicate that the duplicate QC had been performed and met the criteria specified in this document.

Appendix I

QC Summary Table

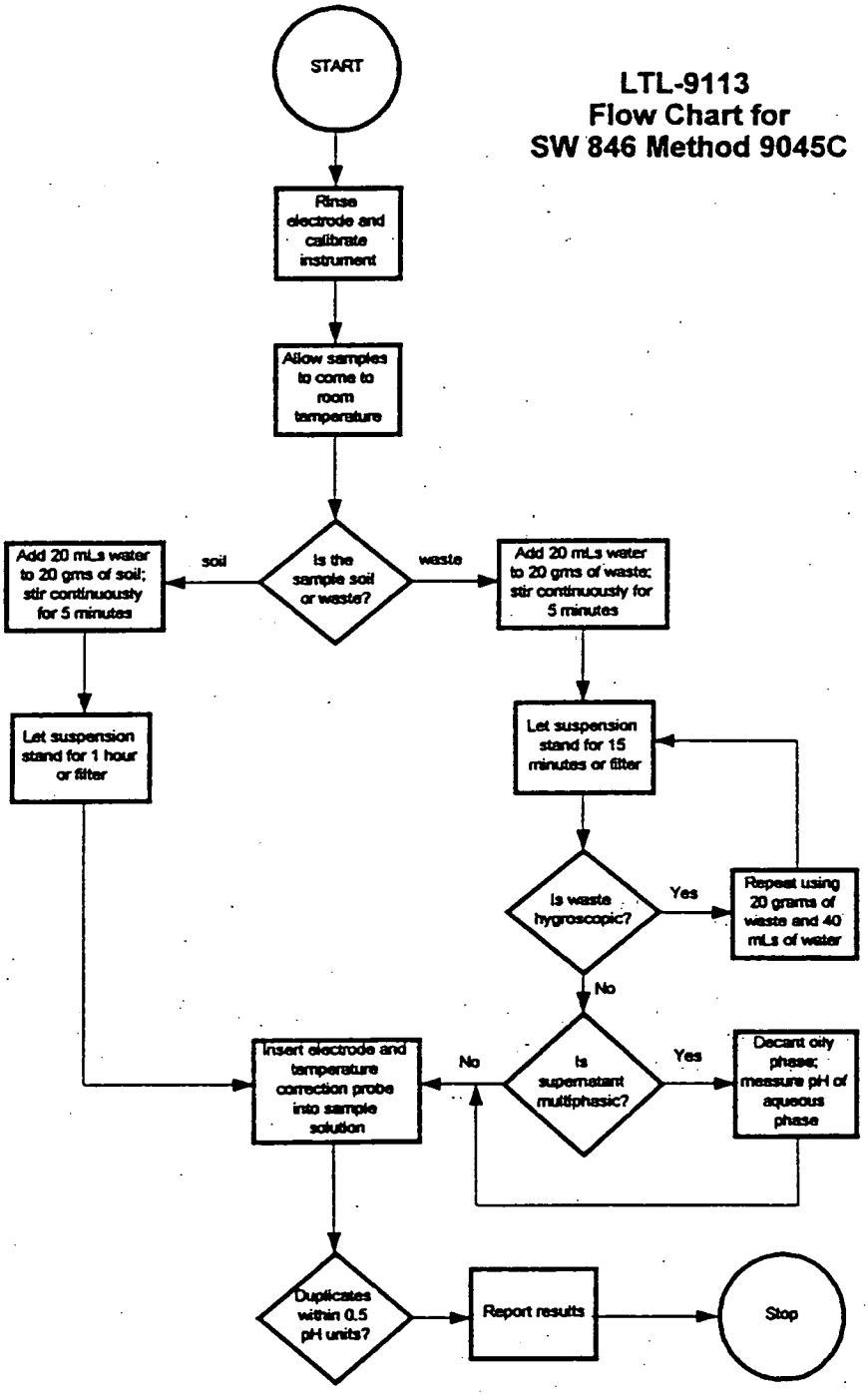
Laucks Testing Laboratories

Method SW 9045C QA Requirements and Corrective Actions

QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
Initial Calibration	Buffer pH meter to bracket sample values	Buffer pH meter between pH 7 & 4 or 10 before analyses (to bracket sample values)	Once before analyzing any samples or QC	None	None
Duplicate % Difference	N/A	within 0.5 pH units of one another	10% or once every 10 samples.	Correct problem Consult QC Officer	QC_DB report form with appropriate commentary

Appendix II

Flow Chart


LTL-9113
Flow Chart for
SW 846 Method 9045C
START
Rinse electrode and calibrate instrument
Allow samples to come to room temperature
Is the sample soil or waste?
soil
waste
Add 20 mLs water to 20 grms of soil; stir continuously for 5 minutes
Add 20 mLs water to 20 grms of waste; stir continuously for 5 minutes
Let suspension stand for 1 hour or filter
Let suspension stand for 15 minutes or filter
Is waste hygroscopic?
Yes
Repeat using 20 grams of waste and 40 mLs of water
No
Is supernatant multiphasic?
No
Yes
Insert electrode and temperature correction probe into sample solution
Decant oily phase; measure pH of aqueous phase
Duplicates within 0.5 pH units?
Report results
Stop

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-9115

Title: **The Determination of Total Organic Carbon in Water Samples by EPA 415.1 and SW846 Method 9060**

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1. Introduction and Scope

1.1 Method Description

1.1.1 This method is used to determine the concentration of total organic carbon (TOC) in a water sample. The acidified sample is purged of inorganic carbon and then sent to the UV reactor where organic carbon is converted to CO_2 by UV-catalyzed persulfate oxidation. Released CO_2 is measured using NDIR detection.

1.1.2 Method SW846 9060 states that all TOC analyses should be performed in quadruplicate. Laucks performs all TOCs singleton, unless previous arrangements have been made with the client.

1.1.3 This method is restricted to use by, or under the supervision of analysts experienced in the technique described. Each analyst performing this method must have demonstrated the ability to perform the described analysis.

1.2 Sample Collection, Sample Storage, Holding Times

1.2.1 It is strongly recommended that samples be collected in glass containers (40mL vials are provided by Laucks Testing Labs), preserved with 0.2% phosphoric acid. Samples collected in plastic run the potential risk of: a) an increased TOC value do to organic carbon leaching from the plastic into the sample and/or b) a decreased TOC value due to the solvents in the sample being incorporated into the plastic container.

1.2.2 In accordance with SW846, plastic containers are permissible. Laucks will, however, make every effort to provide glass containers.

1.2.3 Upon receipt, samples should be stored at 4 ± 2°C.

1.2.4 The maximum recommended holding time for waters is 28 days from the date of sample collection. If the holding time is exceeded, the analyst should notify the project manager so they may notify the client.

1.3 Interferences

1.3.1 This procedure is applicable only to homogenous samples which can be injected reproducibly into the apparatus. The opening of the syringe limits the maximum particle size which may be included in the sample.

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.

1.4.2 **CCB** - Continuing Calibration Blank - This is the same acronym used in the CLP program. This is a blank which is analyzed immediately after the CCV (almost always after every 10 samples and at the end of the analytical run) during the analysis sequence to determine whether the instrument or system has maintained a stable baseline or is exhibiting carry-over from the CCV.

1.4.3 **CCV** - Continuing calibration verification. - This is the same acronym used in the CLP program. This is a standard analyzed at some prescribed frequency (almost always after every 10 samples and at the end of the analytical run) during the analysis sequence to determine whether the instrument or system has remained in calibration.

1.4.4 **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 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.

1.4.5 **Corr Coef, CC, r** - 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

1.4.6 **DIW** - Deionized water - Lab reagent water. This water should be free of virtually all analytes.

1.4.7 **ICB** - Initial calibration blank - This term is borrowed from CLP. An instrument blank is prepared in the same way as calibration standards, without target analytes.

1.4.8 **ICV** - Initial calibration verification - This term is borrowed from the CLP protocol. It is a standard which is analyzed at the start of each analytical run that is compared to the initial multi-point calibration to determine whether the instrument calibration is accurate.

1.4.9 **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 determined empirically by Laucks. See section 4.1 for a more detailed discussion of MDL determination.

1.4.10 **SRM or LCS** - Standard Reference Material or Laboratory Control Sample. This is a material of approximately the same matrix as the samples, containing a known and usually certified amount of target analyte and which is prepared and analyzed in the same manner as a typical sample. This sample is used to demonstrate that the analytical system is in control.

1.4.11 **QC period** - Quality control period - An analysis sequence initiated by the analysis of one or more standards, followed by samples, and terminated with a standard and blank analysis. A QC period can be open-ended chronologically, but calibration verification must be documented using the procedures in this SOP.

1.4.12 **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. A measure of the similarity of the values one to another.

1.4.13 **Sequence**- A set of sample extracts and standard solutions injected into an instrument in a chronologically continuous group. See also QC period.

2. Equipment List and Standards

2.1 Equipment List

2.1.1 Instrument

2.1.1.1 TOC analyzer, Tekmar-Dohrmann Phoenix 8000, or equivalent.

2.1.1.2 Autosampler

2.1.2 Analytical Balance: 0.1 mg sensitivity.

2.2 Reagents

2.2.1 21 % Phosphoric Acid Reagent: 188 mL DIW into rinsed bottle. Add 37 mL concentrated phosphoric acid (H_3PO_4). This reagent should be prepared monthly.

2.2.2 10% persulfate and 5% phosphoric acid: 213 mL DIW into rinsed bottle. Add 9 mL concentrated H_3PO_4 and add 25 g of high purity sodium persulfate ($Na_2S_2O_8$). This reagent should be prepared weekly.

2.2.3 Purified air, hydrocarbon free, 35 psi.

2.3 Standards

2.3.1 All standards should be preserved with 0.2% phosphoric acid.

2.3.2 **50 ppm dextrose ICV/SRM stock solution**: Dissolve 0.125 g of AR grade dextrose in DIW. Add a small amount phosphoric acid (H_3PO_4) for preservation and dilute to a final volume of one liter.

2.3.3 **10 ppm dextrose ICV/SRM working standard**: Weigh 8.0 g of the 50 ppm dextrose ICV/SRM stock solution into 40 mL vial and bring the total weight up to 40.0 g with DIW.

2.3.4 **2000 ppm potassium biphthalate (KHP) stock solution**: vendor supplied solution.

2.3.5 **40 ppm potassium biphthalate (KHP) stock calibration standard**: Dilute 20.0 mL of the 2000 ppm. KHP stock solution to 1 liter with DIW.

2.3.6 **20 ppm potassium biphthalate (KHP) calibration standard**: Dilute 20.0 g of the 40 ppm potassium biphthalate (KHP) stock calibration standard to 40.0 g with DIW.

2.3.7 **10 ppm potassium biphthalate (KHP) calibration standard**: Dilute 10.0 g of the 40 ppm potassium biphthalate (KHP) stock calibration standard to 40.0 g with DIW.

2.3.8 **5 ppm potassium biphthalate (KHP) calibration standard**: Dilute 5.0 g of the 40 ppm potassium biphthalate (KHP) stock calibration standard to 40.0 g with DIW.

2.3.9 **2 ppm potassium biphthalate (KHP) calibration standard**: Dilute 2.0 g of the 40 ppm potassium biphthalate (KHP) stock calibration standard to 40.0 g with DIW.

2.3.10 **1 ppm potassium biphthalate (KHP) calibration standard**: Dilute 1.0 g of the 40 ppm potassium biphthalate (KHP) stock calibration standard to 40.0 g with DIW.

3. Safety precautions and Waste Disposal

3.1 Safety Precautions

3.1.1 All standards, samples and sample solutions should be handled as if they are 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.

3.2 Waste Disposal

3.2.1 Waste products from this process are not considered harmful and are therefore collected at the instrument and disposed of down the sink.

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 Method Detection Limit Study

4.1.1 Prior to the analysis of any samples, it is necessary to establish method detection limits. This procedure is fully described in Laucks SOP on MDL studies. Briefly, it involves the analysis of seven 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. The LTL estimated MDL is 0.5 mg/L.

4.2 Initial Multi-Point Calibration

4.2.1 Analyze standard solutions using at least 5 different concentration levels.

4.2.2 Calibration Curve:

Concentration	Preparation
0 ppm standard	0.2% phosphoric acid
1 ppm standard	Described in 2.3.10
2 ppm standard	Described in 2.3.9
5 ppm standard	Described in 2.3.8
10 ppm standard	Described in 2.3.7
20 ppm standard	Described in 2.3.6

4.2.3 Analyze the standards from lowest concentration to highest concentration.

4.2.4 A multi-point calibration of the system is not required with every analytical run.

4.2.4.1 If the previous calibration is verified by an ICV, the calibration is considered valid and the instrument does not require recalibration.

4.2.4.2 A curve is not valid for longer than six months. It is recommended that a curve is run when any significant change in instrumentation, reagents, or standards occurs.

4.2.5 Criteria

4.2.5.1 Initial calibration data is evaluated using the correlation coefficient of a linear regression analysis. The correlation coefficient must be 0.995 or greater for a 5-point calibration. All CCVs and sample extract concentrations must be computed using the regression equation.

4.2.6 Corrective action

4.2.6.1 If the criteria are not met, the instrument must be recalibrated.

4.3 Initial Calibration Verification

4.3.1 Immediately after the calibration curve, analyze a standard from a source other than that from which the calibration material was obtained.

4.3.2 Criteria

4.3.2.1 The calculated concentration of the ICV should not exceed 90%-110% of the true value.

4.3.3 Corrective action

4.3.3.1 If the ICV criteria are not met, no samples can be analyzed. Perform system maintenance and re-check the ICV. If the criteria still cannot be met, the system must be recalibrated.

4.4 Initial Calibration Blank

4.4.1 After the analysis of the ICV standard an instrument blank (ICB) is analyzed. The levels of target analytes in the ICB should not exceed the reporting limit *(one-half the reporting limit for USACOE work).*

4.4.2 Corrective action

4.4.2.1 If the ICB contains target analyte levels above the reporting limit *(one-half the reporting limit for USACOE work)*, the system is out of control. The source of contamination must be identified and corrected before proceeding with the analysis.

4.5 Continuing Calibration Verification (CCV) and Blank (CCB)

4.5.1 A mid-range calibration standard is analyzed after every 10 samples. Immediately following the CCV, a blank solution is analyzed. In addition, this standard and blank must be the last samples analyzed in the run.

4.5.1.1 The CCV must fall within ± 10% of the true value.

4.5.2 The levels of target analytes in the CCB should not exceed the reporting limit *(one-half the reporting limit for USACOE work)*.

4.5.2.1 Corrective action

4.5.2.2 If CCV limits are exceeded, check calculations or perform instrument maintenance. Recalibrate and reanalyze. No sample results may be reported that are not bracketed by a successful calibration and a CCV which is in control or by preceding and following CCVs which are within limits.

4.5.2.3 If the CCB contains target analyte levels above the reporting limit *(one-half the reporting limit for USACOE work)*, the system is out of control. The source of contamination must be identified and corrected and the affected samples re-analyzed. As with the CCVs, no sample results may be reported that are not bracketed by a successful initial and continuing calibration blank which are in control or by preceding and following CCBs which are within limits.

4.6 Method Blanks

4.6.1 Method blanks are used to verify contamination free reagents and apparatus. They are prepared with every set of samples prepared at the same time or at least one blank every 20 samples which ever is more frequent. Any analyte response above the reporting limit is reported. Method blank control limits specify that contamination should not exceed the reporting limit *(one-half the reporting limit for USACOE work)*. In this case the Method Blank and the ICB are the same.

4.6.2 Corrective action

4.6.2.1 Corrective action may necessitate re-preparation and re-analysis of the sample set. For example if an analyte were found in the blank but not in any of the

associated samples then sample group may not require re-analysis. In addition, if sample levels exceed 10 times the blank, the level of contamination may be considered insignificant. In any case, if re-preparation and re-analysis is not being undertaken, the analyst must first discuss the issue with the Quality Assurance Officer. It is the laboratory's responsibility to ensure that method interferences caused by contaminants in acids, solvents, reagents, glassware, and other sample processing hardware leading to discrete artifacts and/or elevated baselines in the analytical run 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.

4.7 Matrix Spike/Matrix Spike Duplicate

4.7.1 Project-specific requirements will dictate whether MS/MSD or MS/Duplicate analysis is to be performed. Unless specified otherwise by the client, 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 preparation. The analyst should attempt to avoid selecting samples which are identified by the client as blanks. As the purpose of the matrix spike is to test the system under "typical" conditions, the analyst may also avoid selecting the most difficult sample of the batch for spiking. It is not always required that a matrix spike analysis be performed with each preparation/analysis batch, however, the minimum frequency for MS analysis is 1 each per 20 samples per matrix. This will be best accomplished by running one with every batch for many analyses. 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:

$$\text{recovery} = \frac{(SS - S) * 100}{SA}$$

where:

SS = concentration in spiked sample
S = native concentration in unspiked sample
SA = spiked added, the amount of spiking material actually added to the sample calculated on the sample basis

4.7.2 Matrix Spikes are prepared by spiking a 40 g aliquot of sample with 200 μL of a 2000 mg/L KHP vendor supplied stock solution (equal to a 10 mg/L spike).

4.7.3 The recovery criteria are detailed in the Quality Control Database and will change from time to time. The current QC limit for recovery for MS/MSD is 70%-119%.

4.7.4 Corrective action

4.7.4.1 Samples with spike recoveries outside control limits will be reviewed for possible corrective action. Corrective action will first involve recalculation, followed by possible re-preparation, and/or reanalysis. This process should also look at the recovery of at the recovery of matrix spiking compounds from the SRM and/or blank spike analysis. In all cases a narrative explanation of the condition is required to detail the corrective actions taken.

4.8 Matrix Spike Duplicate

4.8.1 The compound recovery criteria are identical to those for the matrix spike sample. In addition, the matrix spike duplicate is used 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:

$$RPD = \frac{|S1 - S2| * 100}{(S1 + S2)/2}$$

where:
S1 = measured concentration for MS sample
S2 = measured concentration for MSD sample

4.8.2 RPD control limits are detailed in the Quality Control Database and will change from time to time. The current qc limit for RPD is 11%.

4.9 Sample Duplicate

4.9.1 Criteria

4.9.1.1 Sample duplicates are required only when the client requests them. At least one duplicate sample per 20 samples per matrix is required when matrix spikes are being performed. When duplicate analysis is all that is being performed or when requested the frequency is 10%. RPD values are calculated in a manner similar to MS/MSD RPDs:

$$RPD = \frac{|S1 - S2| * 100}{(S1 + S2)/2}$$

where:

S1 = measured concentration in the initial analysis
S2 = measured concentration in the duplicate analysis

4.9.1.2 The RPD control limits are detailed in the Quality Control Database and will change from time to time. The current control limit for RPD is 11%.

4.9.2 Corrective action

4.9.2.1 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. Generally, if recoveries are in control and no analyte of interest was detected in any of the samples, no immediate action will be taken on that sample set. If integrity of reported sample values is in doubt, re-analysis may be called for. Corrective actions should be discussed with the Quality Control Officer.

5. Operation procedures

5.1 Sample Analysis

5.1.1 Ensure that there are ample amounts of reagents to complete an entire analysis.

5.1.2 It is recommended that the priming method then the cleaning method be run prior to calibration or sample analysis.

5.1.3 Analysis sequence

ICV/SRM
ICB/MB
Sample 1
Sample 1ms (or dup depending on client specifications)
Sample 1msd (or ms depending on client specifications)
Sample 2-8
CCV1
CCB1
Continue with samples with CCVs and CCBs every 10 injections.
Close with a CCV and a CCB.

Note: Samples are run in Singleton, unless clients specify otherwise.

5.2 Instrumental Conditions

5.2.1 The instrument should be in the ready mode for a minimum of two hours to allow for NDIR stabilization.

5.2.2 Gas flow rate should be around 200 cc/min.

5.3 Analytical Operation

5.3.1 Calibration Setup

5.3.1.1 Select Calibration Standards from the Setup Menu.

5.3.1.2 Save the calibration standards as MMDDYY where M=month, D=day, Y=year.

5.3.1.3 Select Calibration Set Active from the Setup Menu.

5.3.1.4 Select the calibration standards named as active in 5.3.1.2.

5.3.1.5 Select [Sample Setup] in the run screen.

5.3.1.6 Setup the Calibration Sequence according to 4.2.2.

5.3.1.6.1 To enter the appropriate standard Select TOC standard in the Sample Type column.

5.3.1.6.1.1 A window will open which allows selection of the appropriate standard.

5.3.1.6.1.2 This process is repeated for all standards.

5.3.1.7 The selected method should be TOC Range 0.1-20ppm C.

5.3.1.8 Make sure vial numbers correspond to the placement of the standards in the autosampler tray.

5.3.1.9 Set all standards to ready.

5.3.1.10 Select [Save/Use] to save the setup.

5.3.1.11 Select [Start] on the Run Screen.

5.3.1.12 After calibration is complete, a window will open. At least five standards should be selected for the calibration curve. Evaluate the curve based on the criteria outlined in 4.3.2.1.

5.3.2 Sample Setup

5.3.2.1 Place samples on the autosampler tray according to the sequence in 5.1.3.

5.3.2.2 Select [Sample Setup] in the run screen.

5.3.2.2.1 Entering QC samples

5.3.2.2.1.1 To enter QC samples (except for MS, MSD, and DUP) Select Calibration Verification in the Sample Type column.

5.3.2.2.1.2 A window will open which will allow for selecting the appropriate standard.

5.3.2.2.1.3 Repeat this process for all standards.

5.3.2.2.2 Entering Unknowns

5.3.2.2.2.1 Type the sample ID in the Sample ID column.

If a dilution is needed, type the dilution factor after the sample ID in the Sample ID column.

5.3.2.2.2.2 Select Sample in the Sample Type Column.

5.3.2.2.3 Set the method to TOC Range 0.1-20ppm C.

5.3.2.2.4 Ensure that the samples are set to ready and vial numbers are correct.

5.3.2.3 Select [Save/Use] to save the setup.

5.3.2.4 Select [Start] on the Run Screen to begin analysis.

5.4 Compound Quantification

5.4.1 Data export

5.4.1.1 Data can be exported into Excel.

5.4.1.1.1 Under the results menu, Select Multiple Analysis.

5.4.1.1.2 A window should open showing the results of the previous analysis.

5.4.1.1.3 Under the Edit Menu, Select Customize View in Excel.

5.4.1.1.4 Continue by following instructions that will appear.

6. Reports

6.1 Data Packet Organization

6.1.1 See Appendix I for a check list detailing data packet organization

6.2 Quality Control Reports

6.2.1 All results for quality control tests are entered into the lab data base. Printouts of all data entered must be included in the data packet. The routine minimum is a method blank report, and an MS/MSD or MS/duplicate report. Many analyses will also require an SRM, blank spike or other 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 limit of detection indicated.

7. Reference

USEPA Method for Chemical Analysis of Water and Wastes, Lastest Edition, Method 415.1

USEPA Test Methods for Evaluating Solid Waste, Latest Edition, Method 9060

Appendix I

Data Packet Organization

Excel Spreadsheet with Calculations
QC_DB form
Raw Data
Out of Control Form (if needed)

Appendix II

QC Summary Table

EPA Method 415.1 and Method SW846 9060 QC Requirements and Corrective Actions

QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
Initial Calibration	per manufacturers instructions	Correlation Coefficient (r) of .995 or higher.	At least every six months or with any significant change in the system. Must be verified with an ICV.	Recalibration.	N/A
Initial Calibration Verification/ Standard Reference Material	verify with independent check standard	±10% of True Value.	Once every 20 samples, or per client request, whichever is more frequent	Perform system maintenance and re-check the ICV/SRM. If the criteria still cannot be met, the system must be recalibrated.	N/A
Initial Calibration Blank/Method Blank	Not specified.	Not to exceed the reporting limit*(one-half the reporting limit for USACOE work)*.	Once every 20 samples, or per client request, whichever is more frequent	If sample concentration exceed 10x the contamination level, no action required. Samples with contaminated Method Blanks must be re-extracted.	Narrative comment in report in quality control data base, and in raw data package.
Continuing Calibration Verification	verify with an independently prepared check standard every 15 samples	±10% of True Value.	After every 10 samples and at the end of analysis.	Check calculations or perform instrument maintenance. Recalibrate and reanalyze.	N/A
Continuing Calibration Blank	Not specified.	Not to exceed the reporting limit *(one-half the reporting limit for USACOE work)*.	After every 10 samples and at the end of analysis.	The source of contamination must be identified and corrected and the affected samples re-analyzed.	N/A
Matrix Spike Recovery	once every 10 samples; no criteria	To meet or exceed criteria in the quality control data base.	Once every 20 samples, or per client request, whichever is more frequent.	Review data, consult QC officer, some conditions may require reanalysis.	Narrative comment in report in quality control data base, and in raw data package.

QC Summary Table (cont.)

Method SW846 9060 QA Requirements and Corrective Actions

MS/MSD RPD	Not specified.	To meet or exceed criteria in the quality control data base.	Once every 20 samples, or per client request, whichever is more frequent.	Review data, consult QC officer, some conditions may require reanalysis.	Narrative comment in report in quality control data base, and in raw data package.
Duplicate % Difference	N/A	To meet or exceed criteria in quality control data base.	Once every 20 samples, or per client request, whichever is more frequent.	Review data, consult QC officer, some conditions may require reanalysis.	Narrative comment in report in quality control data base, and in raw data package.

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #: LTL-9116

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METHOD SW 9060 (MODIFIED FOR SOIL/SEDIMENT) QA REQUIREMENTS AND CORRECTIVE ACTIONS 19

APPENDIX II **22**

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1. Introduction and Scope

1.1 Method Description

1.1.1 This method is used to determine the concentration of total organic carbon in a soil or sediment sample. Inorganic carbon (carbonates) is removed by treatment of the homogenized sample with 1:1 nitric acid. The treated sample is then combusted in a furnace and the carbon dioxide evolved as a combustion product is measured using an infrared detector.

1.1.2 This method is based on SW846 method 9060, modified to accommodate the analysis of soils and sediments.

1.1.3 Assuming a 1:5 dilution factor, using 10 to 100 mg of diluted sample, the stated calibration curve allows for a concentration range of 0.1 to 2.0% carbon in the sample. This range can be extended in either direction by adjusting the sample dilution.

1.1.4 This method is restricted to use by, or under the supervision of analysts experienced in the technique described. Each analyst performing this method must have demonstrated the ability to perform the described analysis.

1.2 Sample Collection, Sample Storage, Holding Times

1.2.1 Samples can be collected in glass or plastic containers. A minimum sample size of 50 grams is recommended.

1.2.2 Samples should be stored at 4°C ± 2°C. The holding time for soil samples is not established, but the holding time for water samples is 28 days from sample collection. For lack of other official guidance, 28 days from sample collection is used for the analytical holding time.

1.3 Definition of Terms

1.3.1 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.

1.3.2 **CCV** - Continuing calibration verification. - This is the same acronym used in the CLP program. This is a standard analyzed at some prescribed frequency (almost always after every 10 samples) during the analysis sequence to determine whether the instrument or system has remained in calibration.

1.3.3 **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 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.

1.3.4 **Corr Coef, CC, r** - Correlation coefficient - A measures 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

1.3.5 **DIW** - Deionized water - Lab reagent water. This water should be free of virtually all analytes.

1.3.6 **ICB** - Initial calibration blank - This term is borrowed from CLP. An instrument blank is made up in the same way as calibration standards, without target analytes.

1.3.7 **ICV** - Initial calibration verification - This term is borrowed from the CLP protocol. It is a standard, which is analyzed at the start of each analytical run that is compared to the initial multi-point calibration to determine whether the instrument calibration is accurate.

1.3.8 **IDL** - Instrument detection limit. The lowest concentration of a target analyte that will yield a signal: noise ratio of least 3x. Used as a starting point for selecting MDL study spiking levels.

1.3.9 **MDL** - Method detection limit - The lowest concentration a sample that will yield a positive result that is greater zero at a known level of confidence. MDLs are determined empirically by Laucks.

1.3.10 **MDL standard** - Method detection limit standard - A standard prepared so that the concentrations of the target analytes are no greater than 4x the empirically determined MDLs. This standard is used to verify that the instrument or system is capable of detecting the target analytes on an ongoing basis.

1.3.11 **SRM or LCS** - Standard Reference Material or Laboratory Control Sample. This is a material of approximately the same matrix as the samples, containing a known and usually certified amount of target analyte and which is prepared and analyzed in the same manner as a typical sample. This sample is used to demonstrate that the analytical system is in control. It may be considered to be a blank spike for most inorganic analyses and is preferred over artificially spiking blank materials.

1.3.12 **QC period** - Quality control period - An analysis sequence initiated by the analysis of one or more standards, followed by samples, and terminated with a standard and blank

analysis. A QC period can be open-ended chronologically, but calibration verification must be documented using the procedures in this SOP

1.3.13 **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. A measure of the similarity of the values one to another.

1.3.14 **Sequence** - A set of sample extracts and standard solutions injected into an instrument in a chronologically continuous group. See also QC period.

2. Interferences

2.1.1 The possibility exists for loss of organic compounds during the drying step. In addition, drying at a temperature lower than 105°C may not be adequate to remove all moisture (and entrained inorganic-carbon compounds) from the sample.

2.1.2 Due to the small sample aliquot size used for analysis it is important that the sample be homogenized. This step is particularly important for samples, which will be diluted using clean sand.

3. Equipment List and Standards

3.1 Equipment

3.1.1 TOC analyzer, Dohrmann Pheonix 8000 or equivalent

3.1.2 Dohrman 183 boat sampler or equivalent

3.1.3 Analytical Balance: 0.1 mg accuracy

3.1.4 Desiccator

3.1.5 Platinum combustion boats

3.1.6 Drying oven set at 70°C

3.1.7 Any laboratory PC equipped with Excel and the TOC template may be used for calculation or the calculations may be done by hand, requiring no computer except for entry into the LIMS database.

3.2 Reagents and Standards:

3.2.1 Nitric acid (HNO_3), AR-Grade - Prepare by diluting 50 mL concentrated HNO_3 to 100 mL with DIW.

3.2.2 ASTM Type II water

3.2.3 Potassium hydrogen phthalate (KHP)Stock Solution, 4000 mg/L carbon: Dissolve 1510 mg ±1 mg KHP (Primary Standard Grade, dried for two hours at 120°C and stored in a desiccator) in a 200 mL volumetric flask. Calibration solutions are prepared from the stock by dilution. They must be stored under refrigeration and preserved with 0.2% H_3PO_4 and expire after one year.

3.2.3.1 Prepare solutions at 500, 1000, 1500, and 2000 mg/L as follows:

Analyte	Stock Conc.	Vol./Wt. taken	Final Vol.	Final Conc.	Solvent
500 mg/l KHP	4000 mg/l	12.5 ml	100 ml	500 mg/l	0.2 % H_3PO_4
1000 mg/l KHP	4000 mg/l	25.0 ml	100 ml	1000 mg/l	0.2 % H_3PO_4
1500 mg/l KHP	4000 mg/l	37.5 ml	100 ml	1500 mg/l	0.2 % H_3PO_4
2000 mg/l KHP	4000 mg/l	50.0 ml	100 ml	2000 mg/l	0.2 % H_3PO_4

3.2.4 Sand (purified and ignited, carbon-free), which has been disk pulverized to pass at least 80 mesh.

3.2.5 Laboratory Control Sample (LCS) is prepared as a 1:20 dilution in clean sand using Reference material ERA Sludge (currently, TV = 2.61%, range = 2.09 - 3.03% as prepared, Lot 17095) or equivalent. The control limits for this and any replacement materials are located in the laboratory's quality control database.

3.2.6 Matrix spike samples are prepared using 40 µL of the 1000 mg/L KHP working standard. Recovery limits are generated periodically as described in Laucks' SOP LTL-1011 and are located in the laboratory's quality control database.

4. Safety precautions and Waste Disposal

4.1 Safety Precautions

4.1.1 All standards, samples and sample solutions should be handled as if they are hazardous substances.

4.1.2 Refer to the instrument manufacturer's manual for routine instrument precautions.

4.1.3 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.

4.1.4 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.

4.1.5 The combustion furnace is heated to approximately 800°C. Care should be taken not to burn oneself when in the proximity of the furnace or objects, which have been recently removed from the furnace.

4.2 Waste Disposal

4.2.1 There is no significant waste generated from this procedure. Any remaining liquids are disposed of by flushing down the sink. Solid material (ash, soil, etc.) may be disposed of in the garbage.

5. Calibration and Quality Control

5.1 Batch Quality Control Limits

5.1.1 All Batch QC precision and recovery criteria are maintained and updated in the Laboratory's Quality Database, which is managed by the Quality Assurance Officer. These criteria should be consulted prior to initiating sample analysis. This includes detection and quantitation/reporting limits and all associated control charts (see LTL-1011 and section 7.2 for control chart discussion).

5.2 Method Detection and Reporting Limits

5.2.1 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, which is in turn derived from 40CFR part 136, Appendix B. 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.

5.2.2 The MDL has historically been no higher than 0.02% based on the standard sample size, and is usually lower. The Army Corps Shell document allows reporting of non-detects (ND) at a level no lower than about twice the MDL and requires flagging of data between that and the quantitation limit (low standard). The laboratory has selected a standard reporting limit of 0.1% to allow for the fluctuation of MDLs and for the slight background TOC expected from the method and diluent sand, which can be controlled but never completely eliminated. A low standard at this level is analyzed with each run to verify its acceptability. The Shell allows for the reporting of flagged results between this low standard and twice the MDL but the laboratory rarely will report any values below the reporting limit represented by this low standard.

5.3 Initial Multi-Point Calibration

5.3.1 The initial, multi-point calibration should be done as needed. A multi-point calibration is not required with each analytical run. If the previous calibration is verified by an ICV, the calibration is considered valid and the instrument does not require recalibration.

5.3.1.1 A curve is not valid for longer than six months.

5.3.2 Calibration Curve

Concentration of KHP	Injection Volume
2000 mg/L	40 µl
1500 mg/L	40 µl
1000 mg/L	40 µl
500 mg/L	40 µl
0 mg/L DIW	40 µl

5.3.3 Calibration Setup

5.3.3.1 Select Calibration Standards from the Setup Menu.

5.3.3.2 Save the calibration standards as MMDDYY where M=month, D=day, Y=year.

5.3.3.3 Select Calibration Set Active from the Setup Menu.

5.3.3.4 Select the calibration standards that you named in 5.3.3.2 as active.

5.3.3.5 Select [Sample Setup] in the run screen.

5.3.3.6 To enter the appropriate standard Select TOC standard in the Sample Type column.

5.3.3.6.1 A window will open which will allow for choosing the appropriate standard.

5.3.3.7 The selected method should be TOC Range 0.1-20ppm C.

5.3.3.8 Select [Save/Use] to save the setup.

5.3.4 A small piece of quartz wool is placed into the boat. This should be replaced daily. A 40 µl aliquot of the 2000 mg/L standard is injected onto the quartz wool.

5.3.5 Press the "start" button, and slide the boat smoothly into the furnace at about two inches per second.

5.3.6 Repeat this procedure with each of the other calibration standards (1500, 1000, and 500 mg/L). In addition, analyze a calibration blank (DIW) just after the last calibration standard. Report this blank as a sample with no dilution.

5.3.7 Criteria

5.3.7.1 Initial calibration data is evaluated using the correlation coefficient of a linear regression analysis. The correlation coefficient must be 0.995 or greater for a 4-point calibration. All CCVs and sample extract concentrations must be computed using the regression equation.

5.3.8 Corrective action

5.3.8.1 If the criteria are not met, the instrument must be recalibrated.

5.4 Initial Calibration Verification

5.4.1 At the start of each analytical run a mid-range standard (1000 ppm C) is analyzed to evaluate the validity of the calibration curve.

5.4.2 Criteria

5.4.2.1 If the ICV is in control, the previous calibration is still valid. A new calibration must be performed when the ICV is out of control. It should read ±10% of the "true" value (between 900 and 1100 mg/L).

5.4.3 Corrective Action

5.4.3.1 Analysis of actual samples should not be started unless calibration of the instrument has been verified. If the ICV criteria are not met, no samples can be analyzed. Perform system maintenance and re-check the ICV. If the criteria still cannot be met, the system must be recalibrated.

5.4.3.2 **No sample values should be reported from any run where the calibration has not been adequately verified.**

5.5 Initial Calibration Blank

5.5.1 After the analysis of the ICV standard an instrument blank (ICB) is analyzed. The levels of target analytes in the ICB should not exceed 1/2 of the reporting limit.

5.5.2 Corrective action

5.5.2.1 If the ICB contains target analyte levels above one half of the reporting limit, the system is out of control. The source of contamination must be identified and corrected before proceeding with the analysis.

5.6 System Blank

5.6.1 Prior to the analysis of any samples, a system blank is analyzed to ensure that the sample boat is free from contamination

5.6.2 Criteria

5.6.2.1 The system blank must read ≤2 ppm at the instrument. If the system blank reads higher than 2 ppm, the source of contamination must be identified and corrected before proceeding with the analysis.

5.7 Method Blanks

5.7.1 Since there is not a "method blank" in this method the diluent blank will be used as a method blank to estimate the level of 'background' contamination. See the diluent blank discussion in section 5.9.

5.8 Field rinsates, field blanks

5.8.1 Criteria

5.8.1.1 Field rinsates and blanks are analyzed only upon client request and are not a routine part of the method. These aqueous samples are analyzed in a manner similar to calibration standards. That is, 40 µl of the aqueous sample is injected onto quartz wool in a combustion boat and ignited. The measured TOC value is computed assuming a 40 mg sample size with no dilution.

5.8.1.2 The TOC content cannot exceed the reporting limit.

5.8.2 Corrective action

5.8.2.1 Reanalyze the affected field QC sample. Notify the client project manager immediately since all samples from the set are potentially adversely affected.

5.9 Diluent Blank

5.9.1 Purified and ignited, carbon-free sand is to be used as the sample diluent. This sand must be confirmed to have carbon content less than the reporting limit for the analysis (0.1%) or produce a reading of less than 5% of the level in any sample for which results are reported. If a measurement of the diluent sand records detectable levels of organic carbon, a minimum of three replicates will be required to be analyzed. The resulting quantitation and reporting limits may be adjusted to reflect this mean detectable level, if necessary, but the routine reporting limit of 0.1% should be adequate to allow for low level contamination without reporting false positive sample results or results with a significant bias.

5.10 Method Detection Limit Standard

5.10.1 No method detection limit standard is utilized for evaluation in this analysis. However, the low standard is very near the reporting limit and must meet the calibration criteria discussed in the calibration section of this method.

5.11 Continuing Calibration Verification (CCV)

5.11.1 Criteria

5.11.1.1 A mid-range (1000 mg/L) calibration standard is analyzed after every 10 samples. In addition, this standard must be the last sample analyzed in the run.

5.11.1.2 The CCV must fall within ± 10% of the true value.

5.11.2 Corrective action

5.11.2.1 If CCV limits are exceeded, check calculations or perform instrument maintenance. Recalibrate and reanalyze. No sample results may be reported that are not bracketed by a successful calibration and a CCV, which is in control or by preceding and following CCVs, which are within limits.

5.12 Continuing Calibration Blank (CCB)

5.12.1 Immediately following the analysis of the CCV standard, a CCB must be analyzed. The CCB is 40 µL of DIW injected directly into the sample boat. The levels of target analytes in the CCB should not exceed 1/2 of the reporting limit.

5.13 Matrix Spike

5.13.1 Criteria

5.13.1.1 A sample is chosen at random from the samples to be analyzed, unless a client has specifically requested that a certain sample be spiked. An appropriate aliquot (generally 40µL) of the 1000 mg/L calibration solution is added to this sample prior to the combustion step. This addition should be at least double the instrument response. As the purpose of the matrix spike is to test the system under "typical" conditions, the analyst may avoid selecting the most difficult sample of the batch for spiking. It is not always required that a matrix spike analysis be performed with each preparation/analysis batch, however, 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 TOC. The TOC recovery is calculated as follows:

$$\%recovery = \frac{(SS - S)}{S_{true}} * 100$$

where:

SS = concentration in spiked sample
S = native concentration in unspiked sample
S_{true} = actual ("true") concentration of spike added

5.13.1.2 The recovery control limits are defined in the QC database. The current QC limit for MS/MSD is 50%-150%.

5.13.2 Corrective action

5.13.2.1 Samples with spike recoveries outside control limits will be reviewed for possible corrective action. Corrective action will first involve recalculation, followed by possible re-preparation, and/or reanalysis. This process should also look at the SRM analysis. In all cases a narrative explanation of the condition is required to detail the corrective actions taken.

5.14 Sample Duplicate

5.14.1 Criteria

5.14.1.1 At least one duplicate sample per 20 samples per matrix is required. The same sample selected as the matrix spike sample is also selected for the duplicate analysis unless the client has specifically requested that another sample be used.

5.14.1.2 RPD values are calculated as follows:

$$RPD = \frac{|S_1 - S_2|}{(S_1 + S_2)/2} * 100$$

where:
S_1 = measured concentration in the initial analysis
S_2 = measured concentration in the duplicate analysis

5.14.1.3 The RPD control limit is defined in the QC database. The current QC limit for RPD is 20%.

5.14.2 Corrective Action

5.14.2.1 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.

5.15 Standard Reference Material

5.15.1 Criteria

5.15.1.1 The standard reference material (SRM) must be analyzed at a frequency of once per 20 samples or per analysis batch whichever is more frequent.

5.15.1.2 The measured TOC value must be within the limits established by the SRM vendor. Alternatively, these limits may be unachievably narrow and may be

defined internally by the QA Officer. Acceptance limits are currently, TV = 2.61%, range = 2.09 - 3.03% as prepared, for ERA Lot 17095. The control limits for this and any replacement materials are located in the laboratory's quality control database.

5.15.2 Corrective Action

5.15.2.1 Appropriate corrective actions may include any or all of the following: check calculations, perform instrument maintenance, recalibrate the instrument, and reanalyze all affected samples. Corrective actions must be accepted by the QA Officer before data may be reported.

5.15.2.2 In any case, the SRM results must be recorded in the QC database and any corrective actions noted.

6. Operation procedures

6.1 Instrumental Conditions

6.1.1 The instrument with boat inlet is assembled according to the manufacturer's instructions.

6.1.2 A gas flow of 200 mL/min O_2 is set for the furnace.

6.1.3 Analysis sequence

6.1.3.1 Calibration standards (including calibration blank)

Aqueous ICV
Aqueous ICB
System Blank
Sand blanks (at least 1 per batch in triplicate)
Reference Material
PBS
10 or fewer samples (may include QC)
midpoint calibration standard (CCV)
calibration blank (CCB)
additional samples (no more than 10)
additional CCVs and CCBs
...
must close with CCV and CCB

6.2 Sample Analysis

6.2.1 Sample preparation

6.2.1.1 It is critical that each sample be thoroughly homogenized before a subsample is taken for analysis. If the sample is already finely divided with no large pieces, a homogeneous sample of 5 to 10 grams is dried in a 70°C oven. If samples contain larger pieces or if they in any way may compromise the analyst's ability to obtain a representative sample, the analyst should utilize sample size of at least 20 grams.

6.2.1.2 If the sample is already finely divided as described above, the dried sample, if it has formed clumps in the drying process, may be ground with a mortar and pestle to pass an 80 mesh sieve.

6.2.1.3 If the sample is sandy, rocky, or as described above, required a larger sample size; it should be ground using the disk pulverizer.

6.2.1.4 Following the grinding step, mix the ground sample thoroughly and combine a weighed, representative portion with clean diluents sand in a ratio of 1 part by weight sample to 4 parts by weight of sand. Record the weights of both sample and sand used. The mixture is placed in a snap-cap vial and tumbled for 90 minutes in the TCLP extractor. Dried, pulverized samples should be held in a desiccator.

6.2.2 Instrument startup

6.2.2.1 The furnace is turned on and the temperature allowed stabilizing. This takes approximately 30 minutes.

6.2.2.2 The instrument is set to the Boat Sampler Mode.

6.2.2.3 Sample combustion

6.2.2.4 Just prior to the combustion analysis, a sample aliquot (20 - 100 mg) is weighed into a combustion boat and wetted with 1:1 HNO_3. The boat is then placed in the 70°C oven and excess HNO_3 driven off (not more than 15 minutes).

6.2.2.5 The sample ID is entered into the sample setup screen and saved.

6.2.2.6 Insert a combustion boat containing treated sample into the wire loop. Close the lid and allow the instrument baseline to stabilize. This normally takes about two minutes.

6.2.2.7 Press the "start" button, and slide the boat smoothly into the furnace at about two inches per second.

6.2.2.8 After the instrument indicates the analysis cycle is complete, remove the boat, and after stabilization of the system, analyze the next sample in the sequence.

6.2.2.9 The same procedure is followed for blanks, samples, SRMs, and matrix spike samples. The size of the platinum boat and the percent carbon in the samples are the limiting factors for optimal sample size. Ten to 100 milligrams of prepared samples are used for analysis, with 40 mg preferred.

6.2.2.10 Total analysis time is approximately 5-6 minutes.

6.2.2.11 In some cases it may be necessary to analyze samples in quadruplicate. Check the LIMS comments to determine whether this is necessary.

6.3 Quantification

6.3.1 Micrograms sample burned

$$\mu g \text{ of sample burned} = \frac{(Ws*100)*Wb*1000}{(Ws+Wd)}$$

where:

W_s = weight (gm) sample diluted with sand
W_d = weight (gm) diluent sand used in sample preparation
W_b = weight (mg) sample combusted

6.3.2 Milligrams sand burned

$$\text{mg sand burned} = \frac{W_d}{W_s + W_d} * W_b$$

6.3.3 "sand correction"

$$C_s = \text{mg sand burned } (W_b) * \text{Corr}$$

where:

C_s = sand correction (response units)
Corr =correction factor for sand which is calculated by taking the average of three consecutive sand blanks.

6.3.4 Net sample reading

$$R_S = R - C_S$$

where:

R_S = net sample reading (response units)
R = uncorrected sample reading (response units)

6.3.5 TOC result

$$\% \text{ TOC} = \frac{R_S * CF * 100}{\mu g \text{ sample burned}}$$

where:

CF = calibration factor. The calibration factor is 0.04 because the instrument adjusts the result for calibration.

7. Reports

7.1 Sample Results and Quality Control Reports

7.1.1 In addition to the sample results, all results for quality control tests are entered into the lab database using the QC Database program. These results include those for the method blank analyses, matrix spike results, duplicate results, and Standard Reference material (SRM) reports. It is not necessary to include with each job a copy of the information entered into the QC Database program. However, for analytical consistency, a copy of the QC Database Report form MUST be included in order to indicate that the QC was evaluated.

7.1.2 Optional reports, which may be provided on client request, include initial and continuing calibration information and raw data.

7.2 Control Chart(s)

7.2.1 The recovery values for the LCS/SRM are plotted on control charts, which also may be supplied to clients upon request. Control limits are computed as discussed in Laucks SOP LTL-1011, "Procedures for the Determination and Reporting of Detection Limits, Reporting Limits, Precision and Accuracy Studies and Control Limits". Basically, warning limits are established as twice the standard deviation of the mean of at least 20 data points and control limits as 3 times the standard deviation. If it is a purchased laboratory control material for which the vendor has computed limits, those limits are used for control purposes. Control charts are developed and interpreted in accordance with section 7.6 of Laucks Quality Assurance Plan. Essentially, a method has exceeded

control when any point exceeds a control limit, when 3 consecutive points have exceeded a single warning limit, 8 or more points are on one side of the mean, or a pattern of increasing or decreasing points or cyclical pattern is readily observable.

7.3 Definitions:

CODE	Definition
U:	The analyte of interest was not detected, to the limit of detection indicated.

7.4 Data Review

7.4.1 Data validation is detailed in a separate SOP (see LTL-9001)

8. References

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, USEPA, 1986, Method 9060.

Appendix I

Laucks Testing Laboratories

Method SW 9060 (modified for soil/sediment) QA Requirements and Corrective Actions

QA Element	Method Criterion (for water)	Laucks Criterion	Frequency	Corrective Action	Documentation
Initial Calibration	per manufacturers instructions	4-point curve. 0.995 or higher correlation coefficient (r)	As needed. Expires after six months.	Fix problem and re-calibrate	in raw data package
Initial Calibration Verification	verify with check standard	Verify the calibration with 1000 mg/L KHP solution	At the beginning of each run	prepare new ICV and/or calibration solutions; service instrument; report no analyses from failed ICV	in raw data package
Initial Calibration Blank	Analyzed immediately after ICV	Must be less than ½ the reporting limit	Analyzed immediately after ICV	Source of contamination must be identified and corrected before proceeding with analysis	in raw data package
Continuing Calibration Verification	verify with an independently prepared check standard every 15 samples	verify with a mid-point standard; CCV must fall within 10% of the true value	after every 10 samples	Fix problem & recalibrate; re-analyze samples which are not bracketed by in-control CCVs	in raw data package

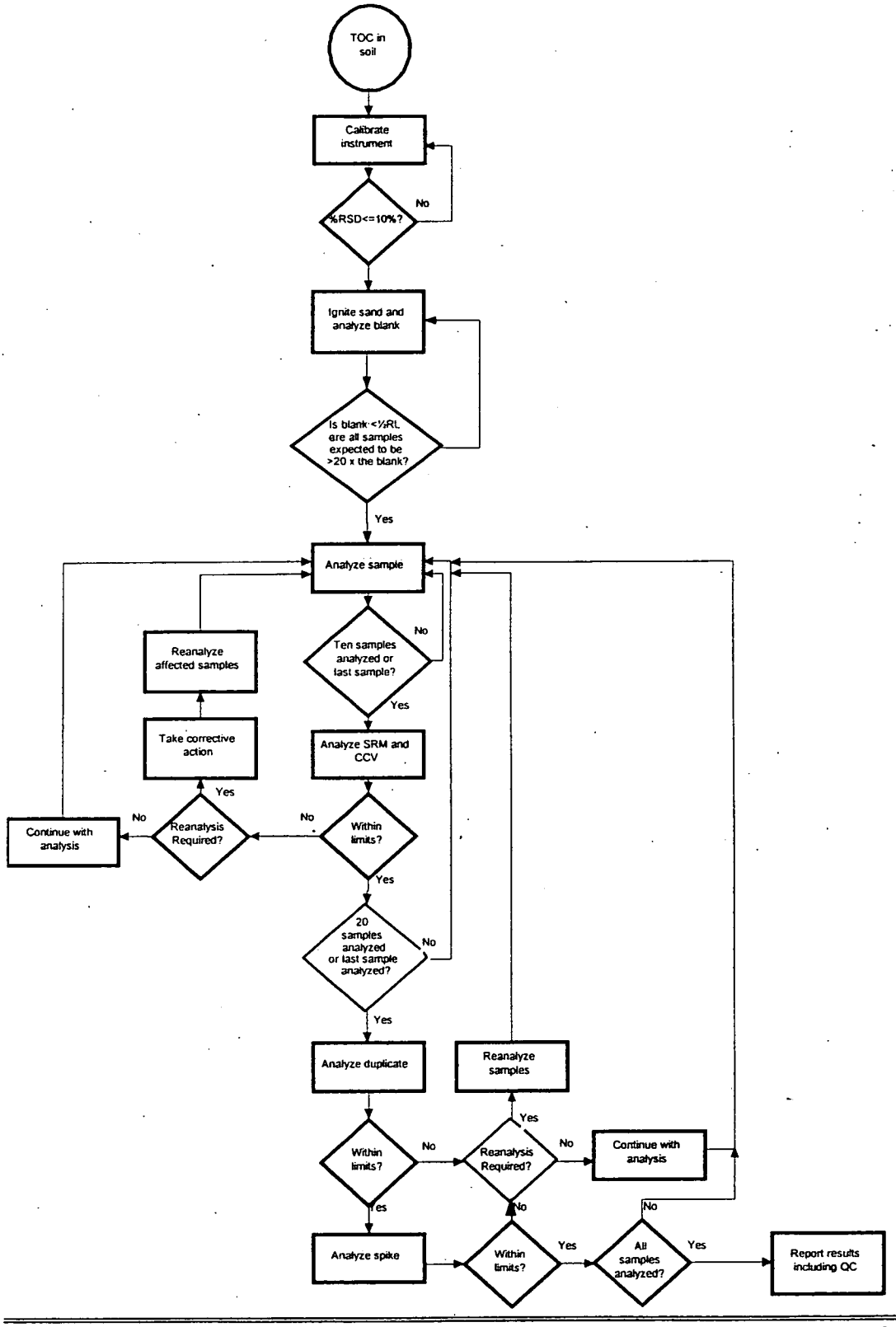
QA Element	Method Criterion (for water)	Laucks Criterion	Frequency	Corrective Action	Documentation
Continuing Calibration Blank	Analyzed immediately after CCV	Must be less than ½ the reporting limit	Analyzed immediately after CCV	Source of contamination must be identified and corrected. Affected samples must be reanalyzed.	in raw data package
Reporting Limit standard recovery	N/A	Must meet initial calibration criteria	Reporting limit standard is incorporated into curve	Recalibrate	in raw data package
System Blank	N/A	Must be ≤2 ppm instrument reading	Once after initial calibration	Check system for leaks; check sample introduction technique; do not analyze samples	in raw data package
Diluent Blank/Method Blank (sand blank)	Once per sample batch; no criteria	Diluent (sand) blank is determined and must be < ½ RL or 5% of any reported sample.	Once per batch or per twenty samples, in at least triplicate	If blank is very high, diluents sand should be re-ignited	in raw data package
Matrix Spike Recovery	once every 10 samples; no criteria	50% - 150% unless criteria are published in lab QC database	once every 20 samples or per batch, whichever is more frequent	Review data; Consult QC Officer; some conditions may require re-analysis	narrative comment in report and raw data package

QA Element	Method Criterion (for water)	Laucks Criterion	Frequency	Corrective Action	Documentation
Duplicate % Difference	N/A	20% unless criteria are published in lab control limits catalog or QC database	once every 20 samples or per batch, whichever is more frequent	Review data; Consult QC Officer; some conditions may require re-analysis	narrative comment in report and raw data package
Standard Reference Material (SRM) Recovery	N/A	ERA Sludge	once every 20 samples or per batch, whichever is more frequent	Review data; Consult QC Officer; some conditions may require re-analysis	narrative comment in report and raw data package

Appendix II

Flow Chart

TOC Analysis of Soils
by modified SW 846 Method 9060



LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-9136

Determination of Perchlorate by Ion Chromatography by EPA Method 314.0

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1. Introduction and Scope

1.1 Method Description

1.1.1 This method describes the technique used to determine perchlorate in surface water, ground water and drinking water using Ion Chromatography. The method is capable of being extended to the analysis of perchlorate in soil matrices if a preliminary leaching step is performed to solubilize the perchlorate

1.1.2 The anions in an aqueous solution are introduced via an autosampler into a flowing eluant stream. Perchlorate is separated by an analytical column. The separation column effluent is then passed through an anion micromembrane suppresser where counter ions are exchanged for hydronium ions. This serves to suppress the conductance of the eluant and enhances the conductance of the perchlorate by forming its complementary acids. Following this exchange the stream is passed through a conductivity detector. The detector output is collected by a data acquisition system, which stores the chromatograms for later calculation and interpretation.

1.1.3 This method is restricted to use by, or under the supervision of analysts experienced in the technique described. Each analyst performing this method must have demonstrated the ability to perform the described analysis.

1.2 Sample Collection, Sample Storage, Holding Times

1.2.1 Samples are collected in 500 or 1000 mL unpreserved plastic or glass bottles. Samples do not need to be shipped iced or stored cold in a refrigerator, but care should be taken not to expose samples to temperature extremes. No preservation is required.

1.2.2 Analysis holding time is 28 days.

1.3 Interferences

1.3.1 Interferences can be caused by substances with retention times that are similar to and overlap those of the anion of interest. Large amounts of an anion can interfere with the peak resolution of an adjacent anion. Sample dilution and/or spiking can be used to solve most interference problems.

1.3.2 Pretreatment cartridges are effective in eliminating certain matrix interferences. Extreme caution should be exercised when using pretreatment cartridges. Artifacts can leach from some cartridges which can cause damage to the columns resulting in a loss of

column capacity. Cartridges should be washed with DIW according to manufacturer's instructions prior to use.

1.3.3 Sample matrices with high concentrations of anions such as chloride, sulfate, and carbonate can cause the baseline to destabilize at the retention time of perchlorate. Sample conductivity is monitored prior to analysis. When the Matrix Conductivity Threshold (MCT) is exceeded, the samples are pretreated to reduce the concentration of the common anions or diluted to reduce interference.

1.3.4 Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baseline in IC.

1.3.5 Samples that contain particles larger than 0.45 microns and reagent solutions that contain particles larger than 0.20 microns require filtration to prevent damage to instrument columns and flow systems.

1.4 Definition of Terms

CCB - Continuing Calibration Blank - This is the same acronym used in the CLP program. This is a blank which is analyzed immediately after the CCV (almost always after every 10 samples and at the end of the analytical run) during the analysis sequence to determine whether the instrument or system has maintained a stable baseline and to estimate carry-over from a mid-level standard (CCV).

CCV - Continuing calibration verification. - This is the same acronym used in the CLP program. This is a standard analyzed at some prescribed frequency (almost always after every 10 samples and at the end of the analytical run) during the analysis sequence to determine whether the instrument or system has remained in calibration. The method refers to the CCV as the Continuing Calibration Check Standard (CCCS)

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 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, r - Correlation coefficient (r)- 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. This water should be free of virtually all analytes.

ICB - Initial calibration blank - This term is borrowed from CLP. An instrument blank is made up in the same way as calibration standards, without target analytes.

ICV - Initial calibration verification - This term is borrowed from the CLP protocol. It is a standard which is analyzed at the start of each analytical run that is compared to the initial multi-point calibration to determine whether the instrument calibration is within control. The method refers to the ICV as the Initial Calibration Check Standard (ICCS)

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 determined empirically by Laucks. See section 4.2 for a more detailed discussion of MDL determination.

SRM or LCS - Standard Reference Material or Laboratory Control Sample. This is a material of approximately the same matrix as the samples, containing a known and usually certified amount of target analyte and which is prepared and analyzed in the same manner as a typical sample. This sample is used to demonstrate that the analytical system is in control. May also be referred to as a blank spike. The method refers to the LCS as the Laboratory Fortified Blank (LFB).

QC period - Quality control period - An analysis sequence initiated by the analysis of one or more standards, followed by samples, and terminated with a standard and blank 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. 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 the IC (or other) column.

RT window - Retention time window - The +/- value which is applied to the individual analyte peaks to establish the time range used to make tentative target analyte identifications.

Sequence - A set of sample extracts and standard solutions injected into an instrument in a chronologically continuous group. See also QC period.

MCT – Method Conductivity Threshold – The highest conductance of a sample, measured prior to analysis, which is used to determine whether a sample should be pretreated or diluted prior to analysis to reduce interferences from common anions.

IPC – Instrument Performance Check Solution – A solution containing a specific concentration of perchlorate and other common anions (chloride, sulfate, and carbonate) used to evaluate the performance of the instrument with respect to a defined set of criteria.

2. Equipment List and Standards

2.1 Equipment

2.1.1 Ion chromatograph, Dionex model DX100 or equivalent consisting of a single piston pump, autosampler, either manual or automated injector, guard column, separator column, anion micromembrane suppresser, and a conductivity detector.

2.1.2 Guard column, Dionex AG16 or equivalent

2.1.3 Chromatographic column, Dionex AS16 or equivalent

2.1.4 Anion Micro Membrane Suppresser, Dionex ASRS-1 or equivalent. *Note: If pretreated sample are analyzed regularly, then cations from the cartridges may bind to the suppressor resulting in reduced peak response or asymmetrical perchlorate peaks. The suppressor should be cleaned regularly according to the manufacturer's instructions.*

2.1.5 Electronic data collection device, AI-450 Chromotography Software or equivalent, or other applicable data collection system.

2.1.6 Conductivity Meter

2.1.7 Analytical Balance

2.1.8 Plastic disposable syringes

2.1.9 Matrix pretreatment cartridges

2.1.9.1 Ba – reduce the matrix levels of sulfate

2.1.9.2 Ag – reduce the matrix levels of chloride

2.1.9.3 H - reduce Ag that may have leached from the Ag cartridge which may damage the suppressor. May indirectly reduce the levels of carbonate by removing the cationic counter ion.

2.2 Standards and Solutions

2.2.1 Perchlorate calibration primary stock solution (1000 mg/L): Dissolve 0.1231 g sodium perchlorate ($NaClO_4$) in DIW and dilute to 100 mL in a volumetric flask.

2.2.1.1 The above solution expires after one year. It may be stored at room temperature.

2.2.1.2 Spiking - Samples are spiked by adding 100µl of solution prepared in 2.2.1.1 to an aliquot of sample and diluting to 500 µl. The dilution of sample and spike are recorded in the dilution column of the batch schedule. The reference number of the spike is recorded in the sample name field of the batch schedule.

2.2.2 Perchlorate calibration secondary stock solution (1.0 mg/L): Dilute 0.5 mL of the perchlorate calibration primary stock solution to a final volume of 500 mL in a volumetric flask. This solution expires after one month. It may be stored at room temperature.

2.2.3 Perchlorate calibration solution #1 (400 µg/L): Dilute 80 mL of perchlorate calibration secondary stock solution to 200 mL in a volumetric flask. This solution expires after one month. It may be stored at room temperature.

2.2.4 Perchlorate calibration solution #2 (25 µg/L): Dilute 0.625 mL of the perchlorate calibration secondary stock solution to a final volume of 25 mL in a volumetric flask. This solution expires after one month. It may be stored at room temperature.

2.2.5 Mixed common anion stock solution: Dissolve the following salts in DIW to a final volume of 25 mL in a volumetric flask:

1.0 g sodium chloride (NaCl)
0.93 g sodium sulfate (Na_2SO_4)
1.1 g sodium carbonate (Na_2CO_3)

2.2.5.1 Each anion concentration in this solution is 25 mg/mL. It is used to prepare simulated common anion samples in the determination of the MCT.

2.2.5.2 The above solution expires after one year. It may be stored at room temperature.

2.2.6 MCT standards: Prepare the following seven standards in separate 25 mL volumetric flasks. Before bringing to volume, add 0.625 mL of the perchlorate calibration secondary stock solution.

Volume (mL) of mixed common anion stock solution	Measured conductivity range (µS/cm at 25°C)
0.20	1350-1500
0.30	1900-2100
0.40	2600-2800
0.50	3200-3700
0.60	3700-4000
0.80	4800-5200
1.00	5900-6400

2.2.7 Instrument performance check standard: a standard containing sulfate, chloride, carbonate and 25 µg/L of perchlorate at which the conductivity is +/-10% of the determined MCT. Confirm the conductance of this standard prior to analysis. If the conductivity has changed by more than 10%, a fresh standard must be prepared.

2.2.8 Perchlorate ICV stock solution (1000 mg/L): Dissolve 0.1393 g potassium perchlorate in DIW and dilute to 100 mL in a volumetric flask. This solution expires after one year. It may be stored at room temperature.

2.2.9 Perchlorate ICV standard (80 µg/L): Dilute 0.080 mL of Perchlorate ICV stock solution to 1 L in a volumetric flask. This solution expires after one year. It may be stored at room temperature.

2.2.10 Conductivity meter calibration solution: Dissolve 0.745 g potassium chloride (KCl) in DIW and dilute to a final volume of 1.0 L in a volumetric flask. The conductance of this solution is 1410 µS/cm at 25°C.

2.2.11 Eluant Solution

2.2.11.1 The eluant is 50 mM sodium hydroxide solution. The eluant is prepared by dissolving 8.0 g of 50% sodium hydroxide in DIW and diluting to a final volume of 2 L. Exposure to the atmosphere should be minimized to reduce possible carbonate contamination. Should be prepared fresh weekly and purged for 10 minutes with helium prior to use. The suppressed conductivity background of this solution should be between 2–5 µS.

3. Safety precautions and Waste Disposal

3.1 Safety Precautions

3.1.1 All standards, samples and sample solutions should be handled as if they are 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.

3.2 Waste Disposal

3.2.1 There is no significant waste generated from this procedure. Any remaining liquids are disposed of by flushing down the sink. Solid material may be disposed of in the garbage.

4. Calibration and Quality Control

4.1 Minimum Conductivity Threshold Study

4.1.1 Prior to the analysis of any samples, it is necessary to establish the minimum conductivity threshold. It involves preparing a series of standards with increasing amounts of common anions (chloride, sulfate, and carbonate) that each contain a constant concentration of perchlorate.

4.1.1.1 Prepare the MCT standards described in section 2.2.7.

4.1.1.2 Measure and record the conductance of each of these prepared solutions on a conductivity meter.

4.1.1.3 Analyze each solution, recording the peak to area height ratio (A/H) and the quantified concentration of perchlorate.

4.1.1.4 Calculate the A/H ratio percent difference ($PD_{A/H}$) between the average A/H ratio for calibration standard #2 ($A/H_{CS\#2}$) and the average A/H ratio for each MCT standard (A/H_{MCT}) using the following equation:

$$PD_{A/H} = \frac{|A/H_{CS\#2} - A/H_{MCT}|}{A/H_{CS\#2}} * 100$$

4.1.1.5 The MCT is set at the conductivity of the highest MCT standard which yielded a $PD_{A/H}$ less than 20%.

4.1.1.6 Finally, confirm the reporting limit of perchlorate with a solution that has a conductivity within 10% of the MCT and a perchlorate concentration at or near that reporting limit. The recovered perchlorate concentration must be between 70-130% the true value. If the recovery falls outside of this criteria, then the MCT must be lowered by 10% and this procedure repeated.

4.1.1.7 The conductivity of all samples must be determined prior to analysis. If the conductivity is greater than the MCT, the sample must be diluted or pretreated.

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 the determination of method detection limits (LTL-1011). This SOP can be found in the SOP manual. Briefly, it involves the analysis of 7 replicate samples spiked at a concentration 1-5 times the anticipated method detection limit. A Student's t-test is then applied to these measured values to calculate the MDL.

4.2.2 MDL studies for the ion chromatograph must be determined at a minimum of every six months, with each new analyst, or whenever there is a significant change in system response. The current approximate MDL is 0.5 µg/L.

4.3 Determination of Retention Time Windows

4.3.1 Every six months, or any time there is a significant change in the system (such as analytical column replacement), the retention time windows need to be determined.

4.3.2 The RT window is determined by taking the retention times of three CCVs (mid range standards) on any one day, and computing the standard deviation. The standard deviation multiplied by three is the retention time window. This procedure is similar to that described in the Laucks SOP on Determination of Retention Time Windows (LTL-8000) except one run is used rather than a 72-hour period. This value is then entered into the AI-450 method. The retention time windows are stored in the method.

4.3.3 This data is generated on an Excel spreadsheet and is archived on the laboratory data base.

4.4 Initial Multi-Point Calibration

4.4.1 The reference method requires a calibration curve consisting of a minimum of five points if the curve extends over two orders of magnitude. LTL currently uses a six point curve. All calibration standards are diluted in sample vials at the instrument just prior to analysis as stated in the following table:

Standard Number	Volume of Standard	Volume DIW	Total Volume	Perchlorate concentration (µg/L)
1	50 µl of Cal #2	450 µl	500 µl	2.5
2	100 µl of Cal #2	400 µl	500 µl	5.0
3	500 µl of Cal #2	0 µl	500 µl	25.0
4	100 µl of Cal #1	400 µl	500 µl	80.0
5	250µl of Cal #1	250 µl	500 µl	200.0
6	500 µl of Cal #1	0 µl	500 µl	400.0

4.4.2 Samples whose responses exceed the high standard must be diluted.

4.4.3 A multi-point calibration of the system is not required with every analytical run.

4.4.3.1 If the previous calibration is verified by an ICV, the calibration is considered valid and the instrument does not require re-calibration.

4.4.3.2 A curve is not valid for a period of greater than six months.

4.4.4 Criteria

4.4.4.1 Initial calibration data is evaluated using the correlation coefficient of a linear regression analysis. The linear correlation coefficient (r) must be 0.995 or greater. All CCVs and sample concentrations must be computed using the regression equation.

4.4.5 Corrective action

4.4.5.1 If the criteria are not met the instrument must be recalibrated. No data may be reported for an analyte that does not have a valid calibration.

4.5 Instrument Performance Check

4.5.1 The MCT must be verified at the beginning of every analysis by analyzing an instrument performance check standard (IPC). The calculated $PD_{A/H}$ (see section 4.1.1.4 for calculations) of this solution must be less than 25% and the percent recovery of perchlorate must be between 80-120% of true value. Samples may not be analyzed and instrument maintenance must be performed or the MCT redetermined if the results fall outside this criteria. Also, the retention time of perchlorate must be within 80% of the original retention time of the column at installation. If the retention times have shifted past this point, then the column must be cleaned or replaced.

4.6 Initial Calibration Verification

4.6.1 At the start of each analytical run, analyze a standard from a source other than that from which the calibration material was obtained.

4.6.2 Criteria

4.6.2.1 The calculated concentration of the ICV for perchlorate must not to exceed ±25% of the true value.

4.6.3 Corrective action

4.6.3.1 If the ICV criteria are not met, no samples can be analyzed. Perform system maintenance and re-check the ICV. If the criteria still cannot be met, the system must be recalibrated. No data can be reported for an analyte that does not have a valid ICV.

4.7 Initial Calibration Blank

4.7.1 After the analysis of the ICV standard an instrument blank (ICB) is analyzed. The levels of target analytes in the ICB should not exceed the 1/2 the reporting limit.

4.7.2 Corrective action

4.7.2.1 If the ICB contains target analyte levels above the 1/2 the reporting limit which is currently 4.0 µg/L the system is out of control. The source of contamination must be identified and corrected before proceeding with the analysis. No data can be reported for an analyte that does not have a valid ICB.

4.8 Blank Spike/LCS

4.8.1 Immediately after the analysis of the ICV and ICB, a blank spike (currently spiked with 50 µL of calibration standard #2) must be analyzed using the same solution used to calibrate the instrument and spike the matrix spikes. This sample is filtered and analyzed as a sample. If some samples are pretreated, then a separate blank spike that is also pretreated must be performed.

4.8.2 The blank spike recovery of perchlorate must be within 85-115%. If the recovery falls outside of this criteria, the source of the problem must be identified and resolved before continuing analysis.

4.9 Continuing Calibration Verification (CCV) and Blank (CCB)

4.9.1 A mid-range calibration standard is analyzed at a minimum of once every 10 sample injections. Immediately following the CCV, a blank solution is analyzed. In addition, at the end of the run, this standard should be run at a different level than preceding CCVs to verify that the curve has remained linear throughout the analysis. A CCB should follow this final CCV.

4.9.2 Criteria

4.9.2.1 The CCV must fall within ± 15% of the true value. The levels of target analytes in the CCB should not exceed the 1/2 the reporting limit of 4.0 µg/L.

4.9.3 Corrective action

4.9.3.1 If CCV limits are exceeded, check calculations or perform instrument maintenance. Recalibrate and reanalyze. No sample results may be reported that are not bracketed by a successful ICV and a CCV which is in control or by preceding and following CCVs which are within limits.

4.9.3.2 If the CCB contains target analyte levels above the 1/2 the reporting limit of 4.0 µg/L, the system is out of control. The source of contamination must be identified and corrected and the affected samples re-analyzed. As with the CCVs, no sample results may be reported that are not bracketed by a successful initial and continuing calibration blank which are in control or by preceding and following CCBs which are within limits.

4.10 Method Blanks

4.10.1 Method blanks are used to verify contamination free reagents and apparatus. They are prepared with every set of samples prepared at the same time, or at least one blank every 20 samples, whichever is more frequent. Any analyte response above the reporting limit of 4.0 µg/L is reported. For the purpose of water analyses, the ICB, CCBs, and the method blank are the same. Method blank control limits are that contamination should not exceed the 1/2 the reporting limit for waters. Method blanks should not exceed the reporting limit of 100 µg/kg for soil leaches.

4.10.2 Corrective action

4.10.2.1 Corrective action may necessitate re-preparation and re-analysis of the sample set. For example if an analyte were found in the blank but not in any of the associated samples then sample group may not require re-analysis. In addition, if sample levels exceed 10 times the blank, the level of contamination may be considered insignificant. In any case, if re-preparation and re-analysis is not being undertaken, the analyst must first discuss the issue with the Quality Control Officer. It is the laboratory's responsibility to ensure that method interferences caused by contaminants in acids, solvents, reagents, glassware, and other sample processing hardware leading to discrete artifacts and/or elevated baselines in the analytical run 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.

4.11 Matrix Spike/Matrix Spike Duplicate

4.11.1 Project-specific criteria will determine whether MS/MSD or MS/Duplicate analysis is to be performed. Samples are spiked by adding 50 µl of calibration solution #1 to an aliquot of sample and diluting to 500 µl. The dilution factor of the sample and the spike are recorded in the dilution field of the batch schedule. The reference number for the spike is recorded in the sample name field of the batch schedule.

4.11.2 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 preparation. The analyst should attempt to avoid selecting samples which are identified by the client as blanks. As the purpose of the matrix spike is to test the system under "typical" conditions, the analyst may also avoid selecting the most difficult sample of the batch for spiking. It is not always required that a matrix spike analysis be performed with each preparation/analysis batch, however, the

minimum frequency for MS analysis is 1 each per 20 samples per matrix. This will be best accomplished by running one with every batch for many analyses. 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:

$$\% \text{ recovery} = \frac{(SS - S) * 100}{SA}$$

where: SS = concentration in spiked sample
S = native concentration in unspiked sample
SA = spiked added, the amount of spiking material actually added to the sample calculated on the sample basis

4.11.3 The recovery criteria are detailed in the Quality Control Database and will change from time to time. The current control limits are 80-120%.

4.11.4 Corrective action

4.11.4.1 Samples with spike recoveries outside control limits will be reviewed for possible corrective action. Corrective action will first involve recalculation, followed by possible re-preparation, and/or reanalysis. This process should also look at the recovery of matrix spiking compounds from the SRM and/or blank spike analysis. In all cases a narrative explanation of the condition is required to detail the corrective actions taken.

4.12 Sample Duplicate

4.12.1 Criteria

4.12.1.1 At least one duplicate sample per 20 is required for Method 314.0. RPD values are calculated in the following manner:

$$RPD = \frac{|S1 - S2| * 100}{(S1 + S2)/2}$$

where: S1 = measured concentration in the initial analysis
S2 = measured concentration in the duplicate analysis

4.12.1.2 The RPD control limits are detailed in the Quality Control Database and will change from time to time. The current control limit is 15%.

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. Generally, if recoveries are in control and no analyte of interest was detected in any of the samples, no immediate action will be taken on that sample set. If integrity of reported sample values is in doubt, re-analysis may be called for. Corrective actions should be discussed with the Quality Control Officer.

5. Operation Procedures

5.1 Initial Multi-Point Calibration

5.1.1 Creating a method

5.1.1.1 To start the Method Editor program double-click on the Method icon in the AI-450 MainMenu.

5.1.1.2 Method Settings:

System: Dionex DX-100
Number of Detectors: 1
Detector 1: Other-COND conductivity detector
1000mV=30.000uS
Run Time: 6-13 min. depending on retention time of sulfate peak
Plot Min.: -1
Plot Max: 30
Sampling Rate: 2 Hz
Timed Events: Init-Pump on
0.1:Offset on, Sampler on, Pump on, Begin Sampling on
Detector 1: Integration- Threshold-10.0, Width-10.0 sec, Reject-1000.0, Reference Peak area reject-2000.0
Data Events- void volume treatment for this peak at Fluoride retention time
Calibration- 4 levels, linear, calibration update- replace, standardization- external, Resp. for unknowns-area. The rest is set with the default settings.
Components- Enter each component that will be analyzed and their respective retention times, retention time windows. Calibrate by area. Reference component #1.

Enter amount of analyte at each calibration level.
Save new method as icMMDDYY.met where M=month, D=day, Y=year.

5.1.2 Creating a Calibration Curve Schedule

5.1.2.1 To start the Schedule Editor Program, double-click on the [Schedule] icon in the AI-450 MainMenu.

5.1.2.2 Enter sample name. For calibration purposes *autocal1r* is the name for the level 1 standard, *autocal2r* is the name for the level 2 standard, etc.

5.1.2.3 Enter the name of the method saved in 5.1.1.2

5.1.2.4 Enter a file name cMMDDYY, where M=month, D=day, Y=year. The program will number the filenames during analysis.

5.1.2.5 Save Schedule as cMMDDYY.sch., where M=month, D=day, Y=year.

5.1.3 Starting a run

5.1.3.1 Double-click on the [run] icon in the AI-450 MainMenu.

5.1.3.2 Load the schedule into the run program.

5.1.3.3 Load autosampler with cartridge containing the 4 levels of standards. Set autosampler to Run.

5.1.3.4 Set DX-100 to relay control.

5.1.3.5 Choose the run menu and start in the Run Program of AI-450.

5.2 Analysis tools and observations

5.2.1.1 If a discrete bottle number is referenced on the sample container, this information must be recorded in the sample name field of the batch schedule.

5.2.1.2 Samples that appear overly turbid or that have suspended or floating particles must be filtered through a 0.45 µm syringe filter prior to analysis. If this procedure is followed it should be documented.

5.2.1.3 Other anomalies should be discussed with the departmental supervisor in order to determine appropriate corrective action.

5.3 Sample Analysis

5.3.1 If samples are stored at 4±2°C, then samples should be brought up to room temperature prior to analysis.

5.3.2 Measure and record sample conductivity. If sample conductivity is less than the MCT, then the sample may be analyzed without pretreatment or dilution. If the sample conductivity is greater than the MCT, then samples must be pretreated or diluted prior to analysis.

5.3.3 Dilution

5.3.3.1 Calculate the dilution factor by dividing the measured sample conductance by the MCT and rounding up to the nearest whole number.

5.3.3.2 After dilution, measure and record the conductivity of the diluted sample to verify that it is below the MCT.

5.3.3.3 The sample reporting limit will change by an equivalent factor.

5.3.4 Pretreatment

5.3.4.1 Thoroughly rinse each filter cartridge with DIW to reduce the risk of contamination.

5.3.4.2 Rinse 3 mL of sample through the rinsed filter cartridges stacked in series (→Ba→Ag→H) at a flow of 1 mL/min. or less. This fraction is discarded.

5.3.4.3 Continue filtering at a rate of 1 mL/min until sufficient volume has been collected to measure the conductivity and analyze the sample.

5.3.4.4 Measure the conductivity of the pretreated sample to ensure that the conductivity is less than the MCT. If the sample conductance is below the MCT, then the sample may be analyzed. If the sample conductance is greater than the MCT, the flow rate through the filters is probably too fast and the sample pretreatment should be repeated with new cartridges.

5.3.4.5 If a batch contains pretreated samples, then a blank spike, method blank, and MS/MSD or MS/Dup must also be pretreated and analyzed.

5.4 Analysis sequence

Calibration standards (from low to high concentration)

IPC
ICV
ICB
Blank spike
Method blank
Pretreated blank spike (if necessary)
Pretreated method blank (if necessary)
10 or fewer injections
midrange standard (CCV)
DIW (CCB)
additional samples (not more than 10 injections)
additional CCVs and CCBs
...
...
must close with CCV and CCB

5.5 Instrumental Conditions

5.5.1 System Conditions

- Eluant flow is approximately 1.5 mL/min
- Injection volume is 500 µL.
- Temperature correction factor is 1.7.
- Detector range is 30 µS.
- Analysis time is approximately 15 minutes.
- Background conductivity is between 2-3 µS .

5.6 Analytical Operation

5.6.1 Analytical procedure for liquid matrixes after any necessary pretreatment.

5.6.1.1 A schedule is constructed for the sample set. This includes the appropriate dilutions for the given samples, the method name that corresponds to the curve that is in effect, and the filename where data for the sample will be saved. The file name extension is updated during analysis, therefore the analyst will not need to type in an extension.

5.6.1.2 The schedule is loaded into the run program of AI-450.

5.6.1.3 An appropriate number of 500 µL sample vials are placed into the auto sampler trays.

5.6.1.4 500 µL of standards, samples and QC events are placed into the sample vials.

5.6.1.5 Dilutions up to 50x can be done directly in the sample vials, greater dilutions will require an external dilution in a Solo cup or a combination of external and sample cup dilutions.

5.6.1.6 Sample vials are capped with filter caps and placed in the auto sampler.

5.6.1.7 The "Control" button on the DX-100 is set on relay and the autosampler is set on local control and run.

5.6.1.8 Choose the run menu and start in the Run Program of AI-450.

5.6.2 Analytical procedure for soil or sludge matrixes.

5.6.2.1 The soil/sludge is leached with DIW by transferring 10 g to a tared, 250 mL digest bottle, adding 100 mL DIW and placing on the shaker for 15 minutes or more at a shaking rate sufficient to suspend the majority of the solids. The solids are then allowed to settle and an aliquot of the supernatant is filtered through a 0.45 µm syringe filter prior to use. The leaching and filtration of the sample must be recorded in the pretreatment field of the batch summary and a prep sheet completed.

5.6.2.2 A 100 mL aliquot of DIW is shaken in a 250 mL digest bottle and used as a method blank.

5.6.2.3 The resulting supernatant is treated as a water sample and is pretreated if necessary.

5.6.2.4 A total solids determination is made on all soil/sludge samples and the results are reported on a dry weight basis.

5.7 Compound Quantification

5.7.1 The data acquisition system generates a report with the chromatogram of the sample, the date analyzed, the sample identification, the method used to quantify the sample, the sample dilution, and the calculated concentration of the sample corrected for dilution.

5.7.2 For soil/sludge samples, the mg/L integrator value is converted to mg/kg DB by the following equation:

Soil: $$Cs = \frac{Ci * Vs * 100}{Ws\ TS}$$

Cs = Sample concentration (mg/kg DB)
Ci = Concentration in sample injected (mg/L)
Vs = Volume of extract (mL)
Ws = Weight of sample extracted (gm)
TS = Total solids (as fraction)

6. Reports

6.1 Sample Results and Quality Control Reports

6.1.1 Data packages shall consist of the sample results summary, the chromatograms for samples in the workorder, and a copy of the QC summary report form. These include the method blank analysis, matrix spike results, duplicate results, and the Standard Reference Material (SRM) reports. A copy of the QC summary report form must be included in order to indicate that the QC was evaluated for analytical consistency.

6.2 Data Qualifying Flags

6.2.1 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.

Appendix I

Method 314.0 QC Requirements and Corrective Actions

QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
Initial Calibration	A minimum five point curve for curves that span two orders of magnitude that brackets the sample concentrations.	A six point curve that brackets the sample concentrations Corr coef r≥ 0.995	As instrument performance dictates, or when any change is made in the analytical system.	Fix the problem and recalibrate.	In the raw data package for all validatable packages and referenced in all other data.
Instrument Performance Check (IPC)	Conductance at ± 10% of the MCT; $PD_{A/H}$ less than 25%; Perchlorate recovery at between 80-120%. Perchlorate retention time greater than 80% the original RT.	Conductance at ± 10% of the MCT; $PD_{A/H}$ less than 25%; Perchlorate recovery at between 80-120%. Perchlorate retention time greater than 80% the original RT.	Prior to analysis.	Repeat the MCT study and reanalyze the IPC; Clean analytical column.	In the raw data package for all validatable packages and referenced in all other data.
Initial Calibration Verification	Not to exceed ±25% of the true value.	Not to exceed ±25% of the true value.	At the beginning of the analysis.	Reanalyze, if reanalysis fails recalibrate and or perform instrument maintenance. No data can be reported if ICV fails.	In the raw data package, and in the quality control data base.
Initial Calibration Blank	Value not to exceed the RL.	Value not to exceed the 1/2 the reporting limit	Immediately following the ICV.	Reanalyze. No data can be reported if ICB fails.	In the raw data package, and in the quality control data base.

QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
Continuing Calibration Verification	Not to exceed ±15% of the true value.	Not to exceed ±15% of the true value.	At a minimum, after every 10 injections and as the final injection.	Samples which are not bracketed by in control CCVs must be reanalyzed.	In the raw data package.
Continuing Calibration Blank	Value not to exceed the RL.	Value not to exceed the 1/2 the reporting limit.	Immediately following a CCVs.	Samples which are not bracketed by in control CCBs must be reanalyzed.	In the raw data package.
Blank Spike/LCS	Spike a blank with the calibration standard at no greater than 10 times the highest perchlorate level in the sample batch; recovery at +/- 15% of true value.	Spike a blank with the calibration standard at no greater than 10 times the highest perchlorate level in the sample batch; recovery at +/- 15% of true value.	Run at a minimum of 1 per 20 samples. A pretreated BS must be run with samples that are pretreated.	Source of the problem identified and fixed prior to analyzing samples.	Run at a minimum of 1 per 20 samples. A pretreated MB must be run with samples that are pretreated.
Method Blank	Value not to exceed the RL.	Not to exceed the 1/2 the reporting limit for waters and the reporting limit for soils.	Run at a minimum of 1 per 20 samples. A pretreated MB must be run with samples that are pretreated.	If sample concentration exceed 10x the contamination level, no action required. Samples with contaminated Method Blanks must be re-extracted.	In the raw data package, and in the quality control database.
Matrix Spike /Matrix Spike Duplicate Recovery	Not to exceed ±20% of the true value. Once every 20 samples.	Not to exceed ±20% of the true value. Once every 20 samples.	Once every 20 samples, or per client request, whichever is more frequent.	Review data, consult QC officer, some conditions may require reanalysis.	Narrative comment in report in quality control database, and in raw data package.

QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
Duplicate/ Relative % Difference (RPD)	Not to exceed 15%. Once every 20 samples	Not to exceed 15%. Once every 20 samples	Once every 20 samples, or per client request, whichever is more frequent.	Review data, consult QC officer, some conditions may require reanalysis.	Narrative comment in report in quality control database, and in raw data package.

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-9202

Title: **Total Suspended Solids (Non-Filterable Residue) Using EPA Method 160.2 / Standard Methods 2540D and Total Volatile Suspended Solids Using Standard Methods 2540 E.**

Revision history:

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1.0	7/11/94
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Paul Swift, Inorganic Division Manager

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Kathy Kreps, Laboratory Director

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1. Introduction and Scope

1.1 Method Description

1.1.1 Scope and Application

1.1.1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes. The practical range of the determination is 4 mg/l to 20,000 mg/l. The detection limit, however, is generally reported as 2 mg/l unless a sample volume greater than 100 mls is used.

1.1.1.2 A well-mixed sample is filtered through a standard glass fiber filter. The filter and residue are dried to constant weight at 103°C-105°C.

1.1.1.3 The filtrate from this method may be used for Total Dissolved Solids (Filterable Residue).

1.1.1.4 If volatile suspended solids are to be determined, the filter and residue are then ignited at 550°C and the loss on ignition determined.

1.1.2 Interferences

1.1.2.1 Samples high in dissolved solids (filterable residue), such as saline waters, brines and some wastes, may be subject to positive interferences due to soluble material which has not been adequately washed from the filter. Care must be taken to ensure that an appropriate filtering apparatus has been selected and the filter adequately washed in order to minimize this possibility.

1.1.2.2 Samples which are very high in suspended material or which have certain particle sizes may plug the filter causing difficulty in filtering. It may be necessary to reduce sample size in order to reduce this tendency.

1.1.2.3 This method is restricted to use by, or under the supervision of analysts experienced in the technique described. Each analyst performing this method must have demonstrated the ability to perform the described analysis.

1.2 Sample Collection, Sample Storage, Holding Times

1.2.1.1 No preservation of the sample is necessary. Refrigeration or icing to 4°C, to minimize microbiological decomposition of solids, is required. Analysis should begin as soon as possible and should in no case exceed 7 days from the date of collection. All exceptions, whether due to laboratory or client cause, must be recorded on a Holding Time Violation Report (HTVR).

1.3 Definition of Terms

1.3.1 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.

DIW - Deionized water - Lab reagent water. This water should be free of virtually all analytes.

MDL - Method detection limit - The lowest concentration a sample which will yield a positive result that is greater zero at a known level of confidence. MDLs are empirically determined by Laucks, although there is no known way to determine the MDL for the TSS or TVSS analyses.

SRM or LCS - Standard Reference Material or Laboratory Control Sample. This is a material of approximately the same matrix as the samples, containing a known and usually certified amount of target analyte and which is prepared and analyzed in the same manner as a typical sample. This sample is used to demonstrate that the analytical system is in control. It may be considered to be a blank spike for most inorganic analyses and is preferred over artificially spiking blank materials. This type of sample is rarely analyzed at Laucks for TSS and there is no known source of TVSS material.

Sequence - A set of samples analyzed in a chronologically continuous group.

Total Suspended Solids (TSS) (nonfilterable residue)- Those solids which are retained on a glass fiber filter of the appropriate retentive ability and dried to constant weight at 103-105C.

Total Volatile Suspended Solids (TVSS) - Suspended solids which are volatile (burn off) at a temperature of 550°C.

2. Equipment List

Glass fiber filter discs, 4.7 cm without organic binder, Gelman A/E or equivalent. Laucks currently uses Pro Weigh 47 mm glass fiber filters from Environmental Express which are designed for TSS analysis. They are pre-washed and pre-weighed and require no additional preparation.

Membrane filter funnel with the capability of adequately supporting 4.7 cm. filters

Suction flask

Drying oven, set at 103°C-105°C.

Muffle furnace set at 550°C ± 50°C

Desiccator charged with active silica gel desiccant

Analytical balance, capable of weighing to 0.1 mg.

3. Safety precautions and Waste Disposal

3.1 Safety Precautions

3.1.1 All standards, samples and sample solutions should be handled as if they are 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 Routine precautions include an awareness of elevated temperatures of both the oven and any samples which have recently been removed from the drying oven or especially the muffle furnace. The temperatures involved in this analysis can cause severe burns if adequate care is not taken.

3.2 Waste Disposal

3.2.1 No waste should be generated from this procedure. Sample residues may be washed out and discarded down the sink.

4. Quality Control

4.1 Method Blanks

4.1.1 Criteria:

4.1.1.1 Method blanks are used to verify contamination free reagents and apparatus. They are prepared with every set of samples prepared at the same time or at least one blank every 20 samples which ever is more frequent. The method blank is prepared by pouring the same amount of deionized water through a filter as one would a typical sample (generally 100 mls.). Any TSS above the detection limit is reported. Method blank control limits are such that contamination should not exceed twice the detection limit. If 100 ml samples are used, Laucks generally considers the detection limit to be 2 mg/L with method blank control limits of 4 mg/L.

4.1.1.2 In making a determination of whether or not the analysis is in control, the analyst should actually be normalizing the blank to whatever volume was used for any sample. It is assumed that any blank is due to washings from the filter and apparatus and is actually independent of sample volume. In other words, the control limit for this analysis is actually 0.4 mg. If blank contamination exceeds that value, the TSS (or TVSS) of samples must be ten times that weight or corrective action should be taken.

4.1.1.3 If TVSS is being determined, the filters are processed in the same manner only are also heated to 550°C. Otherwise, the detection limits, criteria, and corrective actions are the same as for TSS.

4.1.2 Corrective action

4.1.2.1 Corrective action may necessitate re-preparation and re-analysis of the sample set. For example if TSS or TVSS were found in the blank but not in any of the associated samples, then the sample group may not require re-analysis. In addition, if sample levels exceed 10 times the blank, the level of contamination may be considered insignificant. In any case, if re-analysis is not being undertaken, the analyst must first discuss the issue with the Quality Control Officer. In all cases where blank contamination exceeds the control limit, a narrative comment must be made which documents the corrective actions taken.

4.2 SRM or LCS

4.2.1 Criteria

4.2.1.1 Analysis of a reference material is not normally required for TSS analysis and no known material is available for TVSS. An SRM/LCS analysis will generally be analyzed only if specifically required for a project. If not otherwise specified in that contract, it would typically

be analyzed at a frequency of once per 20 samples. Vendor specified control limits would be used for any such material.

4.2.2 Corrective Action

4.2.2.1 Re-analysis of all associated samples may be required if this sample exceeds it's limits. The QC Officer should be consulted for any other corrective actions and all instances of out-of-control events and any actions taken must be documented in the QC narrative of the report.

4.3 Sample Duplicate

4.3.1 Criteria
At least one duplicate sample per 10 samples is required. RPD values are calculated as follows:

$$RPD = \frac{|S1 - S2| * 100}{(S1 + S2)/2}$$

where
S1 = measured concentration in the initial analysis
S2 = measured concentration in the duplicate analysis

4.3.1.1 The RPD control limits are detailed in the Quality Control Database (QC_DB) and will change from time to time. For samples with values which are less than 5 times the detection limit, the control limit is equal to 5 times the detection limit. For values greater than 5 times the detection limit, the control limit is a calculated percent RPD.

4.3.2 Corrective action

4.3.2.1 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. If integrity of reported sample values is in doubt, re-analysis of all associated samples may be called for. Corrective actions should be discussed with the Quality Control Officer.

5. Operation procedures

5.1 Sample Analysis

5.1.1 Analysis sequence

Method Blank
SRM or LCS (if required)
up to 20 samples plus duplicates

5.1.2 Analytical Operation

5.1.2.1 Drying, ashing or cooling times in this section are those typically used in the laboratory and are not specifically required by the method. The method requires a minimum of 1 hour drying or ashing times and analysis to constant weight. This may be achieved through either shorter or longer time periods than those specified in this SOP. Experience has also shown that the beakers or other weighed containers must be cooled to room temperature for the weights to be stable and accurate. As long as proper and complete cooling has been allowed to occur in an environment where the dried or ashed sample cannot re-absorb water or be otherwise contaminated, these times are not specified in the published method and are thus also flexible.

5.1.2.2 Preparation of glass fiber filter disc if Environmental Express Pro Weigh filters are being used: Remove the filter from it's aluminum weighing dish and place the disc on the membrane filter apparatus with the wrinkled side up. While vacuum is applied, rinse the disc with a small amount of deionized water in order to seat the disk in the filter device.

5.1.2.3 Preparation of glass fiber filter disc if pre-washed and pre-weighed filters are NOT being used: Place the glass fiber filter on the membrane filter apparatus (if 4.7 mm filters are being used) or insert into bottom of a suitable Gooch crucible (if 2.4 cm filters are being used) with the wrinkled surface up. While vacuum is applied, wash the disc with three successive 20 ml volumes of distilled water. Remove all traces of water by continuing to apply vacuum after water has passed through. Remove filter from membrane filter apparatus (if 4.7 mm filter) or both crucible and filter if Gooch crucible is used, and dry in an oven at 103°C-105°C for one hour or at 550°C ± 50°C if TVSS is to be determined. Remove to desiccator and store until needed. Repeat the drying cycle until a constant weight is obtained (weight loss is less than 0.5 mg). Weigh immediately before use. After weighing, handle the filter or crucible/filter with forceps or tongs only. As in the procedure for the pre-weighed filters above, wet the filter slightly before use in order to properly seat it in the filtration apparatus.

5.1.2.4 Assemble the filtering apparatus and begin suction, taking care to have wet the filters as described in either procedure above. Shake the sample vigorously and rapidly transfer 100 ml to the funnel by means of a 100 ml graduated cylinder. If this volume takes longer than 5-10

minutes to pass through the filter, sample volume must be reduced such that the filtration time will not be exceeded. If that volume is less than or equal to 10 mls, it should be dispensed with a 10 ml Mohr (graduated glass) pipet which has a wide enough tip opening so as not to inhibit the passing of solid pieces of material.

5.1.2.5 Filter the sample through the glass fiber filter, rinse the graduate and filter with three successive 10 ml portions of deionized water, allowing the rinsate to pass completely through the filter between washings, and continue to apply vacuum for about 3 minutes after filtration is complete to remove as much water as possible.

5.1.2.6 If the sample contains large pieces of material which make it difficult or impossible to achieve a representative, homogeneous sample, it may be necessary to thoroughly mix the sample in a blender prior to filtration. If this is done, however, care should be taken to assure that air bubbles aren't entrained in the measured sample volume to the extent that it could affect the actual volume dispensed. In other words, let the bubbles and subsequent foaming subside before dispensing the sample.

5.1.2.7 Carefully remove the filter from the filtration device, taking care not to leave pieces of filter on the support apparatus, and place it in the aluminum weighing dish appropriate to that filter and sample.

5.1.2.8 Dry the filter overnight at 103°C-105°C.

5.1.2.9 Remove the filter and aluminum dish from the oven and place in a desiccator to cool. The samples MUST be cooled prior to weighing or the apparent weight will be affected.

5.1.2.10 Repeat the cycle of drying, desiccating, cooling and weighing until the filter/dish attain a constant weight, changing by no more than 0.5 mg.

5.1.2.11 Record the final weight for calculation of TSS.

5.1.2.12 If TVSS is to be determined, repeat step 5.1.2.9 using a muffle furnace pre-heated to 550°C ± 50°C for 90 minutes. Record the final weight for calculation of TVSS.

5.2 Quantification

5.2.1 Residue concentrations are calculated using the following equations:

$$TSS = \frac{(W_f - tare) \times 1000}{V_i}$$

$$TVSS = \frac{W_f - W_a \times 1000}{V_i}$$

where:
V_i = volume of sample used in mls
W_f = weight of dried residue & filter
W_a = weight of ignited residue (after ignition @ 550°C) & filter in mg
tare = tare weight (weight in mg of filter before filtration of sample)

5.2.2 TSS and TVSS are generally reported on a mg/L as received basis.

6. Reports

6.1 Data Packet Organization

6.1.1 The data package for this analysis consists of the data sheet and a quality control database (QC_DB) report form.

6.2 Quality Control Reports

6.2.1 All results for quality control tests are entered into the lab data base using the QC_DB program. Printouts of all data entered need not be included in the package. However, all must be referenced on the report form. This includes the blank and duplicate results and any other QC which might have been analyzed by special request (such as an SRM/LCS).

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 limit of detection indicated.

Appendix I

QC Summary Table

Laucks Testing Laboratories

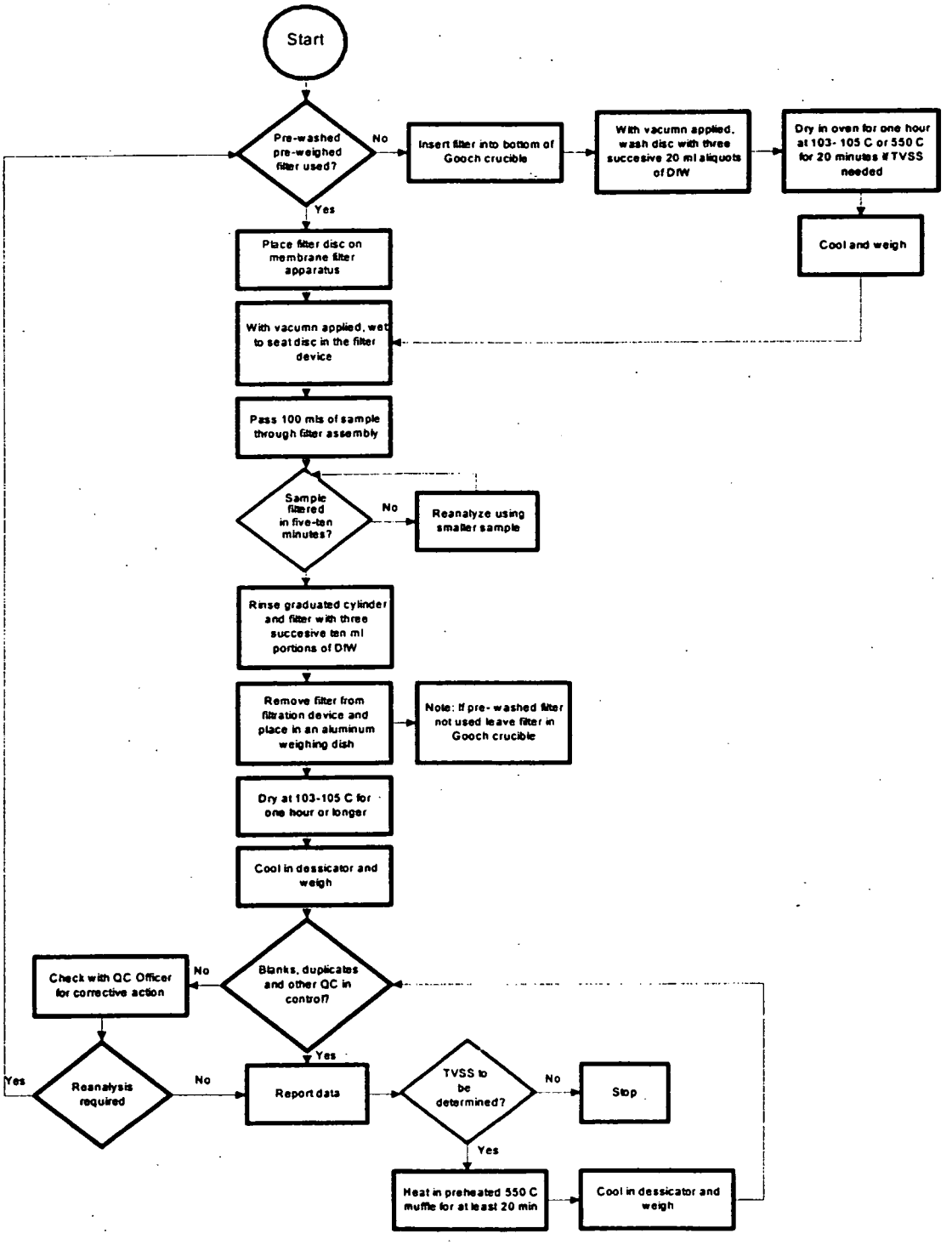
Method EPA 160.2 / SM 2540D & E QC Requirements and Corrective Actions

QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
Method Blank	None	<4 mg/L or no more than twice the detection limit	5% frequency (1 per 20 samples)	Re-analyze all samples <10x the actual weight of the solids. Consult QC Officer for any other actions	QC_DB report form with appropriate commentary
Duplicate % Difference	None	See current control limits catalog or QC_DB database	10% frequency (1 per 10 samples)	Discuss with QC Officer. If impact appears serious, may need to re-analyze samples	QC_DB report form with appropriate commentary
Standard Reference Material (SRM) Recovery	None	Within vendor supplied limits or 90%-110% recovery	If required, at frequency specified, or 5% if not specified	Discuss with QC Officer. If impact appears serious, may need to re-analyze samples	QC_DB report form with appropriate commentary

Appendix II .

Flow Chart

Total Suspended Solids (TSS) and Total Volatile Suspended Solids (TVSS)
EPA 160.2 and/or SM 2540D&E



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NON-CONFORMANCE				
TLI SOP No.	2.04	Version:	6	Date Revised: July 27, 2001

Author: Jennifer Hass

Effective Date: 1 August 2001

Authorization: Donald Horan
Management

Date Authorized: 30 July 2001

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I. **DEFINITION:** A Non-Conformance is the failure to comply with one or more criteria established for the acceptance of data.

II. **SCOPE AND APPLICATION:** The purpose of this SOP is to describe the decision and documentation process applied to non-conformance's or analytical elements which fail to meet the applicable acceptance criteria. This SOP applies to all analytical data and associated data reports, and must be followed by all members of the TLI staff.

III. **RESPONSIBILITY:** The staff member who identifies a non-conformance issue is responsible for evaluating the failure condition and initiating the applicable course of action.

IV. **PROCEDURE:**

A. When analytical data do not satisfy the acceptance criteria, the staff member evaluates the extent of the failure using the Allowed Exceptions section of this SOP as a guideline.

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B. Allowed Exceptions

1. All Methods

Issue	Allowed Exception
Blank Contamination	1. if blank contamination is less than 5% of that analyte concentration in the client samples 2. if client samples have ND for that analyte 3. if client samples have "B" Flag and "J" Flag for that analyte
Instrument Spike	if it does not affect quantitation of analyte or put the standard out of ratio
MS/MSD analyte recoveries and relative percent differences	if it does not look like an obvious sample preparation error and the native client sample has high levels of analytes such that the amount of spike is small relative to the native amount
Quantitative Interference or Interference	if only in client samples and it appears to be a matrix problem
Ratio Out	for client samples only if due to high levels of analytes or obvious interference
Saturation	all conditions for only client samples, but project scientist must be notified

2. Method 8290 and Method 23

Issue	Allowed Exception
LCS/LCSD analyte recoveries	up to two analytes may have % recoveries as high as 145% and as low as 60% as long as associated relative percent differences meet criteria
LCS/LCSD relative percent differences	up to two relative percent differences may be 20-35% as long as the associated percent recoveries meet criteria
Labeled Standard Recoveries	internal standard recoveries may be as low as 25% if signal to noise is 10:1 for associated standard

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NON-CONFORMANCE	
TLI SOP No. 2.04 Version: 6	Date Revised: July 27, 2001

3. Method 8280

Issue	Allowed Exception
LCS/LCSD analyte recoveries	up to two analytes may have % recoveries as high as 165% and as low as 40% as long as associated relative percent differences meet criteria
LCS/LCSD relative percent differences	Up to two relative percent differences may be 50-65% as long as the associated percent recoveries meet criteria
Labeled Standard Recoveries	internal standard recoveries may be as low as 25% if signal to noise is 10:1 for associated standard

4. Method 1613

Issue	Allowed Exception
Blank Contamination	All blank contamination below the target detection limit is allowed by the method
Standard recovery limits for tetra-octa analyses	1. 13C12-2378-TCDD: 25%-164% 2. 13C12-2378-TCDF: 24%-169% 3. 37Cl4-2378-TCDD: 35%-197%

5. High resolution PCB analysis

Issue	Allowed Exception
Blank contamination	if blank contamination is less than 10% of that analyte concentration in the client samples
Low standard recoveries	Mono, di, and tri standards do not have recovery limits. However, if the recovery is less than 10%, an NCR should be created and the project scientist must approve it.

6. Method 680

Issue	Allowed Exception
Low standard recoveries	Mono, di, and tri standards do not have recovery limits. However, if the recovery is less than 10%, an NCR should be created and the project scientist must approve it.

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C. A project with a non-conformance which is not addressed in the Allowed Exceptions section of this SOP must have a Non-Conformance Report(NCR) initiated. The special instructions for an individual project override the Allowed Exceptions section of this SOP. Projects for which NCRs are initiated must be taken to the project scientist for approval prior to shipment. All non-conformances must be addressed in the case narrative, regardless of whether an NCR was created.

D. A completed NCR shall include the following:

1. Initials of the persons identifying the non-conformance and creating the non-conformance report;
2. Date the non-conformance is identified;
3. Identification of the affected project data (including identification of any associated batched projects);
4. A description of the failure or non-conformance;
5. The initiator's plan for resolution of the non-conformance
6. Project scientist is responsible for documenting a description of the planned actions, action associated with the investigation, and resolution of the non-conformance; and
7. Project scientist is responsible for documenting conclusions regarding the impact of the non-conformance on other project data.

E. Data in the NCRs shall be documented as required in the SOP for recording raw data.

F. Completed NCRs are reviewed and accepted by a Project Scientist. The Project Scientist evaluates the proposed actions and the potential impact on other data.

G. Technical guidance is sought from the Area Manager or appropriate member of senior management until an adequate solution has been defined for the non-conformance.

H. Project Scientist defines the planned action for resolving the non-conformance and documents resolution in MILES. Verbal acceptance by Project Scientist may be given after full discussion of the NCR issues. In such cases, the person on-site must document the verbal acceptance.

I. After resolution of NCR, a copy of the NCR and any supporting data not already in the project file are placed in the project file.

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J. Data associated with an NCR cannot be reported to the client until the NCR has been accepted. Any NCR issues and their affect on the data must be reported in the case narrative.

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SAMPLE RECEIPT, IDENTIFICATION, HANDLING AND STORAGE		
TLI SOP No. 5.01	Version: 10	Date Revised: August 13, 2001

Author: Anzor Gatchetchiladze Effective Date: 08-27-2001

Authorization: Donald Harvan Date Authorized: 20 Aug 2001
Management

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I. **PURPOSE:** To describe the standard operating procedures (SOPs) to be followed to ensure sample security and integrity from the time of receipt to the time of final disposal. This includes procedures for sample inspection, log in, storage, and disposal.

II. **SCOPE:** The procedures described in this SOP are applicable to all samples that are received by TLI's Environmental and Pharmaceutical Divisions.

III. **RESPONSIBILITY:** The primary responsibility for sample security and integrity belongs to the Sample Management Group or designated alternate(s), who initiates the procedures described in this SOP. However it is the responsibility of all personnel at TLI, who handle samples, to ensure the security and integrity of the samples under their control and to document on a COC form the movement of those samples.

IV. **SAFETY CONSIDERATION:** Incoming samples may contain harmful substances. Gloves, lab coat, and safety glasses must always be worn when handling samples. Some situations may require wearing a respirator. These situations include the receipt of leaking or highly volatile samples, or certain samples for which specific hazards are known prior to receipt. For samples of specific known hazards, refer to the appropriate appendix in this SOP for additional handling instructions. See Appendix A for handling samples contaminated with the hantavirus, and Appendix B for handling human blood and other potentially infectious material (OPIM). For additional safety information, consult the Safety and Health Officer or the "Safety and Health Manual".

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V. PROCEDURES:

NOTE: Special instructions from study specific protocols or EPA methodology supersede this SOP.

A. SAMPLE RECEIPT:

1. At the time a sample shipment is received, the receiving individual will document, the time and date received, who received it, and the general condition of the package(s). For Pharmaceutical samples Shipping Container Internal Custody Form must be filled out at this time.

   When the customer delivers the samples, also document the name of the individual making the delivery.

2. Open shipping container and carefully take all the samples out of the container. Take temperature of the samples (see paragraph B.3 of this SOP). Immediately count all the samples in the shipment and document on the Shipping Container Internal Custody Form (applies only to pharmaceutical samples). Examine all the documentation arrived with the shipment such as the Chain-of-Custody Report, Specimen Shipment Verification Form, Sample Traffic Report Form, Shipping Container Internal Custody Form, etc. Verify and confirm that number of actual samples in the shipment matches the number of samples indicated in the paperwork.

   NOTE: If any discrepancy is found at this point between the actual sample count and the shipment paperwork, stop the log-in process and notify the appropriate Project Scientist and the Sample Management Coordinator immediately. Do not proceed until clear instructions are obtained from the Project Scientist.

   a) If the external documentation indicates that the samples could potentially be contaminated with the hantavirus (i.e. deer mice, squirrels, cotton mice, field mice, etc.), refer to Appendix A for specific instructions.

      Notify the appropriate Project Scientist and Sample Management Coordinator immediately. It is the responsibility of the Project Scientist to contact the client so tracing procedures can be implemented.

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NOTE: At this point, if samples cannot be processed immediately, place the shipping container(s) in the appropriate cold storage location (See section D). It is not necessary to place frozen samples in the freezer if there is sufficient dry ice in the shipping container to keep the samples frozen until full inspection and log in can be performed. Document when and where the shipment was stored.

3. Take the shipment to the designated sample receiving area to be inspected and logged in. If the receiving individual does not perform the inspection/log in or the sample shipment was stored prior to inspection, document when and by whom the inspection/log in was performed.

   NOTE: All the samples must be logged-in within 24 hours of receipt unless instructed otherwise by Sample Management Coordinator or a Project Scientist.

4. Create a project number for each sample or group of samples received using the TLI's Management Information for the Lab Environment System (MILES). Project numbers are assigned sequentially by MILES. For samples of specific known hazards, follow the handling instructions detailed in the appropriate appendix for sample inspection and log in.

   NOTE: Only the Sample Custodian or a designated alternate may open sample shipping containers unless permission obtained from the Sample Management Coordinator.

B. SHIPMENT INSPECTION: The inspection of each shipment is documented in MILES, referencing the appropriate project number on each shipping document. Items to be documented include:

1. Shipping Container(s)
   - a) Presence/absence of custody seals
   - b) Condition of custody seal - intact/broken
   - c) Description of shipping container (e.g. ice chest, Styrofoam cooler, box) and its general condition
   - d) Carrier and airbill number(s)
2. Shipping Documents
   - a) Presence/absence of client COC.

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b) Presence/absence of Sample Management Office (SMO) Forms (for EPA samples only).

c) Presence/absence of airbills and/or bills of lading.

3. Status of Preservation/Temperature Conditions

a) Presence/absence of coolant.

Is there frozen coolant present? Is there evidence that coolant was present but thawed en route? Is there no evidence of coolant ever having been present (i.e. shipped at ambient temperature)? Document what is observed.

b) For all samples received with some evidence of coolant (other than dry ice) and for samples to be analyzed by methods specifying preservation at 4 ± 2°C measure and record the temperature. For samples received on dry ice record on the Chain of Custody: "Dry Ice". No temperature should be recorded for these samples.

(1) If in doubt about preservation requirements/evidence of coolant, measure and record the temperature.

(2) Measure the temperature of the single randomly selected sample using a calibrated Infrared (IR) thermometer gun. NOTE: See Table 1 for common Emissivity values for materials.

(3) If the IR thermometer gun is unavailable for any reason, place an in-house temperature blank (a scintillation vial of deionized water which has been stored at approximately 4°C) in the shipping container (close the container) for at least one half hour and measure the temperature with a calibrated Celsius thermometer.

4. If the samples are not received under the specified temperature conditions, proceed with inspection/log in and notify the Project Scientist/Principal Investigator immediately to obtain further handling instructions from the client. Order Acknowledgement specifying sample conditions at the time of the sample receipt will be faxed to the client as soon as sample log-in/initiation process is complete.

5. Observe and document conditions of the sample containers:

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a) Presence/absence of sample custody seals.

b) If wild rodent carcasses are present but not indicated on external documentation, immediately close and secure the sample container and notify the Health and Safety Officer (HSO).

c) Condition of the samples (intact, broken, leaking, etc.) and action taken, if applicable.

(1) Photograph unfavorable sample shipments and file photos along with the copies of client COC in "Damaged Sample Logbook" maintained by Sample Management Group.

(2) Salvage leaking or broken sample(s), when doing so will not increase the likelihood of further sample loss or contamination as follows:

(a) If a leaking sample is discovered, it may suffice to simply tighten the lid. Otherwise, treat it like a broken sample (Note loose lid on the COC).

(b) If a bottle containing a solid sample is cracked, but remains intact, wrap the bottle in aluminum foil and place the container in a plastic bag with a "zipper" closure.

(c) Isolate each broken sample into an appropriate new container, which is labeled with the client sample ID.

(i) Wrap fish and paper in clean foil, with the dull side towards the sample.

(ii) If a tube containing a biohazard sample is cracked, but the sample is still frozen and intact, place the tube in a clean beaker. Allow the sample to thaw, then transfer to a new labeled test tube. This procedure must be performed by qualified Chemist.

(3) Presence/absence of Contract Laboratory Program (CLP) tags and numbers. Tags are normally attached around the neck of the bottle they apply to. Document

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any discrepancies between the number on the tag and the client paperwork. CLP sample tags will be removed from the samples and shipped with the data package.

(4) Notify the appropriate Project Scientist and Sample Management Coordinator immediately of any damaged or unidentifiable samples. It is the responsibility of the Project Scientist to contact the client to obtain further instructions on how to proceed with the affected sample(s) and verify any known or suspected hazards associated with the affected sample.

(5) The Sample Management Group will properly dispose of samples that cannot be recovered, after the Project Scientist's authorization.

6. Compare client COC, if present, with sample identification. Document any discrepancies, such as missing samples, samples present but not listed on the client COC, missing information or differences in information contained on the sample label/tag and the client COC. Notify the Project Scientist immediately of any discrepancies listed above. It is the responsibility of the Project Scientist to determine if the discrepancies require client's attention.

7. Return non-disposable shipment containers and coolant packs, which belong to the client, to the return address found on the airbill or client COC.

C. SAMPLE LOG IN AND IDENTIFICATION:

1. Every incoming sample is logged in into MILES "virtual logbook" which then creates TLI project number and TLI sample IDs for every sample or group of samples. From this point on every logged in sample can be tracked throughout the entire process until disposed or shipped back to the client.

2. TLI IDs assigned to samples are unique ID that represent:

a) "Virtual Logbook" Number - Page Number - Sample Sequence Number. For example: sample logged into Virtual

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Logbook # 258, on page # 16, sample sequence # 2 will translate into TLI sample ID: 258-16-2

b) If a single sample is submitted in more than one container, each container is uniquely identified by appending sequential letters (A through Z) to the Sample Sequence Number. Ex: 258-16-2A, 258-16-2B, etc.

3. For each sample, record the client sample identifier as stated on the sample label and client COC. Also, record sample matrix, and the initial sample storage location. If samples will be scanned with Bar-code scanner refer to the appropriate SOP for using, recording, and transferring data obtained with bar-code scanner.

4. Securely label each sample with the TLI project number and both, TLI and client sample IDs.

5. Generate the TLI COC, sign and date it. If applicable, generate any other necessary paperwork, such as: Log in Form, Extract COC and Project Communication forms (usually required for Pharmaceutical samples only). Sign and date the paperwork.

6. The nature of the project determines the exact storage location of all original shipping and log in documents for the project.

   a) In all cases, documentation will be identified by project number and will be maintained in such a manner as to prevent destruction or loss (i.e. file cabinet, study binder, project file, etc.).

   b) Any copies of these documents will be clearly labeled as such and will be initialed and dated.
   NOTE: During the entire log in process, including sample inspection and labeling, all samples must be maintained at a temperature that insures sample integrity.

D. SAMPLE STORAGE:

1. Place samples in boxes, crates or coolers, as appropriate for the sample matrix. Label storage container with TLI project number in such a way as to avoid breakage and cross contamination.

   a) Never store samples together with chemical standards in the same refrigerator/freezer.

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b) For Pharmaceutical projects, note the location of the samples on the appropriate inventory list.

c) Store Pharmaceutical samples in freezers designated by Project Scientist on the Sample Log in And Initiation Form.

2. Actual storage requirements are dependent upon the matrix, the analysis requested, and client's protocols or specifications. Storage temperature can vary from Room Temperature to 4°C, - 20°C or - 70°C.

E. SAMPLE TRACKING:

1. All personnel handling samples (extracts) at any time before, during or after analysis, will document the movement of the sample on the original TLI COC form. Original TLI COC forms are stored in the storage containers along with the samples. For Pharmaceutical samples original TLI COC forms are placed in the binders located outside of every freezer door. Copies of COC forms (Log-in Forms for Pharmaceutical projects) are placed in the project folders. Documentation includes:

   a) The identification of the sample being moved.

   b) The initials of the person who removed and returned the sample from and to the storage location.

   c) Date when the sample was removed and returned from and to storage. If returned to a different location - the new storage location.

2. In addition, the sample's whereabouts within the analytical process will be tracked via MILES system.

   NOTE: Copies of COC forms must be clearly labeled as such and be signed and dated. Entries and updates must be made on the original document.

F. SAMPLE DISPOSAL OR RETURN:

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1. Sample disposal will be performed in compliance with the state and federal regulations. Unless instructed otherwise by the client, samples will be disposed as follows:

   a) All samples will remain in the appropriate storage location throughout the analysis process.

   b) Environmental samples will be disposed 30 days after the complete data package ships to the client. It is a client's responsibility to arrange sample storage for longer than 30 days if necessary. Sample storage fees may apply in this case.

   c) Pharmaceutical samples will be disposed 90 days after the final report is issued. During this 90 days client will be contacted by Project Scientist and further storage, disposal or sample return will be arranged. Sample storage fees may apply if client chooses to keep samples at Triangle Labs storage locations longer than 90 days.

   d) After samples are disposed the original TLI COC form will be updated and then archived.

   e) In addition the MILES system will be updated as soon as the original COC is updated. For details, please see Sample Disposal SOP.

2. Sample Return

   a) Obtain client's authorization and packing/shipping instructions before returning any samples.

   b) Sign and date original client's COC and/or packing list for all samples being returned. Original will accompany the shipment and a copy will be retained for the project (study) file at TLI.

   c) Pack samples to prevent breakage and contamination.

   d) Pack samples/extracts on ice, dry ice or without coolant at all, as requested by the client.

   e) Document sample return on TLI COC form and update MILES.

If this SOP can not be followed notify your supervisor immediately.

Original stamped in blue: ORIGINAL

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APPENDIX A

PROCEDURE FOR HANDLING RODENT SAMPLES POTENTIALLY CONTAMINATED WITH HANTAVIRUS

NOTE: CONTACT THE SAFETY/HEALTH OFFICER IMMEDIATELY. DO NOT OPEN THE SHIPPING CONTAINER UNTIL AUTHORIZED BY HIM/HER.

I. **SCOPE AND APPLICATION:** The purpose of this document is to outline the supplies and specific procedures for the safe handling of rodent samples (i.e. deer mice, squirrels, cotton mice, field mice, etc.) that are potentially contaminated with hantaviruses of significance to human beings.

II. **SUPPLIES REQUIRED:**

- Two half-mask respirators with organic vapor/acid gas/HEPA cartridges.
- Two non-vented splash goggles.
- Two tyvek coveralls.
- Two plastic splash aprons.
- Four pairs latex gloves.
- Commercially available chlorinated bleach diluted 1:10 with water. (10% bleach disinfectant) in a spray bottle.

III. **PROCEDURE:**

A. The samples will be delivered directly to Triangle Laboratories. Shipping containers will remain closed until they are ready for processing. Freezing of the entire unopened shipping containers is allowed if they arrive late in the day for processing during the subsequent six hours.

B. All processing of rodent samples will be done in a designated closed lab. Only individuals wearing the required protective clothing, and who have

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been certified for respirator use by the Triangle Laboratories Occupational Health-Respiratory Safety Program, are allowed in the room during specimen processing. These room access restrictions are removed after all rodent specimen processing has been completed, working surfaces have been decontaminated, contaminated disposables have been properly stowed, and the room has been aired out for at least 30 minutes.

C. Required protective clothing for specimen processing includes tyvek coveralls, a plastic apron, disposable boot covers, two pairs of latex gloves, non-vented safety goggles, and a properly fit half-mask respirator with organic vapor, acid-gas/HEPA filter cartridges.

D. The animals **must** be packaged as follows:

1. Each individual animal must be packaged separately, even if compositing is required. The chain of custody should contain all compositing information. The individual animals will be ground first in methylene chloride. Compositing will take place once each animal has been ground and can be safely handled.

2. Each individual animal should be wrapped in two layers of aluminum foil, shiny side away from the animal. The outside of the foil encased animal should be labeled with the sample identification number.

3. Each foil encased animal should be placed inside a sealed ziplock bag that is also labeled with the sample identification (ID). This ziplock bag should then be placed inside another ziplock bag such that the seal from the inner bag is at the bottom of the outer ziplock bag. The outer bag should also be labeled with the sample ID.

4. If there are non-rodent samples collected at the same site, these must be shipped ***separately*** from the mice samples. This will allow the laboratory to effectively quarantine the infected samples prior to preparation.

E. For greatest efficiency, two technicians should participate in specimen processing. One technician will be considered "dirty" and will directly handle specimen bags and contents, while the other technician will be considered "clean" and will handle specimen log in forms, blender vessels and tops, and solvent. All direct contact (especially hands) and indirect contact (surfaces of items touched by "dirty" technician) between technicians should be avoided. These roles are not to be switched mid-processing.

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F. After both technicians have donned their protective clothing and the doors to the processing room have been closed, the "dirty" technician should open the shipping container, being careful not to tear his/her latex gloves or tyvek suit.

G. The vertical safety sash on the chemical fume hood should be left in the lowered position to increase the inward linear flow-rate of the fume hood, thereby helping to contain and exhaust any aerosolized virus hazard.

H. The "dirty" technician should sit or stand to the right of the "clean" technician throughout the processing. He/she should remove a specimen from the shipping container, read and/or show the samples identification information to the "clean" technician for log in. The "dirty" technician should not touch the pen or any of the log in supplies.

I. The "clean" technician should load the appropriate amount of methylene chloride solvent into a clean blender vessel and hold it inside the hood work zone within reach of the "dirty" technician. The "dirty" technician should then open and hold the plastic bags containing the specimen and, without directly touching the rodent or the outside of the blender vessel, drop the rodent into the vessel containing the solvent.

J. The "clean" technician should then place a clean lid on the blender vessel, place the vessel on the blender motor, and emulsify the specimen for the appropriate amount of time.

K. The "dirty" technician should then place the empty specimen bags and associated potentially contaminated tags or packing material into the incineration waste container.

L. Steps G-J of this document, above, are then repeated until all specimens have been processed. After emulsification, the "clean" technician is allowed to decant the contents of each blender vessel into another container for storage, and may then remove the vessel from the fume hood work zone if necessary for cleaning and reloading of solvent.

M. If a pair of gloves becomes torn at any time during this procedure, the gloves and any exposed human skin are thoroughly wetted with 10% bleach disinfectant in a continuous hand-washing like manner. If skin has been broken or penetrated by a potentially contaminated object, the gloves are removed after bleach disinfection, and the wound is washed under running water with disinfectant soap for no less than 5 minutes, after which appropriate medical attention is sought. If no injury to the skin has occurred

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a new pair (two pair if necessary) of gloves are donned and the torn pair of gloves are placed in the incineration waste container.

N. All remaining packing material in the shipping container, including any transport ice packs, are then placed into the incineration waste container.

O. When all above steps have been completed, a spray bottle containing 10% bleach disinfectant is used to wet down the sash and horizontal surface of the fume hood, the outside of all other potentially contaminated work surfaces, the outer pair of gloves over the hands of both technicians, the inside and outside of the shipping container, and the spray bottle itself.

P. With gloves wet with bleach disinfectant, the "clean" and "dirty" technicians then grab the outer surface of their left glove with their right double-gloved enabling them to pull off the outer glove on their left hand and drop it into the incineration waste container. The dry inner glove of their left hand is now exposed, which they use to pull off the outer glove on their right hand by slipping a finger under the collared wrist area of the glove as they stand over the incineration waste container.

Q. Wearing the dry inner pair of latex gloves, the technicians should then remove, in the following order, their plastic apron, their disposable boot covers, their tyvek coveralls, their goggles, and their inner gloves (in the manner described above), placing each disposable clothing item into the incineration waste container as it is removed. Any splash contaminated area on their protective clothing should be sprayed with a 10% bleach disinfectant prior to removal. The incineration waste container is then closed and sealed.

R. The floor surface directly around the specimen processing area and shipping container is then sprayed with 10% bleach disinfectant.

S. Wearing their respirators, the technicians then leave the specimen processing room and allow it to ventilate for at least 30 minutes before allowing room re-entry. Outside of the room, they remove their respirators and thoroughly wash their hands with soap and water.

T. The incineration waste container is processed for incineration at the next available opportunity.

U. Subsequent processing of methylene chloride emulsified rodent specimens can then commence without any residual biohazard.

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APPENDIX B

PROCEDURES FOR HANDLING BLOOD AND OTHER POTENTIALLY INFECTIOUS MATERIALS (OPIM)

I. **SCOPE AND APPLICATION:** Procedures delineated in this document are to be applied whenever human blood or OPIM are handled.

II. **SAFETY CONSIDERATIONS:** In the handling of human blood samples or samples containing other human body fluids, it is essential that the precautions delineated below be followed without exception. Precautions must be followed consistently. The approach and procedures delineated below are those recommended by the US Center for Disease Control and Prevention (CDCP). The Hepatitis B (HBV) and the HIV and HTLV-III/LAV viruses (AIDs viruses) appear to be incapable of penetrating the skin. Infection may nevertheless occur as a result of blood or infectious fluids coming in contact with mucus membranes or open wounds. Any individual working with human blood or body fluids must undergo a HBV vaccination program, prove immunity or that a past vaccination is still satisfactory to prevent infection.

III. **PROCEDURE:**

Recommended precautions for handling all blood or other human body fluid samples must be appropriate to prevent contamination, regardless of the knowledge or the lack thereof regarding the infectious state of the media. In the laboratory environment, the greatest risk for transmission involves exposure to a needle or other sharp instrument contaminated with infected blood. Great care must therefore be undertaken to prevent possible transmission via a puncture wound (e.g. needle, sharp glass, etc.)

A. Standard Precautions

1. Handle all human blood and/or body fluids samples as potentially infectious regardless of possible knowledge to the contrary.

2. When working with raw human blood or other body fluids, all work must be done in a hood. Disposable gloves as well as protective eyewear and clothing must be worn. In addition, a disposable mask

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or face shield must be worn whenever procedures, that are likely to generate droplets or aerosols, are performed.

3. Sharp items (needles, glass, etc.) having contacted blood or body fluids should be considered as potentially infective and be handled with extraordinary care. Minimize handling and thus risks associated with such items. Prevent accidental punctures.

4. Disposable syringes, glass pipettes and plastic pipette tips should be placed in puncture resistant containers located as close as possible to the area in which they are being used. If work is being performed in a hood, place the disposal container in the hood, immediately next to or as close as possible to the hood.

5. Hands should be washed immediately and thoroughly with soap and water if contaminated with blood or following glove removal after work with blood or other human body fluid samples. Practice standard good hygiene procedures. Do not handle with contaminated gloves or hand anything a co-worker may handle unprotected (i.e. phone, doorknob, etc.).

6. Spills of blood or other body fluids should be immediately cleaned with soap and water or a household detergent. Individuals performing such cleaning must wear disposable gloves. A freshly prepared solution of sodium hypochlorite (tenfold dilution of off-the-shelf commercial bleach) solution should be used to wipe the area after cleaning in order to thoroughly disinfect the affected area. An alternative to this is to spray the area well with Lysol™.

7. In the event of an exposure (i.e. an accidental puncture wound with a sharp object having contacted blood), immediately wash the area thoroughly with a germicidal soap and water and contact your supervisor for the appropriate follow up procedures.

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TABLE 1: COMMON EMISSIVITY VALUES

Non-Metals

Material	Emissivity
Asbestos	.95
Asphalt	.95
Basalt	.70
Brick	.95
Carborundum	.90
Ceramic	.95
Clay	.95
Concrete	.95
Cloth	.95
Glass Plate	.85
Gravel	.95
Gypsum	.80-.95
Ice	.98
Ice Bath	.95
Limestone	.98
Organic Materials (food, plants, oil, some chemicals)	.90-.98
Paint (non-Al)	.90-.95
Paper (any color)	.95
Plastic (opaque, over 20 mils)	.95
Rubber	.95
1.	.70-.90

Non-Metals

Material	Emissivity
Sand	.90
Snow	.90
Soil	.90-.98
Water	.93
Wood, natural	.90-.95

Metals

Material	Emissivity
Alloy A3003 Oxidized	.30
Brass:	
Burnished	.30
Oxidized	.50
Carbon:	
Unoxidized	.80-.90
Graphite	.70-.80
Iron:	
Oxidized	.50-.90
Rusted	.50-.90
Wrought, dull	.90
Lead:	
Roughened	.40
Steel:	
Oxidized	.70-.90
Cold rolled	

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EXTRACTION OF PCDD/PCDF FROM SOLIDS (NOT TISSUE) - 8290

TLI SOP No. DSP105	Version: 16	Effective Date:	03/02/2001
Author:	Don Harvan	Date Written:	January 10, 2001
Authorization: Phil Alfro (Management)		Date Authorized:	02/23/2001

I. **PURPOSE:** This method provides procedures for the extraction of polychlorinated dibenzo-p-dioxin (tetra- through octachlorinated homologues; PCDDs) and polychlorinated dibenzofuran (tetra- through octachlorinated homologues; PCDFs) from solid samples.

II. **SCOPE** It may be applied to the extraction of non-tissue solids, including but not limited to soil, sediment, pulp, sludge, paper and/or cardboard, according to SW-846 Method 8290. Only the extraction procedure is contained in this SOP.

III. **SAFETY CONSIDERATIONS:** Samples may contain harmful substances. Wear labcoat, appropriate eyewear and gloves. Toluene and ethanol are flammable; avoid flames and sparks. The procedure has been validated for either heptane or hexane, since heptane is much less of a health hazard, it should be used instead of hexane whenever possible, but hexane can be used if heptane is unavailable. Do not breathe the vapors, and avoid contact with skin or eyes, as these solvents may cause irritation, nausea, and dizziness. For additional safety information, see the TLI Safety and Health Manual and the appropriate MSDS.

NOTES: **Slight procedural differences exist for specified sample types in this SOP. Be careful not to overlook these differences.**

IV. **REAGENTS:**

A. Heptane- pesticide grade (< 1 ppm residue)

B. Toluene- pesticide grade (< 1 ppm residue)

C. Ethanol- OmniSolve grade

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D. Ethanol/toluene (68/32 v/v) - Take 68 parts (by volume) of Ethanol and mix well with 32 parts (by volume) of Toluene.

V. GLASSWARE PREPARATION

A. All glassware used in this procedure must have been prepared according to glassware washing SOP.

B. The following glassware is needed for each sample:

1. beaker
2. 500 mL
3. forceps
4. spatula
5. thimble holder - acetone rinsed
6. Soxhlet extractor - acetone rinsed
7. thimble - pre-Soxhlet extracted and ready to use

C. If wet sample ≥ 15 g, Soxhlet Dean Stark (SDS) extractor must be used in addition to the Soxhlet extractor.

D. The flask, thimble holder and Soxhlet or SDS extractor must be the same size.

E. If SDS is required, assemble the SDS extractor with stopcock.

F. Rinse all glassware with n-heptane.

G. Label each beaker and flask by placing a color coded sample label on top of a strip of colored lab tape. The colored lab tape is necessary because the adhesive on the color coded labels is difficult to remove from the glass and will cause contamination problems.

H. All flasks require two labels - one on the side of the flask and one on the neck.

VI. EXTRACTION PROCEDURE:

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EXTRACTION OF PCDD/PCDF FROM SOLIDS (NOT TISSUE) - 8290	
TLI SOP No. DSP105 Version: 16	Date Written: January 10, 2001

A. Plan the extraction batch. An extraction batch can contain up to twenty (20) samples and must include a method blank and at least one(1) Lab Control Spike (LCS). Complete the QC batch form, including all samples and QC samples in the extraction batch.

B. Observe and document the physical appearance and consistency of each sample on form PSTMF 7 for later entry into the wet lab observation log in MILES. Mix the sample well before taking an aliquot for extraction. Make sure homogeneity is maintained--exclude anything that does not constitute sample's natural matrix.

C. Zero balance. Weigh sample and its container.

D. Record the gross weight before on the Sample Preparation Management and Tracking Form (PSTMF 7).

E. Tare the beaker containing the extraction thimble.

F. Weigh into the thimble the amount of sample needed to provide 10g dry weight according to the moisture determination. If the moisture determination has not been completed yet, it is appropriate for the chemist to make an estimate of the amount of sample needed based on its appearance and consistancy.

G. Record the sample weight on the Sample Preparation Management and Tracking Form (PSTMF 7).

(Y)=There is enough sample left to perform re-extraction
(N)=There is NOT enough sample left to perform re-extraction

H. Zero balance. Weigh leftover sample and its container.

I. Record the gross weight "after" on the Sample Preparation Management and Tracking Form (PSTMF 7).

J. Clean the balance by swiping with heptane.

Prepare the blank using pre-extracted G-8 filters for pulps and all <u>dried and ground samples</u>. Prepare the blank using pre-extracted sand for all normal ash/sediment/soil/sludge samples. Weight 10 grams +/- 0.4 g using the same

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EXTRACTION OF PCDD/PCDF FROM SOLIDS (NOT TISSUE) - 8290	
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matrix as the blank for any laboratory control samples (OPR or LCS and/or LCSD).

L. Prepare the Soxhlet apparatus by:

1. Use a 500 mL setup, place 400 mL toluene* in the flatbottom flask. Add 5-6 Teflon boiling chips in each flask.
2. Place the label containing information for the concentration process on the boiling flask on top of the colored lab tape. Write the solvent used on the flask.
3. Place the thimble holder on top of the flask.

M. ***NOTE:** GP pulp sludge samples require 68:32 ethanol or reagent alcohol/toluene instead of toluene. GP pulp samples require ethanol or reagent alcohol instead of toluene. The volume remains 400 mL for 500 mL setup.

N. Place the thimble with the sample into the thimble holder. Be sure to seat the thimble at the bottom of the holder.

O. **NOTE:** While the Soxhlet apparatus is sitting on the counter, keep the top capped with aluminum foil to avoid contamination.

P. Spike the samples according to the SOP on adding spike standards to samples.

Q. After spiking place a glass wool plug on top of the sample in each thimble. Use pre-extracted glasswool.

R. Place the Soxhlet on top of the thimble holder. If Soxhlet Dean Stark (SDS) is being used, be sure the stopcock is closed.

S. Place the Soxhlet apparatus on the heating mantle and connect the Soxhlet apparatus to the condenser at the ground glass joint. Cap the top of the condenser with aluminum foil.

T. Wrap the thimble holder and Soxhlet extractor with foil. Do not cover the condenser.

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EXTRACTION OF PCDD/PCDF FROM SOLIDS (NOT TISSUE) - 8290	
TLI SOP No. DSP105 Version: 16	Date Written: January 10, 2001

U. **NOTE:** If using ethanol or reagent alcohol as the sole solvent, do not wrap any of the apparatus with aluminum foil.

V. Place a piece of colored tape on the condenser to indicate it is being used for a sample.

W. Turn on the heat to a level at which each unit should be cycling at a rate of five times per hour.

X. Check the units after one-half hour (1/2) hour. Open the aluminum foil on the thimble holder to check the cycling action and close the wrapping. Each unit should be cycling, have no leaks and have sufficient solvent. Make adjustments as necessary.

Y. If adjustments were required, check the units again in one-half hour (1/2) hour. Periodic checks should be made throughout the required time to ensure proper cycling.

Z. If the weighed sample is >30g, drain the water from the SDS halfway through the extraction (i.e., approximately 8 hours after turning on the heaters).

AA. Extract the sample for 16 hours.

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EXTRACTION OF PCDD/PCDF FROM SOLIDS (NOT TISSUE) - 8290	
TLI SOP No. DSP105 Version: 16	Date Written: January 10, 2001

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EXTRACTION OF DIOXINS/FURANS FROM WATER FOR METHODS 1613, 8290 AND 551		
TLI SOP No. DSP161	Version: 18	Date Revised: October 9, 2001

Author: Patrice L Singletary Effective Date: 3/12/02

Authorization: P. Ragsdale Date Authorized: 12/31/01
Management

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I. **PURPOSE:** This SOP provides procedures for the extraction of polychlorinated dibenzo-p-dioxin and polychlorinated dibenzofuran (PCDD and PCDF) from water samples.

II. **SCOPE** . It may be applied to the extraction of tetrachlorodibenzo-p-dioxins and tetrachlorodibenzofuran from water in accordance with method 1613, 8290 or 551. See the SOP on Preparation for Extraction of Dioxins / Furans from Water before using the present SOP.

III. **SAFETY CONSIDERATIONS:** Samples may contain harmful substances. Wear labcoat, appropriate eyewear, and gloves. These solvents are flammable; avoid flames and sparks. Do not breathe the vapors, and avoid contact with skin and eyes. They may cause irritation, nausea, dizziness, and, in extreme cases, death. For additional safety and health information, see the TLI Safety and Health Manual and the appropriate MSDS.

IV. **REAGENTS:**

A. HPLC Grade Water

B. Heptane-pesticide grade or better quality, less than 1 ppm residue on evaporation.

C. Sodium sulfate-anhydrous, pesticide grade.

D. Methylene Chloride-pesticide grade or better quality.

E. Toluene-pesticide grade or better quality.

V. **GLASSWARE PREPARATION:**

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A. All glassware used in this procedure must have been prepared according to the SOP entitled "Glassware Cleaning".

B. The following glassware is needed for each sample:

2 L separatory funnel with stopper and Teflon© stopcock or a continuous liquid-liquid extractor

medium glass powder funnel

receiving flask

500 mL extraction flask and regular thimble holder

thimble (pre-Soxlet extracted)

Soxhlet Dean-Stark (SDS) extractor

C. Assemble the separatory funnel(s) with stopcock and stopper.

D. Rinse the following with heptane:

separatory funnel(s) or continous liquid-liquid apparatus

graduated cylinder(s)

all flasks

glass powder funnel(s)

E. While rinsing the separatory funnel(s), close the stopcock and check for leaks. Drain the funnel into a waste container.

F. After rinsing, invert all flasks and allow to fully drain.

G. Plug the powder funnel(s) with pre-cleaned glasswool. Fill the powder funnel 3/4 full with anhydrous sodium sulfate.

VI. PREPARING SAMPLES FOR EXTRACTION:

A. Plan the extraction batch according to the SOP on batching projects. An extraction batch can contain up to twenty (20) samples and must include a method blank, a spike pair, and at least one (1) Lab Control Spike (LCS).Complete the QC batch form, including all samples and QC samples in the extraction batch.

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B. Remove the samples from storage (cooler) and place them on clean lab bench. Allow sufficient time for samples to reach ambient temperature.

C. Check sample IDs on sample containers against IDs on Sample Preparation Tracking and Management Form. If there are any discrepancies contact the Project Scientist for further instructions.

D. Shake each sample bottle for one minute. If the available volume is less than 900 mL, hold the extraction and contact the Project Scientist for further instructions.

Note: An aliquot cannot be taken of an aqueous sample. The entire contents of the bottle must be used.

E. Use 1000 mL of HPLC water for the blank.

F. Record sample volume in the Wet Lab Observation menu in the MILES.

G. Pour the measured sample volume into a 2 L separatory funnel.

H. Keep the labeled graduated cylinders and sample bottles together. These containers will be rinsed with the extraction solvent in a later step.

I. Record pH and observations of physical appearance of samples (i.e. color, viscosity) in the Wet Lab Observation menu in the Miles.

J. Spike samples according to the WAG on adding spike standards to samples.

K. Shake the spiked water samples for 1 minute.

L. If filtration is required, filter each sample using the suction filtering system. If necessary, rinse the sample bottle and separatory funnel with 50 mL HPLC water and also filter. Transfer the filtered sample back into the 2 L separatory funnel.

M. Extract the filters and all filtered solids according to one of the SOP's for extracting solids. Appropriate extraction methods include the accelerated solvent extractor (ASE) or soxhlet extractor.

VII. SEPARATORY FUNNEL EXTRACTION PROCEDURE:

Note: For samples being analyzed by 8290, when the sample is judged to contain 1 percent or more solids, the sample must be filtered through a glass fiber filter that has been rinsed with toluene. If the suspended solids content is too great to filter through the filter, decant, and then filter the aqueous phase. For samples being analyzed by 1613, when the sample contains greater than 1 percent solids, a sample aliquot

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sufficient to provide 10g of dry solids is used. Decant excess water. If necessary to remove water, filter the sample through a glass-fiber filter and discard the aqueous liquid.

A. If it has not already been done in the preparation of the sample for extraction, pour the sample volume into a 2 L separatory funnel. Rinse the sample bottle and filtration flask if used with 120 mL of methylene chloride and transfer to the separatory funnel.

B. Extract the aqueous phase with methylene chloride as follows:

1. Shake the separatory funnel with water sample and methylene chloride for 2 minutes by hand. Be sure to vent the funnel periodically to avoid pressure buildup.

2. Allow the solvent layers to settle for 10 minutes. If emulsions occur, filter the water + emulsion through a G8 filter or glass wool with a methylene chloride rinse. Add the methylene chloride rinses to the methylene chloride extract.

3. Drain the methylene chloride layer through anhydrous sodium sulfate into a receiving flask.

4. Repeat steps above steps two more times using 60 mL methylene chloride for each extraction. A total of three extractions are required for each sample.

5. Rinse the sodium sulfate twice with 10 mL methylene chloride. Collect the methylene chloride rinses in the receiving flask containing the sample extract.

6. Measure the volume used for each sample using a graduated cylinder.

VIII. CONTINUOUS LIQUID-LIQUID EXTRACTION PROCEDURE:

Note: The use of the continuous liquid-liquid extractor is always allowed as an alternative to separatory funnel extraction in method 8290. It is the technique of choice when a given sample type is known to produce difficult emulsions. Use this technique with methods 1613 (B) and 551 whenever a re-extraction is needed because of low recoveries during the separatory funnel extraction step. Be sure to indicate on the extraction form whenever L-L extraction was used.

Note 2: The L-L extractor simply substitutes for a separatory funnel; therefore all considerations of filtering, determination of solids or particulate solids, or water vs.

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sludge described in the SOP on Preparation for Extraction of Dioxins / Furans from Water for Methods 1613, 8290 and 551 still apply.

A. Assemble Glassware

1. Rinse the extractor body and 500 mL flat bottom flask with methylene chloride. Discard rinse as waste.

2. Place 5-6 methylene chloride pre-extracted boiling chips in the flat bottom flask. Add approximately 250 mL of clean methylene chloride to the flask.

3. Add approximately 150 mL of methylene chloride to the extractor body.

4. Attach extractor body to the flask with green plastic clamp.

5. Label flat bottom with solvent, project number and sample number using color labels.

B. Preparation of Water Sample

1. Measure and record 1 liter of Reagent water each for blank and either OPR (1613), or LCS/LCSD (8290) utilizing a 1000 mL graduated cylinder.

2. Measure the volume of sample and transfer the well mixed sample into the extractor body. Record this volume on the sample preparation and tracking form. Note: If the sample does not contain 1000 mL, record the volume it does contain, but make up the difference with Reagent water. The L-L apparatus needs 1000 mL of water to operate correctly. The sample size to use in calculations, however, is the actual sample size not including make-up water.

3. Rinse the sample bottle three times with 20 mL methylene chloride and transfer rinses to the extractor body.

C. Extraction

1. Place Continuous Liquid-Liquid setup on condenser/hot plate and seat securely in place. Use aluminum foil shimmies to align body vertically and to fill any space between hotplate and bottom of the flask.

2. Turn hotplate on to 400 degrees.

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3. Extract for 18 hours.

4. Dismantle setup after they have cooled. Keep only the methylene chloride in the flat bottom flask.

   Discard water and methylene chloride in extractor body as waste.

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PCDDs AND PCDFs BY HRGC/HRMS - METHOD 8290 & TO-9	
TLI SOP: DHR182 Version: 9	Date Written: March 20, 2002

Author: Jennifer Hass Effective Date: April 1, 2002

Authorization: R. Rogoski Date Authorized: March 25, 2002
Management

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I. **PURPOSE:** This SOP is intended to describe the procedures to implement Method 8290.

II. **SCOPE:** This method provides procedures for the analysis of polychlorinated dibenzo-p-dioxins (tetra- through octachlorinated homologues; PCDDs), and polychlorinated dibenzofurans (tetra- through octachlorinated homologues; PCDFs) from extracts of samples prepared according to SW 846 Method 8290 and TO-9.

III. **SAFETY CONSIDERATIONS:** The 2,3,7,8-TCDD isomer has been found to be acenegenic, carcinogenic, and teratogenic in laboratory animal studies. Other PCDDs and PCDFs containing chlorine atoms in the 2,3,7,8 positions are known to have toxicities comparable to that of 2,3,7,8-TCDD. Extreme care must be exercised in all handling of extracts and standards in the application of this SOP. For additional safety information, see the TLI Safety and Health Manual and the appropriate MSDSs.

IV. **SAMPLE COLLECTION, PRESERVATION, AND HANDLING:** See TLI SOP No. 5.01 for sample collection, preservation, and handling information.

V. **PROCEDURE:** The High-Resolution Gas Chromatograph/High-Resolution Mass Spectrometer/Data System (GC/MS/DS) equipment utilized for this analysis includes the following:

A. Gas Chromatographs: Hewlett Packard 5890 or 5890 Series II (equipped for temperature programming and capillary columns)

B. High Resolution Mass Spectrometers: VG 70 Series, VG 70-SE Series, VG Autospec.

C. Data Systems: VG Analytical PDP11 with 11-250 software or VAX Alpha with Opus 3.2 software.

D. <u>GC Injection Port</u> - The GC injection port is designed for capillary columns. Typically, 2 µL injection volumes are used unless otherwise noted.

E. <u>Gas Chromatograph/Mass Spectrometer(GC/MS) Interface</u> - The GC/MS interface components can withstand 350°C. The interface has been designed so

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that the separation of 2,3,7,8-TCDD from the other TCDD isomers achieved in the gas chromatographic column is not appreciably degraded. The GC column is fitted directly into the mass spectrometer ion source without being exposed to the ionizing electron beam. Graphite ferrules should be avoided in the injection port because they may adsorb the PCDDs and PCDFs. Vespel™, or equivalent, ferrules are recommended.

F. Mass Spectrometer - The static resolving power of the instrument must be maintained at a minimum of 10,000 (10 percent valley).

G. Data System - A dedicated data system is employed to control the rapid selected-ion monitoring (SIM) process and to acquire the data. Quantitation data (peak areas or peak heights) and SIM traces (displays of intensities of each ion signal being monitored including the lock-mass ion as a function of time) must be acquired during the analyses and stored. Quantitation may be reported based upon computer generated peak areas or upon measured peak heights. The data system is set to acquire data as low as 10 ions in a single scan. Table 1. presents a listing of the ions which are typically monitored. The data system is set to switch to different sets of ions (descriptors) at specified times during an HRGC/HRMS acquisition. The data system provides hard copies of individual ion chromatograms for selected gas chromatographic time intervals. It also acquires mass spectral peak profiles and provides hard copies of peak profiles to demonstrate the required resolving power. Measurements of noise on the base line are performed using the hard copies of individual ion chromatograms provided by the data system.

NOTE: The detector ADC zero setting must be set to allow peak-to-peak measurement of the noise on the base line of every monitored channel and allow for good estimation of the instrument resolving power.

H. GC Columns

1. In order to have an isomer specific determination for 2,3,7,8-TCDD and to allow the detection of OCDD/OCDF within a reasonable time interval in one HRGC/HRMS analysis, the 60 m DB-5 fused silica capillary column is used.

2. The 2,3,7,8-TCDF isomer must be confirmed on a 30 m DB-225 fused silica capillary column, when 2,3,7,8-TCDF is detected on the DB-5 column at a level greater than or equal to the target detection limit.

VI. STANDARDS:

A. Calibration Solutions Six nonane solutions containing 17 unlabeled PCDDs and PCDFs and 18 $^{13}C_{12}$ -labeled PCDDs and PCDFs at known concentrations are used to calibrate the instrument. The analyte concentration ranges are

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homologue dependent, with the lowest values for the tetrachlorinated dioxin and furan (0.5 pg/µL) and the highest values for the octachlorinated congeners (2000 pg/µL) (Table 2.).

B. Recovery Standard Solution - This nonane solution contains two recovery standards, $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD, at a nominal concentration of 100 pg/µL per compound. A 20 µL of this solution is spiked into each sample extract before the HRGC/HRMS analysis.

C. GC Column Performance/Retention Window Check Solution (RTCHK)- This solution contains the first and last eluting isomers for each homologous series from tetra- through heptachlorinated congeners. The solution also contains a series of closely eluting TCDD and TCDF isomers for the purpose of documenting the chromatographic resolution (Table 3).

D. Acceptance Criteria for Newly Prepared Standards - All components and concentrations of each calibration standard, recovery standard, internal standard, and matrix spike solutions are verified prior to use for the analysis of samples. Testing consists of back to back analysis of the "test" solution (the newly prepared solution) and a "control" solution (an independent, second source solution purchased from a qualified vendor). Control solutions are isolated from the production standards in a protected location. Both the control and test solutions are evaluated versus the current continuing calibration standard and versus each other. Each component of the test solution must be within 80 - 120% of the true concentration when calculated versus the control standard. The control standard must be within 80 - 120% of the true value when calculated versus the continuing calibration standard.

Note: The control solution is a second source standard that is purchased ready to use from a qualified vendor such as Cambridge Isotape Laboratories

E. Standards are stored in 1/2 dram amber glass vials at room temperature.

VII. SYSTEM PERFORMANCE CRITERIA

System performance criteria are presented below. It must be documented that all applicable system performance criteria specified in this Section are met before analysis for any sample is performed. Table 4 provides recommended GC conditions that can be used to satisfy the required criteria. During a typical 12-hour analysis sequence, the GC column performance and mass spectrometer resolving power checks must be performed at the beginning of the 12-hour period of operation. A routine calibration verification is required at the beginning and end of each 12-hour period during which samples are analyzed. A method blank or HRGC/HRMS solvent blank is required between a calibration run and the first sample run.

A. GC Column Performance

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1. Inject the column performance check solution described in the standards section of this SOP.Acquire selected-ion monitoring (SIM) data using the equipment and settings described in the equipment section of this SOP.

2. The chromatographic separation between 2,3,7,8-TCDD and the peaks representing any other TCDD isomers or between 2,3,7,8-TCDF and the peaks representing other TCDF isomers must be resolved with a valley of $\leq$ 25% (Fig. 1.), where:

   Valley Percent = (x/y) x 100

   x = height of valley measured between 2,3,7,8-TCDD or 2,3,7,8-TCDF and the closest TCDD or TCDF eluting isomers, and

   y = the peak height of 2,3,7,8-TCDD or 2,3,7,8-TCDF.

3. The acquisition time windows must be set to allow observation of the first and last eluting isomer of each congener. All first and last eluters of a homologous series should be labeled and identified on chromatograms.

B. Mass Spectrometer Performance

1. The mass spectrometer must be operated in the electron ionization mode. It is recommended that the ionization potential be set to optimize sensitivity for the given column flow and source design. A static resolving power of at least 10,000 (10% valley definition) must be demonstrated at appropriate masses before any analyses are performed. Static resolving power checks must be performed at the beginning and at the end of each 12-hour period of operation. It is recommended, however, that a check of the static resolution be made and documented by using the peak matching unit before and after each analysis. Corrective actions must be implemented whenever the resolving power does not meet the requirement.

2. Chromatography time for PCDDs and PCDFs exceeds the long-term mass stability of the mass spectrometer. Because the instrument is operated in the high-resolution mode, mass drifts of a few ppm can have serious adverse effects on instrument performance. Therefore, a mass-drift correction is mandatory. To that effect, use a lock-mass ion from the reference compound Perfluorokerosene (PFK) used for tuning the mass spectrometer and monitor and record the lock-mass ion channel during SIM acquisitions. The level of the reference compound (PFK) metered inside the ion chamber during HRGC/HRMS analyses should be adjusted so that the amplitude of the selected lock-mass ion signal, regardless of

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the description number, does not exceed 10% of the full scale deflection for a given set of detector parameters. Under those conditions, sensitivity changes that might occur during the analysis can be more effectively monitored.

3. Using PFK molecular leak and an appropriate ion within the scan window, tune the instrument to meet the minimum required resolving power of 10,000 (10% valley).

   a) Documentation of the mass spectrometer resolving power is accomplished by recording the peak profile of the high-mass reference signal (m/z 416.9760) obtained during a peak matching experiment by using the low-mass PFK ion at m/z 330.9792 (or lower in mass) as a reference.

   b) The format of the peak profile representative allows manual determination of the peak resolution. The peak width (at 5% peak height) of the high-mass reference ion must not exceed 100 ppm (resolving power: 10,000). Peak width is determined by triangulation with no more than 10% allowance for sampling error. Instrumental ion transmission and resolution will be checked, adjusted and documented in case the resolution is below the minimum required 10,000 resolving power.

VIII. CALIBRATION PROCEDURES:

A. Initial Calibration (ICAL)- Initial calibration of the instrument is required before any samples are analyzed for PCDDs and PCDFs. Initial calibration is also required if any continuing calibration does not meet the required criteria listed in Section VI. B..

1. All six calibration solutions listed in Table 2. must be used for the initial calibration.

2. Tune the instrument with PFK to achieve a static resolving power of at least 10,000 (10% valley) as described in the section on mass spectrometer performance.

3. Inject 2 µL of the GC column performance check solution and acquire SIM mass spectral data –using the equipment and settings described in the equipment section of this SOP. Further analysis must not be performed the column performance criteria listed in the GC column performance section has been met and documented.

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4. Using the same GC and MS conditions that produced acceptable results for the column performance check solution, analyze a 2 µL portion of each of the six calibration solutions with the following requirements:

   a) The ratio of integrated ion current for the ions appearing in Table 5 (homologous series quantitation ions) must be within the indicated control limits (set for each homologous series).

   b) The ratio of integrated ion current for the ions belonging to the carbon-labeled internal, surrogate, alternate, and recovery standards must be within the control limits stipulated in Table 5.

   NOTE: Ion ratios for all 17 native analytes and 18 carbon-labeled internal and recovery standards must be within the specified control limits simultaneously in one run for each of the six (6) calibration standard solutions. If the ion abundance ratios are outside the limits, corrective action must be taken and acceptable abundance ratios achieved before any samples may be analyzed.

   c) For each SICP and for each GC signal representing the elution of a target analyte the signal-to-noise ratio (S/N) must be better than or equal to 10:1.

   d) Referring to Table 6., calculate the 17 relative response factors (RRF) for unlabeled target analytes relative to their appropriate internal standards, according to the following formula:

$$RRF(n) = \frac{A_x \times Q_{is}}{Q_x \times A_{is}}$$

Where:

RRF(n)=		Analyte RRF
A_x	=	sum of the integrated ion abundances ofthe quantitation ions (Table 1.) for unlabeled PCDDs/PCDFs,
A_{is}	=	sum of the integrated ion abundances of the quantitation ions (Table 1.) for the labeled internal standards,
Q_{is}	=	quantity of the internal standard injected (pg),
Q_x	=	quantity of the unlabeled PCDD/PCDF analyte injected (pg).

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The RRF(n) is a dimensionless quantity; the units used to express Q_{is} and Q_x must be the same.

e) Calculate the average analyte $\overline{RRF}$ and their respective percent relative standard deviations (%RSD) for the six calibration solutions.

$$\overline{RRF}_{(n)} = \frac{1}{6}\sum_{j=1}^{6} RRF_{(n)j}$$

Where n represents a particular PCDD/PCDF (2,3,7,8 substituted congener), and j is the injection number (or calibration solution number).

f) The relative response factors to be used for the determination of the concentration of total isomers in a homologous series are calculated as follows:

(1) For congeners that belong to a homologous series containing only one isomer (e.g., OCDD and OCDF) or only one 2,3,7,8-substituted isomer (TCDD, PeCDD, HpCDD, and TCDF), the mean RRF used will be the same as the mean RRF calculated for the associated unlabeled target analyte.

NOTE: The calibration solutions do not contain $^{13}C_{12}$-OCDF as an internal standard. This is because a minimum resolving power of 12,000 is required to resolve the $[M+6]^+$ ion of $^{13}C_{12}$-OCDF from the $[M+2]^+$ ion of OCDD (and $[M+4]^+$ from $^{13}C_{12}$-OCDF with $[M]^+$ of OCDD). Therefore, the RRF for OCDF is calculated relative to $^{13}C_{12}$-OCDD.

(2) For congeners that belong to a homologous series containing more than one 2,3,7,8-substituted isomer (PeCDF - two, HxCDF - four, HxCDD - three, HpCDF - two) the mean RRF used for those homologous series will be the average of the mean RRFs calculated for all individual 2,3,7,8-substituted congeners.

NOTE: HRGC/HRMS responses of all isomers in a homologous series that do not have the 2,3,7,8-substitution pattern are assumed to be the same as the responses of one or more of the 2,3,7,8-substituted isomer(s) in that homologous series.

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g) Referring to Table 7. and 8. calculate relative response factors (RRF) and average relative response factors (RRF) for internal, surrogate, and alternate standards relative to their appropriate recovery standards, according to the following formula:

$$RRF_{(m)} = \frac{A_s \times Q_{rs}}{Q_s \times A_{rs}}$$

$$\overline{RRF}_{(m)} = \frac{1}{6}\sum_{j=1}^{6} RRF_{(m)j}$$

Where:

m	=	congener type,
j	=	injection number,
A_s	=	sum of the integrated ion abundances of the quantitation ions for a given standard,
A_{rs}	=	sum of the integrated ion abundances of the quantitation ions for the appropriate recovery standard,
Q_{rs}, Q_s	=	quantities of, respectively, the recovery standard (rs) and a particular standard injected (pg),
$RRF_{(m)}$	=	relative response factor of a particular standard relative to an appropriate recovery standard, as determined from one injection, and
$\overline{RRF}_{(m)}$	=	calculated mean relative response factor of a particular labeled standard relative to an appropriate recovery standard, as determined from the six initial calibration injections.

5. Acceptance Criteria for Initial Calibration - The criteria listed below for acceptable calibration must be met before any analysis is performed.

a) The percent relative standard deviations for the mean response factors from the 17 unlabeled standards must not exceed ± 20 percent, and those for the labeled reference compounds must not exceed ± 30%.

b) The S/N ratio for the GC signals present in every SICP (including the ones for the labeled standards) must be ≥ 10.

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c) The isotopic ratios (Table 5.) must be within the specified control limits.

NOTE: If the criterion for acceptable calibration is met, the analyte specific RRF can then be considered independent of the analyte quantity for the calibration concentration range. The mean RRFs will be used for all calculations until the continuing calibration criteria are no longer met. At such time, new mean RRFs will be calculated from a new set of injections of the initial calibration solutions.

B. Continuing Calibration Check (CONCAL) - Continuing calibrations must be performed at the beginning of a 12 hour period after successful mass resolution and QC resolution performance checks. A continuing calibration is also required at the end of a 12 hour shift.

1. Inject 2 µL of the CONCAL solution HRCC-3 standard (Table 2) using the same HRGC/HRMS conditions described in the system performance criteria section. and used to acquire the initial calibration data.

2. Acceptance Criteria for Continuing Calibration - The following criteria must be met before further analyses are performed.

a) The measured RRFs for the unlabeled standards obtained during the continuing calibration runs must be within ± 20 percent of the mean values established during the initial calibration.

b) The measured RRFs for the labeled standards obtained during the routine calibration must be within ± 30 percent of the mean values established during the initial.

c) The ion-abundance ratios (Table 5.) must be within the allowed control limits.

d) If either one of the RRF criteria listed above is not satisfied, repeat one more time. If these criteria are still not satisfied, the entire continuing calibration process must be reviewed.

e) If the continuing calibration at the end of a 12-hour period fails no more than 25% RPD for the unlabeled compounds and 35% RPD for the labeled reference compounds, use the mean RRFs from the two daily calibration runs to compute analyte concentrations, instead of the RRFs obtained from the initial calibration.

NOTE: If RRFs for up to two labeled standards fail by more than 35%, the calibration is considered acceptable, as long as corresponding unlabeled analytes meet criteria.

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f) Continuing calibrations analyzed at the end of the 12 hour period which fail by more than 25% RPD for the unlabeled compounds and 35% RPD for the labeled reference compounds must be documented according to the non-conformance SOP.

IX. ANALYSIS

A. A valid analysis of column performance check, calibration and method or instrument blank must have been obtained prior to the analysis of any sample.

B. Remove the sample extract (blown to dryness) or blank from storage. Add 20 µL of recovery standard and mix thoroughly. Care must be taken to coat the walls of the vial several times to dissolve the sample material deposited on the walls during the concentration process.

NOTE: A final volume of 20 µL or more should be used whenever possible. A 10 µL final volume is difficult to handle, and injection of 2 µL out of 10 µL leaves little sample for confirmations and repeat injections, and for archiving.

C. Inject a 2 µL aliquot of the extract into the GC, operated under the GC conditions that have produced acceptable CONCAL and RTCHK results.

D. Acquire SIM data using the same acquisition and mass spectrometer operating conditions previously used to determine the relative response factors.

NOTE: The acquisition period must at least encompass the PCDD/PCDF overall retention time window previously determined. Selected ion current profiles (SICP) for the lock-mass ions (one per mass descriptor) must also be recorded and included in the data package. These SICPs must be true representations of the evolution of the lock-mass ions amplitudes during the HRGC/HRMS run. The analyst may be required to monitor a PFK ion, not as a lock mass, but as a QC ion, in order to meet this requirement. It is recommended to examine the QC ion or lock-mass ion SICP for obvious basic sensitivity and stability changes of the instrument during the GC/MS run that could affect the measurements. Report any discrepancies in the case narrative.

E. Identification Criteria - For a gas chromatographic peak to be identified as a PCDD or PCDF, it must meet all of the following criteria:

1. Retention Times

a) For 2,3,7,8-substituted congeners, which have an isotopically labeled internal or recovery standard present in the sample extract (this represents a total of 10 congeners including OCDD; Table 1.), the retention time (RRT; at maximum peak height) of the sample components (i.e., the two ions used for quantitation

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purposes listed in Table 1.), must be within -1 to +3 seconds of the isotopically labeled standard.

b) For 2,3,7,8-substituted compounds that do not have an isotopically labeled internal standard present in the sample extract (this represents a total of eight congeners; Table 1.), the retention time must fall within 0.005 retention time units of the relative retention times measured in the continuing calibration. Identification of OCDF is based on its retention time relative to $^{13}C_{12}$-OCDD as determined from the 12 hour continuing calibration results.

c) For non-2,3,7,8-substituted compounds (tetra through octa; totaling 119 congeners), the retention time must be within the corresponding homologous retention time windows established by analyzing the RTCHK solution.

d) The ion current responses for both ions used in quantitation (e.g., for TCDDs: m/z 319.8965 and 321.8936) must reach maximum simultaneously (± 2 seconds).

e) The ion current responses for both ions used for the labeled standards (e.g., for $^{13}C_{12}$-TCDD: m/z 331.9368 and m/z 333.9339) must reach maximum simultaneously (± 2 seconds).

2. Ion Abundance Ratios

The integrated ion current for the two ions used for quantitation purposes must have a ratio between the lower and upper limits established for the homologous series to which the peak is assigned (Table 5.).

3. Signal-to-Noise (S/N) Ratio

All ion current intensities must be ≥ 2.5 times noise level for positive identification of a PCDD/PCDF compound or a group of coeluting isomers.

4. Polychlorinated Diphenyl Ether Interferences

In addition to the above criteria, the identification of a GC peak as a PCDF can only be made if no signal having a S/N ≥ 2.5 is detected, at the same retention time (± 2 seconds), in the corresponding polychlorinated diphenyl ether (PCDPE, Table 1.) channel or if the PCDPE signal is less than 10% of the PCDF signal.

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F. Quantitation

1. For gas chromatographic peaks that have met specified criteria calculate the concentration of the PCDD or PCDF compounds using the formula:

$$C_x = \frac{A_x \times Q_{is}}{A_{is} \times W \times \overline{RRF}_{(n)}}$$

Where:

C_x = concentration of unlabeled PCDD/PCDF congeners (or group of coeluting isomers within an homologous series) in pg/g,

A_x = sum of the integrated ion abundances of the quantitation ions (Table 1.) for unlabeled PCDDs/PCDFs,

A_{is} = sum of the integrated ion abundances of the quantitation ions (Table 1.) for the labeled internal standards,

Q_{is} = quantity, in pg, of the internal standard added to the sample before extraction,

W = weight or volume, in grams or liters, of the sample (solid or liquid), and

$\overline{RRF}_{(n)}$ = calculated mean relative response factor for the analyte.

2. Calculate the percent recovery of the nine internal standards measured in the sample extract, using the formula:

$$\text{Internal Standard Recovery} = \frac{A_{is} \times Q_{rs}}{Q_{is} \times A_{rs} \times \overline{RRF}_{(m)}} \times 100$$

Where:

A_{is} = sum of the integrated ion abundances of the quantitation ions (Table 1.) for the labeled internal standard,

A_{rs} = sum of the integrated ion abundances of the quantitation ions (Table 1.) for the labeled recovery standard; the selection of the recovery standard depends on the type of congeners (Table 7.),

Q_{is} = quantity, in pg, of the internal standard added to the sample before extraction,

Q_{rs} = quantity, in pg, of the recovery standard added to the cleaned-up sample residue before HRGC/HRMS analysis, and

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$\overline{RRF}_{(m)}$ = calculated mean relative response factor for the labeled internal standard relative to the appropriate (see Table 7) recovery standard.

3. Calculate the percent recovery of seven surrogate and alternate standards using the same equation used to calculate percent recovery of the internal standards.

4. If the concentration in the final extract of any of the fifteen 2,3,7,8-substituted PCDD/PCDF compound exceeds the dynamic range of the instrument (i.e., saturation in a mass channel) then solvent will be added to the extract to bring the signal level into the instrument's dynamic range. Any dilutions must be pre-approved by the client.

5. The total concentration for each homologous series of PCDD and PCDF is calculated by summing up the concentrations of all positively identified isomers of each homologous series. Therefore, the total should also include the 2,3,7,8-substituted congeners. The total number of GC signals included in the homologous total concentration value must be specified in the report.

6. Sample Specific Estimated Detection Limit - The sample specific estimated detection limit (EDL) is the concentration of a given analyte required to produce a signal with a peak height of at least 2.5 times the background signal level. An EDL is calculated for each 2,3,7,8-substituted congener that is not identified, regardless of whether or not other non-2,3,7,8-substituted isomers are present. Two methods of calculation can be used, depending on the type of response produced during the analysis of a particular sample.

   a) Samples giving a response for at least one quantitation ion that is less than 2.5 times the background level.

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The area of the analyte is replaced by the noise level measured in a region of the chromatogram clear of genuine GC signals multiplied by an empirically determined factor. The detection limits represent the maximum possible concentration of a target analyte that could be present without being detected.

$$DL = \frac{2.5 \times H \times Q_{is}}{H_{is} \times RRF_{(n)} \times W}$$

Where:

DL	=	estimated detection limit for a target analyte, expressed in ng or pg.
2.5	=	minimum signal/ noise required for a GC signal to be accepted.
H	=	height of the noise.
H_{is}	=	integrated current of the characteristic ions of the corresponding internal standard.
Q_{is}	=	amount of internal standard added to sample before extraction.
$\overline{RRF}_{(n)}$	=	mean analyte relative response factor from the initial calibration.
W	=	sample weight or volume.

b) Samples characterized by a response above the background level with a S/N of at least 2.5 for both quantitation ions.

When the response of a signal having the same retention time as a 2,3,7,8-substituted congener has a S/N in excess of 2.5 and does not meet ion ratio requirements (Table 5.) calculate the "Estimated Maximum Possible Concentration" (EMPC) using the equation shown at the beginning of this section for the quantitation of PCDD or PCDF compounds except that A_x should represent the sum of the area under the smaller peak and of the other peak area calculated using the theoretical chlorine isotope ratio.

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PCDDs AND PCDFs BY HRGC/HRMS - METHOD 8290 & TO-9	
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X. QUALITY CONTROL REQUIREMENTS

A. GC column performance must be demonstrated initially and verified prior to analyzing any sample in a 12-hour period. The GC column performance check solution must be analyzed under the same chromatographic and mass spectrometric conditions used for other samples and standards.

B. Routine calibrations must be performed at the beginning of a 12-hour period after successful mass resolution and GC resolution performance checks and at the end of a 12-hour period following the analysis of samples.

C. The quantitation limits (or target detection limits) will be the following:

1. Quantitation limits for waters (sample size - 1L):

   ≤ 10 ppq TCDD & TCDF

   ≤ 50 ppq Penta - HeptaCDD & CDF

   ≤ 100 ppq OCDD & OCDF

2. Quantitation limits for solids (sample size - 10g):

   ≤ 1 ppt TCDD & TCDF

   ≤ 5 ppt Penta - HeptaCDD & CDF

   ≤ 10 ppt OCDD & OCDF

3. Quantitation limits for air or Wipes (sample size - 1):

   ≤ 50 pg TCDD & TCDF

   ≤ 250 pg Penta - HeptaCDD & CDF

   ≤ 500 pg OCDD & OCDF

D. Method Blank

1. Percent recoveries of all labeled standards should be between 40 - 135%. Method blank with standard recoveries below 40% (but ≥ 25%) is acceptable as long as signal to noise for affected standards is ≥ 10:1.

2. Qunatitation limites (target detection limits) must be met for each analyte.

3. No reportable analytes should be present in the Method Blank. Up to 3 analytes may be present at levels below 1/2 Target Detection Limit (TDL) as long as the compounds were not reported in the previous analysis.

4. For Method Blanks associated with high level samples, the analyte level in the blank must be < 5% of the quantity present in the samples.

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E. LCS/ LCSD and MS/ MSD

1. Percent recoveries of all labeled standards should be between 40 - 135%. LCS/ LCSD or MS/ MSD with labeled standard recoveries below 40% (but ≥ 25%) are acceptable as long as signal to noise for affected standards is ≥ 10:1.
2. Percent recoveries of all analytes should be between 70 - 130%. For up to two analytes, recoveries may be as high as 145% or as low as 60%, as long as the associated relative percent differences (%RPDs) meet criteria.
3. Relative percent difference between LCS and LCSD or MS and MSD should be ≤ 20% for all analytes. For up to two analytes, %RPDs may be higher (up to 35%), as long as the associated percent recoveries meet criteria.
4. If percent recovery or relative percent difference criteria in MS/MSD pair is not met:
   a) Evaluate data for possible matrix influence
   b) Evaluate LCS data for compliance.
   c) If cause of non-compliance is not determined, reextract sample batch.

F. Samples

1. Percent recoveries of all labeled standards should be between 40 - 135%. Samples with standard recoveries below 40% (but ≥ 25%) are acceptable as long as signal to noise for affected standards is ≥ 10:1. In the case of OCDD internal standards, the OCDF analyte must be below TDL also.
2. Specific detection limits must not exceed the target detection limits unless prohibited by a limited sample size or the need for dilution.
3. If the method blank contains reportable analytes but those analytes are not detected in the sample, the sample data may be reported.
4. Samples which fail acceptance criteria listed above or are associated with failing method blank or LCS/ LCSD must be reextracted and reanalyzed. Exceptions may be made for sample matrices which require extreme additional cleanup procedures.

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XI. **REFERENCES:** This method is used for the analysis of sample extracts prepared by any of the following methods, SOP DSP104, DSP105, DSP108, DSP112, DSP115, DSP124, DSP130, DSP131, DSP133, DSP134, DSP150, DSP154, DSP161, DSP218, DSP254, DSP260, DSP261, DSP272, DSP276, DSP278, DSP280, DSP290, and/or DSP294.

XII. **INTERFERENCES**

A. Phthalate interferences are characterized by major quantitative interference in the PeCDF and PeCDD regions. Samples with phthalates receive additional clean up using the alumina clean up detailed in DSP 260D.

B. Interferences caused by the presence of sulfur in a sample are characterized by quantitative interference in the TCDF and TCDD regions. Samples containing sulfur should receive additional clean up using the copper clean up detailed in DSP 277.

C. Interferences caused by the presence of three-ring PAHs are characterized by quantitative interference in the Tetra through HexaCDD and CDF regions. Samples containing three-ring PAHs should receive additional clean up using sulfuric acid, alumina, and/or carbon clean up detailed in DSP 280 and 260D. Samples that contain fluorescing residue and show this pattern of quantitative interference should be cleaned up using the silver nitrate clean up detailed in DSP 260D.

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TABLE 1: ELEMENTAL COMPOSITIONS AND EXACT MASSES OF THE IONS MONITORED BY HRGC/HRMS FOR PCDDs AND PCDFs

Descriptor Number[b]	Accurate Mass[a]	Ion Type	Elemental Composition	Analyte
2	292.9825	LOCK	C_7F_{11}	PFK
	303.9016	M	$C_{12}H_4{}^{35}Cl_4O$	TCDF
	305.8987	M+2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF
	315.9419	M	$^{13}C_{12}H_4{}^{35}Cl_4O$	TCDF (S)
	317.9389	M+2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF (S)
	319.8965	M	$C_{12}H_4{}^{35}Cl_4O_2$	TCDD
	321.8936	M+2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD
	327.8847	M	$C_{12}H_4{}^{37}Cl_4O_2$	TCDD (S)
	330.9792	QC	C_7F_{13}	PFK
	331.9368	M	$13C_{12}H_4{}^{35}Cl_4O_2$	TCDD (S)
	333.9339	M+2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD (S)
	375.8364	M+2	$C_{12}H_4{}^{35}Cl_5{}^{37}ClO$	HxCDPE
	339.8597	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF
	341.8567	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF
	351.9000	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF (S)
	353.8970	M+4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF (S)
	355.8546	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD
	357.8516	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD
	367.8949	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD (S)
	369.8919	M+4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD (S)
	409.7974	M+2	$C_{12}H_3{}^{35}Cl_6{}^{37}ClO$	HpCDPE
3	373.8208	M+2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF
	375.8178	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDF
	383.8639	M	$^{13}C_{12}H_2{}^{35}Cl_6O$	HxCDF (S)

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TABLE 1 CONTINUED

Descriptor Number[b]	Accurate Mass[a]	Ion Type	Elemental Composition	Analyte
3 Continued	385.8610	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF (S)
	389.8157	M+2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD
	391.8127	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD
	392.9760	LOCK	C_9F_{15}	PFK
	401.8559	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD (S)
	403.8529	M+4	$13C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD (S)
	445.7555	M+4	$C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2O$	OCDPE
	430.9729	QC	C_9F_{13}	PFK
4	407.7818	M+2	$C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF
	409.7789	M+4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O$	HpCDF
	417.8253	M	$^{13}C_{12}H^{35}Cl_7O$	HpCDF (S)
	419.8220	M+2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF (S)
	423.7766	M+2	$C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD
	425.7737	M+4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD
	435.8169	M+2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD (S)
	437.8140	M+4	$^{13}C_{12}H^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD (S)
	479.7165	M+4	$C_{12}H^{35}Cl_7{}^{37}Cl_2O$	NCDPE
	430.9729	LOCK	C_9F_{17}	PFK
	441.7428	M+2	$C_{12}{}^{35}Cl_7{}^{37}ClO$	OCDF
	443.7399	M+4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O$	OCDF
	457.7377	M+2	$C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD
	459.7348	M+4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD
	469.7779	M+2	$^{13}C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD (S)
	471.7750	M+4	$^{13}C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD (S)

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TABLE 1 CONTINUED

Descriptor Number[b]	Accurate Mass[a]	Ion Type	Elemental Composition	Analyte
4 Continued	513.6775	M+4	$C_{12}{}^{35}Cl_8{}^{37}Cl_2O$	DCDPE
	442.9728	QC	$C_{10}F_{17}$	PFK

a) The following nuclidic masses were used:

H = 1.007825
C = 12.000000
^{13}C = 13.003355
F = 18.9984
O = 15.994915
^{35}Cl = 34.968853
^{37}Cl = 36.965903

S = Labeled Standard
QC = Ion Selected for Monitoring the Instrument Stability During the GC/MS Analysis

b) Descriptor 1 contains mono-, di- and trichlorinated dibenzodioxins and dibenzofurans that are not quantitated by Method 8290.

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TABLE 2: COMPOSITION OF THE INITIAL CALIBRATION SOLUTIONS

Compound	Concentrations (pg/µL) Sol. Number: 1	2	3	4	5	6
Unlabeled Analytes						
2,3,7,8-TCDD	0.5	1	10	50	100	200
2,3,7,8-TCDF	0.5	1	10	50	100	200
1,2,3,7,8-PeCDD	2.5	5	50	250	500	1000
1,2,3,7,8-PeCDF	2.5	5	50	250	500	1000
2,3,4,7,8-PeCDF	2.5	5	50	250	500	1000
1,2,3,4,7,8-HxCDD	2.5	5	50	250	500	1000
1,2,3,6,7,8-HxCDD	2.5	5	50	250	500	1000
1,2,3,7,8,9-HxCDD	2.5	5	50	250	500	1000
1,2,3,4,7,8-HxCDF	2.5	5	50	250	500	1000
1,2,3,6,7,8-HxCDF	2.5	5	50	250	500	1000
1,2,3,7,8,9-HxCDF	2.5	5	50	250	500	1000
2,3,4,6,7,8-HxCDF	2.5	5	50	250	500	1000
1,2,3,4,6,7,8-HpCDD	2.5	5	50	250	500	1000
1,2,3,4,6,7,8-HpCDF	2.5	5	50	250	500	1000
1,2,3,4,7,8,9-HpCDF	2.5	5	50	250	500	1000
OCDD	5	10	100	500	1000	2000
OCDF	5	10	100	500	1000	2000
Internal Standards						
$^{13}C_{12}$-2,3,7,8-TCDD	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	100	100	100	100	100

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TABLE 2 CONTINUED

Compound	Concentrations (pg/µL) Sol. Number: 1	2	3	4	5	6
Internal Standards Continued						
$^{13}C_{12}$-OCDD	200	200	200	200	200	200
$^{13}C_{12}$-2,3,7,8-TCDF	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	100	100	100	100	100
Surrogate Standards						
$^{37}Cl_4$-2,3,7,8-TCDD	0.5	1	10	50	100	200
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	100	100	100	100	100
Alternate Standard						
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	100	100	100	100	100
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	100	100	100	100	100
Recovery Standards						
$^{13}C_{12}$-1,2,3,4-TCDD	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	100	100	100	100	100

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TABLE 3: GC RETENTION TIME WINDOW DEFINING SOLUTION AND ISOMER SPECIFICITY TEST STANDARD (SECTION IV. C.)

DB-5 COLUMN GC RETENTION TIME WINDOW DEFINING SOLUTION

CDD/ CDF	FIRST ELUTED	LAST ELUTED
TCDF	1,3,6,8	1,2,8,9
TCDD	1,3,6,8	1,2,8,9
PeCDF	1,3,4,6,8	1,2,3,8,9
PeCDD	1,2,4,7,9	1,2,3,8,9
HxCDF	1,2,3,4,6,8	1,2,3,4,8,9
HxCDD	1,2,4,6,7,9	1,2,3,4,6,7
HpCDF	1,2,3,4,6,7,8	1,2,3,4,7,8,9
HpCDD	1,2,3,4,6,7,9	1,2,3,4,6,7,8

DB-5 COLUMN TCDD SPECIFICITY TEST STANDARD

1,2,3,7 + 1,2,3,8 - TCDD
2,3,7,8 - TCDD
1,2,3,9 - TCDD

DB-225 COLUMN TCDF ISOMER SPECIFICTY TEST STANDARD

2,3,4,7 - TCDF
2,3,7,8 - TCDF
1,2,3,9 - TCDF

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TABLE 4: GAS CHROMATOGRAPHY CONDITIONS

Column type	**DB-5**	**DB-225**
Length (m)	60	30
i.d. (mm)	0.25	0.25
Film Thickness (um)	0.25	0.25
Carrier Gas	Helium	Helium
Carrier Gas Flow (mL/min)	1-2	1-2
Injection Mode	⇐ splitless ⇒	
Valve Time (s)	60	60
Initial Temperature (°C)	150	130
Injection Port Temperature (°C)	250	250
Program Temperature	⇐ See Note ⇒	

Note: The GC temperature program is subject to change. Refer to work area guidelines for exact definitions of the current run conditions and descriptor name.

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TABLE 5. ION-ABUNDANCE RATIO ACCEPTABLE RANGES FOR PCDDs AND PCDFs

Number of Chlorine Atoms	Ion Type	Theoretical Ratio	Control Limits	
			Lower	Upper
4	M/M+2	0.77	0.65	0.89
5	M+2/M+4	1.55	1.32	1.78
6	M+2/M+4	1.24	1.05	1.43
6a	M/M+2	0.51	0.43	0.59
7b	M/M+2	0.44	0.37	0.51
7	M+2/M+4	1.04	0.88	1.20
8	M+2/M+4	0.89	0.76	1.02

a) Used only for ^{13}C-HxCDF
b) Used only for ^{13}C-HpCDF

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TABLE 6. UNLABELED ANALYTES QUANTITATION RELATIONSHIPS

Analyte	Standard Used During Quantitation
2,3,7,8-TCDD	$^{13}C_{12}$-2,3,7,8-TCDD
Other TCDDs	$^{13}C_{12}$-2,3,7,8-TCDD
1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,7,8-PeCDD
Other PeCDDs	$^{13}C_{12}$-1,2,3,7,8-PeCDD
1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
1,2,3,7,8,9-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
Other HxCDDs	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD
Other HpCDD	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD
OCDD	$^{13}C_{12}$-OCDD
2,3,7,8-TCDF	$^{13}C_{12}$-2,3,7,8-TCDF
Other TCDFs	$^{13}C_{12}$-2,3,7,8-TCDF
1,2,3,7,8-PeCDF	$^{13}C_{12}$-1,2,3,7,8-PeCDF
2,3,4,7,8-PeCDF	$^{13}C_{12}$-1,2,3,7,8-PeCDF
Other PeCDFs	$^{13}C_{12}$-1,2,3,7,8-PeCDF
1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF
1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF
1,2,3,7,8,9-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF

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TABLE 6 CONTINUED

Analyte	Standard Used During Quantitation
2,3,4,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF
Other HxCDFs	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF
1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF
1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF
Other HpCDFs	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF
OCDF	$^{13}C_{12}$-OCDD

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TABLE 7: INTERNAL STANDARDS QUANTITATION RELATIONSHIPS

Internal Standard	Standard Used During Percent Recovery Determination
$^{13}C_{12}$-2,3,7,8-TCDD	$^{13}C_{12}$-1,2,3,4-TCDD
$^{13}C_{12}$-1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,4-TCDD
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-OCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-2,3,7,8-TCDF	$^{13}C_{12}$-1,2,3,4-TCDD
$^{13}C_{12}$-1,2,3,7,8-PeCDF	$^{13}C_{12}$-1,2,3,4-TCDD
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD

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PCDDs AND PCDFs BY HRGC/HRMS - METHOD 8290 & TO-9	
TLI SOP: DHR182 Version: 9	Date Written: March 20, 2002

TABLE 8: SURROGATE/ALTERNATE STANDARDS QUANTITATION RELATIONSHIPS

Surrogate/Alternate/Cleanup Standard	Standard Used During Percent Recovery Determination
$^{37}Cl_4$-2,3,7,8-TCDD	$^{13}C_{12}$-1,2,3,4-TCDD
$^{13}C_{12}$-2,3,4,7,8-PeCDF	$^{13}C_{12}$-1,2,3,4-TCDD
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	13C_{12}-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD

NOTE : For air samples (PUF and M-0023A) recoveries of surrogate standards are quantitated relative to their appropriate internal standards.

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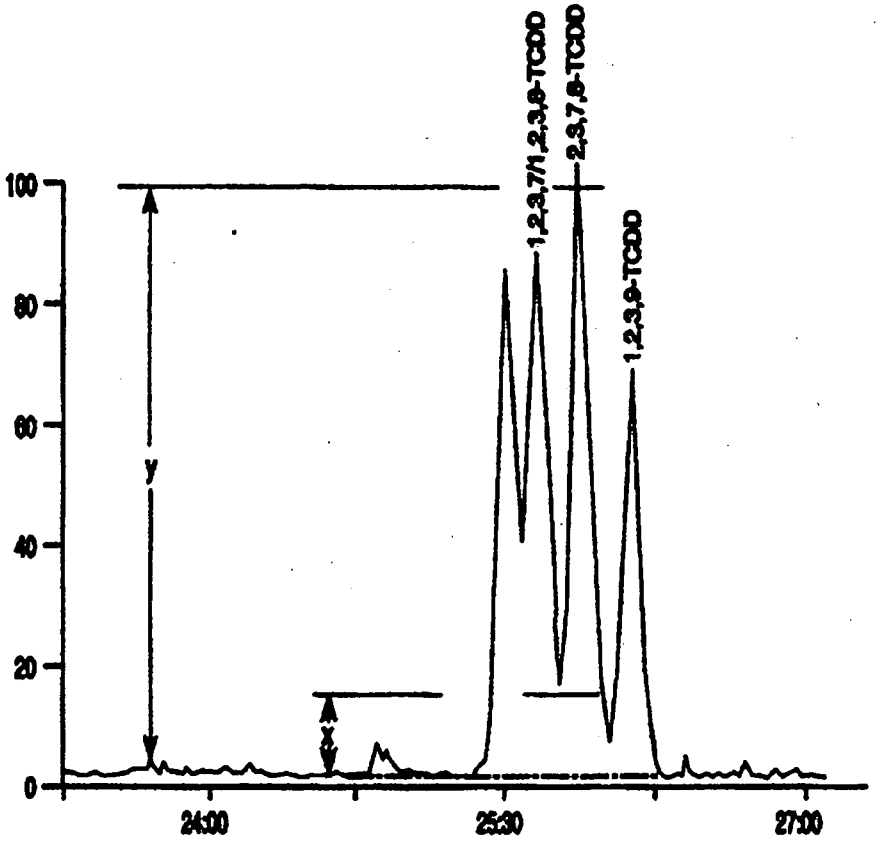

FIGURE 1. Valley between 2,3,7,8 - Tetrachlorodibenzo-p-dioxin and Other Closely Eluting Isomers.

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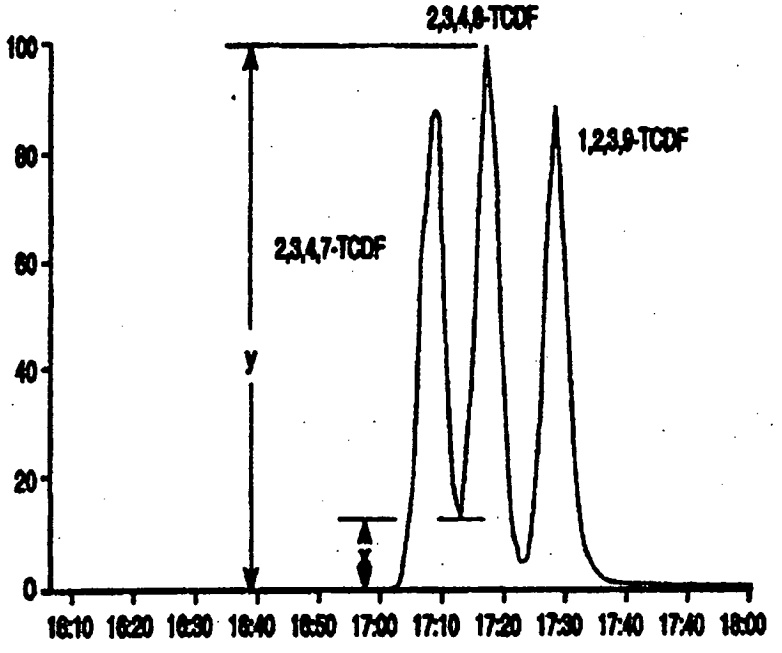

FIGURE 2. Valley between 2,3,7,8 - Tetrachlorodibenzofuran and Other Closely Eluting Isomers.

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APPENDIX 1

Deviations from and improvements to US EPA Method 8290
POLYCHLORINATED DIBENZODIOXINS (PCDDs) AND POLYCHLORINATED DIBENZOFURANS (PCDFs) BY HIGH-RESOLUTION GAS CHROMATOGRAPHY/ HIGH-RESOLUTION MASS SPECTROMETRY (HRGC/ HRMS)
as performed at Triangle Laboratories, Inc.

See Section	
• VI. A. and Table 2.	Triangle Laboratories uses 6 calibration points ranging from 0.5 pg/µL to 200 pg/µL for tetrachlorinated dioxin and furan. Concentrations of penta- through heptachlorinated analytes are 5 times higher than tetra congeners and octachlorinated analytes are 10 times higher (Compare with Table 5., Method 8290).
• VI. A.	Seven more labeled PCDDs/ PCDFs are used as surrogate and alternate standards to provide additional quality control information.
• VI. A.	The 1,2,3,6,7,8 - hexachlorodibenzofuran (HxCDF) is used as an internal standard instead of 1,2,3,4,7,8 - HxCDF. Triangle Laboratories uses 1,2,3,4,7,8 - HxCDF as a surrogate standard.
• VI. A.	Each carbon-labeled standard in the initial calibration solution has a concentration of 100 pg/µL except $^{13}C_{12}$ - OCDD, which is at 200 pg/µL. Concentrations of $^{13}C_{12}$ - labeled standards in sample fortification solutions are the same as in the initial calibration solution (See section 5.9., Method 8290).
• VII.	The method blank does not need to be analyzed on each analysis clock that samples are analyzed. Once a valid analysis is provided for the method blank it may be replaced with HRGC/ HRMS solvent blank (See section 8.2., Method 8290).
• VII. B. 3. a)	Documentation of the mass spectrometer resolving power is accomplished by recording the peak profile of m/z 416.9760 and 330.9792 (See section 8.2.2.3., Method 8290).
• IX. F. 6. a)	To calculate the sample specific Estimated Detection Limit, noise equivalent area is used instead of noise height (See section 7.9.5.1.1., Method 8290).
• XI. D. - F. 1.	The Internal Standard recoveries in all QC samples and field samples are considered valid as long as the signal to noise ratio is greater than 10:1, the recovery is ≥ 25% and target detection limits for the analytes are met (See section 8.4., Method 8290).
• X. E. 2.	For up to two analytes in LCS/ LCSD and MS/ MSD, recoveries may be as high as 145% or as low as 60%, as long as the associated relative percent differences (%RPDs) meet criteria.

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APPENDIX 1 Continued

- X. E. 3. For up to two analytes in LCS/ LCSD and MS/ MSD, %RPDs may be higher (up to 35%), as long as the associated percent recoveries meet criteria.

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DATA PACKAGE ASSEMBLY AND SHIPPING

TLI SOP No. DPA104	Version: 12	Effective Date:	11/30/98
Author:	David Chu	Date Written:	October 1, 1998
Authorization: Phil Albro Management		Date Authorized:	11/20/98

I. **SCOPE AND APPLICATION:** The purpose of this SOP is to describe the procedures to follow when assembling and shipping all data packages at Triangle Laboratories, Inc. The deliverables of the standard data package contain an identification document stating that Triangle Laboratories, Inc. produced the results.

II. **PROCEDURE:**

A. Assemble the data package, including: the address documentation, the signed case narrative, Triangle Labs list of certifications, document control or project description section, all Sample Data Summary sheets with chromatograms and calibration data for each project. Paginate everything that is going to the client. Go to the last page of the Case Narrative and, in the space provided, enter the total number of pages in the document. Unless the client has requested otherwise, send them the original case narrative and the copy of other deliverables.

NOTE: To obtain the address documentation, go into MILES and Select "F", enter project number, printout destination, Select "M" for Marked for shipment. If it is to be shipped out the door, then type "Y" for transfer to archive. If not, type "N".

B. For high resolution data packages only, locate all calibration data pertaining to the project. Refer to the Reporting Option located in the Reporting Requirements of the Sample Tracking and Project Management Form. Copy only summary sheets for CONCALs and ICALs to send to customer. Some clients request full calibration data which includes summary data sheets and chromatograms for CONCALs, ICALs and retchecks. Calibration data for all other projects should be furnished.

C. Before copying data package, go to the MILES system. At the main menu, select "F" for Shipping/Archiving. On Shipping/Archiving Information Sub-menu, select "Sample shipment Update/Inquiry."

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DATA PACKAGE ASSEMBLY AND SHIPPING					
TLI SOP No.	DPA104	Version:	12	Date Written:	October 1, 1998

D. Enter project number, extension (if applicable) and "M" for marked for shipment, "T" for transfer to archive. Also enter password for this screen.

E. The samples for this project will appear on the screen. The project must be in shipping (D-SH, O-SH, I-SH, S-SH) in order to perform this function. If not, go back to the shipping sub-menu and select option "Production By Project and/or Worklist." Transfer project to shipping.

F. All samples for project will be tagged if project is in shipping. Press <F10> to transfer shipping information to accounting. The computer will issue a printout with all the shipping information including price, address, and special instructions.

G. Follow all instructions closely. Copy data packages according to instructions listed on the printout.

H. The computer will automatically archive all projects if you indicate it to do so by typing "Y".

I. See SOP on shipping projects.

NOTE: When copying BNA projects, set the copier on 93% reduction to avoid chopping off the interim.

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EXTRACTION OF PCDD/PCDF FROM WATER FOR METHODS 1613, 8290 AND 551

TLI SOP No. DSP161	Version: 16	Effective Date:	October 23, 1998
Author:	Phil Albro	Date Written:	October 2, 1998
Authorization: Phil Albro (Management)		Date Authorized:	10/18/98

I. **SCOPE AND APPLICATION:** This SOP provides procedures for the extraction of polychlorinated dibenzo-p-dioxin and polychlorinated dibenzofuran (PCDD and PCDF) from water samples in accordance with methods 1613 or 8290. It may also be applied to the extraction of tetrachlorodibenzo-p-dioxins and tetrachlorodibenzofuran from water in accordance with method 551. See the SOP on Preparation for Extraction of PCDD/PCDF from Water before using the present SOP.

II. **SAFETY CONSIDERATIONS:** Samples may contain harmful substances. Wear labcoat, appropriate eyewear, and gloves. These solvents are flammable; avoid flames and sparks. Do not breathe the vapors, and avoid contact with skin and eyes. They may cause irritation, nausea, dizziness, and, in extreme cases, death. For additional safety and health information, see the TLI Safety and Health Manual and the appropriate MSDS.

III. **REAGENTS:**

A. Organic-free reagent water- Either Dracor or Fisher HPLC Grade

B. Heptane-pesticide grade or better quality, less than 1 ppm residue on evaporation.

C. Sodium sulfate-anhydrous, pesticide grade.

D. Methylene Chloride-pesticide grade or better quality.

E. Toluene-pesticide grade or better quality.

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EXTRACTION OF PCDD/PCDF FROM WATER FOR METHODS 1613A 8290 AND 551	
TLI SOP No. DSP161 Version: 16	Date Written: October 2, 1998

IV. **GLASSWARE PREPARATION:**

A. All glassware used in this procedure must have been prepared according to the SOP entitled "Glassware Cleaning".

B. The following glassware is needed for each sample:

2 L separatory funnel with stopper and Teflon© stopcock

A. 1000 mL graduated cylinder

medium glass powder funnel

250 mL round bottom flask

500 mL extraction flask and regular thimble holder (pre-Soxlet extracted).

Soxlet extractor (pre-Soxlet extracted).

Soxhlet Dean-Stark (SDS) extractor - pre-soxhlet extracted and ready for use

A. Assemble the separatory funnel(s) with stopcock and stopper.

B. Rinse the following with heptane:

separatory funnel(s)

graduated cylinder(s)

all flasks

glass powder funnel(s)

A. While rinsing the separatory funnel(s), close the stopcock and check for leaks. Drain the funnel into a waste container.

B. After rinsing, invert all flasks and allow to fully drain.

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C. Plug the powder funnel(s) with pre-cleaned glasswool. Fill the powder funnel 3/4 full with anhydrous sodium sulfate.

I. SEPARATORY FUNNEL EXTRACTION PROCEDURE:

A. If has not already been done in the preparation of the sample for extraction, pour the sample volume into a 2 L separatory funnel. Rinse the sample bottle with 60 mL of methylene chloride and transfer to the separatory funnel.

B. Extract the aqueous phase with methylene chloride as follows:

1. Shake the separatory funnel with water sample and methylene chloride for 5 minutes using Glas-Col Automatic Shaker (or 2 minutes by hand). Be sure to vent the funnel periodically to avoid pressure buildup.

   Note: If using the Gas-Col shaker, set the timer for 5 minutes and turn the power on. Slowly increase the speed to 40 or the maximum speed possible without displacing any sample through the vent.

   Allow the solvent layers to settle for 10 minutes. If emulsions occur, filter the water + emulsion through a G8 filter or glass wool with a methylene chloride rinse. Add the methylene chloride rinses to the methylene chloride extract.

2. Drain the methylene chloride layer through anhydrous sodium sulfate into a 250 mL flask.

3. Repeat steps 1-3 two more times using 60 mL methylene chloride for each extraction. A total of three extractions are required for each sample.

1. Rinse the sodium sulfate twice with 10 mL methylene chloride. Collect the methylene chloride rinses in the 250 mL flask containing the sample extract.

I. EXTRACTING THE FILTER:

A. Soxhlet extract the filters, glasswool used to break emulsions, and all filtered solids as follows:

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1. Place filters in a toluene pre-Soxhlet extracted thimble (500 mL size).

2. For methods 1613 and 8290, add 375-400 mL of toluene to the 500 mL boiling flask; For method 551, use 400 mL of ethanol: toluene 68:32 (v/v) to the 500 mL flask.

3. Add 5-6 Teflon boiling chips to the boiling flask.

4. Place the label containing information for the concentration process on the boiling flask on top of colored lab tape. Write solvent used on flask with marker.

   a) Do not place set up on hotplates until extraction of the water phase is completed to insure no additional emulsions need to be filtered and the filter or glasswool placed into the thimble with the first filter.

2. Extract using pre-Soxhlet extracted Soxhlet apparatus for 16 hours.

3. After extraction, let cool and ensure the label indicating that this extract is to be combined with the methylene chloride extract from the water phase is still intact.

II. CONTINUOUS LIQUID-LIQUID EXTRACTION PROCEDURE:

Note: The use of the continuous liquid-liquid extractor is always allowed as an alternative to separatory funnel extraction in method 8290. It is the technique of choice when a given sample type is known to produce difficult emulsions. Use this technique with methods 1613 (A or B) and 551 whenever a re-extraction is needed because of low recoveries during the separatory funnel extraction step. Be sure to indicate on the extraction form whenever L-L extraction was used.

Note 2: The L-L extractor simply substitutes for a separatory funnel; therefore all considerations of filtering, determination of solids or particulate solids, or water vs. sludge described in the SOP on Preparation for Extraction of PCDD/PCDF from Water for Methods 1613, 8290 and 551 still apply.

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EXTRACTION OF PCDD/PCDF FROM WATER FOR METHODS 1613A 8290 AND 551	
TLI SOP No. DSP161 Version: 16	Date Written: October 2, 1998

A. Assemble Glassware

1. Using pre-extracted glassware, rinse the extractor body and 500 mL flat bottom flask with methylene chloride. Discard rinse as waste.

2. Place 5-6 methylene chloride pre-extracted boiling chips in the flat bottom flask. Add approximately 250 mL of clean methylene chloride to the flask.

3. Add approximately 150 mL of methylene chloride to the extractor body.

4. Attach extractor body to the flask with green plastic clamp.

5. Label flat bottom with solvent, project number and sample number using color labels.

B. Preparation of Water Sample

1. Measure and record 1 liter of Reagent water each for blank and either OPR (1613), or LCS/LCSD (8290) utilizing a 1000 mL graduated cylinder.

2. Measure 1000 mL of well mixed sample and transfer to the extractor body. Record this volume on the sample preparation and tracking form. Note: If the sample does not contain 1000 mL, record the volume it does contain, but make up the difference with Reagent water. The L-L apparatus needs 1000 mL of water to operate correctly. The sample size to use in calculations, however, is the actual sample size not including make-up water.

3. Rinse the 1000 mL graduated cylinder three times with 20 mL methylene chloride and transfer rinses to the extractor body.

C. Extraction

1. Place Continuous Liquid-Liquid setup on condenser/hot plate and seat securely in place. Use aluminum foil shimmies to align body vertically and to fill any space between hotplate and bottom of the flask.

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2. Turn hotplate on to 400 degrees.

3. Extract for 18 hours.

4. Dismantle setup after they have cooled. Keep only the methylene chloride in the flat bottom flask.

5. Discard water and methylene chloride in extractor body as waste.

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Quality Assurance and Control Plan

Explosive Sciences Branch
Naval Surface Warfare Center Crane
300 Highway 361
Crane, IN 47522

March 28, 2001

Approvals:

Name	Nancey J. Maegerlein
Title	Branch Manager
Signature	Nancey J. Maegerlein
Name	Michelle L. Spellman
Title	Quality Assurance Officer
Signature	Michelle L. Spellman

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I. SCOPE AND APPLICATION

The Explosive Sciences Branch (ESB), Code 4052 of the Crane Division, Naval Surface Warfare Center provides scientific laboratory support to the various military services and private constituents. Analysis is normally performed in a laboratory environment. Explosive work is performed both in the laboratory and in remote locations when necessary.

The overall Quality Assurance objective of the laboratory is to develop and implement procedures that will provide sound measurements. This Quality Assurance/Quality Control (QA/QC) Plan is intended to provide the necessary guidance for the laboratory in the development of data that is technically sound and legally defensible. Through teamwork and accountability, the ESB laboratory strives to meet and exceed customer expectations per the Code 405 Quality Plan.

II. SUMMARY OF METHOD

A. Regulations

This method is consistent with ISO 9000 standard requirements and all state and federal testing, safety, and environmental requirements. The table below outlines the branch's mechanism for addressing each element of the standard:

Table 1: Code 4052 ISO Standard Assessment

Element	Applicable Procedure
4.1 Management Responsibility	CR4052-PD-0001
4.2 Quality System	CR4052-PD-0001
4.3 Contract Review	CR4052-PD-0350
4.4 Design Control	N/A
4.5 Document and Data Control	CR4052-PD-0100
4.6 Purchasing	CR4052-PD-0220
4.7 Control of Customer-Supplied Product	CR4052-PD-0500, Method PD's
4.8 Product ID and Traceability	CR4052-PD-0500, CR4052-PD-0150, CR4052-PD-0600
4.9 Process Control	CR4052-PD-0200, Method PD's
4.10 Inspection and Testing	CR4052-PD-0600, CR4052-PD-0500, CR4052-PD-0450
4.11 Control of inspection, measuring, test equip	CR4052-PD-0250
4.12 Inspection and Test Status	N/A
4.13 Control of Nonconforming Product	CR4052-PD-0600
4.14 Corrective and Preventative Action	Code 405 Procedure
4.15 Handling, storage, packaging, preservation and delivery	N/A
4.16 Control of quality records	CR4052-PD-0150
4.17 Internal Quality Audits	Navy Instruction 4855.12A
4.18 Training	CR4052-PD-0300
4.19 Servicing	N/A
4.20 Statistical Techniques	CR4052-PD-0230

B. Objectives

The objective of the laboratory quality assurance program is to assure the accuracy and precision, as well as the reliability of laboratory results produced for our customers, or at the request of regulatory or accrediting bodies. Management, administrative, statistical, investigative, preventive, and corrective techniques will be employed to maximize reliability of the data.

Specific objectives are:

1. To establish the level of quality of the laboratory's routine performance as a baseline against which to measure the effectiveness of quality improvement efforts.

2. To monitor the routine operational performance of the laboratory through participation in appropriate Performance Evaluation programs and to provide for corrective actions as necessary.

3. To improve and validate laboratory methodologies by performing method validation studies.

C. Organization and Responsibility

This section is designed to identify the responsibilities of Quality Assurance within the overall structure of the laboratory organization. Other position descriptions are found in personnel department files and in the training procedures.

The direct and ultimate responsibility for assuring data quality at the ESB laboratory rests with the ESB Manager. The chemist/laboratory analyst will provide the first level of data review in the laboratory, however, the ESB Manager provides the final quality assurance/control of all data gathered or reported for compliance testing. Results may also be reviewed by the customer, regulating agency, or certification body upon request.

All personnel shall strive to meet the requirements of the QA programs. All personnel shall have access to procedure and technical documents and are encouraged to discuss the contents with the management at any time.

CR4052-PD-0001(1) provides an organizational chart within the Explosive Sciences Branch.

1. Explosive Sciences Branch Manager

The Explosives Sciences Branch Manager is primarily responsible for ensuring the QA/QC program within the laboratory is in compliance and data quality adheres to this compliance. In delegating QA responsibilities/authorities, the ESB Manager depends on the Quality Assurance Officer to coordinate all necessary QA requirements. The ESB Manager is responsible for assuring that quality planning is developed, implemented, monitored and updated. The ESB Manager maintains training records and documents for each analyst in all methods in which the analyst is proficient and capable of performing.

2. Quality Assurance Officer

The Quality Assurance Officer is responsible for the performance of the ESB Quality Control program and for taking or recommending measures to ensure the fulfillment of the quality objectives of management while ensuring continued accuracy and precision of the data produced. Duties include but are not limited to the following:

a. Monitors quality control programs, including statistical procedures and techniques, which will enable the laboratory to meet desired quality standards; and advises and assists management in the installation, staffing, and supervision of such programs.

b. Monitors quality control activities of the laboratory to determine conformance with authorized policies and procedures and with sound practice; and makes appropriate recommendations for correction and improvement as may be necessary.

c. The QAO should prepare an annual written Quality Assurance Summary Report.

d. Seeks out and evaluates new technology, methods, and equipment in the field of quality control and recommends means for their application wherever advisable.

e. Prepares for internal and external audits.

f. Advises the purchasing agents with regard to the quality of purchased equipment, materials, reagents, and chemicals.

g. Provides information to the ESB Manager for Management Reviews.

h. Initiates an in-house proficiency evaluation program involving blind samples as required.

i. Maintains appropriate paper copies of procedures and attachments.

2. ESP Laboratory Manager

Duties of the Laboratory Manager include but are not limited to the following:

a. Direct and oversees all laboratory personnel in the enactment of the required analytical procedures and necessary quality control activities.

b. Assists the Quality Assurance Officer in fulfilling the objectives of the Quality Assurance Plan.

c. Reviews the Annual Quality Assurance Summary Report and addresses any outstanding deficiencies.

d. Assures that a complete set of controlled procedures is maintained for all test procedures used by the ESB laboratory.

e. Ensures that only analysts who have completed training conduct analytical methods independently. An analyst in training is directly supervised by an analyst who has completed training.

4. Chemist/Laboratory Analyst

Duties of the Chemist/Laboratory Analyst include but are not limited to the following:

a. Maintains proper log-in and sample tracking documents and active chain-of-custody files.

b. Provides for appropriate disposal of all samples after completion of the analysis.

c. Performs quality control on all samples analyzed utilizing appropriate procedures and providing the necessary documentation as required by the department procedures.

d. Carries out quality control programs, including statistical procedures and techniques, which will enable the laboratory to meet desired quality standards and advise and assist management in the installation, staffing, and supervision of such programs.

e. Monitor quality control activities of the laboratory to determine conformance with authorized policies and procedures and with sound practice; and make appropriate recommendations for correction and improvement as may be necessary.

5. Document Control Coordinator

Duties of the Document Control Coordinator include but are not limited to the following:

a. Maintains controlled electronic procedure copies.

b. Alerts Quality Assurance Officer of required procedure reviews.

III. QUALITY ASSURANCE

The ESB is committed to continuous quality improvement through identifying and managing variation within each analytical process. The policy of the ESB laboratory is to apply the quality system requirements to all testing and analytical activities and includes the following:

A. Quality activities shall emphasize the prevention of quality problems rather than detection and correction of problems after they occur. Periodic internal audits will be conducted and control charts maintained. The laboratory shall proactively identify methods or technology to improve the quality of services provided.

B. All employees engaged in making decisions affecting the quality of laboratory output shall undergo training programs designed to be commensurate with their positions, duties, and responsibilities.

C. The laboratory shall use a single approved analytical test method for each parameter tested, consistent with customer needs for precision, accuracy, and sensitivity, in compliance with State and Federal regulatory programs.

D. The laboratory shall retain copies of all tracking, test and analytical reports in a manner and for a period specified by regulatory or accrediting bodies.

E. Each analyte and associated analytical method requested for certification/accreditation will have an initial demonstration of capability (IDC) performed before any actual sample analysis takes place.

F. The laboratory shall have a comprehensive calibration program involving all instrumentation used for making determinations, the results of which are reported.

G. The laboratory shall practice a supply management program to ensure sufficient supply availability and quality.

H. The laboratory shall participate in an inter laboratory testing program as prescribed by the cognizant certification authority, accrediting organization, or upon customer request.

I. The laboratory shall practice a preventative maintenance program to ensure maximum equipment operating efficiency.

J. The laboratory shall report results in a format and timeframe consistent with consumer requirements.

IV. APPARATUS

Not applicable.

V. SAMPLE HANDLING AND PRESERVATION

Not applicable.

VI. REAGENTS

Not applicable.

VII. PROCEDURE

A. Quality Assurance Summary Report

On an annual basis, the Quality Assurance Officer will prepare a Quality Assurance Summary Report for review by the ESB Manager. The ESB will use this information to establish priorities and modify this procedure, as required. The report will include the following information:

1. Date of last review of this Quality Assurance Summary Report.

2. A statistical summary of any certification testing including a comparison of blanked or spiked samples.

3. A list of qualified laboratory personnel and the test methods each is certified to perform, including date of most recent certification (see training procedures).

4. Status of annual quality training.

5. Preventative maintenance status.

6. Continuous improvement plan status.

7. A summary of the resolution of any and all corrective actions, preventative actions, audits, and SOP reviews for the previous year.

B. Control Plan

The Code 4052 Control Plans are attached. Separate control plans are included for the different types of analysis performed by the ESB.

C. Quarterly Branch Reviews

The Code 4052 Branch will review quality issues on a quarterly basis. Content of the review will be similar to that of the annual Quality Assurance Summary Report. Notes from these reviews will be taken and maintained per Record Retention, CR4052-PD-0150(1).

VIII. DATA ANALYSIS AND REPORTING

None.

IX. ATTACHMENTS

CR4052-PD-001(1) Code 4052 Organizational Chart, 11/1/00

CR4052-PD-0001(2) Code 4052 Control Plan: NPDES Water, 3/28/01

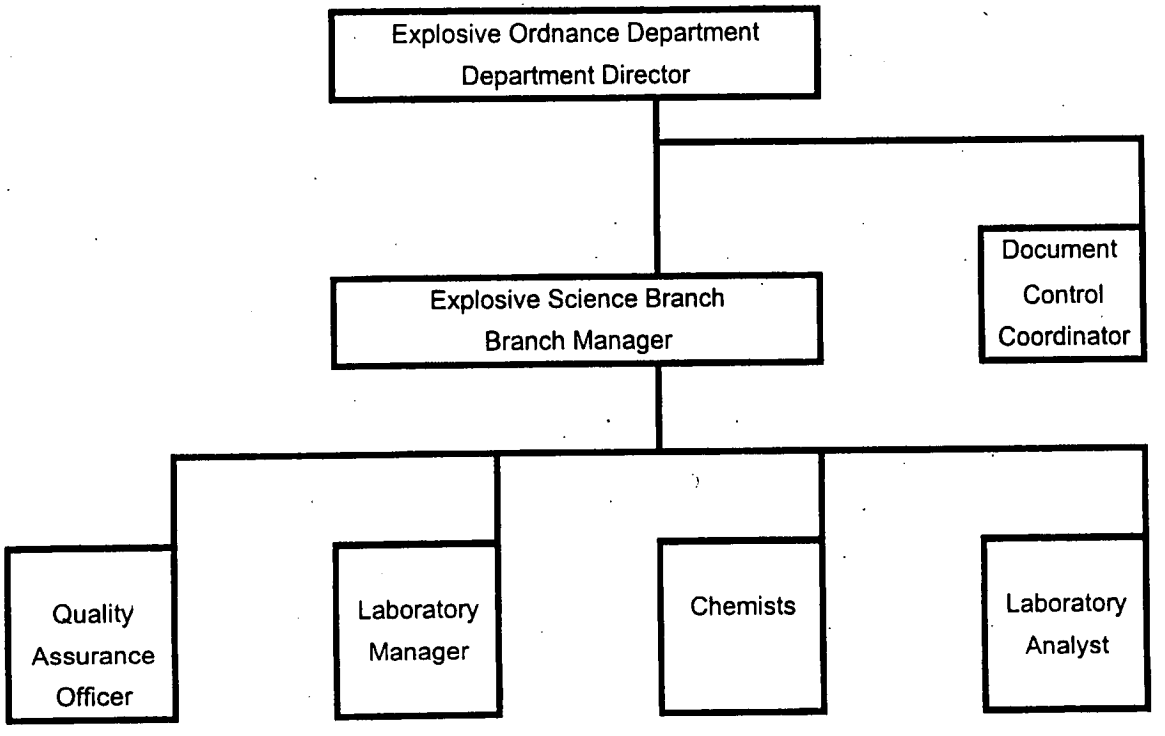
X. REFERENCES

None.

XI. REVISION BLOCK

REV	DATE	REVISION	AUTHOR
0	11/1/00	Original issue.	MLS
1	3/28/01	Added Table 1. Updated attachment (2). Added Branch Quarterly Review process.	MLS

Code 4052 Organizational Chart



Process Step	Operation Description		Characteristic: Sample	Characteristic: Test	Tolerance	Measure	Reaction Plan
1. Prepare Laboratory	1.1	Ensure sufficient supply stock to perform routine testing.	Raw materials known quality.	None.	Chemical Supply Management, CR4052-PD-0220	N/A	Refer to Chemical Supply Management CR4 PD-0220 if material is accepted on an "excep basis.
	1.2	Ensure equipment calibrated.	None.	Results suspect.	Calibration, CR4052-PD-0250	Calibrate equipment prior to each test according to test procedure.	Refer to Calibration CR4052-PD-0250 an Preventative Maintenance CR4052-PD-02
	1.3	Ensure analyst properly trained.	Sample preparation compromised.	Test run improperly.	Training, CR4052-PD-0300; Training: Water, CR4052-PD-0310	Performance evaluations.	Refer to Performance Evaluations, CR4052-PD-0450
2. Receive Sample	2.1	Document and Classify Customer Name, Tests Required, Sample Type	Sample mis-labeled.	Improper test run.	Chain of Custody, CR4052-PD-0500	N/A	Improper test, repeat test procedure.
3. Prepare Sample	3.1	Cadmium, Copper, Lead, Silver, Chromium, Nickel, Zinc, Molybdenum, Potassium	Improper preparation.	N/A	Sample Preparation, CR4052-PD-1000	N/A	If improper standard prepared, repeat preparation procedure.
	3.1	TKN	Improper preparation.	N/A	TKN, CR4502-PD-1210	N/A	If improper standard prepared, repeat preparation procedure.
	3.1	T-Phosphorous	Improper preparation.	N/A	Total Phosphorous, CR4052-PD-1220	N/A	If improper standard prepared, repeat preparation procedure.
Select appropriate test:	3.1	Ammonia-N	Improper preparation.	N/A	Ammonia-N, CR4052-PD-1230	N/A	If improper standard prepared, repeat preparation procedure.
	3.1	Total Solids	Improper preparation.	N/A	Total Solids, CR4052-PD-1240	N/A	If improper standard prepared, repeat preparation procedure.
	3.1	Arsenic, Selenium	Improper preparation.	N/A	Arsenic/Selenium, CR4052-PD-1200	N/A	If improper standard prepared, repeat preparation procedure.
	3.1	Mercury	Improper preparation.	N/A	Mercury, CR4052-PD-1300	N/A	If improper standard prepared, repeat preparation procedure.
	3.1	Hexavalent Chromium	Improper preparation.	N/A	Hexavalent Chromium, CR4052-PD-1400	N/A	If improper standard prepared, repeat preparation procedure.
	3.1	E-Coli - Wastewater	Improper preparation.	N/A	E-coli in Wastewater, CR4052-PD-1500 Sterilization Procedure, CR4052-PD-0710	N/A	If improper standard prepared, repeat preparation procedure.
	3.1	HMX, RDX, TNT	Improper preparation.	N/A	HMX, RDX, TNT, CR4052-PD-1600	N/A	If improper standard prepared, repeat preparation procedure.
	3.1	Nitrate-N	Improper preparation.	N/A	Nitrate - N, CR4052-PD-1700	N/A	If improper standard prepared, repeat preparation procedure.
	3.1	Oil & Grease	Improper preparation.	N/A	Oil and Grease, CR4052-PD-1800	N/A	If improper standard prepared, repeat preparation procedure.
	3.1	T. Cyanide	Improper preparation.	N/A	Total Cyanide, CR4052-PD-1900	N/A	If improper standard prepared, repeat preparation procedure.
4. Test Sample	4.1	Cadmium, Copper, Lead, Silver, Molybdenum	Damaged sample.	Invalid test.	Graphite Furnace, CR4052-PD-1100 Flame AA, CR4052-PD-1150	Performance Evaluations, CR4052-PD-0450 Data Validation, CR4052-PD-0230	If data unacceptable, re-run test.
	4.1	Chromium, Nickel, Zinc, Potassium	Damaged sample.	Invalid test.	Flame AA, CR4052-PD-1150	Performance Evaluations, CR4052-PD-0450 Data Validation, CR4052-PD-0230	If data unacceptable, re-run test. Refer to Performance Evaluation, CR4052-PD-0450
	4.1	Arsenic, Selenium	Damaged sample.	Invalid test.	Arsenic/Selenium, CR4052-PD-1200	Data Validation, CR4052-PD-0230	If data unacceptable, re-run test.
Select appropriate test:	4.1	TKN	Damaged sample.	Invalid test.	TKN, CR4502-PD-1210	Data Validation, CR4052-PD-0230	If data unacceptable, re-run test.
	4.1	T-Phosphorous	Damaged sample.	Invalid test.	Total Phosphorous, CR4052-PD-1220	Data Validation, CR4052-PD-0230	If data unacceptable, re-run test.
	4.1	Ammonia-N	Damaged sample.	Invalid test.	Ammonia-N, CR4052-PD-1230	Performance Evaluations, CR4052-PD-0450 Data Validation, CR4052-PD-0230	If data unacceptable, re-run test. Refer to Performance Evaluation CR4052-PD-0450
	4.1	Total Solids	Damaged sample.	Invalid test.	Total Solids, CR4052-PD-1240	Data Validation, CR4052-PD-0230	If data unacceptable, re-run test
	4.1	Mercury	Damaged sample.	Invalid test.	Mercury, CR4052-PD-1300	Performance Evaluations, CR4052-PD-0450 Data Validation, CR4052-PD-0230	If data unacceptable, re-run test Refer to Performance Evaluation CR4052-PD-0450
	4.1	Hexavalent Chromium	Damaged sample.	Invalid test.	Flame AA, CR4052-PD-1400	Data Validation, CR4052-PD-0230	If data unacceptable, re-run test
	4.1	E-Coli - Wastewater	Damaged sample.	Invalid test.	E-coli in Wastewater, CR4052-PD-1500	Data Validation, CR4052-PD-0230	If data unacceptable, re-run tes
	4.1	HMX, RDX, TNT	Damaged sample.	Invalid test.	HMX, RDX, TNT, CR4052-PD-1600	Data Validation, CR4052-PD-0230	If data unacceptable, re-run tes
	4.1	Nitrate-N	Damaged sample.	Invalid test.	Nitrate - N, CR4052-PD-1700	Performance Evaluations, CR4052-PD-0450 Data Validation, CR4052-PD-0230	If data unacceptable, re-run tes Refer to Performance Evaluatio CR4052-PD-0450
	4.1	Oil & Grease	Damaged sample.	Invalid test.	Oil and Grease, CR4052-PD-1800	Performance Evaluations, CR4052-PD-0450 Data Validation, CR4052-PD-0230	If data unacceptable, re-run te Refer to Performance Evaluati CR4052-PD-0450
	4.1	T. Cyanide	Damaged sample.	Invalid test.	Total Cyanide, CR4052-PD-1900	Performance Evaluations, CR4052-PD-0450 Data Validation, CR4052-PD-0230	If data unacceptable, re-run te Refer to Performance Evaluati CR4052-PD-0450
5. Report Data	5.1	Write report	N/A	Inaccurate report	Customer Reports, CR4052-PD-0600	N/A	Revise/reissue report.
6. File Data	6.1	Distribute data to appropriate personnel and maintain copies as required.	N/A	N/A	Record Retention, CR4052-PD-0150	N/A	N/A

Note 1: All tests are consistent with EPA Methods as noted in the PD.

Document Control

Explosive Sciences Branch
Naval Surface Warfare Center Crane
300 Highway 361
Crane, IN 47522

March 28, 2002

Approvals:

Name	Nancey J. Maegerlein
Title	Branch Manager
Signature	Nancey J. Maegerlein
Name	Jacquelyn J. Karty
Title	Quality Assurance Officer
Signature	Jacquelyn J. Karty

MASTER

CONTROLLED COPY
NSWC REPOSITORY 08
CODE 405
COPY NO. 3

I. SCOPE AND APPLICATION

This procedure describes the control of documents in Code 4052, including origination, review and revision, approval, use and control.

Documents utilized in Code 4052 will be maintained with current information and will be easily accessible.

II. SUMMARY OF METHOD

This method is consistent with ISO 9000 standard requirements.

III. QUALITY ASSURANCE

Quality is assured by distributing the responsibility for document control as follows:

Position	Responsibility
Branch Manager	Reviews and approve all changes in documents.
	Insures that all procedures are being followed.
Document Control Coordinator (DCC)	Maintains controlled electronic copies of all documents. Generates Master Document List upon request.
	Monitors document status to determine when review is required.
	Issues new controlled paper copies of procedures and attachments. Destroys old copies as appropriate.
Quality Assurance Officer (QAO)	Routes documents review and approval to the appropriate individuals.
	Provides periodic reports of document review status to Branch Manager.
	Issues procedure numbers for new documents.
	Assists others in the preparation of new procedures or modification of old procedures to ensure compliance with the Document Control Procedure and ISO Standards.
Laboratory Managers and Analysts	Reviews and creates documents as appropriate.
	Performs analysis and documentation according to documented procedures.
	Initiates document review as the procedures are modified.

IV. APPARATUS

Not applicable.

V. SAMPLE HANDLING AND PRESERVATION

Not applicable.

VI. REAGENTS

Not applicable.

VII. PROCEDURE

A. Master Document List

The Master Document List is maintained as part of the electronic document repository system through Code 405. A current Master Document List can be generated by the DCC upon request.

Included in this procedure is a list of the location of controlled procedure copies, CR4052-PD-0100(1). For location of additional attachments, refer to CR4052-PD-0100(2). When a procedure is updated, the QAO provides a list to the DCC of appropriate places to send controlled copies.

B. Types of Procedures

Code 4052 operates using two types of procedures: Equipment Operating Procedures and Method Procedures.

1. Equipment Operating Procedures (EOP)
   The EOP is specific to a piece or system of equipment. The intent of the procedure is to describe in general terms the theory and proper operation/maintenance of the particular piece of equipment. The EOP includes further reference to the appropriate Operation Manual provided by the manufacturer.

2. Method Procedures (PD)
   The Method Procedure details the step-by-step application of the equipment and reagents in order to analyze a sample in a particular way. These procedures include sample preparation techniques, detailed equipment settings, and data analysis approaches for the methods routinely applied in the Code 4052 laboratory.

C. Common Formatting and Content

All EOP's and PD's are to have the following characteristics:

1. Cover Page
   Each procedure includes a cover page to provide the title and approval information for the procedure. Refer to the cover page in this procedure for the proper format.

2. General Formatting
   a. Procedures are created using MS Word.
   b. Font: Ariel, 12pt.
   c. All margins: 1".
   d. Header ½" from the top.

e. Left justified.

D. Equipment Operating Procedure (EOP) Formatting and Content

1. EOP Body
EOP's include the following sections. If a section doesn't apply to the particular process, indicate "Not applicable" or "None", rather than omitting the section. Each section describes the type of information which may be appropriate to include, but does not limit the content of that section (note the capital letters in the section headers).

a. SCOPE AND APPLICATION: Identify the equipment to which the EOP is applicable. Include model numbers when available.

b. THEORY OF OPERATION: General description of the theory by which the equipment operates. This section includes basic principles and assessment of the equipment capability (describe the type of data the equipment generates).

c. FUNDAMENTAL OPERATION: Describe the general ways in which the equipment can be operated. Relate the equipment settings to the Theory of Operation.

d. PREVENTATIVE MAINTENANCE: Describe the required preventative maintenance recommended by the manufacturer or defined by operational experience. Define frequencies and material requirements of the maintenance. Refer to CR4052-PD-0200 as required.

e. CALIBRATION: Describe the required calibration recommended by the manufacturer or defined by operational experience. Define frequencies and material requirements of the calibration. Refer to CR4052-PD-0250 as required.

f. ATTACHMENTS: List all forms and attachments to the procedure. Each attachment is marked with procedure and attachment number, the revision number, and date (mm/dd/yy). Note the method in which the attachment is listed in this procedure.

Attaching uncontrolled reference documents is avoided. However, if necessary, these references can be attached if stamped "For Reference Only".

g. REFERENCES: List references that are not attached, but could be useful. Refer to the manufacturer's Operational Manual if available.

h. REVISION BLOCK: The revision table box includes revision number, date, description of the revision, and initials of the author of the revision. Refer to the revision block in this procedure for the appropriate format.

2. EOP Procedure Designation
Each procedure includes a header to list the procedure number, revision number, revision date, and page number of total pages excluding attachments. Refer to the header in this procedure for proper format (note 8pt Ariel font).

All Code 4052 methodology procedures are formatted as "CR4052-EOP-####".

E. Method Procedure (PD) Formatting and Content

1. PD Procedure Body
As in this procedure, documents include the following sections. If a section doesn't apply to the particular process, indicate "Not applicable" or "None", rather than omitting the section. Each section describes the type of information which may be appropriate to include, but does not limit the content of that section (note the capital letters in the section headers).

a. SCOPE AND APPLICATION: Describes the depth of the procedure, background discussion, and to whom the procedure applies.

b. SUMMARY OF METHOD: General description of the method and basis for the method, if applicable (such as EPA, Standard Methods, ISO Requirement).

c. QUALITY ASSURANCE: Describe any interferences that might be encountered in this method. Also highlight what steps this method incorporates for assuring quality. Examples may include the use of blanks, spikes, and raw samples. If this test is included in the performance evaluation process, refer to that procedure here.

d. APPARATUS: List of materials or equipment that may need to be gathered prior to beginning the procedure. Include any comments on special cleaning requirements (sterilization, for example).

e. SAMPLE HANDLING AND PRESERVATION: Includes containers, temperature, time, and preservation information for samples.

f. REAGENTS: List reagents required, preparation techniques, shelf life, etc.

g. PROCEDURE: Provide step-wise instructions designed for someone who is familiar with general laboratory work. Also include special clean-up requirements.

h. DATA ANALYSIS AND REPORTING: Describe the proper methods to handle data and refer to reporting requirements described in the reporting procedure.

i. ATTACHMENTS: List all forms and attachments to the procedure. Each attachment is marked with procedure and attachment number, the revision number, and date (mm/dd/yy). Note the method in which the attachment is listed in this procedure.

Attaching uncontrolled reference documents is avoided. However, if necessary, these references can be attached if stamped "For Reference Only".

j. REFERENCES: List references that are not attached, but could be useful.

l. REVISION BLOCK: The revision table box includes revision number, date, description of the revision, and initials of the author of the revision. Refer to the revision block in this procedure for the appropriate format.

2. PD Procedure Designation
Each procedure includes a header to list the procedure number, revision number, date, and page number of total pages excluding attachments. Refer to the header in this procedure for proper format (note 8pt Ariel font).

The number scheme is as follows:

a. All Code 4052 methodology procedures are formatted as "CR4052-PD-####".
b. A 4-digit number is selected to group the procedure by the type of application:
   1) 0000 – 0699: Code 4052 Overall ISO System PD's
   2) 0700 – 0999: Code 4052 Overall Process PD's
   3) 1000 – 1999: NPDES Water Testing PD's
   4) 2000 – 2499: Drinking Water Testing PD's
   5) 2500 – 2999: Dye Project PD's
   6) 3000 – 3999: Sensitivity Testing PD's
   7) 4000 – 4999: Liquid Chromatography PD's
   8) 5000 – 5999: FBM Process PD's
   9) 6000 – 6999: Thermal Analysis Process PD's

C. Procedure Review Process

1. Frequency

All procedures will be reviewed as often as necessary to assure that they reflect current operating practices, including changes that result from changes in the method, technology, equipment, etc.

In addition, revisions may be initiated or suggested by any department personnel to improve instructions, correct mistakes, or modify operation requirements.

At minimum, each procedure will be reviewed every 4 years.

2. Process
   a. When a review is required, the QAO will make sure an appropriate person is reviewing the procedure, providing assistance as required.
   b. An uncontrolled, paper copy or electronic copy of the procedure can be requested from the DCC.

c. The marked-up copy or a corrected electronic copy will be given to the DCC to edit the controlled electronic file, issue new copies stamped "Controlled Copy" to the appropriate person as designated in CR4052-PD-0100(1,2). Controlled copies will be tracked using the receipts described in CR-405-3001.

d. Obsolete controlled documents will be returned to the DCC and retained according to procedure CR-405-3001.

3. Documenting Revision Content
Notes will be made in the revision block describing the nature of the revisions.

4. Approvals
Two approvals are required for each procedure. One approver must be the Branch Manager. The other approver must be a person who is familiar with the operation described in the procedure.

5. Training
Those reviewing the document will decide whether changes made were significant enough to warrant immediate training. Should training be warranted, the Branch Manager will be notified. Training will proceed as described in CR4052-PD-0300, Training.

D. Using the Procedures

1. Location of Controlled copies
Controlled paper copies will be distributed as described in CR4052-PD-0100(1). When possible, a copy will be located in the vicinity of the applicable process.

Controlled electronic copies will be maintained by the DCC in the document repository.

a. Document Receipt Log
Document Receipts (9ND-NWSCC 4430/10) will be controlled by the QAO and will be recorded on CR4052-PD-0100(3) Code 4052 Document Receipt Log.

It is the responsibility of the Receiving Person to ensure that the QAO is provided the receipt and to notify the QAO when the document is returned.

2. Making Copies

Copies of procedures cannot be made except by the DCC. These copies will be marked "Uncontrolled" and are not to be used for operation.

3. Marking-up Controlled Copies
The Quality Assurance Officer may make minor, temporary changes to a controlled copy of a procedure to ensure proper performance until the procedure can be revised. Any changes should be dated and initialed. Revisions should be complete within 3 months. It is not permissible for any other individuals to mark-up controlled copies.

E. Deleting a Procedure
Deleting a procedure will require the same level of approval as did the review or creation of a procedure. Simply mark "Deleted" in the revision block and handle as other revisions are handled. The document will be removed from the Master Document List.

VIII. DATA ANALYSIS AND REPORTING

A. Purpose

Test data is reported according to the operating procedure for the particular test. When appropriate, test logbooks (a logbook specific to a particular type of test) or instrument logbooks (a logbook for a particular instrument) are utilized to document activity.

B. Responsibility

It is the responsibility of the analyst to complete the appropriate information in the logbook. Notebooks should be maintained in a neat, orderly, and technically understandable manner. Ink should be used. Any errors made while entering data into the laboratory notebook will be crossed out with a single line, dated, and initialed.

C. Record Retention

Logbooks will be retained and located according to attachment CR4052-PD-0150(1). Removal of pages should be minimized; if it is necessary to remove a page(s), it should be noted in the logbook.

IX. ATTACHMENTS

CR4052-PD-0100(1) Code 4052 Master Document List, 10/01/2001

CR4052-PD-0100(2) Code 4052 Controlled Attachment Copy Inventory, 10/01/2001

CR4052-PD-0100(3) Code 4052 Document Receipt Log, 10/01/2001

X. REFERENCES

None.

XI. REVISION BLOCK

REV	DATE	REVISION	AUTHOR
0	11/1/00	Original issue.	MLS
1	3/28/01	Updated attachments.	MLS
2	10/01/2001	Added Document Receipt Log Requirements and Attachment and Changed header requirements and updated attachments.	CAW
3	3/28/2002	Updated Attachment CR4052-PD-0100(1)	CAW

Code 4052 Master Document List

PD Number	PD Title	Copy Locations (Note 1)
	4052 Overall Quality System PD's	
CR4052-PD-0001	Quality Assurance and Control Plan	C = Code 4052 QAO, Hunsicker
CR4052-PD-0100	Document Control	C = Code 4052 QAO, Hunsicker
CR4052-PD-0150	Record Retention	C = Code 4052 QAO, Hunsicker
CR4052-PD-0200	Preventative Maintenance	C = Code 4052 QAO, Hunsicker
CR4052-PD-0220	Chemical/Supply Management	C = Code 4052 QAO, Hunsicker
CR4052-PD-0230	Data Validation	C = Code 4052 QAO, Hunsicker
CR4052-PD-0250	Calibration	C = Code 4052 QAO, Hunsicker
CR4052-PD-0300	Training Overview	C = Code 4052 QAO, Hunsicker
CR4052-PD-0310	Training: Water Testing	C = Code 4052 QAO, Hunsicker
CR4052-PD-0450	Performance Evaluations	C = Code 4052 QAO, Hunsicker
CR4052-PD-0500	Chain of Custody: Soil and Water Samples	C = Code 4052 QAO, Hunsicker
CR4052-PD-0600	Customer Reports	C = Code 4052 QAO, Hunsicker
	4052 Overall Process PD's	
CR4052-PD-0700	Glassware Cleaning Procedure	C = Code 4052 QAO, Hunsicker
CR4052-PD-0710	Sterilization Procedure	C = Code 4052 QAO, Hunsicker
	NPDES Water Testing PD's	
CR4052-PD-1000	Metal Analysis Sample Preparation	C = Code 4052 QAO, Hunsicker
CR4052-PD-1100	Graphite Furnace	C = Code 4052 QAO, Hunsicker
CR4052-PD-1150	Flame AA Method	C = Code 4052 QAO, Hunsicker
CR4052-PD-1200	Arsenic/Selenium Sample Preparation & Analysis	C = Code 4052 QAO, Hunsicker
CR4052-PD-1210	TKN	C = Code 4052 QAO, Hunsicker
CR4052-PD-1220	Total Phosphorous	C = Code 4052 QAO, Hunsicker
CR4052-PD-1230	Ammonia-Nitrogen	C = Code 4052 QAO, Hunsicker
CR4052-PD-1240	Total Solids Determination	C = Code 4052 QAO, Hunsicker
CR4052-PD-1300	Mercury Sample Preparation & Analysis	C = Code 4052 QAO, Hunsicker
CR4052-PD-1400	Hexavalent Chromium Sample Preparation & Analysis	C = Code 4052 QAO, Hunsicker
CR4052-PD-1500	Escherichia Coli (E-Coli) in Wastewater	C = Code 4052 QAO, Hunsicker
CR4052-PD-1600	Pink Water Analysis	C = Code 4052 QAO, Hunsicker
CR4052-PD-1700	Nitrate - Nitrogen	C = Code 4052 QAO, Hunsicker
CR4052-PD-1800	Oil and Grease Sample Preparation & Analysis	C = Code 4052 QAO, Hunsicker
CR4052-PD-1900	Total Cyanide Preparation and Analysis	C = Code 4052 QAO, Hunsicker
CR4052-PD-2000	Total Coliforms and Eschericha Coli Analysis in Drinking Water	C = Code 4052 QAO, Hunsicker
	4052 FBM Process PD's	
CR4052-PD-5100	Cold Potting of Metallographic Test Specimens Using Epoxy Resins Araldite and Epoxicure	C = Code 4052 QAO
CR4052-PD-5200	Sample Order Maintenance in Lot Acceptance Testing of 95 and 150 grains per foot Flexible Linear Shape Charges (95 and 150 gr/ft FLSC)	C = Code 4052 QAO
CR4052-PD-5300	Sample Order Maintenance in Lot Acceptance Testing of 14.25 grains per foot Separation Linear Shape Charges (14.25 gr/ft SLSC)	C = Code 4052 QAO
	4052 Thermal Analysis Process PD's	
CR4052-PD-6000	Thermal Analysis Process Applications	C = Code 4052 QAO

Note 1: C=Controlled Copy, U=Uncontrolled Copy

Code 4052 Controlled Attachment Copy Inventory

Procedure Reference	Attachment Name	Location
Paper Copies		
CR4052-PD-0100(1)	Code 4052 Master Document List	QAO Office
CR4052-PD-0100(2)	Controlled Attachment Copy Inventory	QAO Office
CR4052-PD-0150(1)	Code 4052 Record Retention Detail	QAO Office
CR4052-PD-0200(2)	Water Systems Maintenance Log	B2707 Main Office Forms Drawer
CR4052-PD-0200(3)	Refrigerator/Freezer Temperature Log	B2707 Main Office Forms Drawer
CR4052-PD-0200(4)	Flame AA Maintenance Log	B2707 Main Office Forms Drawer
CR4052-PD-0200(5)	Code 4052 Maintenance Log	B2707 Main Office Forms Drawer
CR4052-PD-0220(1)	General Laboratory Supplies Inventory	B2707 Main Office Forms Drawer
CR4052-PD-0220(2)	NPDES Water Testing Supplies Inventory	B2707 Main Office Forms Drawer
CR4052-PD-0250(2)	Monthly Balance Verification	B2707 Main Office Forms Drawer
CR4052-PD-0300(1)	Code 4052 New Employee Orientation Training	B2707 Main Office Forms Drawer
CR4052-PD-0300(2)	Chemical Hygiene Plan Annual Review	B2707 Main Office Forms Drawer
CR4052-PD-0300(3)	Code 4052 Additional Training Form	B2707 Main Office Forms Drawer
CR4052-PD-0500(1)	Chain of Custody, NPDES Waste Water Samples	B2707 Main Office Forms Drawer
CR4052-PD-0500(2)	Chain of Custody, Sludge and Soil Samples	B2707 Main Office Forms Drawer
CR4052-PD-0500(3)	Code 4052 Internal Chain of Custody Form	B2707 Main Office Forms Drawer
CR4052-PD-0710(1)	Autoclave Use Report	B2707 Main Office Forms Drawer
CR4052-PD-1100(1)	Graphite Furnace Burn Log	B2707 Main Office Forms Drawer
CR4052-PD-1230(1)	Ammonia-Nitrogen Data	B2707 Main Office Forms Drawer
CR4052-PD-1400(1)	Hexavalent Chromium Data Analysis	B2707 Main Office Forms Drawer
CR4052-PD-1500(1)	E-Coli Analysis	B2707 Main Office Forms Drawer
CR4052-PD-1500(2)	Daily Temperature Record of Coliform Incubator	B2707 Main Office Forms Drawer
CR4052-PD-1700(1)	Nitrate-Nitrogen Analysis	B2707 Main Office Forms Drawer
CR4052-PD-1800(1)	Oil and Grease Analysis	B2707 Main Office Forms Drawer
CR4052-PD-1900(1)	Cyanide Data Sheet	B2707 Main Office Forms Drawer
Electronic Copies		
CR4052-PD-0600(1)	Sludge Testing Report	f:\Code4076\ISOForms
CR4052-PD-0600(2)	Water Testing Report	f:\Code4076\ISOForms
CR4052-PD-0600(3)	NPDES Report Cover Sheet	f:\Code4076\ISOForms
CR4052-PD-1150(1)	Water Analysis Metal Results Sheet	f:\Code4076\ISOForms
CR4052-PD-1150(2)	Sludge Analysis Metal Results Sheet	f:\Code4076\ISOForms
CR4052-PD-1200(1)	Arsenic in Sludge Analysis	f:\Code4076\ISOForms
CR4052-PD-1200(2)	Selenium in Sludge Analysis	f:\Code4076\ISOForms
CR4052-PD-1200(3)	Arsenic in Drinking Water Analysis	f:\Code4076\ISOForms
CR4052-PD-1200(4)	Selenium in Drinking Water Analysis	f:\Code4076\ISOForms
CR4052-PD-1210(1)	TKN Analysis	f:\Code4076\ISOForms
CR4052-PD-1220(1)	Total Phosphorous Analysis	f:\Code4076\ISOForms
CR4052-PD-1230(2)	Ammonia-Nitrogen Analysis	f:\Code4076\ISOForms
CR4052-PD-1300(1)	Mercury Data Analysis in Wastewater	f:\Code4076\ISOForms
CR4052-PD-1300(2)	Mercury Data Analysis in Sludge	f:\Code4076\ISOForms
CR4052-PD-1400(2)	Hexavalent Chromium Data Analysis	f:\Code4076\ISOForms
CR4052-PD-1900(2)	Total Cyanide Data Analysis	f:\Code4076\ISOForms

Code 4052 Document Receipt Log

Serial Number	Document Title or No.	Revision & Copy No.	Issuing Code	Date Received	Person Received	Date Returned

Record Retention

Explosive Sciences Branch
Naval Surface Warfare Center Crane
300 Highway 361
Crane, IN 47522

March 28, 2002

Approvals:

Name	Nancey J. Maegerlein
Title	Branch Manager
Signature	Nancey J. Maegerlein
Name	Jacquelyn J. Karty
Title	Quality Assurance Officer
Signature	Jacquelyn J. Karty

MASTER

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CODE 409
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I. SCOPE AND APPLICATION

This procedure describes the retention of quality records created and/or filed in Code 4052. This includes but is not limited to test records, instrument records, instrument logbooks, and laboratory notebooks.

II. SUMMARY OF METHOD

This method is consistent with ISO standard requirements.

III. QUALITY ASSURANCE

All Code 4052 personnel are responsible for understanding and complying with the Code 4052 Record Retention procedure. The following personnel have specific responsibilities:

Position	Responsibility
Quality Assurance Officer (QAO)	Maintains controlled copies in forms drawer.
	Audit retention of documents and initiate proper disposal.
Laboratory Managers and Analysts	Copies blank forms from Forms Drawer.
	Complete and file forms, notebooks, records according to procedure.

IV. APPARATUS

Not applicable.

V. SAMPLE HANDLING AND PRESERVATION

Not applicable.

VI. REAGENTS

Not applicable.

VII. PROCEDURE

A. Hard Copy Files

1. Hardcopy records may be filed in specified locations within Code 4052.
2. Record disposal will be via shredding when the retention time has been exceeded.
3. Records will be accessible to all individuals supporting the operation of the building.

B. Code 4052 Records, General

Quality Record	ISO 9000 Reference	Code 4052 Records	Record Retention Comments
Management Responsibility	4.1	Code 4052 Quality Assurance Summary Report	The Quality Assurance Summary Report is maintained by the Branch Manager. The current year plan and the previous year plan are retained at minimum.
Product ID and Traceability Inspection and Testing Control of Non-Conforming Product	4.8/4.10/ 4.13	Customer Reports (excluding NPDES)	Reports logged and retained per Naval Instructions.
Calibration	4.11	Internal Calibrations (Code 4052); External Calibrations (outside Code 4052)	Internal calibration records and environmental devices Calibration Reports will be retained per CR4052-PD-0150(1); External calibration records will be maintained by the calibrator.
Audit Results	4.17	External Audit Reports (outside 4052)	External Audit Reports are maintained by the Quality Assurance Officer for five years beyond the verification of all CARS.
Training Records	4.18	Training records for Code 4052 personnel	Records are retained per attachment CR4052-PD-0150(1); tests and additional training records are maintained by the Branch Manager for the period in which the employee is working in Code 4052.

C. Record Retention Detail

See attachment for detailed information concerning Code 4052 records not specifically described above.

D. Electronic Files

Document Control attachment CR4052-PD-0100(2) lists several documents maintained on the F:\ Code4076\ISOFORMS directory. The contents of this drive can be altered only by the Quality Assurance Officer. These documents are used to generate reports and analyze data. Results are printed and maintained per CR4052-PD-0150(1) and represent the official quality record. In addition, completed electronic forms are renamed and stored on the F:\Code4076\ISODATA subdirectory. Retention of these files allows for the efficient creation of corrected quality records if errors are discovered in the review process. THESE FILES DO NOT REPRESENT THE OFFICIAL QUALITY RECORDS. This directory will be maintained with no more than 5 years of data.

VIII. DATA ANALYSIS AND REPORTING

When contractually agreed upon, applicable test data is made available to the customer upon request.

IX. ATTACHMENTS

CR4052-PD-0150(1) Code 4052 Record Retention Detail, 3/28/01

X. REFERENCES

None.

XI. REVISION BLOCK

REV	DATE	REVISION	AUTHOR
0	11/1/00	Original issue.	MLS
1	2/8/01	Updated attachment 1. Added f:\code4076\ISODATA explanation.	MLS
2	6/06/01	Modified headers. Removed internal audit procedure reference	JJK
3	10/09/2001	Updated attachment 1. To include Certificates of Analysis in response to Audit Incident.	CAW
4	03/28/2002	Updated attachment 1. To include Calibration Reports for environmental devices.	CAW

Code 4052 Record F tion Detail

Area	Form or Record	Procedure Reference	Location of Form	Location of Record	Retention Time (Current Fiscal Year + ___)	Method of Indexing	Filing Responsibility
Overall System	Quarterly Quality Meeting Notes	CR4052-PD-0001	---	MA Office	3 years	Folder, Reverse-chronological	Management Assistant
	Monthly Routine Maintenance Log	CR4052-PD-0200(2)	B2707, Main Office	Water Lab	3 years	Folder, Reverse-chronological	Lab Analyst
	Weekly Controlled Temperature Log	CR4052-PD-0200(3)	B2707, Main Office	Water Lab	3 years	Binder; Folder, Reverse-chronological	Lab Analyst
	Flame AA Maintenance Log	CR4052-PD-0200(4)	B2707, Main Office	Water Lab	4 years	Folder, Reverse-chronological	Lab Analyst
	Semi-Annual Code 4052 Maintenance List	CR4052-PD-0200(5)	B2707, Main Office	Water Lab	5 years	Folder, Reverse-chronological	Lab Analyst
	Annual Code 4052 Maintenance List	CR4052-PD-0200(6)	B2707, Main Office	Water Lab	6 years	Folder, Reverse-chronological	Lab Analyst
	General Laboratory Supplies Inventory	CR4052-PD-0220(1)	B2707, Main Office	B2707, Main Office	1 year	Folder, Reverse-chronological	Lab Analyst
	NPDES Water Testing Supplies Inventory	CR4052-PD-0220(2)	B2707, Main Office	Water Lab	1 year	Folder, Reverse-chronological	Lab Analyst
	Data Validation Control Charts	CR4052-PD-0230	---	Water Lab	10 years	Binder, sorted by source	QAO
	Monthly Balance Verification	CR4052-PD-0250(2)	B2707, Main Office	Water Lab	3 years	Binder; Folder, Reverse-chronological	Lab Analyst
	Calibration Records	CR4052-PD-0250	---	Water Lab	5 years	Folder	Lab Analyst
	Chemical Hygiene Plan Annual Review	CR4052-PD-0300(2)	---	MA Office	3 years	Folder, Reverse-chronological	Management Assistant
	Code 4052 Additional Training Form	CR4052-PD-0300(3)	---	MA Office	3 years	Folder, Reverse-chronological	Management Assistant
	Code 4052 Job Traveler	CR4052-PD-0350(1)	B2707, Main Office	B2707, Main Office	3 years	Folder, Reverse-chronological	Program Manager
	Corrective Action Report Form	CR4052-PD-0400(1)	B2707, Main Office	B2707, Main Office	3 years	Active = Binder, Report number Complete=Folder, Report number	QAO
	Preventative Action Report Form	CR4052-PD-0400(2)	B2707, Main Office	B2707, Main Office	3 years	Complete=Folder, Report number	QAO
	Performance Evaluation Reports	CR4052-PD-0450	---	B2707, Main Office	5 years	Folder, Reverse-report number	QAO
	Chain of Custody: NPDES Water Samples	CR4052-PD-0500(1)	B2707, Main Office	Water Lab	5 years	Folder, Reverse-chronological	Lab Analyst
	Chain of Custody: Sludge and Soil Samples	CR4052-PD-0500(2)	B2707, Main Office	Water Lab	5 years	Folder, Reverse-chronological	Lab Analyst
	Code 4052 Internal Chain of Custody Form	CR4052-PD-0500(3)	B2707, Main Office	B2707, Main Office	5 years	Folder, Reverse-chronological	Lab Analyst
	Customer Reports (Data, Cover Sheet)	CR4052-PD-0600 (1-3)	F:\Drive	Water Lab	5 years	Binder, Reverse-chronological	Lab Manager
Overall Process	Autoclave Use Report	CR4052-PD-0710(1)	B2707, Main Office	Water Lab	2 years	Binder, Chronological	Lab Analyst
NPDES	Graphite Furnace Burn Log	CR4052-PD-1100(1)	B2707, Main Office	PW	3 years	Binder; Folder, Reverse-chronological	Lab Analyst
	GFAA Analysis Records	CR4052-PD-1100	---	Water Lab	3 years	Binder; Folder, Reverse-chronological	Lab Analyst
	Metal Analysis Log Book	CR4052-PD-1150	---	Water Lab	5 years	Cabinet	Lab Analyst
	Water Analysis Metal Results Sheet	CR4052-PD-1150(1)	F:\Drive	Water Lab	2 years	Folder, Reverse-chronological	Lab Analyst
	Sludge Analysis Metal Results Sheet	CR4052-PD-1150(2)	F:\Drive	Water Lab	2 years	Folder, Reverse-chronological	Lab Analyst
	Arsenic in Sludge Analysis	CR4052-PD-1200(1)	F:\Drive	Water Lab	2 years	Folder, Reverse-chronological	Lab Analyst
	Selenium in Sludge Analysis	CR4052-PD-1200(2)	F:\Drive	Water Lab	3 years	Folder, Reverse-chronological	Lab Analyst
	Arsenic in Drinking Water Analysis	CR4052-PD-1200(3)	F:\Drive	Water Lab	4 years	Folder, Reverse-chronological	Lab Analyst
	Selenium in Drinking Water Analysis	CR4052-PD-1200(4)	F:\Drive	Water Lab	5 years	Folder, Reverse-chronological	Lab Analyst
	TKN Analysis	CR4052-PD-1210(1)	F:\Drive	Water Lab	2 years	Folder, Reverse-chronological	Lab Analyst
	TKN Log Book	CR4052-PD-1210	---	Water Lab	5 years	Cabinet	Lab Analyst
	Total Phosphorous Analysis	CR4052-PD-1220(1)	F:\Drive	Water Lab	2 years	Folder, Reverse-chronological	Lab Analyst
	Total Phosphorous Log Book	CR4052-PD-1220(1)	---	Water Lab	5 years	Cabinet	Lab Analyst
	Ammonia-Nitrogen Data	CR4052-PD-1230(1)	B2707, Main Office	Water Lab	2 years	Spiral bound; chronological	Lab Analyst
	Ammonia-Nitrogen Analysis	CR4052-PD-1230(2)	F:\Drive	Water Lab	2 years	Binder, Reverse-chronological	Lab Analyst
	Sludge Log Book	CR4052-PD-1240	---	Water Lab	5 years	Cabinet	Lab Analyst
	Mercury Data Analysis in Wastewater	CR4052-PD-1300(1)	F:\Drive	Water Lab	2 years	Folder, Reverse-chronological	Lab Analyst
	Mercury Data Analysis in Sludge	CR4052-PD-1300(2)	F:\Drive	Water Lab	2 years	Folder, Reverse-chronological	Lab Analyst
	Hexavalent Chromium Analysis Data	CR4052-PD-1400(1)	B2707, Main Office	Water Lab	2 years	Spiral bound; chronological	Lab Analyst
	Hexavalent Chromium Data Analysis	CR4052-PD-1400(2)	F:\Drive	Water Lab	2 years	Binder, Reverse-chronological	Lab Analyst
	Media Log Book	CR4052-PD-1500	---	Water Lab	5 years	Cabinet	Lab Analyst
	E-Coli Analysis	CR4052-PD-1500 (1)	B2707, Main Office	Water Lab	2 years	Spiral bound; chronological	Lab Analyst
	Daily Temperature Record of Coliform Incubator	CR4052-PD-1500 (2)	B2707, Main Office	Water Lab	2 years	Binder; Chronological	Lab Analyst
	Explosive Water Log Book	CR4052-PD-1600	---	HPLC Lab	5 years	Cabinet	Lab Analyst
	Explosive Water HPLC Results	CR4052-PD-1600	---	Water Lab, HPLC Lab	2 years	Binder; Reverse-chronological	Lab Analyst
	Nitrate-Nitrogen Analysis	CR4052-PD-1700(1)	B2707, Main Office	Water Lab	2 years	Spiral bound; chronological	Lab Analyst
	Nitrate-Nitrogen LogBook	CR4052-PD-1700	---	HPLC Lab	5 years	Cabinet	Lab Analyst
	Nitrate-Nitrogen IC Results	CR4052-PD-1700	---	Water Lab	2 years	Binder; Reverse-chronological	Lab Analyst
	Oil and Grease Log Book	CR4052-PD-1800	---	Water Lab	5 years	Cabinet	Lab Analyst
	Oil and Grease Analysis	CR4052-PD-1800(1)	B2707, Main Office	Water Lab	2 years	Spiral bound; chronological	Lab Analyst
	Total Cyanide Logbook	CR4052-PD-1900	---	Water Lab	5 years	Cabinet	Lab Analyst
	Cyanide Data Sheet	CR4052-PD-1900(1)	B2707, Main Office	Water Lab	2 years	Spiral bound; chronological	Lab Analyst
	Total Cyanide Data Analysis	CR4052-PD-1900(2)	F:\Drive	Water Lab	2 years	Binder, Reverse-chronological	Lab Analyst
	Certificate of Analysis	---	B2707, Main Office	B2707, Main Office	Until use is completed	Cabinet	Lab Analyst
	C[illegible]ration Reports (environmental devices)	---	B2707, Main Office	B2707, Main Office	5 years	Cabinet	Lab Analyst

Preventative Maintenance

Explosive Sciences Branch
Naval Surface Warfare Center Crane
300 Highway 361
Crane, IN 47522

January 14, 2002

Approvals:

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Signature	Nancey J. Maegerlein
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Signature	Jacquelyn J. Karty

MASTER

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I. SCOPE AND APPLICATION

This procedure describes the Explosive Sciences Branch Preventative Maintenance program.

II. SUMMARY OF METHOD

This method is consistent with ISO 9001 standard requirements.

III. QUALITY ASSURANCE

The laboratory personnel will conduct an orderly program of positive actions (equipment cleaning, reconditioning, adjusting, and/or testing) to prevent instruments or equipment from failure during use. The purpose of this preventative maintenance program is to increase measurement system reliability and thus data completeness and analysis efficiency.

Quality is assured by distributing the responsibility for preventative maintenance as follows:

Position	Responsibility
Branch Manager	Review PM progress in annual report.
Quality Assurance Officer (QAO)	Inspects maintenance log sheets for completeness.
Laboratory Managers and Analysts	Performs analysis and documentation according to documented procedures.

IV. APPARATUS

Not applicable.

V. SAMPLE HANDLING AND PRESERVATION

Not applicable.

VI. REAGENTS

Not applicable.

VII. PROCEDURE

Based on the purpose of each test, environmental influences, physical location of equipment, and manufacturer recommendations, a complete preventative maintenance plan has been developed, CR4052-PD-0200(1). The plan includes those steps completed when the equipment is used, steps completed when the equipment indicates that they are necessary, and steps taken on a routine basis.

A. CR4052-PD-0200(2) Water Systems Maintenance Log

This attachment is used to log the water conductivity for the water purification system (CR4052-IN-4000) and the automatic water still (CR4052-IN-4010).

B. CR4052-PD-0200(3) Controlled Temperature Log

This attachment is used to monitor temperature on a daily basis during the normal 5-day workweek.

C. CR4052-PD-0200(4) Flame AA Maintenance Log

Contains monthly and quarterly checklist for Flame AA Maintenance.

D. CR4052-PD-0200(5) Code 4052 Maintenance List

Includes miscellaneous tasks performed on a routine basis: graphite furnace lenses cleaning, UV-vis calibration, membrane replacement, various equipment cleaning, filter changes, and timer operation verification.

E. CR4052-PD-0200(6) Temperature Log for Oven Incubator

This attachment is used to record the temperatures for the oven incubator and water bath. The oven incubator has a thermometer on the top shelf and one on the bottom shelf. Both temperatures must be recorded 2 times per day. The reading must be at least 4 hours apart.

VIII. DATA ANALYSIS AND REPORTING

Maintenance records and status reports will be retained and located according to CR4052-PD-0150.

Any additional required maintenance beyond that described in CR4052-PD-0200(1) will be noted in the appropriate log books or data sheets.

IX. ATTACHMENTS

CR4052-PD-0200(1) Code 4052 Preventative Maintenance Summary

CR4052-PD-0200(2) Water Systems Maintenance Log

CR4052-PD-0200(3) Controlled Temperature Log

CR4052-PD-0200(4) Flame AA Maintenance Log

CR4052-PD-0200(5) Code 4052 Maintenance Log

CR4052-PD-0200(6) Temperature Log for Oven Incubator

X. REFERENCES

None.

XI. REVISION BLOCK

REV	DATE	REVISION	AUTHOR
0	12/1/00	Original issue.	MLS
1	5/02/01	Changed header requirements. Revised Section VII and attachments	JJK
2	10/19/01	Added CR4052-IN-4090 to attachments. Corrected references in CR4052-PD-0200(1).	JJK
3	01/14/02	Added CR4052-PD-0200(6) and CR4052-IN-4025.	JJK

Code 4052 Preventative Maintenance Summary

Code 4052 Instrument Number	Instrument Description	PM Each Time Used	Maintenance As Needed	Routine Maintenance
CR4052-IN-3020	ATOMIC ABSORPTION SPECTROMETER (GF/FLAME)	1. Verify adequate rinse water supply. 2. Verify drain is not full. 3. Check delivery tube alignment with graphite tube. 4. Calibrate with standards. 5. Record activity in log, CR4052-PD-1100(1).	1. Change graphite tube approximately every 200 runs. Check alignment after installation. Note in CR4052-PD-0200(2).	1. Clean lenses semiannually. Note in CR4052-PD-0200(5).
CR4052-IN-4020	REFRIGERATOR - FISHER	1. Read and log thermometer temperature readings, CR4052-PD-0200(3). 2. Check for spillage and wet areas around refridgerator.	N/A	1. Clean montlhly with soap and water. Note in CR4052-PD-0200(5).
CR4052-IN-4025	REFRIGERATOR - ROPER	1. Read and log thermometer temperature readings, CR4052-PD-0200(3). 2. Check for spillage and wet areas around refridgerator.	N/A	1. Clean monthly with soap and water. Note in CR4052-PD-0200(5).
CR4052-IN-4100	HOOD - WATER LAB (1 OF 2)	N/A	1. Change bulbs as required.	N/A
CR4052-IN-4200	ASPIRATOR PUMP - WATER LAB (1 OF 2)	N/A	N/A	N/A
CR4052-IN-4230	OIL AND GREASE EXTRACTION	N/A	N/A	N/A
CR4052-IN-3000	ATOMIC ABSORPTION SPECTROMETER (FLAME)	1. Align lamps for optimum energy. 2. Align burner head for optimum absorbance. 3. Calibrate with standards.	N/A	1. Disassemble burner head, nebulizer and clean assembly with distilled water followed by acetone quarterly. Record in CR4052-PD-0200(4). 2. Clean optics quartely. Record in CR4052-PD-0200(4). 3. Check gaskets and o-rings quarterly. Record in CR4052-PD-0200(4). 4. Clean slot in burner monthly. After use, rinse burner and spray chamber with distilled water followed by acetone. Record in CR4052-PD-0200(4).
CR4052-IN-3010	As/Se HYDRIDE SYSTEM	1. Rinse with DI water after run complete. 2. Insert hydride solution for storage.	N/A	N/A
CR4052-IN-4250	EDL POWER SUPPLY	N/A	N/A	N/A
CR4052-IN-4260	EDL POWER SUPPLY II	N/A	N/A	N/A
CR4052-IN-4300	HOT PLATE/STIRRER	N/A	N/A	N/A
CR4052-IN-4150	pH METER	1. Calibrate meter with appropriate buffer solutions.	1. Replace electrode/probe and batteries.	NA

Code 4052 Preventativ[illegible] [illegible]ntenance Summary

Code 4052 Instrument Number	Instrument Description	PM Each Time Used	Maintenance As Needed	Routine Maintenance
		2. Clean electrode after use and immerse in capped buffer reagent.		
CR4052-IN-4400	AUTOCLAVE	1. Fill reservoir. 2. Check for spillage and wet areas around drain. 3. Information recorded for each time cycle of operation in CR4052-PD-0710(1). 4. Sterility strips used with each cycle of operation. 5. Check drain screen, clean as necessary.		1. Automatic timer operation verified annually. Record in CR4052-PD-0710(1). 2. Clean with soap and water every 6 months. Record in CR4052-PD-0710(1).
CR4052-IN-4410	MICROPROCESSOR OVEN	1. Clean after each use if spills occur. 2. Set temperature settings and limits.	N/A	N/A
CR4052-IN-4500	BALANCE, TOP LOAD	1. Clean after each use.	1. Verify calibration with weights monthly per CR4052-PD-0250(2).	1. External certified calibration annually.
CR4052-IN-4510	BALANCE, TOP LOAD	1. Clean after each use.	1. Verify calibration with weights monthly per CR4052-PD-0250(2).	1. External certified calibration annually.
CR4052-IN-3030	MERCURY ANALYZER SYSTEM	1. Clean with water. 2. Check for leakage around tubing. 3. Calibrate high standard to 75% on chart recorder.	1. Clean with soap and water. 2. Replace Hg absorbing solution as needed.	N/A
CR4052-IN-4600	RECORDER	N/A	N/A	N/A
CR4052-IN-4420	OVEN	1. Clean after each use if spills occur. 2. Set temperature settings and limits.	N/A	N/A
CR4052-IN-4430	FURNACE	1. Check vent connection.	N/A	N/A
CR4052-IN-4610	DESCICATING CABINET	1. Verify N2 purge operational.	1. Change fittings as needed.	N/A
CR4052-IN-4620	DESCICATING CABINET	1. Verify N2 purge operational.	1. Change fittings as needed.	N/A
CR4052-IN-4520	BALANCE, ANALYTICAL	1. Clean after each use.	INACTIVE	INACTIVE
CR4052-IN-4700	COLIFORM INCUBATOR BATH	1. Check for spillage and wet areas around cover. 2. Ensure temperature setting is correct.	N/A	1. Verify thermostat setting with thermometer monthly when in use. Record in CR4052-PD-0200(3).
CR4052-IN-4710	COLONY COUNTER	N/A	1. Change bulbs as required.	N/A

Code 4052 Preventativ Maintenance Summary

Code 4052 Instrument Number	Instrument Description	PM Each Time Used	Maintenance As Needed	Routine Maintenance
CR4052-IN-4780	CULTURE INCUBATOR	1. Thermometer immersed in liquid and placed on shelf. 2. Temperature log twice daily during operation Apr - Nov per CR4052-PD-1500(2).	N/A	1. Clean with soap and water every annually. Record in CR4052-PD-0200(5).
CR4052-IN-3040	TOTAL ORGANIC CARBON ANALYZER	1. Check and or/replace pump tubing. 2. Prepare fresh reagent and standards. 3. Calibrate with standard.	1. Check reagent, waste, and gas flows. 2. Replace injection septum.	N/A
CR4052-IN-3050	UV/VIS SPECTROPHOTOMETER	1. Clean cells prior to and after each use. 2. Calibrate with standards.	N/A	1. Monitor lamp with didymium glass calibration filter every 6 months. Record in CR4052-PD-0200(5).
CR4052-IN-4730	MICROWAVE DIGESTION SYS.	1. Purge pressure monitoring line with 50 ml DI water. 2. Ensure exhaust fans (ICP, microwave) are on and working. 3. Ensure inside fan isn't touching vessels.	1. Check pressure monitoring tubing at vessel end.	1. Perform power calibration. Record in CR4052-PD-0250(3). 2. Clean with soap and water annually. Record in CR4052-PD-0200(5).
CR4052-IN-4110	HOOD - WATER LAB (2 OF 2)	N/A	1. Change bulbs as required.	N/A
CR4052-IN-4210	ASPIRATOR PUMP - WATER LAB (2 OF 2)	N/A	N/A	N/A
CR4052-IN-4740	CYANIDE DISTILLATION UNIT	1. Clean with water on external surfaces. 2. Check for leakage and ensure cold water head is snug in distillation tube. 3. Ensure heater in distillation housing unit is working.	N/A	1. Clean with soap and water annually. Record in CR4052-PD-0200(5). 2. Automatic timer operation verified annually. Record in CR4052-PD-0200(5).
CR4052-IN-4030	REFRIGERATOR - AVANTI	1. Read and log thermometer temperature readings, CR4052-PD-0200(3). 2. Check for spillage and wet areas around refridgerator.	N/A	1. Clean monthly with soap and water. Note in CR4052-PD-0200(5).
CR4052-IN-4750	WATER BATH	1. Check for spillage and wet areas around cover.	1. Clean with soap and water.	N/A
CR4052-IN-4800	THERMOMETERS	N/A	N/A	1. Externally calibrated.
CR4052-IN-4000	WATER PURIFICATION SYSTEM	1. Conductivity checked and logged monthly or when used in CR4052-PD-0200(2).	N/A	1. Change filters annually. Record in CR4052-PD-0200(5).
CR4052-IN-4760	FLASKSCRUBBER GLASSWARE WASHER	1. Wipe off soap dispenser.	N/A	N/A

Code 4052 Preventativ ıintenance Summary

Code 4052 Instrument Number	Instrument Description	PM Each Time Used	Maintenance As Needed	Routine Maintenance
CR4052-IN-4010	AUTOMATIC WATER STILL	1. Conductivity checked and logged monthly or when used in CR4052-PD-0200(2).	1. Filter cartridges replaced as needed.	N/A
CR4052-IN-4040	REFRIDGERATOR - LAB-LINE	1. Read and log thermometer temperature readings, CR4052-PD-0200(3). 2. Check for spillage and wet areas around refridgerator.	N/A	1. Clean monthly with soap and water. Note in CR4052-PD-0200(5).
CR4052-IN-4530	ANALYTICAL BALANCE	1. Clean after each use.	1. Verify calibration with weights monthly per CR4052-PD-0250(2).	1. External certified calibration annually.
CR4052-IN-4160	ION ANALYZER	N/A	N/A	N/A
CR4052-IN-4170	AMMONIA SPECIFIC ION ELECTRODE	1. Calibrate meter with appropriate calibration solutions. 2. Clean electrode after use and immerse in capped buffer reagent. 3. Ensure slope is 60±3mV for ammonia per CR4052-PD-1230.	1. Replace electrode/probe as needed.	1. Every month, replace membrane and internal electrode solution. Record in CR4052-PD-0200(5).
CR4052-IN-2430 CR4052-IN-2140 CR4052-IN-21430 CR4052-IN-2150	AUTOSAMPLER CONDUCTIVITY DETECTOR LIQUID CHROMATOGRAPHY PUMP TEMP. CONTROL UNIT	1. Set column heater to 30°C. 2. Ensure rinse water bottle is full. 3. Calibrate with standards. 4. Check level mobile phase reservoir. Filter new mobile phase and purge reservoir line before use.	1. Repair/rebuild pumps, injection ports, install columns and seals.	N/A
CR4052-IN-4770	ULTRASONIC CLEANER	N/A	1. Change water as needed (DI water).	N/A
CR4052-IN-2060 CR4052-IN-2050	PHOTODIODE ARRAY DETECTOR SEPARATIONS MODULE	1. Calibrate with standards 2. Ensure adequate mobile phase. Fill reservoir before use if required. 1. Set column heater to 30°C.	1. Replace lamp 1. Repair/rebuild pumps, injection ports, install columns and seals as required. 2. Manufacturer representative for instrument PM service on internal components as requested.	1. Rebuild check valves, and replace pumps seals yearly.
CR4052-IN-4050	REFRIDGERATOR - SNAKE PIT	1. Read and log thermometer temperature readings, CR4052-PD-0200(3). 2. Check for spillage and wet areas around refridgerator.	N/A	1. Clean monthly with soap and water. Note in CR4052-PD-0200(5).
CR4052-IN-4310	HOT PLATE/STIRRER	N/A	N/A	N/A

Code 4052 Preventative Maintenance Summary

Code 4052 Instrument Number	Instrument Description	PM Each Time Used	Maintenance As Needed	Routine Maintenance
CR4052-IN-4630	DESCICATING CABINET	N/A	N/A	N/A
CR4052-IN-4220	ASPIRATOR PUMP	N/A	N/A	N/A
CR4052-IN-2010	MILLENNIUM CHROMATOGRAPHY SOFTWARE	N/A	N/A	1. Archive Projects monthly.
CR4052-IN-2030 CR4052-IN-2020 CR4052-IN-2040	PHOTODIODE ARRAY DETECTOR SEPARATIONS MODULE - 2690 TEMP. CONTROL UNIT	1. Calibrate with standards 2. Ensure adequate mobile phase. Fill reservoir before use if required. 3. Set column heater to 30°C.	1. Replace lamp 1. Repair/rebuild pumps, injection ports, install columns and seals as required. 2. Manufacturer representative for instrument PM service on internal components as requested.	1. Rebuild check valves, and replace pumps seals yearly.
CR4052-IN-2070	MILLENNIUM CHROMATOGRAPHY SOFTWARE	N/A	N/A	1. Archive Projects monthly.
CR4052-IN-2080 CR4052-IN-2100 CR4052-IN-2090 CR4052-IN-2110	AUTOSAMPLER MULTI-WAVELENGTH DETECTOR LIQUID CHROMATOGRAPHY PUMP TEMP. CONTROL UNIT	1. Ensure rinse bottle if full 2. Calibrate with standards 4. Check level mobile phase reservoir. Filter new mobile phase and purge reservoir line before use.	1. Repair/rebuild pumps, injection ports, install columns and seals. 2. Replace lamp.	1. Rebuild check valves, and replace pumps seals yearly.
CR4052-IN-2170	LIQUID CHROMATOGRAPHY PUMP	1. Check level mobile phase reservoir. Filter new mobile phase and purge reservoir line before use.		1. Rebuild check valves, and replace pumps seals yearly.
CR4052-IN-4060	REFRIGERATOR - GE	1. Read and log thermometer temperature readings, CR4052-PD-0200(3).	N/A	1. Clean monthly with soap and water. Note in CR4052-PD-0200(5).
CR4052-IN-4070	REFRIGERATOR - MAGIC CHEF	1. Read and log thermometer temperature readings, CR4052-PD-0200(3).	N/A	1. Clean monthly with soap and water. Note in CR4052-PD-0200(5).
CR4052-IN-4080	FREEZER - COOL-LAB	1. Read and log thermometer temperature readings, CR4052-PD-0200(3).	N/A	1. Annually clean with soap and water. Note in CR4052-PD-0200(5).
CR4052-IN-4090	REFRIGERATOR/FREEZER-ROPER	1. Read and log thermometer temperature readings, CR4052-PD-0200(3).	N/A	1. Clean monthly with soap and water. Note in CR4052-PD-0200(5).
CR4052-IN-4540	ANALYTICAL BALANCE	1. Clean after each use.	1. Verify calibration with weights monthly per CR4052-PD-0250(2).	1. External certified calibration annually.
CR4052-IN-4550	ANALYTICAL BALANCE	1. Clean after each use.	1. Verify calibration with weights monthly per CR4052-PD-0250(2).	1. External certified calibration annually.

Code 4052 Preventativ intenance Summary

Code 4052 Instrument Number	Instrument Description	PM Each Time Used	Maintenance As Needed	Routine Maintenance
CR4052-IN-4560	ANALYTICAL BALANCE	1. Clean after each use.	1. Verify calibration with weights monthly per CR4052-PD-0250(2).	1. External certified calibration annually.
CR4052-IN-4570	BALANCE, TOP LOAD	1. Clean after each use.	1. Verify calibration with weights monthly per CR4052-PD-0250(2).	1. External certified calibration annually.
CR4052-IN-4580	ANALYTICAL BALANCE	1. Clean after each use.	1. Verify calibration with weights monthly per CR4052-PD-0250(2).	1. External certified calibration annually.
CR4052-IN-4590	ANALYTICAL BALANCE	1. Clean after each use.	1. Verify calibration with weights monthly per CR4052-PD-0250(2).	1. External certified calibration annually.

Water Systems Maintenance Log

Date	CR4052-IN-4000 Water Purification System Conductivity	CR4052-IN-4010 Automatic Water Still Conductivity	Initials

Controlled Temperature Log

Select	Equipment Number	Description	Temperature Range	Thermometer Serial Number	Correction Factor
	CR4052-IN-4020	Freezer	-20 - -10		
	CR4052-IN-4020	Refrigerator	1 – 5		
	CR4052-IN-4025	Freezer	-20 - -10		
	CR4052-IN-4025	Refrigerator	1 – 5		
	CR4052-IN-4030	Refrigerator	1 – 5		
	CR4052-IN-4040	Refrigerator	1 – 5		
	CR4052-IN-4050	Refrigerator	1 – 5		
	CR4052-IN-4060	Freezer	-20 - -10		
	CR4052-IN-4060	Refrigerator	1 – 5		
	CR4052-IN-4070	Refrigerator	1 – 5		
	CR4052-IN-4080	Freezer	-20 - -10		
	CR4052-IN-4090	Freezer	-20 - -10		
	CR4052-IN-4090	Refrigerator	1 – 5		
	CR4052-IN-4700	Water bath	44.5 ± 0.2		

Date	Reading[1] (°C)	Corrected Temperature[2] (°C)	Initials	Comments[3]

Note 1: Temperature as displayed on thermometer's stem.
Note 2: Temperature after adjustment by the thermometer's correction factor.
Note 3: Any corrective actions performed.

Flame AA Maintenance Log
CR4052-IN-3000

Monthly PM: Clean Burner Slot

Quarterly PM: Disassemble burner head, nebulizer and clean assembly with DI water, acetone
Clean optics.
Check gaskets and o-rings.

Date Competed	Check if Monthly PM	Check if Quarterly PM (Note 1)	Initials

Code 4052 Maintenance Log

Select	Equipment Number	Equipment Description	Maintenance Description	Frequency (Months)
	CR4052-IN-4170	Ammonia Ion Electrode	Replace membrane	1
	CR4052-IN-3020	Graphite Furnance	Clean lenses	6
	CR4052-IN-3050	UV-vis	Calibration	6
	CR4052-IN-4000	Water Purification System	Change Filters	12
	CR4052-IN-4400	Autoclave	Clean w/soap and water	6
			Verify proper timer operation	12
	CR4052-IN-4720	Culture Incubator	Clean w/soap and water	12
	CR4052-IN-4730	Microwave Digestion System	Clean w/soap and water	12
			Calibration	12
	CR4052-IN-4740	Cyanide Distillation Unit	Clean w/soap and water	12
	CR4052-IN-4020	Freezer	Defrost; clean w/soap and water	12
	CR4052-IN-4020	Refrigerator	Clean w/soap and water	1
	CR4052-IN-4025	Freezer	Defrost; clean w/soap and water	12
	CR4052-IN-4025	Refrigerator	Clean w/soap and water	1
	CR4052-IN-4030	Refrigerator	Clean w/soap and water	1
	CR4052-IN-4040	Refrigerator	Clean w/soap and water	1
	CR4052-IN-4050	Refrigerator	Clean w/soap and water	1
	CR4052-IN-4060	Freezer	Defrost; clean w/soap and water	12
	CR4052-IN-4060	Refrigerator	Clean w/soap and water	1
	CR4052-IN-4070	Refrigerator	Clean w/soap and water	1
	CR4052-IN-4080	Freezer	Defrost; clean w/soap and water	1
	CR4052-IN-4090	Freezer	Defrost; clean w/soap and water	12
	CR4052-IN-4090	Refrigerator	Clean w/soap and water	1

Date	Initials	Comments

Temperature Log for Oven Incubator

Thermometer	Serial Number	Correction Factor
Top Shelf		
Bottom Shelf		

Date	Time[1]	Top Shelf		Bottom Shelf		Initials	Comments
		Reading[2] (°C)	Corrected Temperature[3, 4] (°C)	Reading[2] (°C)	Corrected Temperature[3, 4] (°C)		

Note 1: The oven incubator temperature must be recorded 2 times per day. The readings must be at least 4 hours apart.
Note 2: Temperature as displayed on stem of thermometer.
Note 3: Temperature after adjustment by the thermometer's correction factor.
Note 4: Target Temperature range: 35 ± 0.5 °C

Chemical/Supply Management

Explosive Sciences Branch
Naval Surface Warfare Center Crane
300 Highway 361
Crane, IN 47522

December 1, 2000

Approvals:

Name	Nancey J. Maegerlein
Title	Branch Manager
Signature	Nancey J. Maegerlein
Name	Louis C. Schwenk
Title	Laboratory Manager
Signature	Louis Schwenk

MASTER

CONTROLLED COPY
NSWC REPOSITORY 08
CODE 405
COPY NO. 3

I. SCOPE AND APPLICATION

This procedure describes the process by which the laboratory ensures adequate quantity and quality of supplies for testing.

II. SUMMARY OF METHOD

This method is consistent with ISO 9001 standard requirements.

III. QUALITY ASSURANCE

A. Responsibility

Quality is assured by distributing the responsibility for document control as follows:

Position	Responsibility
Laboratory Manager	Performs routine supply audit.
	Orders supplies as required.
Laboratory Analyst	Labels and dates supplies appropriately.
	Notifies the laboratory manager of any additional supplies required.

B. Quality Practices

The following quality practices will be observed:

1. Standards to be used for calibration purposes are traceable to the National Institute of Standards and Technology (NIST).

2. Standard makeup solutions are prepared according to method specifications and documented in the specific analytical laboratory notebook with method of preparation, manufacturer, lot number, date of preparation, concentration, and analyst.

3. Purchased standards and laboratory standards will be stored in accordance with method or manufacturer requirements and recommendations.

4. The ESB shall label all reagents, solutions, and preservatives to indicate identity, concentration (where applicable), and the grade or quality of the material. Labeling shall also indicate the preparation or date the reagent was opened.

5. Outdated reagents and solutions will not be used unless their integrity is verified by testing.

IV. APPARATUS

Not applicable.

V. SAMPLE HANDLING AND PRESERVATION

Not applicable.

VI. REAGENTS

Not applicable.

VII. PROCEDURE

A. Routine Inventory

The laboratory manager performs a routine inventory of supplies routinely consumed through testing.

1. General Lab Supplies

The general supplies required to operate the laboratory are listed in CR4052-PD-0220(1). This table indicates items required, suppliers, specification requirements, and minimum quantities. An inventory on these items is performed on a quarterly basis. Based on the current inventory and minimum quantity requirements, an appropriate order is placed and items in inventory beyond their shelf lives will be discarded appropriately.

Any receipts or documentation received in the ordering process is attached to the inventory sheet and filed according to Record Retention, CR4052-PD-0150.

2. NPDES Water Testing Supplies

The supplies required for NPDES water testing are listed in attachment CR4052-PD-0220(2). This table indicates items required and minimum quantities. An inventory on these items is performed on a monthly basis. Based on the current inventory and minimum quantity requirements, an appropriate order is placed and

items in inventory beyond their shelf lives will be discarded appropriately.

Any receipts or documentation received in the ordering process is attached to the inventory sheet and filed according to Record Retention, CR4052-PD-0150.

B. Additional Supplies Required

The laboratory manager is notified when it is observed that additional supplies are needed. The laboratory manager will either place an order at that time or wait until the next inventory period.

VIII. DATA ANALYSIS AND REPORTING

None.

IX. ATTACHMENTS

CR4052-PD-0220(1) General Laboratory Supplies, 12/1/00

CR4052-PD-0220(2) NPDES Water Testing Supplies, 12/1/00

X. REFERENCES

None.

XI. REVISION BLOCK

REV	DATE	REVISION	AUTHOR
0	12/1/00	Original issue.	MLS

General Laboratory Supplies

Inventory Completed by: _____ **Date:** _____

Item	Spec	Supplier	Minimum Quantity	Current Inventory	Amount Ordered
Chemicals					
Methanol	HPLC Grade	Fisher	4 x 4L		
Acetonitrile	HPLC Grade	Fisher	4 x 4L		
Supplies					
Chemwipes	NSN 7920-00-965-1709	Horizon Ind.	2 boxes		
Disposable Lab Coats, L	1209034	Safety & First Aid	1 box		
Disposable Lab Coats, XL	1209035	Safety & First Aid	1 box		
Disposable Lab Coats, 2XL	1209036	Safety & First Aid	1 box		
Disposable Lab Coats, 3XL	1209037	Safety & First Aid	1 box		
Disposable Lab Coats, 4XL	NS-4XL-SMS	Safety & First Aid	1 box		
Disposable Lab Coats, 5XL	NS-5XL-SMS	Safety & First Aid	1 box		
5cc disposable syringes	14-823-35	Fisher	2 boxes		
HPLC Columns	CP28079	Varian	2		
HPLC Guard Cartridges	CP28141	Varian	2		
Nitrile Gloves, XL	40101-350	VWR	2 boxes		
Nitrile Gloves, L	40101-348	VWR	2 boxes		
Nitrile Gloves, M	40101-346	VWR	2 boxes		
Syringe Filters, Nylon, PP Housing, 0.2 micron	26066	Restek	2 boxes		

NPDE[illegible]ter Testing Supplies

Item	Test	Minimum Quantity	Current Inventory	Amount Ordered
Chemicals				
Nitric Acid, Trace metal grade (Fisher Scientific)	Mercury, Metals	5, 5-pint bottles		
AA Standards, ~ 20 elements (Env. Res. Ass.)	Mercury, Metals	100 / 500 ml bottles		Reorder 2 months before expiration date
Stannous chloride - suitable for mercury analysis	Mercury, Metals	500 g		
Hydroxylamine hydrocholoride, 50% solution - suitable for mercury analysis	Mercury, Metals	500 ml		
Potassium permanganate, 5% solution - suitable for mercury analysis	Mercury, Metals	2 L		
Potassium persulfate, 5% solution - suitable for mercury analysis	Mercury, Metals	2 L		
1% $NH_4H_2PO_4$ in 1% HNO_3 matrix modifier - suitable for mercury analysis	Mercury, Metals	100 ml		
1% Palladium solution matrix modifier - suitable for mercury analysis	Mercury, Metals	100 ml		
1% $Mg(NO_3)_2$ solution matrix modifier - suitable for mercury analysis	Mercury, Metals	100 ml		
Sodium borohydride	As/Se	200 g		
Sodium iodide	As/Se	200 g		
Ammonium pyrrolidine dithiocarbamate (APDC)	Hexavalent chromium	20 g		
Yellow mercuric oxide	TKN	100 g		
H_2SO_4, Trace metal grade	TKN, Phosphorous, Mercury/metals	5, 5-pint bottles		
K_2SO_4	TKN	500 g		
NaOH	TKN, Total Cyanide, Phosphorous +	2 kg		
Ammonium chloride	TKN	500 g		
Sodium dihydrogenphosphate	Total Cyanide	1 kg		
KCn	Total Cyanide	100 g		
Silver nitrate, 0.0192N	Total Cyanide	2 L		
P-dimethyl-amino-benzalrhodonine	Total Cyanide	10 g		
Chloramine - T	Total Cyanide	100 g		
Barbituric acid	Total Cyanide	200 g		
Magnesium chloride powder (mg $Cl_2 \bullet 6\ H_2O$)	Total Cyanide	500 g		
Sulfamic acid	Total Cyanide	250 g		
Hydrochloric acid	As/Se	5, 5-pint bottles		
Sodium sulfate drying cartridges, 50/pack	Oil & Grease	2 packs		
Hexodecane	Oil & Grease	300 ml		
Stearic acid	Oil & Grease	500 g		
Hexane	Oil & Grease	2, 4-L bottles		

NPDES [illegible]ter Testing Supplies

Item	Test	Minimum Quantity	Current Inventory	Amount Ordered
Acetone	Oil & Grease	2, 4-L bottles		
Antimony potassium tartrate	Phosphorous	100 g		
Ammonium molybdate	Phosphorous	250 g		
Ascorbic acid	Phosphorous	100 g		
Potassium dihydrogen phosphate	Phosphorous	100 g		
Ammonium persulfate	Phosphorous	100 g		
m-TEC agar	E-coli	250 g		
Urea	E-coli	250 g		
Supplies				
Extraction disks, 10/box	Oil & Grease	3 boxes		
0.45 micron 47mm cellulose esters membrane, 100/box		2 boxes		
Type A/E glass fiber filter, 47 mm, 100/box		2 boxes		
Sterile pipets, 5 ml		2 boxes		
Sterile pipets, 10 ml		2 boxes		
Sterile petri dishes, 55mm		2 boxes		
0.45 micron membrane filters, 47mm, gridded, sterile		2 boxes		
Absorbent pads, cellulose, 47mm		2 boxes		
Polycarbonate sample bottles, sterile, dechloromator added, 100 ml, 200 bottles/box		2 boxes		
Colilert, mo/mugg presence/absense reagent, 20 testers/box		8 boxes		
Colilert, presence/absense color comparator		2 comparitors		
PE known organisms, 3 coliform types				
PE coliform/E-coli sample sets		1 year		
Try ptic soy broth		500 g		
Autoclave sterilization strip indicator		1 box		
Graphite carbon tubes for graphite furnace, 25/box		1 box		

Inventory Completed by: _____

Date: _____

Data Validation

Explosive Sciences Branch
Naval Surface Warfare Center Crane
300 Highway 361
Crane, IN 47522

January 22, 2001

Approvals:

Name	Nancey J. Maegerlein
Title	Branch Manager
Signature	Nancey J. Maegerlein
Name	Michelle L. Spellman
Title	Quality Assurance Officer
Signature	Michelle L. Spellman

MASTER

I. SCOPE AND APPLICATION

This procedure describes the Code 4052 data validation process.

II. SUMMARY OF METHOD

As performance data (% recovery, duplicate analysis, etc.) is collected, it is compiled in a software program to statistically characterize the analytical process in terms of percent relative standard deviation (%RSD).

Duplicate samples are used to monitor method precision; spiked percentage recovery data is used to monitor method accuracy.

III. QUALITY ASSURANCE

Quality is assured by distributing responsibility as follows:

Position	Responsibility
Quality Assurance Officer (QAO)	Enters data into program and interprets results.
Laboratory Managers and Analysts	Provides analytical process data.

IV. APPARATUS

The Code 4052 laboratory uses Windowchem™ Software's ControlChart! ™ software to generate quality control charts.

V. SAMPLE HANDLING AND PRESERVATION

Not applicable.

VI. REAGENTS

Not applicable.

VII. PROCEDURE

A separate control chart will be prepared for each concentration range represented in the outfall data.

Data Type	Source	Test	File Location
Spike Recovery	001	Silver	F:\CODE4076\CCPRO\ccpropls\qechart\001-spike\AG.ccp
		Cadmium	F:\CODE4076\CCPRO\ccpropls\qechart\001-spike\CD.ccp
		Chromium	F:\CODE4076\CCPRO\ccpropls\qechart\001-spike\CR.ccp
		Copper	F:\CODE4076\CCPRO\ccpropls\qechart\001-spike\CU.ccp
		Cyanide	F:\CODE4076\CCPRO\ccpropls\qechart\001-spike\CYAN.ccp
		Hex Chromium	F:\CODE4076\CCPRO\ccpropls\qechart\001-spike\HEXCR.ccp
		Mercury	F:\CODE4076\CCPRO\ccpropls\qechart\001-spike\HG.ccp
		Ammonia – N	F:\CODE4076\CCPRO\ccpropls\qechart\001-spike\NH3.ccp
		Nickel	F:\CODE4076\CCPRO\ccpropls\qechart\001-spike\NI.ccp
		Nitrate-N	F:\CODE4076\CCPRO\ccpropls\qechart\001-spike\No3spike.ccp
		Lead	F:\CODE4076\CCPRO\ccpropls\qechart\001-spike\PB.ccp
		Zinc	F:\CODE4076\CCPRO\ccpropls\qechart\001-spike\ZN.ccp
	101	Oil and Grease	F:\CODE4076\CCPRO\ccpropls\qechart\101-spike\O&G.ccp
	107	Nitrate-N	F:\CODE4076\CCPRO\ccpropls\qechart\107-spike\NO3.ccp
		Ammonia-N	F:\CODE4076\CCPRO\ccpropls\qechart\107-spike\NH3.ccp
		Oil and Grease	F:\CODE4076\CCPRO\ccpropls\qechart\107-spike\O&G.ccp
	301	Ammonia-N	F:\CODE4076\CCPRO\ccpropls\qechart\301-spike\NH3.ccp
		Nitrate-N	F:\CODE4076\CCPRO\ccpropls\qechart\301-spike\NO3.ccp
		Oil and Grease	F:\CODE4076\CCPRO\ccpropls\qechart\301-spike\O&G.ccp
	Exp.	HMX (107)	F:\CODE4076\CCPRO\ccpropls\qechart\exp-spike\HMX_107.ccp
		RDX (107)	F:\CODE4076\CCPRO\ccpropls\qechart\exp-spike\RDX_107.ccp
		TNT (107)	F:\CODE4076\CCPRO\ccpropls\qechart\exp-spike\TNT_107.ccp
		HMX (301)	F:\CODE4076\CCPRO\ccpropls\qechart\exp-spike\HMX_301.ccp
		RDX (301)	F:\CODE4076\CCPRO\ccpropls\qechart\exp-spike\RDX_301.ccp
		TNT (301)	F:\CODE4076\CCPRO\ccpropls\qechart\exp-spike\TNT_301.ccp
	OPR	Oil and Grease	F:\CODE4076\CCPRO\ccpropls\qechart\OPR-spike\O&G.ccp
	Metals	Silver Blank	F:\CODE4076\CCPRO\ccpropls\qechart\metalsblank-spike\AG.ccp
		Cadmium Blank	F:\CODE4076\CCPRO\ccpropls\qechart\metalsblank-spike\CD.ccp
		Chromium Blank	F:\CODE4076\CCPRO\ccpropls\qechart\metalsblank-spike\CR.ccp

		Copper Blank	F:\CODE4076\CCPRO\ccpropls\qechart\metalsblank-spike\CU.cc[illegible]
		Mercury Blank	F:\CODE4076\CCPRO\ccpropls\qechart\metalsblank-spike\HG.ccp
		Nickel Blank	F:\CODE4076\CCPRO\ccpropls\qechart\metalsblank-spike\NI.ccp
		Lead Blank	F:\CODE4076\CCPRO\ccpropls\qechart\metalsblank-spike\PB.ccp
		Zinc Blank	F:\CODE4076\CCPRO\ccpropls\qechart\metalsblank-spike\ZN.ccp
Duplicates	001	Silver	F:\CODE4076\CCPRO\ccpropls\qechart\001-duplicate\AG.ccp
		Cadmium	F:\CODE4076\CCPRO\ccpropls\qechart\001-duplicate\CD.ccp
		Chromium	F:\CODE4076\CCPRO\ccpropls\qechart\001-duplicate\CR.ccp
		Copper	F:\CODE4076\CCPRO\ccpropls\qechart\001-duplicate\CU.ccp
		Cyanide	F:\CODE4076\CCPRO\ccpropls\qechart\001-duplicate\CYANIDE.ccp
		Hex Chromium	F:\CODE4076\CCPRO\ccpropls\qechart\001-duplicate\HEXCR.ccp
		Mercury	F:\CODE4076\CCPRO\ccpropls\qechart\001-duplicate\HG.ccp
		Ammonia – N	F:\CODE4076\CCPRO\ccpropls\qechart\001-duplicate\NH3.ccp
		Nickel	F:\CODE4076\CCPRO\ccpropls\qechart\001-duplicate\NI.ccp
		Lead	F:\CODE4076\CCPRO\ccpropls\qechart\001-duplicatefPB.ccp
		Zinc	F:\CODE4076\CCPRO\ccpropls\qechart\001-duplicate\ZN.ccp
	101	Cyanide	F:\CODE4076\CCPRO\ccpropls\qechart\101-duplicate\CYANIDE.c[illegible]
		Hex. Chromium	F:\CODE4076\CCPRO\ccpropls\qechart\101-duplicate\HEXCHROM[illegible]cp
		Oil and Grease	F:\CODE4076\CCPRO\ccpropls\qechart\101-duplicate\O&G.ccp
	107	Nitrate – N	F:\CODE4076\CCPRO\ccpropls\qechart\107-duplicate\NO3.ccp
		Oil and Grease	F:\CODE4076\CCPRO\ccpropls\qechart\107-duplicate\O&G.ccp
	301	Ammonia – N	F:\CODE4076\CCPRO\ccpropls\qechart\301-duplicate\NH3.ccp
		Nitrate – N	F:\CODE4076\CCPRO\ccpropls\qechart\301-duplicate\NO3.ccp
		Oil & Grease	F:\CODE4076\CCPRO\ccpropls\qechart\301-duplicate\OG.ccp
	Exp.	HMX (107)	F:\CODE4076\CCPRO\ccpropls\qechart\exp-duplicate\HMX_107.ccp
		RDX (107)	F:\CODE4076\CCPRO\ccpropls\qechart\exp-duplicate\RDX_107.ccp
		TNT (107)	F:\CODE4076\CCPRO\ccpropls\qechart\exp-duplicate\TNT_107.ccp
		HMX (301)	F:\CODE4076\CCPRO\ccpropls\qechart\exp-duplicate\HMX_301.ccp
		RDX (301)	F:\CODE4076\CCPRO\ccpropls\qechart\exp-duplicate\RDX_301.ccp
		TNT (301)	F:\CODE4076\CCPRO\ccpropls\qechart\exp-duplicate\TNT_301.ccp
PE Samples	3260	Silver	F:\CODE4076\CCPRO\ccpropls\qechart\3260QE\Ag_qe.ccp
		Cadmium	F:\CODE4076\CCPRO\ccpropls\qechart\3260QE\Cd_qe.ccp
		Cyanide	F:\CODE4076\CCPRO\ccpropls\qechart\3260QE\Cn_qe.ccp
		Chromium	F:\CODE4076\CCPRO\ccpropls\qechart\3260QE\Cr_qe.ccp

		Copper	F:\CODE4076\CCPRO\ccpropls\qechart\3260QE\Cu_qe.ccp
		Mercury	F:\CODE4076\CCPRO\ccpropls\qechart\3260QE\Hg_qe.ccp
		Ammonia – N	F:\CODE4076\CCPRO\ccpropls\qechart\3260QE\Nh3_qe.ccp
		Nickel	F:\CODE4076\CCPRO\ccpropls\qechart\3260QE\Ni_qe.ccp
		Nitrate – N	F:\CODE4076\CCPRO\ccpropls\qechart\3260QE\No3_qe.ccp
		Oil and Grease	F:\CODE4076\CCPRO\ccpropls\qechart\3260QE\O&g_qe.ccp
		Lead	F:\CODE4076\CCPRO\ccpropls\qechart\3260QE\Pb_qe.ccp
		Zinc	F:\CODE4076\CCPRO\ccpropls\qechart\3260QE\Zn_qe.ccp
	WPO	Ammonia – N	F:\CODE4076\CCPRO\ccpropls\qechart\WPOQE\NH3_QE.ccp
		Cadmium	F:\CODE4076\CCPRO\ccpropls\qechart\WPOQE\CD_QE.ccp
		Chromium	F:\CODE4076\CCPRO\ccpropls\qechart\WPOQE\CR_QE.ccp
		Copper	F:\CODE4076\CCPRO\ccpropls\qechart\WPOQE\CU_QE.ccp
		Cyanide	F:\CODE4076\CCPRO\ccpropls\qechart\WPOQE\CN_QE.ccp
		Lead	F:\CODE4076\CCPRO\ccpropls\qechart\WPOQE\PB_QE.ccp
		Mercury	F:\CODE4076\CCPRO\ccpropls\qechart\WPOQE\HG_QE.ccp
		Nickel	F:\CODE4076\CCPRO\ccpropls\qechart\WPOQE\NI_QE.ccp
		Nitrate – N	F:\CODE4076\CCPRO\ccpropls\qechart\WPOQE\NO3_QE.ccp
		Oil and Grease	F:\CODE4076\CCPRO\ccpropls\qechart\WPOQE\O&G_QE.ccp
		Silver	F:\CODE4076\CCPRO\ccpropls\qechart\WPOQE\AG_QE.ccp
		Zinc	F:\CODE4076\CCPRO\ccpropls\qechart\WPOQE\ZN_QE.ccp

VIII. DATA ANALYSIS AND REPORTING

Data will be entered into the appropriate program the day of analysis, before the samples are discarded.

A. Data Entry

1. Spike Analysis

Spike result, sample result, and amount of spike added are entered by the user. The percentage recovery is calculated and graphed. Standard deviations are calculated and graphed.

2. Duplicate Analysis

Multiple results are entered by the user. The program calculates %RSD and graphs appropriately, indicating standard deviation performance on the graph.

B. Data Interpretation

The QAO and lab analyst validate the quality of the duplicate and spiked sample data. If further analysis is required, it is then conducted and re-evaluated. Any unusual observations are recorded in the laboratory notebook.

IX. ATTACHMENTS

None.

X. REFERENCES

None.

XI. REVISION BLOCK

REV	DATE	REVISION	AUTHOR
0	1/22/01	Original issue.	MLS

Calibration

Explosive Sciences Branch
Naval Surface Warfare Center Crane
300 Highway 361
Crane, IN 47522

June 21, 2001

Approvals:

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Title	Chemist
Signature	Jacquelyn Karty

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I. SCOPE AND APPLICATION

This procedure describes the Explosive Sciences Branch Calibration program. The procedure includes a list of equipment used by the ESB and the process for calibrating the equipment.

II. SUMMARY OF METHOD

This method is consistent with ISO 9001 standard requirements.

III. QUALITY ASSURANCE

Appropriate calibration checks will be performed to verify the stability and validity of the sample and the performance of testing and analytical equipment.

Quality is assured by distributing the responsibility for calibration as follows:

Position	Responsibility
Branch Manager	Review calibration/verification progress in annual report.
Quality Assurance Officer (QAO)	Inspects calibration/verification log sheets for completeness.
Laboratory Managers and Analysts	Performs analysis and documentation according to documented procedures.

IV. APPARATUS

Not applicable.

V. SAMPLE HANDLING AND PRESERVATION

Not applicable.

VI. REAGENTS

Not applicable.

VII. PROCEDURE

Based on the purpose of each test, environmental influences, physical location of equipment, and manufacturer recommendations, a complete calibration program has been developed, CR4052-PD-0250(1). The program includes an equipment list and a description of the type of calibration performed. Some calibrations are performed as the analysis is completed, some calibration is done routinely by the laboratory, some are performed by external calibration personnel, and some calibration is supported by internal laboratory verification.

A. CR4052-PD-0250(2) Monthly Balance Verification

This attachment is used to verify performance on a monthly basis. An externally calibrated weight (calibrated annually) is placed on the balance and the result recorded. If the weight falls within the acceptable range, no further action is required. If the balance performance is not successfully verified, additional external calibration will be ordered and the equipment re-verified.

Verification can also be performed if it is suspected that the balance may not be performing correctly. Non-routine verification will be documented on the same attachment.

These balances are routinely calibrated externally on an annual basis

VIII. DATA ANALYSIS AND REPORTING

All external calibrations are documented and retained by the calibrator.

Internal calibrations and verifications are documented in the attachments to this procedure and are retained and located according to CR4052-PD-0150.

Any additional required calibration will be noted in the appropriate logbooks or data sheets.

IX. ATTACHMENTS

CR4052-PD-0250(1) NPDES Water Analysis Equipment

CR4052-PD-0250(2) Monthly Balance Verification

X. REFERENCES

None.

XI. REVISION BLOCK

REV	DATE	REVISION	AUTHOR
0	1/17/01	Original issue.	MLS
1	6/21/01	Updated attachments. Removed microwave power calibration.	JJK

NPDES Water / [illegible]is Equipment

Code 4052 Instrument Number	Crane Tag Number	Instrument Description	Purchased	Manufacturer	Model	Serial Number	Location	Calibration (Note 1)
CR4052-IN-3020		ATOMIC ABSORPTION SPECTROMETER (GF/FLAME)	1994	PERKIN ELMER	300/3300		PW	S
CR4052-IN-4020	No tag.	REFRIGERATOR - 1 OF 2	-	FISHER SCI.	-		Water Lab	NA
CR4052-IN-4100	No tag.	HOOD - 1 OF 2		FISHER SCI.	93-408Q	2704-4	Water Lab	NA
CR4052-IN-4200	No tag.	ASPIRATOR PUMP - 1 OF 2		BOEKEL	177000		Water Lab	NA
CR4052-IN-4230	No tag.	OIL AND GREASE EXTRACTION	1995	ENVIRONMENTAL EXPRESS	ENVIRON. STEP SAVER		Water Lab	NA
CR4052-IN-3000	00164053451000	ATOMIC ABSORPTION SPECTROMETER (FLAME)	1985	PERKIN ELMER	5000	128122	Water Lab	S
CR4052-IN-3010	No tag.	As/Se HYDRIDE SYSTEM	1990	PERKIN ELMER	MHS-10		Water Lab	S
CR4052-IN-4250	No tag.	EDL POWER SUPPLY					Water Lab	NA
CR4052-IN-4260	No tag.	EDL POWER SUPPLY II					Water Lab	NA
CR4052-IN-4300	Not listed on inventory: 164M008383	HOT PLATE/STIRRER	1980	LAB-LINE	NO. 1268	1093-4008	Water Lab	NA
CR4052-IN-4150	Not listed on inventory: 164M008384	pH METER	1986	ORION RESEARCH	EA920	TW38A	Water Lab	S
CR4052-IN-4400	No tag.	AUTOCLAVE	1999	MARKET FORGE	STERILMATIC		Water Lab	X
CR4052-IN-4410	10000029958000	MICROPROCESSOR OVEN	1987	LAB-LINE	3489M, IMPERIAL IV	02970358	Water Lab	NA
CR4052-IN-4500	No tag.	BALANCE, TOP LOAD	1999	METTLER	PB1501-SRS	1118461722	Water Lab	X/Lab
CR4052-IN-4510	No tag.	BALANCE, TOP LOAD	1981	OHAUS	GT4100		Water Lab	X/Lab
CR4052-IN-3030	10000111192000	MERCURY ANALYZER SYSTEM	1984	PERKIN ELMER	MAS 50A	57984	Water Lab	S
CR4052-IN-4600	164M028003	RECORDER	1998	THOMAS SCI.	SERVOGOR 102	AZ5101100000	Water Lab	NA
CR4052-IN-4420	Not listed on inventory: 60036000133000	OVEN		VWR SCI.			Water Lab	NA
CR4052-IN-4430	10000029962000	FURNACE	1987	THERMOLYNE	F30420C	41200516	Water Lab	NA
CR4052-IN-4610	Not listed on inventory: 164M018758	DESCICATING CABINET		FISHER SCI.			Water Lab	NA
CR4052-IN-4620	10000121371000	DESCICATING CABINET	1992	BOEKEL	---	---	Water Lab	NA
CR4052-IN-4520	10000029978000	BALANCE, ANALYTICAL	1987	OHAUS	G160R	001640	Storage	Inactive
CR4052-IN-4700	No tag.	COLIFORM INCUBATOR BATH	1999	PRECISION	MDL-251	699060329	Water Lab	NA
CR4052-IN-4710	No tag.	COLONY COUNTER		LEICA - QUEBEC DARKFIELD	3325	223451	Water Lab	NA
CR4052-IN-4720	164M028044	CULTURE INCUBATOR	1998	HACH	15E	0700498	Water Lab	NA

NPDES Water A[illegible]sis Equipment

Code 4052 Instrument Number	Crane Tag Number	Instrument Description	Purchased	Manufacturer	Model	Serial Number	Location	Calibration (Note 1)
CR4052-IN-3040	00164050714000	TOTAL ORGANIC CARBON ANALYZER	1984	DOHRMANN	DC-80	HD1179	Water Lab	S
CR4052-IN-3050	00164026902000	UV/VIS SPECTROPHOTOMETER	1979	PERKIN ELMER	552	26842	Water Lab	S
CR4052-IN-4730	00164057957000	MICROWAVE DIGESTION SYS.	1989	CEM CORPORATION	MDS -2000	C50236	Water Lab	LAB
CR4052-IN-4110	No tag.	HOOD - 2 OF 2		FISHER SCI.	93-608Q	2704-5	Water Lab	NA
CR4052-IN-4210	No tag.	ASPIRATOR PUMP - 2 OF 2		BOEKEL	177000		Water Lab	NA
CR4052-IN-4740	164M010857	CYANIDE DISTILLATION UNIT	1996	ANDREWS GLASS CO.	MIDI-DIST		Water Lab	NA
CR4052-IN-4030	No tag.	REFRIGERATOR - 2 OF 2	-	AVANTI	-		Water Lab	NA
CR4052-IN-4750	No tag.	WATER BATH	1995	PRECISION	184	12Y6	Snake Pit	NA
CR4052-IN-4800	SC 91038	THERMOMETER: CR4052-IN-3300	---	---	---	9533	Snake Pit	X
CR4052-IN-4810	---	THERMOMETER: CR4052-IN-2300/2500	---	---	---	9110	Water Lab	X
CR4052-IN-4820	---	THERMOMETER: CR4052-IN-2300/2500	---	---	---	9510	Water Lab	X
CR4052-IN-4830	SC 91037	THERMOMETER: SPARE	---	---	---	64620	---	X
CR4052-IN-4840	OPL 91037	THERMOMETER: SPARE	---	---	---	---	---	X
CR4052-IN-4000	164M008376	WATER PURIFICATION SYSTEM	1989	MILLIPORE	---	10566C	Utility Lab	NA
CR4052-IN-4760	164M036412	FLASKSCRUBBER GLASSWARE WASHER	2000	LABCONCO	230V	000910953K	Utility Lab	NA
CR4052-IN-4010	164M003153	AUTOMATIC WATER STILL	1980	STOKES	171-2	78926	Utility Lab	NA
CR4052-IN-4040		REFRIDGERATOR					Utility Lab	NA
CR4052-IN-4530	10000111223000	ANALYTICAL BALANCE	1985	METTLER	AE160	D85657	IR LAB	X/Lab
CR4052-IN-4160	164M008389	ION ANALYZER		CORNING	250		Chromatography Lab	S
CR4052-IN-4170		AMMONIA SPECIFIC ION ELECTRODE		ORION			Chromatography Lab	S
CR4052-IN-2430	164M009621	AUTOSAMPLER		SHIMADZU	SIL-9A	80283DN	Chromatography Lab	S
CR4052-IN-2140	00164053476000	CONDUCTIVITY DETECTOR	1986	WATERS	430	430000659	Chromatography Lab	S
CR4052-IN-2170	164M009602	LC PUMP		WATERS	510		Chromatography Lab	S
CR4052-IN-2100	00164053476001	MULTI-WAVELENGTH DETECTOR	1986	WATERS	490	490001861	Chromatography Lab	S
CR4052-IN-2150	164M009615	TEMP. CONTROL UNIT	1990	WATERS	---	TCM-002038	Chromatography Lab	S

NPDES Water A[illegible]s Equipment

Code 4052 Instrument Number	Crane Tag Number	Instrument Description	Purchased	Manufacturer	Model	Serial Number	Location	Calibration (Note 1)
CR4052-IN-4770	10000050479000	ULTRASONIC CLEANER	1985	BRANSON	B-42	B104548	Chromatography Lab	NA
CR4052-IN-2050	164M036192	SEPARATIONS MODULE	2000	WATERS	2690 XE	G00SM4736M	Chromatography Lab	S
CR4052-IN-4050	1000001739000	REFRIDGERATOR					Snake Pit	NA
CR4052-IN-4310	10000109639000	HOT PLATE/STIRRER	1980	LAB-LINE	NO. 1268		Snake Pit	NA
CR4052-IN-4630	10000017478000	DESCICATING CABINET	1973	BOEKEL	121027	---	Snake Pit	NA
CR4052-IN-4220	No tag.	ASPIRATOR PUMP		BOEKEL	177000		Snake Pit	NA

Calibration Definitions: "Lab" - Laboratory personnel calibrated, "X" - External calibration performed, "S" - Calibrated with calibration standards, "NA" - Not applicable

Monthly Balance Verification

Select	Equipment Number	Crane Tag Number	Equipment Description	Location	Test Weight, g	Acceptable Range, g
	CR4052-IN-4500	SC 095347	Mettler Balance, Top Load	Water Lab	50	+/- 0.1
	CR4052-IN-4510	10000121369000 SC068835	Ohaus Balance, Top Load	Water Lab	50	+/- 0.1
	CR4052-IN-4520	10000029978000 SC057687	Ohaus Balance, Analytical	Storage	INACTIVE	INACTIVE
	CR4052-IN-4530	10000111223000 SC054068	Mettler Balance, Analytical	IR Lab	5	+/- 0.0003
	CR4052-IN-4540	10000111193000 SC051577	Mettler Balance, Analytical	Water Lab	5	+/- 0.0003
	CR4052-IN-4550	10000111224000 SC054211	Mettler Balance, Analytical	Thermal Lab	5	+/- 0.0003
	CR4052-IN-4560	00164050707000 SC049230	Mettler Balance, Analytical	Thermal Lab	INACTIVE	INACTIVE
	CR4052-IN-4570	SC 095346	Ohaus Balance, Top Load	IR Lab	50	+/- 0.1
	CR4052-IN-4580	1000002994300 SC057688	Ohaus Balance, Analytical	Chromatography Lab	5	+/- 0.0003
	CR4052-IN-4590	10000111225000 SC054067	Mettler Balance, Analytical	Chromatography Lab	5	+/- 0.0003

Date	Weight Set (SC #)	Weight, g	Initials	Comments

Training Overview

Explosive Sciences Branch
Naval Surface Warfare Center Crane
300 Highway 361
Crane, IN 47522

December 1, 2000

Approvals:

Name	Nancey Maegerlein
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Signature	Nancey J. Maegerlein
Name	Michelle Spellman
Title	Quality Assurance Officer
Signature	Michelle Spell

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I. SCOPE AND APPLICATION

The purpose of this procedure is to define the training process for Code 4052 personnel.

II. SUMMARY OF METHOD

This method is consistent with ISO 9001 standard requirements.

III. QUALITY ASSURANCE

Quality is assured by distributing the responsibility for document control as follows:

Position	Responsibility
Branch Manager	Maintains personnel files containing training documentation.
	Qualifies employees.
Code 4052 Personnel	Administer training in areas of qualification, verifies training as required.

IV. APPARATUS

Not applicable.

V. SAMPLE HANDLING AND PRESERVATION

Not applicable.

VI. REAGENTS

Not applicable.

VII. PROCEDURE

A. Training Overview

1. New Employee Orientation Training
Each new employee will receive orientation training. Refer to the attachment CR4052-PD-0300(1) for details. After the new employee has completed this initial training, job qualification training begins.

2. Annual Refresher Training
All employees must successfully participate in annual refresher training in the following areas:

a. Explosive Certification
The Branch Manager must observe the behavior and recommend each employee for continued explosive certification on an annual basis. A form is provided and retained by the safety department documenting that the individual has been recommended for certification on all of the procedures associated with explosives in Code 4052. The Branch Manager verifies continued knowledge through a passing test score on the Explosive Certification Training II Test and the Building Safety Orientation Test (refer to CR4052-PD-0300(1)).

b. Chemical Hygiene Plan
The Chemical Hygiene Plan is reviewed and discussed by the team on an annual basis. The Branch Manager orally questions to team to verify knowledge. Satisfied that the group understands the procedure, the Branch Manager qualifies the group as documented in CR4052-PD-0300(2).

3. Job Qualification: Water Testing
For employees involved in water testing, refer to CR4052-PD-0310. This procedure includes initial training and refresher training requirements.

B. Training Administration
All training will be administered by an individual qualified in that particular job.

C. Verification

1. Method of Verification

Job knowledge is verified by the training administrator in a manner appropriate for the particular segment of the training. The training checklists describe specific verification techniques.

If the trainee is unable to pass any portion of this training process, the Branch Manager will determine the appropriate course of action.

2. Documentation of Qualification

After the appropriate portions of the training documentation has been completed, it is reviewed and signed by the Branch Manager. At this point, the employee is qualified for that portion of their job.

D. Assessment of Training Needs

1. Job Qualification Training

The employee and the Branch Manager will determine which Job Qualification Training is appropriate.

2. Additional Training

Additional Training can come from any of the following sources:

a. Code 4052 personnel suggestions
b. Quality audits, Corrective Action Requests, Preventative Action Requests, etc.

Additional training is either documented in the Code 4052 Additional Training Form or in an individual's personal development plan as appropriate.

E. Retraining

Personnel off the job are retrained as determined on a case by case basis.

VIII. DATA ANALYSIS AND REPORTING

A. Record Retention

Training documentation and any written tests administered by Code 4052 in the orientation process will be retained per CR4052-PD-0150.

IX. ATTACHMENTS

CR4052-PD-0300(1) Code 4052 New Employee Orientation Training, 12/1/00

CR4052-PD-0300(2) Chemical Hygiene Plan Annual Review, 12/1/00

CR4052-PD-0300(3) Code 4052 Additional Training Form, 12/1/00

X. REFERENCES

None.

XI. REVISION BLOCK

REV	DATE	REVISION	AUTHOR
0	12/1/00	Original issue.	MLS

Code 4052 New Employee Orientation Training

Employee Name: _____

Training	Provided by:	Training Material	Verification Method	Verified by (2):	Date Completed
Explosive Certification Training I	Safety Department	Family Tests, Interactive Computer Test, Video	Passing Test Scores (1)		
Explosive Certification Training II	Code 4052	NAVSEAINST 8020.9A NAVSEA OP5, Chapter 3 Building Procedure CR4052-2707-0003A	80% Passing Test Score ("Qualification Evaluation for All Families of Explosive Materials")		
Building Safety Orientation	Code 4052	Ordnance Operations of Bldg. 143 CR4052-0143-001 Operations of Building 142 CR4051-142-0012 Standard Operation Procedure for the Demil Facility CR4052-DEMIL-0021	80% Passing Test Score ("Proficiency Evaluation of Explosive Safety Criteria in the Following Explosive Sciences Branch Personnel Occupied Facilities: Demil, Bldg. 143, and Bldg. 142")		
Materials Orientation	Code 4052	Chemical Hygiene Plan	Team Discussion		
FBM Orientation	Code 4052	FBMPI-2000 per D-4052-1002	80% Passing Test Score		
Department Quality Orientation	Code 4052	Quality Assurance, CR4052-PD-0001 Document Control, CR4052-PD-0100 Record Retention, CR4052-PD-0150 Preventative Maintenance, CR4052-PD-0200 Chemical Supply Management, CR4052-PD-0220 Corrective and Preventative Actions, CR4052-PD-0400 Chain of Custody, CR4052-PD-0500 Quality Assurance Plan, Code 405	80% Passing Test Score ("Code 4052 Quality Training")		

(1) Passing test score determined by department administering the test.
(2) Not required by training administered by outside department.

Qualification Certified by:	Date:

Chemical Hygine Plan Annual Review

Employee Name	Review Date

Qualification Certified by:	Date:

Code 4052 Additional Training Form

Description of Training:	
Reason for Training: (Audit #, CAR #, PAR #, etc.):	
Reference Number (SOP#, etc.):	
Date of Training:	
Training Administrator:	
Verification Method:	

Trainees:

Performance Evaluation

Explosive Sciences Branch
Naval Surface Warfare Center Crane
300 Highway 361
Crane, IN 47522

January 19, 2001

Approvals:

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Signature	Nancey J. Maegerlein
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Title	Quality Assurance Officer
Signature	Michelle L. Spellman

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I. SCOPE AND APPLICATION

This procedure describes the Code 4052 Performance Evaluation program for NPDES Water Testing.

II. SUMMARY OF METHOD

Performance evaluation (PE) audits are routinely conducted to ensure data quality. PE audit results are used to evaluate laboratory technician, instrumentation, and analytical system performance.

The ESB laboratory participates in an annual blind Discharge Monitoring Report (DMR) submitted to the Federal EPA as well as quarterly double blind Proficiency Testing reported to Code 095.

This procedure also includes an internal blind testing program whereby samples of known composition are submitted internally to analysts for evaluation.

This method is consistent with ISO 9001 standard requirements.

III. QUALITY ASSURANCE

Quality is assured by distributing the responsibility for document control as follows:

Position	Responsibility
Branch Manager	Review results of performance evaluations testing.
Quality Assurance Officer (QAO)	Review results of performance evaluation testing. Issue CAR/PAR if appropriate.
	Generate and analyze quality control charts.
	Incorporates PE results in the Annual Quality Assurance Summary Report.
Laboratory Managers and Analysts	Performs analysis and documentation according to documented procedures.

IV. APPARATUS

Not applicable.

V. SAMPLE HANDLING AND PRESERVATION

Not applicable.

VI. REAGENTS

Not applicable.

VII. PROCEDURE

A. Routine Tests Performed

The following table summarizes the routine performance testing content:

Test	Procedure	Annual DMR Blind	Quarterly PT Double Blind
Total Solids	CR4052-PD-1240	X	
Ammonia-Nitrogen	CR4052-PD-1230	X	X
Total Cyanide	CR4052-PD-1900	X	X
Oil and Grease	CR4052-PD-1800	X	X
Nitrate – Nitrogen	CR4052-PD-1700	X	X
Cadmium	CR4052-PD-1000/1100/1150	X	X
Copper	CR4052-PD-1000/1100/1150	X	X
Chromium	CR4052-PD-1000/1100/1150	X	X
Lead	CR4052-PD-1000/1100/1150	X	X
Nickel	CR4052-PD-1000/1100/1150	X	X
Silver	CR4052-PD-1000/1100/1150		X
Zinc	CR4052-PD-1000/1100/1150	X	X
Mercury	CR4052-PD-1300	X	X

B. Test Procedure: External performance samples

1. The ESB receives samples. These samples were prepared with a known composition and preserved by an outside laboratory.

2. The ESB analyzes the samples according to the proper procedures for the tests requested.

3. The ESB reports double blind results to customer per CR4052-PD-0600; blind DMR results are reported on the form included with the samples.

4. The customer submits the results to the outside laboratory.

5. The customer provides identification numbers of study and samples to the ESB.

5. The outside laboratory compares results to target values and the performance of other laboratories participating in the study. The outside laboratory then returns an assessment of the ESB data to the customer.

6. The customer sends a copy of the outside laboratory comparison to the ESB with a cover letter summarizing the performance and listing any actions requested.

7. Appropriate CARs will be issued, investigated and documented per CR4052-PD-0400.

C. Test Procedure: Internal performance samples

The ESB periodically has the need to conduct additional internal performance testing. The ESB may conduct internal performance testing for tests not covered in the external testing, certification of a new analyst, modification of a procedure or equipment, etc. The samples for these tests may be purchased or internally prepared. Samples are analyzed according to the appropriate procedures. If Corrective or Preventative action is necessary, CR4052-PD-0400 will then be followed.

VIII. DATA ANALYSIS AND REPORTING

All feedback from the customer and results from the outside laboratory is filed according to CR4052-PD-0150(1).

IX. ATTACHMENTS

None.

X. REFERENCES

None.

XI. REVISION BLOCK

REV	DATE	REVISION	AUTHOR
0	1/19/01	Original issue.	MLS

Chain of Custody: Soil and Water Samples

Explosive Sciences Branch
Naval Surface Warfare Center Crane
300 Highway 361
Crane, IN 47522

February 12, 2001

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Signature	Jacquelyn Karty

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I. SCOPE AND APPLICATION

Sample custody procedures are necessary to provide and maintain data validity and control. Samples must be under the control of the laboratory at all times after their transfer from the sample courier and during sample analysis. A chain-of-custody program provides legal support to the analytical results and tracking for each sample that is brought into the laboratory and during sample analysis.

This procedure describes the method for completing, maintaining, and storing the sample tracking mechanisms for soil and water samples received by the Explosive Sciences Branch (ESB).

II. SUMMARY OF METHOD

Proper sample tracking is accomplished with a Chain-of-Custody (CoC) form and the Inert Sample Log. The CoC form is generated in the field and used to record a sample's identity. The CoC shall accompany samples from the time of sampling until the time they are delivered and logged into the ESB electronic Inert Sample Log.

In addition, some customers require the use of an Internal Chain of Custody (ICoC) record to track a sample from delivery at the laboratory through preparation, analysis, and disposal.

This method is consistent with ISO 9000 standard requirements as well as state and federal testing regulations.

III. QUALITY ASSURANCE

Quality is assured by distributing the responsibility for chain of custody as follows:

Position	Responsibility
Quality Assurance Officer (QAO)	Accept and log samples.
Laboratory Managers and Analysts	Accept, log, analyze, and ship samples as required.

IV. APPARATUS

Not applicable.

V. SAMPLE HANDLING AND PRESERVATION

A. General

The ESB laboratory will not be involved directly in sampling projects except in rare cases, in which at the time a sampling plan will be written. The laboratory may, however, be involved in assisting the client or others in designing and planning the sampling project. The laboratory will recommend such items as the proper sample containers and preservatives to be used, valid sample numbers, matrices and location, the use of background and composite samples, blanks, duplicates, appropriate parameters and analytical methods, sample packaging, handling, and shipment.

The main objective of any sampling effort is to obtain information that can be used to characterize the sample. It is imperative that the specific information desired is defined first. The ESB laboratory will allow for planning of the sampling project and reduce the possibility of wasted effort. If the information is to be used in a regulatory manner for program compliance, it is very important that the correct procedures are used for sampling and analysis. How the information will be used will dictate how to establish the specific project, sampling, analytical, and data objectives.

B. Sample Containers and Preservatives

The ESB laboratory will provide the necessary sample containers and preservatives upon request from any client. The containers provided by the laboratory will be obtained from an independent source. The containers will be provided to the client in the same condition as they were when supplied by the manufacturer. The containers and preservatives will comply with method requirements being utilized for the analysis.

VI. REAGENTS

Not applicable.

VII. PROCEDURE

A. Receiving and Identifying Samples

All laboratory personnel that perform water sample analysis or the Quality Assurance Officer can accept samples delivered to the laboratory. These laboratory personnel will acknowledge the receipt of the sample by signing the Chain of Custody form. If a sample is brought in without a Chain of Custody form, one will be completed and signed by the courier and the laboratory personnel receiving the sample (CR4052-PD-0500(1), CR4052-PD-0500(2)).

The Chain of Custody form is used to record a sample's identity and provide a record showing custody from sampling to delivery. The Chain of Custody shall accompany samples from the time of sampling until the time they are delivered and logged into the ESB electronic Inert Sample Log.

Samples that cannot be related to an associated Chain of Custody because of inadequate, ambiguous, or nonexistent labeling, will be discarded unless the requestor is able to provide immediate identification. Only under those circumstances where sample identification is fairly obvious, will laboratory personnel make a special effort to identify and correlate unidentified samples.

B. Inspecting Samples

Upon receipt of the sample shipment and Chain of Custody forms, the receiving laboratory personnel will inspect all containers, sample documentation, sample identification, sample preservation, and holding time to verify sample integrity. Sample integrity refers to the cumulative end result of those factors which contribute to the overall validity of a sample. Sample integrity is promoted and preserved by adhering to adequate custodial, handling, and identification procedures by those individuals collecting the samples, up to the point of receipt of samples by the laboratory. When the samples are received for testing or analysis they are checked for:

1. Physical damage to samples because of inadequate packing and protection. Physical damage to the sample container may be the fault of the carrier due to abusive handling or may be the fault of the sender because of faulty packaging. If damage to the container is evident, the package will be carefully opened and its contents inspected. In the event of damage to the sample because of damage to the shipping container, the sender will be notified and the invalid sample discarded.

2. Loss of samples because of inadequate or improper sealing. This includes leakage of liquids from vials, loss of particulate material from filters or containers, inadequate sealing of solid absorbent sampling tubes, etc.

3. Contamination of samples due to inadequate separation of sample types or bulk sampling materials.

4. Improper use of special shipping procedures designed to preserve the samples at temperatures other than ambient. Most violations will result in the need to determine the loss of integrity and a decision regarding the disposition of the sample.

Any samples which do not meet this inspection will be rejected and/or the discrepancies noted on the CoC form and in the ESB Inert Sample Log. The receiving laboratory personnel will then sign the Chain of Custody and provide a copy of the Chain of Custody to the courier, if requested. The customer's point of contact will be immediately notified of the discrepancies.

C. Tracking Samples: Inert Sample Log

After the sample is identified and inspected by the ESB laboratory, the sample is entered into the Inert Sample Log, which is maintained on the branch file server and backed up daily. It is then properly stored until analysis is performed.

1. Open the file F:/Code4076/Samp_log/Inert00.xls. This is the Inert Sample Log.

2. Input information into file:

   a. Name of the person receiving the sample
   b. Date the sample was received
   c. Customer Name
   d. Sample identification and description
   e. Analysis requested
   f. Laboratory sample identification number
   g. Analyst assigned to the analysis

3. Save the file

4. After logging in the samples, the laboratory personnel will write the laboratory sample identification number on the sample container with permanent marker.

5. The laboratory personnel will then properly store the sample. The sample will remain secure until it is removed by the individual analyzing the sample.

6. The ESB laboratory will then file the original Chain of Custody form according to CR4052-PD-0150.

D. Additional Sample Tracking: Internal Chain of Custody

When required by the customer, an Internal Chain of Custody (ICoC) form is completed after the samples are entered into the inert sample log. This form will be kept near the place of storage for easy access during sample preparation and analysis. The ICoC is attached, CR4052-PD-0500(3).

Each time a sample is placed in or removed from the storage location, the movement is recorded on the ICoC.

When the ICoC sheet is full, the page number is filled out, a new sheet is initiated, and the full sheet is filed with the CoC forms.

When the project is completed, ICoC sheets are filed with the CoC forms.

E. Shipping Samples

Should sample shipment be required, the following guidelines will be considered:

1. Check the method to determine if packing and shipping instructions are included. If so, follow the Instructions given.

2. Divide samples into appropriate and compatible shipping groups. Liquids will be kept separate from other materials.

3. Select appropriate shipping container and packing material.

4. Make sure that the sample is properly and accurately identified in the Chain of Custody form and that all necessary paperwork accompanies the shipment.

F. Storage and Disposal

Upon completion of an analysis, samples will be stored and/or properly disposed of in accordance with local, state, and federal environmental laws.

VIII. DATA ANALYSIS AND REPORTING

Records are filed per CR4052-PD-0150(1).

IX. ATTACHMENTS

CR4052-PD-0500(1) NSWC, Crane Division, Chain of Custody Form, NPDES Waste Water Samples, 2/12/01

CR4052-PD-0500(2) NSWC, Crane Division, Chain of Custody Form, Sludge and Soil Sampling, 2/12/01

CR4052-PD-0500(3) Code 4052 Internal Chain of Custody Form, 2/12/01

X. REFERENCES

None.

XI. REVISION BLOCK

REV	DATE	REVISION	AUTHOR
0	12/1/00	Original issue.	MLS
1	2/12/01	Updated attachments. Added internal chain of custody.	MLS

NSWC, C[illegible] Division
Chain of Custody Form: NPDES Waste Water Samples

Customer Address:

COMMANDER
CODE 0953 BLDG 3260
NAVSURFWARCENDIV
300 HIGHWAY 361, CRANE IN 47522

Report to:

Nann Stone
Phone No. (812) 854-3382
Fax No. (812) 854-4177

Control Number: _____

Parameters to be Tested	Preservative Used	Hold Time	Laboratory Sample No.	Name of Collector	Time of Collection	Sampling Date	GRAB = G COMP = C	Sample ID	Laboratory Sample No.	Name of Collector	Time of Collection	Sampling Date	GRAB = G COMP = C	Sample ID
NH_3-(N)	H_2SO_4	28 Days												
Cadmium	HNO_3	6 Mo.												
Chromium	HNO_3	6 Mo.												
Copper	HNO_3	6 Mo.												
Lead	HNO_3	6 Mo.												
Nickel	HNO_3	6 Mo.												
Silver	HNO_3	6 Mo.												
Zinc	HNO_3	6 Mo.												
Mercury	HNO_3	28 Days												
Cyanide	NAOH	14 Days												
Oil and Grease	H_2SO_4	28 Days												
NO_3-N	Not Required	48 hours												
Explosives (TNT, HMX, RDX)	Not Required	30 Days												
Hexavalent Chromium	Not Required	24 hours												
E-COLI (4/1 - 10/31 Only)	Not Required	6hours												

Relinquished by:	Date/Time	Received by	Date/Time	COMMENTS:

NSWC, Crane Division
Chain of Custody Form: Sludge and Soil Sampling

Customer Address:

COMMANDER
CODE 0953 BLDG 3260
NAVSURFWARCENDIV
300 HIGHWAY 361, CRANE IN 47522

Report to:

Nann Stone
Phone No. (812) 854-3382
Fax No. (812) 854-4177

Control Number: _____

Parameters	Preservative Used	Hold Time	Laboratory Sample No.	Name of Collector	Time of Collection	Sampling Date	Sample ID	Plastic or Glass	Rush 0008AA	Rush 0008AB
Cadmium	HNO_3	6 mo.						Plastic		
Chromium	HNO_3	6 mo.						Plastic		
Copper	HNO_3	6 mo.						Plastic		
Lead	HNO_3	6 mo.						Plastic		
Nickel	HNO_3	6 mo.						Plastic		
Silver	HNO_3	6 mo.						Plastic		
Zinc	HNO_3	6 mo.						Plastic		
Molybdenum	HNO_3	6 mo.						Plastic		
Arsenic	HNO_3	6 mo.						Plastic		
Selenium	HNO_3	6 mo.						Plastic		
Mercury	H_2SO_4	14 Days						Plastic		
% Total Solids	Not Required	7 Days								
Potassium	HNO_3	6 mo.						Plastic		
NO_3-N	Not Required	48 hrs.						Plastic		
TKN	H_2SO_4	48 hrs.						Plastic		
Phosphorous	H_2SO_4	28 Days						Plastic		
Ammonia-N	H_2SO_4	28 Days						Plastic		

Relinquished by:	Date/Time	Received by:	Date/Time

Code 4052 Internal Chain of Custody Form

Project Name:	Project Leader:	Customer
Job Order Number:	Date:	Customer POC
Charge Number:	Page: of	Address & Phone #

Sample ID	Date	Time	Reason for Handling

Customer Reports

Explosive Sciences Branch
Naval Surface Warfare Center Crane
300 Highway 361
Crane, IN 47522

September 13, 2001

Approvals:

Name	Nancey J. Maegerlein
Title	Branch Manager
Signature	Nancey J Maegerlein
Name	Steve C. Weddle
Title	Quality Assurance Officer
Signature	Steve C Weddle

MASTER

CONTROLLED COPY
NSWC REPOSITORY 08
CODE 405
COPY NO. 3

I. SCOPE AND APPLICATION

This procedure describes the Code 4052 customer data reporting process. Customer data reports are products.

II. SUMMARY OF METHOD

When a customer relationship is established, the requirements for the format and timing of data reporting is defined per CR4052-PD-0350. It is the intention of the ESB to report all data in the most timely, accurate, and understandable way possible.

This method is consistent with ISO 9000 standard and Navy reporting requirements.

III. QUALITY ASSURANCE

Quality is assured by distributing the responsibility for customer reporting as follows:

Position	Responsibility
Branch Manager	Reviews and approves all customer reports.
Quality Assurance Officer (QAO)	Reviews and approves customer reports for NPDES testing.
Laboratory Managers and Analysts	Generates, reviews, and issues customer reports.

IV. APPARATUS

Not applicable.

V. SAMPLE HANDLING AND PRESERVATION

Not applicable.

VI. REAGENTS

Not applicable.

VII. PROCEDURE

A. NPDES Reports

Specific procedures have been established for reporting NPDES data as described in this section.

1. Report Timing and Format

a. Routine NPDES Testing

1) Sludge Testing

Sludge samples are generally received at the beginning of the month. Data is reported to the customer per CR4052-PD-0600(1) as soon as possible.

2) Water Testing

Various water samples are received throughout a given month. The data is compiled and reported by the 10th of the month as stated in the Memorandum of Understanding, (dated 1/11/98, Reference Section) using CR4052-PD-0600(2). This report includes the following tests: Metals, Nitrate-Nitrogen, Ammonia-Nitrogen, Hexavalent Chromium, E-coli, Explosives, Oil and Grease, and Total Cyanide. The inert sample log is used as a checklist to make sure all data is reported.

Explosive water test results are verbally reported per CR4052-PD-1600.

b. Non-routine NPDES Testing

When non-routine NPDES tests are requested, results are included in the monthly report format. If the sample is designated Rush, results will be delivered in 5-7 days; Emergency samples will be reported as soon as possible.

2. Report Approval Process

a. Levels of Approval

Each report must be approved at three levels: Laboratory Manager, Quality Assurance Officer, and Branch Manager.

Each level of approval has the responsibility, upon discovery of a nonconformance, to return the report to the prior level for correction or further return back through the process. A CAR/PAR will be initiated where/when appropriate.

1) Laboratory Manager Approval

The Laboratory Manager review of the report includes but is not limited to following attributes:

a) Check the data reliability: review the logbooks and the spreadsheets to verify that each analysis was performed correctly and that the data is reasonable.

b) Check dates, sample designations, etc, with logbooks to ensure accuracy.

2) Quality Assurance Officer Approval

The Quality Assurance Officer review of the report includes but is not limited to the following attributes:

a) The data is validated per CR4052-PD-0230.

b) The QAO verifies that all forms have been filed out and retained completely.

3) Branch Manager

The Branch Manager review of the report includes but is not limited to the following attributes:

a) Analysis complete within appropriate hold times.

b) Results vs. Detection Limits: Make sure a number below detection limit is not inadvertently reported.

b. Cover Sheet

As each individual approves the report, a cover sheet is signed. The basic cover sheet is attached to this procedure, CR4052-PD-0600(3).

c. Issuing Report

After the report has been approved appropriately, the Laboratory Manager will issue the report to the customer.

B. General Reports

1. Report Formant

Reports generated by Code 4052 outside of the NPDES scope are created in the format given in attachment CR4052-PD-0600(4). This format is consistent with Navy requirements to ensure professional and precise reporting.

Overall formatting guidelines include:

a. The standard font for these reports is Courier 12.
b. Margins are 1" on all sides. The first page must have a 2" top margin to accommodate the letterhead.
c. There are 2 spaces after each period (sentences and numbers).
d. There is 1 space after a set of parentheses, "()".
e. Justification is to the left.
f. Abbreviations are avoided.
g. Enclosures are mentioned in order (for example, Enclosure 1 is mentioned in the body of the report before Enclosure 2).
h. Enclosures numbers are denoted at the bottom right corner.
i. File/codes typically found in reports include:

File/Code	Activity
8000/2	Off Station Correspondence
8000/3	Crane Army
8000/5	Code 09
8000/11	Code 40
8000/12	Code 60
8000/13	Code 70
8000/14	Code 80

j. Every new page of the report must have the subject line at the top of the page with 1 blank line separating the subject line from the report contents.
k. Tables should be centered in the page, when possible. One blank line should be left before and after the table.

l. Paragraphs in the body of the report are numbered according to CR4052-PD-0600(4).

2. Report Approval

After the report is completed, it is printed and approved by the Branch Manager. After the Branch Manager has approved and signed the original report, a date stamp is placed in the upper right side below the Ser number.

3. Report Distribution

a. When a report is completed, it is logged in the Branch logbook.

b. Prior to issuing the original report to the customer, three copies of the full report are made.

1) Author copy: Copy to be retained by the originator of the report.

2) Code 40211: A copy of the report is sent to status accounting.

3) Code 4052 Copy: A copy of the report is retained at the Branch.

c. A Green Board copy of the cover page is stamped with the circulation stamp at the bottom right corner, circulated, and filed according to Navy instructions.

VIII. DATA ANALYSIS AND REPORTING

NPDES completed reports/cover sheets will be stapled and filed together per CR4052-PD-0150(1).

Other reports will be handled according to Navy instructions.

IX. ATTACHMENTS

CR4052-PD-0600(1) Sludge Testing Report, 3/19/01

CR4052-PD-0600(2) Water Testing Report, 3/19/01

CR4052-PD-0600(3) NPDES Report Cover Sheet, 3/19/01

CR4052-PD-0600(4) Code 4052 General Report Format, 3/19/01

X. REFERENCES

Memorandum of Understanding between Code 40 and Public Works, 1/11/98.

XI. REVISION BLOCK

REV	DATE	REVISION	AUTHOR
0	1/19/01	Original issue.	MLS
1	3/19/01	Updated attachments. Added attachment (4) and general report formatting requirements.	MLS
2	9/13/01	Revised to identify reports as products and provide response to non-conformances discovered during approval process. Updated attachments to reflect revision and date.	CAW

EXPLOSIVES SCIENCE BRANCE COL 052 ANALYTICAL REPORT

DATE OF REPORT:	SAMPLING DATE:
SAMPLE ID:	RECEIPT DATE:

TO: NANNETTE STONE

SLUDGE ANALYSES

ANALYSIS	METHOD/ PROCEDURE	LAB NUMBER (N)	DATE ANALYZED	WET SLUDGE RESULT (NOTE 1)	UNIT	DRY SLUDGE RESULT	UNIT
CADMIUM	EPA 3015 SW 846 , SM 311B CR4052-PD-1000 CR4052-PD-1150				MG/L		MG/KG
CHROMIUM	EPA 3015 SW 846 , SM 311B CR4052-PD-1000 CR4052-PD-1150				MG/L		MG/KG
COPPER	EPA 3015 SW 846 , SM 311B CR4052-PD-1000 CR4052-PD-1150				MG/L		MG/KG
LEAD	EPA 3015 SW 846 , SM 311B CR4052-PD-1000 CR4052-PD-1150				MG/L		MG/KG
NICKEL	EPA 3015 SW 846 , SM 311B CR4052-PD-1000 CR4052-PD-1150				MG/L		MG/KG
SILVER	EPA 3015 SW 846 , SM 311B CR4052-PD-1000 CR4052-PD-1150				MG/L		MG/KG
ZINC	EPA 3015 SW 846 , SM 311B CR4052-PD-1000 CR4052-PD-1150				MG/L		MG/KG
MOLYBDENUM	EPA 3015 SW 846 , SM 311B CR4052-PD-1000 CR4052-PD-1150				MG/L		MG/KG
ARSENIC	SM 3114B CR4052-PD-1200				MG/L		MG/KG
SELENIUM	SM 3114B CR4052-PD-1200				MG/L		MG/KG
MERCURY	EPA 245.1 CR4052-PD-1300				MG/L		MG/KG
% TOTAL SOLIDS	EPA 160.2 CR4052-PD-1240				%	---	---
POTASSIUM	EPA 3015 SW 846 , SM 311B CR4052-PD-1000 CR4052-PD-1150				MG/L	#DIV/0!	%
TOTAL NITROGEN (SUM OF TKN & TOTAL NO_3-N)	EPA 300.3, 351.4 CR4052-PD-1700, CR4052-PD-1210				MG/L	#DIV/0!	%
TOTAL PHOSPHORUS	EPA 365.2 CR4052-PD-1220				MG/L	#DIV/0!	%
NITRATE-NITROGEN	EPA 300.3 CR4052-PD-1700				MG/L	#DIV/0!	%
AMMONIA-NITROGEN	EPA 350.3 CR4052-PD-1230				MG/L	#DIV/0!	%

Note 1: [illegible] upon 1kg/l density.

DRY SLUDGE MG/KG = MG[illegible] / (TOTAL S[illegible] .01)

DRY SLUDGE WT. PERCENT (%) = MG/L, NUTRIENT / (% TOTAL SOLIDS) X 100)

CR4052-PD-0600(1), Rev 2

Explosive Science Branch Code 4052
Analytical Analysis

To: Nannette Stone
Date of Report:

Explosive Analysis Results

Analyst:

Detectable Limit: 0.01 mg/l
Method Basis: EPA Method 8330
ESB Procedure: CR4052-PD-1600

Sample ID	Lab ID Number	Date Sampled	Date Received	Date Analyzed	HMX	RDX	TNT

Note: BDL = Below Detectable Limits

CR4052-PD-0600(2), Rev 2
9/13/01

Explosive Science Branch Code 4052
Analytical Analysis

To: Nannette Stone
Date of Report:

Total Cyanide Results

Analyst:

Detectable Limit: 0.005 mg/l
Method Basis: EPA Method 335.3
ESB Procedure: CR4052-PD-1900

Sample ID	Lab ID Number	Date Sampled	Date Received	Date Analyzed	Total Cyanide, mg/l

Note: BDL = Below Detectable Limits

Explosive Science Branch Code 4052
Analytical Analysis

To: Nannette Stone
Date of Report:

Oil and Grease Results

Analyst:

Detectable Limit: 1.4 mg/l
Method Basis: EPA Method 1664
ESB Procedure: CR4052-PD-1800

Sample ID	Lab ID Number	Date Sampled	Date Received	Date Analyzed	Oil and Grease, mg/l

Note: BDL = Below Detectable Limits

Explosive Science Branch Code 4052
Analytical Analysis

To: Nannette Stone
Date of Report:

E-Coli Results

Analyst:

Detectable Limit:
Method Basis: EPA Method 1103.1
ESB Procedure: CR4052-PD-1500

Sample ID	Lab ID Number	Date Sampled	Date Received	Date Analyzed	Colony Count/100ml

Note: BDL = Below Detectable Limits

Explosive Science Branch Code 4052
Analytical Analysis

To: Nannette Stone
Date of Report:

Nitrate-Nitrogen Results

Analyst:

Detectable Limit: 0.1 mg/l
Method Basis: EPA Method 300.0
ESB Procedure: CR4052-PD-1700

Sample ID	Lab ID Number	Date Sampled	Date Received	Date Analyzed	Nitrate-Nitrogen, mg/l

Note: BDL = Below Detectable Limits

Explosive Science Branch Code 4052
Analytical Analysis

To: Nannette Stone
Date of Report:

Ammonia-Nitrogen Results

Analyst:

Detectable Limit: 0.03 mg/l
Method Basis: EPA Method 350.3
ESB Procedure: CR4052-PD-1230

Sample ID	Lab ID Number	Date Sampled	Date Received	Date Analyzed	Ammonia-Nitrogen, mg/l

Note: BDL = Below Detectable Limits

CR4052-PD-0600(2), Rev 2
9/13/01

Explosive Science Branch Code 4052
Analytical Analysis

To: Nannette Stone
Date of Report:

Hex Chrome Results

Analyst:

Detectable Limit: 0.005 mg/l
Method Basis: EPA Method 218.4
ESB Procedure: CR4052-PD-1400

Sample ID	Lab ID Number	Date Sampled	Date Received	Date Analyzed	Hex Chrome, mg/l

Note: BDL = Below Detectable Limits

From: Code 4052 (Louis Schwenk)
Phone: 854-5511 Fax: 854-5054

To: Code 095 (Nannette Stone)
Phone: 854-3382 Fax: 854-4177

Date: _____

Subject: NPDES AND OTHER PUBLIC WORKS SAMPLES ANALYSIS RESULTS FOR THE MONTH OF _____.

1. As requested in the Memorandum of Understanding (MOU) between Code 40 and Code 09 analysis data results are being forwarded to Code 095 by means of this facsimile.

2. Data included:

Data	Included
Total solids	
Potassium	
Nitrate-nitrogen	
Total cyanide	
Oil and Grease	
Ammonia-nitrogen	
Total kjeldahl nitrogen	
Total phosphorous	
Hexavalent chromium	
Metals	
E-coli	
Explosives	

REPORT REVIEWED BY:	DATE:
REPORT REVIEWED BY: QA/QC OFFICER	DATE:
REPORT REVIEWED BY:	DATE:

Code 4052 General Report Format

file code 8000/?
our code/report s/n Ser 4052/????
Refer to CR4052-PD-0600 for code listing. The 2nd line must be flush right and the 1st line aligned directly above line 2.
MEMORANDUM *(ALL CAPS) There are 2 blank lines between Ser line and MEMORANDUM line. 1 blank line after MEMORANDUM line.*
From: 4052 *2 blank spaces after colon.*
To: Name *Everything between here and the body of the report*
Address *is aligned directly under code above.*
1 blank line to separate address from subject line.
Subj: SUBJECT LINE MUST BE ALL CAPS
1 Blank line to separate subject line from references.
Ref: (a) First reference
(b) Second reference
1 blank line to separate references from enclosures.
Encl: (1) First enclosure *Confirm that this title matches*
(2) Second enclosure *title on the enclosure.*
1 blank line to separate enclosures from body of the report.
1. Background *Indent the paragraph line with 4 spaces.*
1 blank line to separate paragraph title and data.
a. Sub paragraphs are indented 4 additional spaces and identified with a small case letter. The second line of subparagraphs will continue to the left margin without indentation.
b. If subparagraphs are needed, use at least two.
1 blank line to separate report information from next paragraph.
2. Introduction
1 blank line to separate paragraph title and data.
Report information here.
1 blank line to separate report information from next paragraph.
3. Analytical Test Procedures
1 blank line to separate paragraph title and data.
Report information here.
1 blank line to separate report information from next paragraph.
4. Results and Discussion
1 blank line to separate paragraph title and data.
Report information here.
1 blank line to separate report information from next paragraph.
5. Closing (POC Paragraph)
1 blank line to separate paragraph title and data.
The closing paragraph must contain the POC, their code, and their extension. Never let proper names continue onto two lines.
4 Blank lines here

NANCEY J. MAEGERLEIN *Name is in all caps*

Glassware Cleaning Procedure

Explosive Sciences Branch
Naval Surface Warfare Center Crane
300 Highway 361
Crane, IN 47522

January 1, 2001

Approvals:

Name	Nancey J. Maegerlein
Title	Branch Manager
Signature	Nancey J. Maegerlein
Name	Jacquelyn J. Karty
Title	Chemist
Signature	Jacquelyn J. Karty

MASTER

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CODE 405
COPY NO. 3

I. SCOPE AND APPLICATION

This document provides the proper cleaning procedure of all glassware in the Explosive Science Branch, Code 4052.

II. SUMMARY OF METHOD

These procedures describe the method for removing surface residuals, washing and drying, and storage of the glassware.

III. QUALITY ASSURANCE

Not applicable.

IV. APPARATUS

The following pieces of apparatus are used in this analysis:

- Flask Scrubber Glassware Washer, Model 230V

V. SAMPLE HANDLING AND PRESERVATION

Not applicable.

VI. REAGENTS

The following reagents are required in this analysis.

A. Dish detergent, concentrated low foaming cleaning agent.

VII. PROCEDURE

A. Rinsing Glassware After Use

Glassware is rinsed after use to minimize the contamination of the dishwasher and the possibility of personnel exposure.

1. Dye-Contaminated Glassware: Rinse 3 times with methanol.
2. Organic-Contaminated Glassware: Rinse with tap water.

B. Removing Surface Residuals

Any tape, label or marker stains must be removed prior to placing in the dishwasher. Tape and labels may be removed with a knife, while marker stains can be removed with acetone.

C. Washing/Drying the Glassware

1. Place all glassware onto steel or plastic-coated racks.
2. Add soap to the dishwasher, both sides of the soap compartment.
3. Close and lock the door.
4. Scroll through programs using the "Select Program" button. Select the "Glass Plus High Heat" cycle.
5. Verify that the "Pure" button has been selected to use DI water rinse.
6. Press "Start" to run the dishwasher.
7. Turn sign to "Clean".

D. Removal and Storage of Glassware

1. After the cycle is complete, unload the dishwasher onto the transporting rack.
2. Turn sign to "Dirty"

3. Return clean glassware to storage cabinets in the appropriate sections or to the appropriate segregation tubs (Oil and Grease analysis, Hexavalent chromium analysis, and Cyanide analysis).

   Note: Store volumetric flasks with caps in place to prevent contamination.

E. Rinsing the Glassware Prior to Use

All glassware should be rinsed three times with the solvent to be used in the particular analysis to be performed.

VIII. DATA ANALYSIS AND REPORTING

None.

IX. ATTACHMENTS

None.

X. REFERENCES

Manual of Analytical Methods for the Analysis of Pesticides in Humans and Environmental Samples.

Flask Scrubber Glassware Washer, Model 230V Operations Manual

XI. REVISION BLOCK

REV	DATE	REVISION	AUTHOR
0	1/1/01	Original issue.	MLS