# ATTACHMENT D
# QUALITY ASSURANCE PROJECT PLAN
# FINAL DESIGN REPORT

## WAUKEGAN MANUFACTURED GAS AND COKE PLANT SITE
## WAUKEGAN, ILLINOIS

US EPA RECORDS CENTER REGION 5
394832

## ATTACHMENT 1

## LABORATORY
## STANDARD OPERATING PROCEDURES

| *Title* | | *SOP Number* |
|---|---|---|
| 1) | Sample Receipt and Sample Control | NC-SC-0005 |
| 2) | Quality Control Program | QA-003 |
| 3) | Statistical Evaluation of Data and Control Charts | NC-QA-0018 |
| 4) | Metals Digestion (Soil) | CORP-IP-0002NC |
| 5) | Metals Digestion (Aqueous) | CORP-IP-0003NC |
| 6) | Metals Analysis (Soil and Aqueous) | CORP-MT-0001NC |
| 7) | PAHs/SVOCs Extraction | CORP-OP-0001NC |
| 8) | SVOCs Analysis | CORP-MS-0001NC |
| 9) | PAHs Analysis (SIM) | NC-MS-0015 |
| 10) | TCLP Extraction | CORP-IP-0004NC |
| 11) | VOCs/BTEX Preparation and Analysis | CORP-MS-0002NC |
| 12) | Mercury Preparation and Analysis | CORP-MT-0005NC |
| 13) | Total Cyanide Preparation | NC-WC-0032 |
| 14) | Total Cyanide Analysis | NC-WC-0031 |

**STL STANDARD OPERATING PROCEDURE**

**TITLE: SAMPLE RECEIVING AND SAMPLE CONTROL**

**(SUPERSEDES: REVISION 6, 09/02/99)**

| | | |
|---|---|---|
| Prepared by: | | 6/27/01 Date |
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# 1 SCOPE AND APPLICATION

1.1 It is the responsibility of Sample Receiving and Control personnel to perform the procedures described herein in full compliance with this SOP.

1.2 It is the responsibility of the Laboratory Director, QA Manager, and departmental Supervisor of the facility to assure that the procedures described are performed in full compliance with this SOP. It is also their responsibility to supply adequate training, materials, and equipment to enable personnel to perform this SOP correctly.

1.3 Analyst

1.3.1 It is the responsibility of the analyst to provide the correct request(s) for bottles to the sample custodian by using the QuantIMS program, PSR024.01 (as described in section 5.3) and to return all bottles to the custodian.

1.4 Sample Custodian

1.4.1 It is the responsibility of the sample custodian or designee to fill all bottle requests in a timely fashion and document the transfers on the request/return forms (Appendix 17.1.6).

1.4.2 It is the responsibility of the sample custodian or designee to correctly document the bottle information required (Appendix 17.1.6).

1.4.3 It is the responsibility of the sample custodian or designee to ensure that the returned bottle is the same as the one relinquished and to return it to the proper storage area.

1.4.4 This document accurately reflects current laboratory standard operating procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary.

# 2 SUMMARY OF METHOD

2.1 Not applicable.

# 3 DEFINITIONS

3.1 Sample Custodian refers to sample control personnel or designee.

3.2 Refer to the glossary in the Laboratory Quality Manual (LQM), latest version

# 4 INTERFERENCES

4.1 Not applicable.

# 5 SAFETY

5.1 Procedures shall be carried out in a manner that protects the health and safety of all STL associates.

5.2 Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. If personnel are required to perform any portion of the procedure in laboratory areas, appropriate personal protective equipment and precautions must be utilized. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately. {VITON gloves may be worn when halogenated solvents are used for extraction or sample preparation, nitrile gloves may be used when other solvents are handled. [Note: VITON is readily degraded by acetone; all solvents will readily pass through disposable latex rubber gloves.]}

5.3 The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory. {The following specific hazards are known} The following specific hazards are known:

5.3.1 The following materials are known to be corrosive: Sulfuric Acid, Nitric Acid, Hydrochloric Acid, Sodium Hydroxide.

5.4 Exposure to chemicals must be maintained as low as reasonably achievable, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.5 The preparation of standards and reagents {and glassware cleaning procedures that involve solvents such as methylene chloride} will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.6 All work must be stopped in the event of a known or potential compromise to the health and safety of a STL associate. The situation must be reported immediately to a laboratory supervisor.

5.7 This document accurately reflects current standard operating procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary by the laboratory QA department.

# 6 EQUIPMENT AND SUPPLIES

6.1 Thermometers

6.2 PPE such as gloves, lab coats, safety glasses, etc.

6.3 Utility knives

6.4 PH paper

6.5 Copier, printer, computer and label generator

6.6 Carts

# 7 REAGENTS AND STANDARDS

7.1 Not applicable.

# 8 SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Not applicable.

# 9 QUALITY CONTROL

9.1 Nonconformance and Corrective Action

9.1.1 Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the facility QA Manager.

# 10 CALIBRATION AND STANDARDIZATION

10.1 Not applicable.

# 11 PROCEDURE

11.1 Any deviations from this procedure must be documented as a nonconformance, with a cause and corrective action described.

11.2 The procedures listed in this document describe the responsibilities of Sample Control personnel in ensuring that data is transmitted correctly from the client samples to all personnel involved with sample analysis and review.

11.3 The intent of the sample custodian maintenance program is to show custody of individual bottles based on workorder number as well as bottle control numbers. This program acts as an internal chain of custody.

11.4 The sample control group opens each cooler and removes the enclosed sample documents. Coolers are prioritized based on rush status and expirable tests. If a COC (chain-of-custody) is marked rush, the following occurs:

24 hour TAT – flag with red folder
48 hour TAT – flag with blue folder
72 hour TAT – flag with yellow folder
1 week TAT – flag with green folder

11.5 If tests on the COC are expirable, the cooler is marked with a manila folder.

11.6 Rush and expirable coolers are to be unpacked first and logged as soon as possible. The lab groups are to be notified with any rush 72 hours or less.

11.7 The following information on the Cooler Receipt/ Narrative Form (Appendix 17.2.1).

11.7.1 Presence of the custody seals on the outside of the cooler

11.7.2 Presence of the custody papers inside the cooler

11.7.3 The custody papers were properly filled out (ink, signed, match labels)

11.7.4 The custody papers were signed in the appropriate place

11.7.5 Presence of the shipper's packing slip

11.7.6 Presence of packing material information: if yes, type of packing material

11.7.7 Conditions of samples at receipt (chilled, etc.).

11.7.7.1 If temp vial is present, it is used to take the temperature. The temperature of the temp vial is taken as soon as it is removed from the cooler. If a temp vial is not present, proceed to section 11.7.7.2.

11.7.7.2 When a temp vial is not present the temp is taken by placing the thermometer probe between the coolant and the sample(s). If a coolant is not present, proceed to section 11.7.7.3.

11.7.7.3 If no coolant is in the cooler, the thermometer probe is placed between two sample bottles and the temperature recorded.

11.7.7.4 If the temperature is outside 4°C ± 2°C, the anomaly is recorded on the cooler receipt form. The project manager is contacted when the temperature is >6°C.

11.7.8 Bottles sealed in separate plastic bags

11.7.9 Condition of bottles upon receipt (good condition, broken, etc.)

11.7.10 Complete bottle labels (date, time, client ID)

11.7.11 Information on bottle labels and tags agree with custody papers

11.7.12 Correct bottles used for the tests indicated

11.7.13 VOA bottles were checked for the presence of air bubbles. Any bubbles exceeding 6 mm in diameter are narrated and the PM is contacted.

11.7.14 Sufficient amount of sample sent in each bottle

11.7.15 Samples were received via overnight courier, client drop off, or other means

11.7.16 pH's are taken, on all preserved samples less Volatiles, TOC, and TOX by removing sample lids and using a droplet of sample from in the lid to test the pH. The pH's are then recorded on the cooler receipt form. The pH paper strips are then discarded.

11.7.16.1 In determining if the sample is preserved to the correct pH for Navy samples, the sample custodian or receiving personnel must take an aliquot of sample out of the sample container either by pouring out a small aliquot or using a disposable pasteur pipette and place a drop of the sample on a pH paper strip.

11.7.17 Purchased prepared vials of preservatives are used if samples are not at the correct pH. The pH is adjusted by adding the appropriate preservative in 5 mL increments up to a maximum of 20 mL or unless there is a reaction. Sulfides are preserved with 5 mL Sodium hydroxide and 1 mL Zinc acetate. The pH adjustment is noted on the cooler receipt form.

11.7.18 The concentrations of the preservatives used:

4N Sodium Hydroxide
1N Zn Acetate
1:1 HCL (18%)
1:4 $HN0_3$ (18%)
1:2 $H_2SO_4$ (33%)

11.7.18.1 If the pH of Navy samples are adjusted, the sample custodian or receiving personnel must record on the cooler receipt form the laboratory assigned reagent ID number.

11.8 The Sample Control person is to remove all sample containers. Any broken, leaking, or dirty sample containers are to be placed inside the fume hood. Dirty sample containers are to be cleaned appropriately, so as not to contaminate the sample storage area. The Sample Control person is to wear disposable latex gloves, safety glasses, and a lab coat while handling any samples.

11.9 Any volatile sample(s) suspected (e.g., odor) or known (client information or site history) to be high in volatile concentration, the volatiles department will be contacted for pick-up and segregation of sample(s).

11.10 The Sample Control person is to examine all documents and compare information from sample container labels and Chain-of-Custody Records to insure that there is no discrepancy between documents, ensuring that all documents are properly completed and signed.

11.11 If any problems or discrepancies are noted during the sample receiving process that compromise sample integrity, such as limited sample volume, sample identification cannot be determined from the COC, incorrect pH levels (or preservatives if known), or broken, leaking samples, the Project Manager is immediately notified. They in turn will contact the client in an attempt to solve discrepancies.

11.12 Expirable tests (hold time 48 hours or less) must be written on the top of the bottles from which they are to be analyzed. If more than one method exists for the analysis, the method must also be written. These bottles designated for expirable tests will be given directly to the wet chem lab group.

11.13 All solid /soil samples received are split off for the total solid analysis. Splitting these samples is the responsibility of the receiving group. A small portion (approx. 5-10 grams) from each sample is put into a small plastic snap-top container designated for the TS analysis. If the TS container is not labeled with a QuantIMS label at the time of splitting off, the TS container must be labeled with handwritten client ID. Containers designed for VOC analysis must not be opened/used for TS aliquot. When only one solid container is received for VOC analysis, receiving group must **not** split off because of possible contamination or possible lost volatiles. An empty TS container with a QuantIMS label is given to the VOC analysis group for each solid. The VOC group will aliquot for the TS when they open container for analysis. TS plastic containers are placed into baggies by lot (project) and the baggies are put into a box inside the walk-in cooler door.

11.14 If all samples recorded on the Chain-of-Custody Record were received by the laboratory and there are no problems observed with the sample shipment, the Sample Control person will sign the Chain-of-Custody Record in the "Received for Laboratory by:" box on the document. If problems are noted, sign for shipment and note the problems. All discrepancies are recorded on Cooler Receipt Form.

11.15 A quote must reflect what is on the chain-of-custody. Any discrepancies must be resolved by the project manager. Likewise, if there is not an associated quote in QuantIMs, the samples are placed on hold until a quote is completed by the project manager.

11.16 In the event that a project is on hold until the next day or longer, all associated paperwork is placed into a black folder and all samples and black folder are put into cold storage. Any project that is on hold must be recorded on the dry-erase board posted on walk-in cooler door.

11.17 The Sample Control person will enter each sample into the laboratory computer (QuantIMS), where a unique lot number is assigned to each project received, and sequential sample numbers are designated for each client identification within the lot.

11.17.1 Lot Numbers: The lot number is nine characters in length and is based on the date of receipt. Lot number A9J010121 is described as follows:

**A** - STL location where the samples were received.

(A = North Canton, B = Tampa, C = Pittsburgh, etc.)

**9** - Last digit of the year (i.e. 1999).

**J** - Month (i.e. A = January, B = February, J = October, etc.)

**01** - The next 2 numeric characters identify the day of the month, in this case, the first day of the month.

**0121** - The next 4 numeric characters are the sequential assignment of numbers specific to each lot received. Each day the first lot logged in receives the number "0101", the second lot receives the number "0102", etc..

For example:

If four bottles were submitted under Client ID numbers AB100-AB103 and the laboratory identification number generated by the computer is A9K100101, then the assigned laboratory number recorded on the Sample Log-In Sheet would be as follows.

| Client ID Sample Number | Assigned Laboratory Number |
|---|---|
| AB 100 | A9K100101-001 |
| AB 101 | A9K100101-002 |
| AB 102 | A9K100101-003 |
| AB 103 | A9K100101-004 |

11.17.2 Sample Numbers: The samples in each lot are assigned a sample number that is attached to the lot number and are reset at each new lot. For example: the first and second samples in the lot above are labeled A9J010121-001 and A9J010121-002.

11.17.3 Sample Suffixes: Each sample also has a 1 character field (which is not a required field for all samples) called the suffix which identifies the sample as specified below.

| | |
|---|---|
| Client Sample | no suffix |
| Method Blank | B |
| Laboratory Control Sample | C |
| Laboratory Control Sample Duplicate | L |
| Matrix Spike | S |
| Matrix Spike Duplicate | D |
| Sample Duplicate | X |
| Serial Dilution | P |
| Sample Confirmation | Y |
| Post Digestion Spike | Z |
| Re-analysis | I |

Example: A9J010121-001X is a sample duplicate for sample A9J010121-001.

11.17.4 Work Order Numbers: Each test requested by the client for an individual sample receives an individual 8 digit work order number assigned by QuantIMS. Work order number A5WE1-2-1C is described as follows:

**A5WE1** - In addition to the three digit sample identification described in 4.7.2 (i.e. - 001 and - 002), the first 5 characters of the work order number also identifies each unique sample. This identification is generated in QuantIMS using a sequential logic that is beyond the scope of this SOP to describe.

**2** - The "modifier" indicates the type of run. In this case this is the second time the sample had to be run. If it needs reprepped and run again, the number would indicate a "3". The original analysis work order number assigns "1" to the modifier position.

**1C** - The "suffix" is the identification of the specific test for that sample. The suffix in this case is not always sequential, but is unique to the test to be performed on the sample.

Example: A5WE1-2-1C is the assigned 8 digit work order number for the reanalysis of the chloride test on the sample A5WE1. A5WE1-1-05 could be the 8 digit work order number for the analysis of SW846 8270 on sample A5WE1.

11.17.5 Each sample container with the same client ID has a unique number. Each container will be labeled with the same 5 digit work order number and then will contain a suffix beginning with – 001, -002, -003, etc. For example, if 5 containers are submitted from the same sample point and the LIMS-generated work order number is CREE4, LIMS will generate 5 labels: CREE4-001, CREE4-002, CREE4-003, CREE4-004, CREE4-005. The specific bottle number is the number used for sample request/removal paperwork.

11.17.6 Expirable tests must be given to the lab groups the day they are received. The expirable test/method is written on top of the bottle and the bottle must be put in the red bin designated for expirables. The work order or sample ID must be recorded on the expirable logsheet – also must record the test to be run, special method if necessary and the initials of the person relinquishing the sample. The wet chem lab group checks this bin throughout the day and is responsible for signing out the sample container when they take it.

11.17.7 Once all sample containers have been properly labeled and all the information has been recorded by the Sample Lot Summary, the Sample Control person will place the samples into the proper storage locations. These locations are as follows:

11.17.8 Organic extractable samples (Semivolatiles, Pesticides/PCBs) are to be placed into the walk-in refrigerators located in Sample Receiving.

11.17.9 Volatile samples are to be stored in the double-door refrigerator located in the Sample Custodian area.

11.17.9.1 Samples known or suspected to be of high concentration are not stored in these refrigerators. The applicable volatile group is contacted to obtain the samples for segregation.

11.17.10 Inorganic samples are to be placed into the walk-in refrigerators located in Sample Receiving.

11.18 Preserved metal samples are placed in a non-refrigerated room located in the Sample Custodian area. Metals samples that need to be lab filtered and preserved are stored in the walk-in cooler. All metals for Navy projects are stored in the walk-in cooler.

11.19 One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.20 Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.21 For clients who request a show of sample transfer from sample receipt to storage, a sample control record is completed (see Appendix 17.2.4 or Appendix 17.2.5). STL LIMS will generate this record for Expanded Deliverable and CLP designated samples. This record is also referred to as an internal chain of custody (COC). The form is completed as follows:

11.21.1 Laboratory sample number - record/list the individual five digit work order number in this column. List all pertaining samples in the project lot. Use an additional sheet if necessary. Do not record multiple lots on a sample control record.

11.21.2 Transferred by - record name of person making the transfer

11.21.3 Date - record date of sample transfer

11.21.4 Entered - "X" or "√" since samples are already logged into the LIMs.

11.21.5 Removed - leave blank since samples are not being removed

11.21.6 Reason - record "storage"

11.21.7 Date returned - leave blank

11.22 The completed sample control record is attached to the summary package. The sample control record can be manually printed using the SAM S31 command in QuantIMS. Note: The report package for the lot must be "D" (Expanded Deliverable) or "C" (CLP) for the report to print.

11.23 Samples are requested by an analyst through the QuantIMS program PSR024.01. This program is accessed from the Sample Receiving Menu (SAM) by selecting option S24 (Sample Removal Requests).

Bottles are requested based on method code, workorder number, prep code, QA batch number, lot number, or method group.

11.24 Each bottle has an associated lot number, sample workorder number, and bottle suffix number (Appendix 17.2.9).

11.25 When an analyst requests bottles and exits the request program, a requisition (Appendix 17.2.6) prints in the custodian's work area. This requisition identifies the requestor and the method/parameter requested. The sample custodian fills the requisition, recording each bottle number on the form. The bottle(s) is/are signed out to the custody of the requestor by indicating the name and the date of transfer. The request is relinquished with the custodian's initials and accepted by the requestor's initials.

11.26 When bottles are returned, the sample custodian records the return on the original requisition form and re-enters custody of the bottles to the sample control area. The custodian initials and dates the return on the form (Appendix 17.2.6).

11.27 When sample bottles are consumed in the analysis process, the empty container is returned to the custodian. The custodian marks a "C" by the appropriate sample on the request form to indicate a consumed sample (Appendix 17.2.6).

11.28 Samples returned after the custodian has left at the end of the day are placed in the walk-in cooler by a custodian designee and recorded as received by the custodian the next working day.

11.28.1 All request forms remain in the sample custodian area while samples are being analyzed. The final form is also kept in the sample custodian area after samples have been analyzed and reported.

11.28.2 When a sample custodian is not available, a designee gets the samples, and all request paperwork is completed properly.

11.29 Subcontracting of samples

11.29.1 Samples that are logged but not analyzed at the laboratory are subcontracted to different laboratories for analysis including other STL facilities.

11.29.2 The LIMs system will automatically print a Sample Analysis Requisition for these samples upon completion of the log-in process (Appendix 17.2.7).

11.29.3 This form contains information necessary for sample analysis. The original form is sent to the subcontracted laboratory and a copy is attached to the summary package. The Sample Analysis Requisition form must have a relinquished signature with a date and time. Any additional information necessary for sample analysis must be handwritten on the form (e.g. list of compounds, homogenizing of samples, limited quantity, etc.). In order to track subcontracted samples, the lab purchase order number on the Sample Analysis Requisition form must be recorded in the subcontracted sample PO book located in the receiving log-in area.

11.29.4 For samples sent to a non QuantIMS lab a chain of custody form is filled out and accompanies the samples.

11.29.5 A sample analysis request (SAR) can be printed from LIMS by entering the Lot Number. The SAR form can be found on Main Screen on receiving computer terminals.

## 12 DATA ANALYSIS AND CALCULATIONS

12.1 Not applicable.

## 13 METHOD PERFORMANCE

13.1 Training Qualifications:

13.1.1 The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

13.1.2 The only personnel authorized to execute this SOP are the Sample Log-In persons.

## 14 POLLUTION PREVENTION

14.1 This method does not contain any specific modifications that serve to minimize or prevent pollution.

## 15 WASTE MANAGEMENT

15.1 All samples may be disposed of 30 days after the report date except for those samples associated with special client retention. Shelves are purged in chronological order. All lots on a specific shelf must be noted. If a lot can be disposed of, a disposal date must be recorded.

15.2 Disposal dates are recorded on a print-out of lots according to a storage location. When clearing samples that cannot yet be disposed of because of special client retention, samples are boxed or stored on carts. Stored samples must have a specific date listed in which samples can be disposed of, or a note that indicates "SAVE" and client name or reason.

15.3 All lots assigned to a certain shelf can be obtained from QuantIMS.

15.3.1 UTL – "Enter"

15.3.2 Type "wrk" – "Enter"

15.3.3 Type "2" by option

15.3.4 Choose one query name and "Enter"

15.3.5 *SLOIS for metals shelves*

15.3.6 CLOIS for cooler shelves C1 – C272

15.3.7 WLOIS for cooler shelves W1-163

15.3.8 Type "1" next to "select records"

15.3.9 Enter the shelf location 3x where prompted (appears on two different screens). Then hit "Enter".

15.3.10 Dates need to be updated every four to six months so shelf locations only print most recent lots assigned.

15.3.11 "F3" to run query and "Enter".

15.3.12 At save definition type "Y" and run option "2" and "Enter".

15.4 Solid samples that can be disposed of are boxed and labeled "SOLIDS NOW."

15.5 Liquid wastes that can be disposed of are boxed and labeled "LIQUID NOW." These boxes are taken to the facility waste building and drummed by the Health and Safety Coordinator or designee.

15.6 Water samples that can be disposed of are placed on carts and purged down the drain in one of the following areas: sample receiving, wet chemistry, or extractions.

15.7 Solvent waste must be disposed of in clearly labeled waste cans.

15.8 Acid waste must be collected in clearly labeled acid waste containers. Solid materials (gloves, soiled paper products, etc.) are placed in the solid debris container. Do not put liquids in the solid waste container.

15.9 Refer to the Laboratory Sample and Waste Disposal plan.

15.10 Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of STL. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by an annual refresher training.

## 16 REFERENCES

16.1 STL Quality Management Plan (QMP), current version.

16.1.1 STL Laboratory Quality Manual (LQM), current version.

16.2 Associated SOPs and Policies, latest version

16.2.1 QA Policy, QA-003

16.2.2 Navy/Army SOP, NC-QA-0016

## 17 MISCELLANEOUS

17.1 Wherever "Sample Control" is mentioned in all SOPs, it is assumed to include the sample custodian or any alternate that is designated by the Sample Control Coordinator.

17.2 Appendix:

17.2.1 Cooler Receipt Form/Narrative

17.2.2 Preservative Preparation

17.2.3 Preservative Requirements

17.2.4 Internal Chain of Custody – CLP

17.2.5 Internal Chain of Custody – Regular Production Organic LIMS generated

17.2.6 Sample Custodian Removal Request

17.2.7 Sample Analysis Requisition

17.2.8 Subcontracted PO Logbook

17.2.9 Laboratory Generated Bottle Label

# 17.1.1

# Example

# Cooler Receipt/Narrative Form

# STL Cooler Receipt Form/Narrative

## North Canton Facility

Client:_____ Project:_____ Quote#:_____

Cooler Received on:_____ Opened on:_____ by: _____

(Signature)

Fedx ☐ Client Drop Off ☐ UPS ☐ Airborne ☐ Other:_____

Cooler ☐ Safe ☐ Foam Box ☐ Client Cooler ☐ Other:_____

STL Shipper No#:_____

1. Were custody seals on the outside of the cooler and intact? Yes ☐ No ☐

   If YES, Quantity_____ Location_____

   Were the custody seals signed and dated? Yes ☐ No ☐ NA ☐

2. Shipper's packing slip attached to this form? Yes ☐ No ☐

3. Were custody papers included inside the cooler and relinquished? Yes ☐ No ☐

4. Did you sign the custody papers in the appropriate place? Yes ☐ No ☐

5. Packing material used:

Peanuts ☐ Bubble Wrap ☐ Vermiculite ☐ Foam ☐ None ☐ Other :_____

6. Cooler temperature upon receipt _____ °C (see back of form for multiple coolers/temp)

METHOD: Temperature Vial ☐ Between Coolant & Sample Container ☐ Against Bottles ☐

COOLANT: Wet Ice ☐ Blue Ice ☐ Dry Ice ☐ Water ☐ None ☐

7. Were all the bottles sealed in separate plastic bags? Yes ☐ No ☐

8. Did all bottles arrive in good condition (Unbroken)? Yes ☐ No ☐

9. Did all bottle labels and tags agree with the custody papers? Yes ☐ No ☐

10. Were samples at the correct pH? Yes ☐ No ☐ NA ☐

11. Were correct bottles used for the tests indicated? Yes ☐ No ☐

12. Were air bubbles >6 mm in any VOA vials? Yes ☐ No ☐ NA ☐

13. Was a sufficient amount of sample sent in each bottle? Yes ☐ No ☐

Contacted PM _____ Date:_____ by:_____ via Voice Mail ☐ Verbal ☐ Other ☐

Concerning:_____

| √ | MACRO | MACRO |
|---|---|---|
| | ***1. CHAIN OF CUSTODY*** | |
| | SR1A | Samples were received under proper custody procedures and without discrepancies. |
| | SR1B | The chain of custody and sample bottles did not agree. The following discrepancies occurred_____ |
| | ***2. SAMPLE CONDITION*** | |
| | SR2A | Sample(s)_____ were received or requested after the recommended holding time had expired. |
| | SR2B | Sample(s) _____ were received with insufficient volume |
| | SR2C | Sample(s)_____ were received in a broken container. |
| | ***3. SAMPLE PRESERVATION*** | |
| | SR3A | Sample(s) _____ were further preserved in sample receiving to meet recommended pH level(s). |
| | SR3B | Sample(s)_____were received with bubble > 6 mm in diameter (cc: PM) |
| | ***4. NCM*** | |
| | SR4A | NCM has been generated. Refer to Clouseau for details |
| | ***5. Other Anomalies (see below or back)*** | |

## STL Cooler Receipt Form/Narrative

## North Canton Facility

| Client ID | pH | Date | Initials |
|---|---|---|---|
| | | | |
| | | | |

**Discrepancies Cont.**

***Macro Name:***

***Macro Name:***

***Macro Name:***

***Macro Name:***

***Other Anomalies:***

# 17.1.2

# Preservative Preparation

## Preservative Preparation

**(If purchased preservative solution vials are not used)**

1:1 Hydrochloric Acid (18%): Slowly add 1000 mL concentrated HCl to 1000 mL reagent water and mix. Store in a well labeled plastic coated acid bottle.

1:2 Sulfuric Acid (33%): In a 2000 mL beaker, SLOWLY and CAREFULLY add 500 mL concentrated $H_2SO_4$ to 1000 mL reagent water and mix. A cool water bath may be needed to cool the solution and beaker. Store in a well labeled plastic acid bottle.

**NOTE:** *All preparations must be performed in a hood and proper personal protective equipment must be worn. All reagents and final preservative solution must be documented in applicable reagent logbooks.*

## 17.1.3

## Preservative Requirements

## PRESERVATIVES, CONTAINERS, AND VOLUMES

| Parameter | Container | Preservative[1,2] | Volume | Parameter | Container | Preservative [1,2] | Volume |
|---|---|---|---|---|---|---|---|
| Asbestos | P | None | 250 mL | Radiological Alpha, Beta, Radium | P | $HNO_3$ | 4 L |
| Acidity | P | None | 250 mL | Hardness | P | $HNO_3$ | 250 mL |
| Alkalinity (Sep) | P | None | 250 mL | Metals | P | $HNO_3$ | 1 L |
| BOD | P | None | 250 mL | Dissolved Metals* | P | $HNO_3$ | 1 L |
| Carbonaceous BOD | P | None | 250 mL | Total Organic Carbon (TOC) | G | HCl | 2 x40 mL |
| Bromide (Br) | P | None | 250 mL | Chemical Oxygen Demand | P | $H_2SO_4$ | 250 mL |
| Chloride (Cl) | P | None | 250 mL | Total Organic Halogens | G | $H_2SO_4$ | 250 mL |
| Chromium, $^{6+}$ | P | None | 250 mL | COD | P | $H_2SO_4$ | 250 mL |
| R. Chlorine | P | None | 100 mL | Ammonia Nitrogen ($NH_3$) | P | $H_2SO_4$ | 500 mL |
| Color | P | None | 50 mL | TKN | P | $H_2SO_4$ | 1L |
| Conductivity | P | None | 250 mL | Nitrate/Nitrite | P | $H_2SO_4$ | 250 mL |
| Corrosivity | P | None | 250 mL | Oil & Grease | G | $H_2SO_4$ | 1 L |
| Dissolved Oxygen | G | None | 300 mL | Phenols | G | $H_2SO_4$ | 1 L |
| Fecal Coliform | P | None | 125 mL | Total Phosphorus | P | $H_2SO_4$ | 250 mL |
| Flashpoint | G | None | 100 mL | TON | P | $H_2SO_4$ | 1 L |
| Fluoride | P | None | 250 mL | | | | |
| Nitrate | P | None | 250 mL | TRPH - IR 418.1 | G | HCl | 2 L |
| Nitrite | P | None | 250 mL | VOC 601 | G | HCl | 3x40 mL |
| pH | P | None | 50 mL | VOC 8010 | G | HCl | 3x40 mL |

## PRESERVATIVES, CONTAINERS, AND VOLUMES

| Parameter | Container | Preservative[1,2] | Volume | Parameter | Container | Preservative [1,2] | Volume |
|---|---|---|---|---|---|---|---|
| Elemental $PO_4$ | G | None | 250 mL | VOC 624 | G | HCl | 8x40 mL |
| Orthophosphate | P | None | 250 mL | BTEX 8020 | G | HCl | 3x40 mL |
| TDS | P | None | 250 mL | VOC 8240 | G | HCl | 3x40 mL |
| TSS | P | None | 250 mL | THM/502.2 | G | HCl | 2x40 mL |
| Total Solids | P | None | 250 mL | 502.2 | G | HCl & Asc. Acid | 2x40 mL |
| TVS | P | None | 250 mL | VOC 624 | G | HCl | 3x40 mL |
| T. Coliform | P | None | 125 mL | VOC 602 | G | HCl | 3x40 mL |
| Settleable Solids | P | None | 1L | 465 C & D | G | HCl | 4x40 |
| Silica | P | None | 250 mL | BTEX 8021 | G | HCl | 3x40 mL |
| Sulfate | P | None | 250 mL | VOC | G | HCl | 3x40 mL |
| Sulfite | P | None | 250 mL | VOC 8260 | G | HCl | 3x40 mL |
| Surfactants (MBAS) | P | None | 250 mL | VOC and VOA | G | HCl | 3x40 mL |
| Turbidity | P | None | 250 mL | VOC 8010/8020 | G | HCl | 3x40 mL |
| TPH-GC | G | None | 2 L | | | | |
| | | | | Total Cyanide | P | NaOH[3] | 250 mL |
| BNAs | G | None | 2 L | Amenable Cyanide | P | NaOH | 250 mL |
| BNA + Dioxin | G | None | 2 L | Free Cyanide | P | NaOH | 250 mL |
| PNA/PAH | G | None | 2 L | Sulfide | P | Zn Acetate & NaOH | 1 L |
| Pesticides | G | None | 2 L | Formaldehyde | G | None | 500 mL |
| Reactive Cyanide | P | None | 1 L | Carbonate | P | None | 250 mL |
| Reactive Sulfide | P | None | 1 L | Bicarbonate | P | None | 250 mL |
| PCB | G | None | 2 L | TPH - Diesel (Ext.) | G | None | 2 L |

## PRESERVATIVES, CONTAINERS, AND VOLUMES

| Parameter | Container | Preservative[1,2] | Volume | Parameter | Container | Preservative [1,2] | Volume |
|---|---|---|---|---|---|---|---|
| Pesticides + PCBs | G | None | 2 L | TPH - Gasoline (P&T) | G | HCl | 2x40 mL |
| Herbicides | G | None | 2 L | Glycols 8015 | G | None | 2x40 mL |
| OPPs | G | None | 2 L | BTEX & MTBE | G | HCl | 3x40 mL |
| | | | | 601/602 | G | HCl | 3x40 mL |

* Filtered in field

[1] HCl, $HNO_3$, and $H_2SO_4$ to pH < 2. NaOH to pH > 12

[2] Temperature = 4°C ± 2°C except for aqueous metals

[3] Samples to be analyzed for Cyanide should be field-filtered for Residual Chlorine. If Residual Chlorine is detected, ascorbic acid (0.6 g) should be added.

## 17.1.4

## Example

## Internal Chain of Custody - CLP

# STL North Canton

## Sample Control Record

Client: _____ Case Number/SDG: _____

Storage Location: _____

| Laboratory Sample Number | Transferred By | Date | Entered | Removed | Reason | Date Returned |
|---|---|---|---|---|---|---|
| 1. | | | | | | |
| 2. | | | | | | |
| 3. | | | | | | |
| 4. | | | | | | |
| 5. | | | | | | |
| 6. | | | | | | |
| 7. | | | | | | |
| 8. | | | | | | |
| 9. | | | | | | |
| 10. | | | | | | |

# 17.1.5

# Internal Chain of Custody

# Regular Production-Organic

# STL North Canton

## Sample Control Record

Client: _____ Case Number/SDG: _____

Storage Location: _____

| Laboratory Sample Number | Transferred By | Date | Entered | Removed | Reason | Date Returned |
|---|---|---|---|---|---|---|
| 11. | | | | | | |
| 12. | | | | | | |
| 13. | | | | | | |
| 14. | | | | | | |
| 15. | | | | | | |
| 16. | | | | | | |
| 17. | | | | | | |
| 18. | | | | | | |
| 19. | | | | | | |
| 20. | | | | | | |

**17.1.6**

**Example**

**Sample Custodian Removal Request Form**

**(LIMS Generated)**

PSR024 6/18/01 17:05:28 MT SAMPLE CUSTODIAN REMOVAL REQUEST PAGE 003

REQUESTED BY: KUHLEJ

METHOD: HL Nitrogen, Ammonia (ISE - 350.3)

| STORAGE LOCATION | WORK ORDER # | PICKED CNTR# | CONTROL # | CLIENT # | ANALYSIS | LOTID | SMP# | SFX | MATRIX DESCRIPTION | QTY RCVD | QTY REQD |
|---|---|---|---|---|---|---|---|---|---|---|---|
| C100 | EEHKF-1-AJ | 6 | 694340 | 002962 | I-88-HL | A1F070186 | 001 | | WATER | 7 | 1 |
| C100 | EEHKR-1-AJ | 7 | 694341 | 002962 | I-88-HL | A1F070186 | 002 | | WATER | 7 | 1 |
| C102 | EEKWJ-1-AJ | 7 | 694342 | 002962 | I-88-HL | A1F080154 | 001 | | WATER | 7 | 1 |
| C102 | EEKW7-1-AJ | 7 | 694343 | 002962 | I-88-HL | A1F080154 | 002 | | WATER | 7 | 1 |
| C102 | EEKW8-1-AJ | 7 | 694344 | 002962 | I-88-HL | A1F080154 | 003 | | WATER | 7 | 1 |
| C102 | EEKXC-1-AJ | 7 | 694345 | 002962 | I-88-HL | A1F080154 | 004 | | WATER | 7 | 1 |
| C111 | EETJ0-1-AG | 2 | 694353 | 057251 | I-88-HL | A1F130158 | 019 | | WATER | 3 | 1 |
| C111 S76 | EETJC-1-AG | 2 | 694346 | 057251 | I-88-HL | A1F130158 | 012 | | WATER | 3 | 1 |
| C111 S76 | EETJK-1-AG | 2 | 694347 | 057251 | I-88-HL | A1F130158 | 013 | | WATER | 3 | 1 |
| C111 S76 | EETJL-1-AT | 6 | 694348 | 057251 | I-88-HL | A1F130158 | 014 | | WATER | 9 | 1 |
| C111 S76 | EETJM-1-AG | 2 | 694349 | 057251 | I-88-HL | A1F130158 | 015 | | WATER | 3 | 1 |
| C111 S76 | EETJQ-1-AG | 2 | 694350 | 057251 | I-88-HL | A1F130158 | 016 | | WATER | 3 | 1 |
| C111 S76 | EETJT-1-AG | 2 | 694351 | 057251 | I-88-HL | A1F130158 | 017 | | WATER | 3 | 1 |
| C111 S76 | EETJW-1-AG | 2 | 694352 | 057251 | I-88-HL | A1F130158 | 018 | | WATER | 3 | 1 |
| C115 | EETWR-1-AJ | 11 | 694354 | 435004 | I-88-HL | H1F130208 | 001 | | WATER | 11 | 1 |
| C95 | EEF2T-1-AA | 2 | 694339 | 056426 | I-88-HL | A1F060238 | 001 | | WATER | 2 | 1 |

| RELINQUISHED BY | RECEIVED BY | DATE/TIME |
|---|---|---|
| | | |
| | lcle | 6-19-01 |

***** END OF REPORT *****

## 17.1.7

## Example Sample Analysis Requisition

Severn Trent Laboratories, Inc
SAMPLE ANALYSIS REQUISITION

LABORATORY: STL Sacramento
880 Riverside Parkway
West Sacramento CA 95605,EZZ OL

NEED ANALYTICAL REPORT BY
7/23/01

ATTN:

LAB PURCHASE ORDER: SR031834

CLIENT CODE: 406422 PROJECT MANAGER: David S. Heakin

NUMBER OF SAMPLES IN LOT: 0002

| SAMPLE I.D. | SAMPLING DATE | ANALYSIS REQUIRED |
|---|---|---|
| A1F260180-001 | 6/25/01 | Perchlorate (314.0) |
| EFHTA-1-AA | | (ICCL04_I) METHOD: 314.0 |
| A1F260180-002 | 6/25/01 | Perchlorate (314.0) |
| EFHTD-1-AA | | (ICCL04_I) METHOD: 314.0 |

NEED DETECTION LIMIT AND ANALYSIS DATE INCLUDED IN REPORT.

SHIPPING METHOD: AIRBORNE DATE: 6/26/01

SEND REPORT TO: DAVE HEAKIN

SAMPLE RECEIVED BY: _____ DATE: _____

PLEASE SEND A SIGNED COPY OF THIS FORM WITH REPORT AT COMPLETION OF ANALYSIS.

THANK YOU.

STL North Canton
INT: ____ 6/26/01 12:12:06
STL Sacramento
880 Riverside Parkway
West Sacramento CA 95605,EZZ OL

RELINQUISHED BY: _____ DATE/TIME: 6/26/01 330

RELINQUISHED BY: _____ DATE/TIME: _____

RECEIVED FOR LAB BY: _____ DATE/TIME: _____

PLEASE RETURN ORIGINAL SAMPLE ANALYSIS REQUISITION

## 17.1.8

## Example Subcontracted PO Logbook

Severn Trent Laboratories, Inc
SAMPLE ANALYSIS REQUISITION

**Laboratory: STL Austin**

Lab Request SR031273 Need Analytical Report 2001-06-14

Client Code: 390133 Project Manager: ALESIA DANFORD

| Sample I.D. | Work Order Number | Client Sample ID | Sampling Date | Analysis Required | |
|---|---|---|---|---|---|
| A1E310129-1 | ED6T6 | HMW-2 | 2001-05-30 | Dissolved Gases in Water | mg/L |
| A1E310129-1 | ED6T6 | HMW-2 | 2001-05-30 | Dissolved Gases in Water | mg/L |
| A1E310129-2 | ED6VR | HMW-3 | 2001-05-30 | Dissolved Gases in Water | mg/L |
| A1E310129-2 | ED6VR | HMW-3 | 2001-05-30 | Dissolved Gases in Water | mg/L |
| A1E310129-3 | ED6VT | HMW-3A | 2001-05-30 | Dissolved Gases in Water | mg/L |
| A1E310129-3 | ED6VT | HMW-3A | 2001-05-30 | Dissolved Gases in Water | mg/L |

Need detection limit and analysis date included in report.

Shipping Method:

Please send a signed copy of this form with the report at completion of analysis.

Relinquished by: [illegible] Date/Time: 5/31/01 0930

Relinquished by: _____ Date/Time: _____

Received for lab by: _____ Date/Time: _____

PLEASE RETURN ORIGINAL SAMPLE ANALYSIS REQUISITION

## 17.1.9

## Laboratory Generated Bottle Label

CT656-001

A9C310142-001
3 VIALS
614MW001-4
MS

375241
3/30/99
8:42

**APPROVAL:**

Director, Quality Assurance

Vice President, Operations Services

## Quanterra Incorporated®

## POLICY NAME

**COMPANY-WIDE**

**Quanterra® Quality Control Program**

Rev. 2, 07/13/98
Supersedes: Revision 1

Policy #: QA-003

### OBJECTIVE:

This policy describes the Quanterra® program of routine analytical quality control (QC) activities. The objective is to generate QC data that demonstrate that the analytical process is in control and that the data meet client and method requirements.

### SCOPE:

This policy is to be enforced and followed throughout the company.

### POLICY:

1.0 Assessments of QC data relative to control limits determine the acceptability of sample test results. Whenever control criteria are not met, the data must be evaluated to determine appropriate corrective action. The initial evaluation is made by the analyst, frequently in

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conjunction with data review software and /or senior analysts or supervisors. Further technical evaluation of the data or data review software output is conducted by second-party data reviewers. Corrective action decisions, particularly whether or not to reanalyze samples, should be done in consultation with the client to the extent possible when operating under project-specific QA plans. Requirements for assessment and corrective action are described in the attachments to this policy. Details concerning technical data review and documentation of the reviews are described in "Technical Data Review Requirements" (Policy QA-012).

2.0 Quanterra's® standard QC program is to be communicated to the client prior to acceptance of work. At the same time, every effort must be made to understand clients' special project requirements. Generally, laboratory project managers serve as a liaison between the clients and the laboratory staff to ensure that requirements are properly communicated in writing to both parties. In the event that alternative QC procedures are not specified by our clients, these standard QC protocols must be followed to ensure the generation of legally and scientifically defensible analytical data.

3.0 Successful implementation of this QC program requires that it is clearly understood by all Quanterra® staff. Training based on this policy will be conducted at each Quanterra® facility and provided to new personnel as appropriate for their functions.

4.0 Quanterra's® QC program applies to the following regulatory programs:

4.1 RCRA and SW-846 Methods - All routine analytical projects performed using SW-846 methods must comply with the requirements described in Quanterra's® Quality Assurance Management Plan (QAMP, Tables 8.4-2 through 8.4-6) and Attachment I to this policy. The Quality Control sections of analytical standard operating procedures (SOPs) referencing SW-846 methods must be consistent with the requirements in Attachment I

4.2 CWA and 40 CFR Part 136 Listed Methods - Any analytical work conducted in support of an NPDES permit or other Clean Water Act compliance activities, must meet the quality control specifications shown in Quanterra's® QAMP tables 8.4-2 through 8.4-6. The quality control requirements for the specific methods listed in the QAMP define the minimum requirements that must be given in laboratory analytical SOPs.

4.3 CERCLA and CLP Methods - Projects performed using USEPA Contract Laboratory Program (CLP) methods must comply with the quality control specifications shown in Quanterra's® Quality Assurance Management Plan (QAMP) table 8.4-7. The quality control sections of the SOPs referencing CLP protocols must be consistent with the QAMP and the relevant CLP Statement of Work.

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4.4 Other Programs or Projects with Clearly Defined QC Requirements

4.4.1 The differences between Quanterra's® standard QC program and special project requirements must be specified in project documents. These documents may include Quality Assurance Project Plans (QAPjPs), Quality Assurance Program Plans (QAPPs), Sampling and Analysis Plans (SAPs), project-specific Quality Assurance Summaries (QASs), SOPs, contracts, or other approved documents.

4.4.2 Documents describing special project requirements must be reviewed and approved by appropriate QA and operations staff.

4.4.3 If the special project requirements appear to result in modifications that contradict federal or state regulatory requirements, the variance must be noted in writing and communicated to the client. A record of this communication must be retained as a permanent part of the project file.

4.4.4 Any special client's project requirements must be communicated to Quanterra's® analysts in advance of releasing samples for analysis, and the work must be clearly differentiated in the analytical documentation, otherwise Attachment I requirements will be followed.

4.5. Projects Without Specific QC Requirements

Any projects for which no specific QC program is specified, regardless of the source of the analytical methods being used, must follow the requirements shown in Attachment I.

4.6 Radiochemistry QC

General QC requirements for radiochemistry analyses are provided in Attachment II.

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# ATTACHMENT I
# QUANTERRA® QUALITY CONTROL PROGRAM

## 1.0 Introduction

This quality control (QC) program is based on the requirements in "Test Methods for Evaluating Solid Waste", USEPA SW-846, Third Edition with promulgated updates. It applies whenever SW-846 analytical methods are used. It also applies in whole or in part whenever project requirements fail to specify some aspect of QC practices described here. It does not apply when other well defined QC programs (e.g. CLP, CLP-like, AFCEE, ACOE, or NFESC) are specified. This policy represents Quanterra's® base QC program for environmental analyses.

Details concerning instrument calibrations, tunes, and QC that are required for specific methods (e.g., interference check samples for ICP and isotopic spikes for dioxin procedures) are not given here. Refer to the method standard operating procedures (SOPs) for information about the frequency, assessment and corrective action required for additional QC elements.

## 2.0 Definitions

2.1 QC Batch - The QC batch is a set of up to 20 field samples plus associated laboratory Q samples that are similar in composition (matrix) and that are processed within the same time period using the same reagent and standard lots.

2.2 Surrogates - Surrogates are organic compounds similar in chemical behavior to the target analytes, but that are not normally found in environmental samples. Surrogates are added to all samples in a batch to monitor the effects of both the matrix and the analytical process on accuracy.

2.3 Method Blank - The method blank (MB) is a control sample prepared using the same reagents used for the samples. As part of a QC batch, it accompanies the samples through all steps of the analytical procedure. The method blank is used to monitor the level of contamination introduced to a batch of samples as a result of processing in the laboratory.

2.4 Instrument/Calibration Blank - The instrument blank is prepared using the same solvents and reagents (e.g. hexane, methylene chloride, or reagent water) used to dilute the prepared sample extracts or digests. Unlike the method blank, it is analyzed without being subject to the preparation steps of the analytical procedure. It is used to monitor laboratory or reagent contamination introduced at the instrumental analysis phase of work. For procedures without a separate preparation step, an instrument blank is equivalent to the method blank, and serves the same purpose.

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2.5 Laboratory Control Sample - A laboratory control sample (LCS) is prepared using a well characterized matrix (e.g. reagent water or Ottawa sand) that is spiked, with known amounts of representative analytes. Alternate matrices (e.g. glass beads) may be used for soil analyses when Ottawa sand is not appropriate. As part of a QC batch, it accompanies the samples through all steps of the analytical process. The LCS is used to monitor the accuracy of the analytical process independent of possible interference effects due to sample matrix.

2.6 Matrix Spike and Matrix Spike Duplicate

2.6.1 Matrix Spike - A matrix spike (MS) is a replicate portion of one field sample in the QC batch that is spiked with known amounts of target analytes. An MS is spiked with the same analytes at the same concentrations that are added to the LCS. As part of the QC batch, it accompanies the field samples through all steps of the analytical process.

2.6.2 Matrix Spike Duplicate - A matrix spike duplicate (MSD) consists of an additional portion of the same sample used to prepare the MS. This portion is spiked and processed exactly as is the MS.

2.6.3 The MS and MSD results are used to determine the effect of the sample matrix on the precision and accuracy of results. Due to the potential variability of the matrix of each sample, the MS and MSD results may not have immediate bearing on any samples except the one spiked.

2.7 Sample Duplicate - A sample duplicate (DU) is a second aliquot of an environmental sample, taken from the same sample container when possible, that is processed with the first aliquot of that sample. That is, sample duplicates are processed as independent samples within the same QC batch. The sample and DU results are compared to determine the effect of the sample matrix on the precision of the analytical process. As with the MS/MSD results, the sample/DU precision results are not necessarily representative of the precision for other samples in the batch.

2.8 Duplicate Control Sample - Duplicate laboratory control samples (LCS/LCSD, also called a DCS pair) consist of a pair of LCSs analyzed within the same QC batch to monitor precision and accuracy independent of sample matrix effects. This QC sample is prepared at the request of the client and/or when insufficient sample volume is received to prepare and analyze an MS/MSD pair. DCS is intended to provide information regarding the precision of the measurement process.

## 3.0 Batch QC Elements & Batch Processing

3.1 A QC batch is designed to determine the quality of the analytical results obtained for a

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group of up to 20 field samples in terms of accuracy and precision. With some exceptions as described in Sections 3.6 through 3.8 below, the minimum QC elements for each QC batch are

- one method blank (MB),
- one laboratory control sample (LCS),
- one matrix spike (MS), and
- one matrix spike duplicate (MSD).

3.2 The identity of each QC batch must be documented and traceable, i.e., each batch of field samples must be clearly associated with the applicable QC samples.

3.3 To the extent possible, samples that require a preparation step should be analyzed together with their associated QC samples. If the samples in a given QC batch require separate analytical runs, the minimum batch QC in each run is an acceptable MB or instrument/calibration blank. To the extent possible, the QC samples should not be analyzed independent of the field samples on a different instrument.

3.4 For analytical procedures that do not include a separate extraction or digestion (e.g., volatile organic analysis by purge and trap), the QC batch must be analyzed sequentially using the same instrument and instrument configuration within the same calibration event. That is, the same calibration curve, calibration factors, or response factors must be in effect throughout the analysis.

3.5 Field QC samples (e.g., trip blanks, equipment rinsates, and field duplicates) count as individual samples, therefore, they add to the QC batch count. Samples that require simple reanalysis (e.g., dilutions to adjust a sample extract to the working range of the instrument), as opposed to reextraction or digestion and reanalysis, do not count as additional samples in the QC batch. For procedures without a separate preparation, a reanalysis within the same calibration event (as defined in Section 3.4) does not add to the batch count.

3.6 MS/MSD pairs are not the only acceptable means of demonstrating precision.

3.6.1 As requested by clients or required by some methods, batch precision may also be demonstrated through the analysis of sample duplicates (DUs). However, the client should be advised that a DU is less likely to provide usable precision statistics depending on the likelihood of finding concentrations below reporting limits.

3.6.2 A duplicate LCS (DCS) may be used to demonstrate method batch precision independent of client's matrix when the client has not supplied sufficient sample quantity to prepare an MS, MSD or DU, if requested by the client.

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3.6.3 On-going monitoring of LCS results can be used to determine long-term (a.k.a., between batch) precision and accuracy for a method.

3.7 Some methods including isotope-dilution methods, pH and ignitability for example, do not use all of the QC elements listed in Section 3.1. Method exceptions to these requirements are listed in the QC tables of Quanterra's® QAMP and in the laboratory's analytical SOPs.

3.8 Deviations from these QC elements must either be noted in project planning documents (QAPPs, QAPjPs, SAPs, SOWs, QAS, or equivalent) or in a NCM.

## 4.0 Data Evaluation and Corrective Action

4.1 General Guidelines

4.1.1 Any QC component that is outside of established control limits is considered an out-of-control event. All out-of-control events must be documented and the associated data evaluated. Depending on the specific circumstances, evaluation can lead to a variety of actions. The following sections and the flowcharts describe the appropriate corrective action for the most common QC failures. However, it is not possible to address all possible data evaluation scenarios in this policy. The guiding principle for all evaluations is that the data and corrective action decisions must be defensible using Quanterra® policies, procedures or scientific evidence, and justified in the project records.

4.1.2 If reanalysis for QC failures is conducted and the second analysis confirms a QC problem that is outside of the laboratory's control, further testing is not necessary. The problem must be documented and the data properly qualified in the project report.

4.1.3 QC failures that are not corrected by reanalysis are documented in NCMs or using an electronic anomaly system as described in SOP # CORP-QA-0010. This does not include QC failures due to sample matrix interferences (particularly MS, MSD and surrogate failures). These failures are a function of the method used and are normally outside of the laboratory's control; trending via NCMs is not required. Other forms (for example, data review checklists) may be used to document matrix QC failures.

4.1.4 When ongoing, systematic problems are identified, work must stop until it can be demonstrated that the system is in control again.

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4.2 Method Blank (MB) Evaluation (also see Figure 1)

4.2.1 Method Blank Acceptance Criteria

The results of the method blank shall be one of the QC measures used to assess batch acceptance. Results are acceptable if all analyte concentrations in the MB meet the following criteria:

- The blank contamination is less than 1/10 of the measured concentration of any sample in the associated preparation batch , or
- The blank contamination is less than the concentration present in the samples and is less than 1/10 of the regulatory limit, or
- The same contaminants were not found in the associated samples, or
- MB results are less than or equal to the reporting limit.

Note: Positive method blank results slightly below the reporting limit should still be evaluated by the analyst for potential impact on sample results at or near the reporting limit.

4.2.2 Corrective Action for Method Blank Failure

- If the method blank does not meet the acceptance criteria, the source of contamination must be investigated and measures taken to correct, minimize or eliminate the problem. Samples associated with the contaminated blank shall be reprocessed for analysis or, under the following circumstances, may be reported as qualified (qualifier flags or narrative comments):
- MB contamination at a level less than the reporting limit with sample results at levels near the RL, based on analyst's judgement shall be flagged, or
- Analyte concentrations in samples are greater than 10 times blank contamination, or
- The contaminate is a common blank contaminate (see below) and the MB concentration is less than 5 times the RL for organics or less than 2 times the RL for inorganics.

Common Laboratory Contaminants:

| Analyte | Method |
|---|---|
| Methylene Chloride | Volatile Organics (GC or GC/MS) |
| Acetone | Volatile Organics (GC or GC/MS) |
| 2-Butanone | Volatile Organics (GC or GC/MS) |
| Phthalate Esters | Semi-Volatile Organics (GC or GC/MS) |
| Copper | Metals (ICP or GFAA) |
| Zinc | Metals (ICP or GFAA) |
| Iron | Metals (ICP or GFAA) |
| [illegible] :ad | Metals (Trace ICP or GFAA) |

Revisions made on 10/01/99

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4.3 Laboratory Control Samples (LCS) Evaluation (also see Figure 2)

4.3.1 Acceptance Criteria
The LCS recovery for the control analytes must be within established control limits. The percent recovery is calculated as follows:

$$\text{LCS Percent Recovery} = \frac{X}{t} \times 100$$

Where: $X$ = observed concentration
$t$ = concentration of spike added

4.3.2 Corrective Action for LCS Failure
- check calculations,
- check instrument performance,
- reanalyze the LCS, and if still outside of control limits,
- reprepare and reanalyze all samples in the QC batch.

Notes: 1. It is acceptable to report the data, if the LCS recovery is out high and analyte of concern was not detected in any of the samples. Successful MS/MSD and surrogate recoveries may also provide evidence of control of accuracy, but this would be decided on a case-by-case basis and only with client approval.

2. In the case of volatile analyses, if the LCS fails, it may be reprepared and reanalyzed within the same tune period.

3. In the case where all target requested analytes are within control, but some other LCS compounds are out of control, the LCS may still be considered acceptable for reporting.

4.4 Duplicate Laboratory Control Samples (LCS/LCSD or DCS) Evaluation (also see Figure 2)

4.4.1 Acceptance Criteria
The recovery for each spike of the pair must be within established control limits. The formula used to calculate LCSD recoveries is the same as the formula for LCS spike recoveries. If a batch includes samples requiring LCS control and samples requiring DCS control, the LCS used will be the first LCS that passes control criteria.

The relative percent difference (RPD) for the pair is calculated as follows:

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$$RPD = \left[ \frac{|X_1 - X_2|}{\frac{(X_1 + X_2)}{2}} \right] \times 100$$

Where: $X_1$ = first observed concentration

$X_2$ = second observed concentration

4.4.2 Corrective Action for LCS/LCSD Recovery (Accuracy) Failure

- check calculations,
- check instrument performance,
- reanalyze and/or reprepare and reanalyze all samples in the QC batch.

Note: If either LCS/LCSD spikes fails and the batch cannot be reanalyzed, the failure must be documented and noted in the final report.Also see notes under Section 4.3.2.

4.4.3 Corrective Action for LCSD Precision Failure

- check calculations;
- check instrument performance;
- if the RPD is out of control but both accuracy recoveries are within acceptance criteria, prepare an NCM, and qualify report.

Note: Because LCS/LCSD limits are based on the standard deviation of data collected over time and include long-term precision, it would be unusual to fail precision limits while meeting accuracy limits. If this occurs with any frequency, control limits should be reevaluated.

4.5 Surrogate Evaluation (also see Figure 3)

4.5.1 Acceptance Criteria

Surrogate recoveries must be within established control limits. Method QC (MB, LCS, and/or LCSD) results are not acceptable unless the surrogate recoveries for those QC samples are within control limits. If MS/MSD, DU or field samples require dilutions beyond the threshold stated in the analytical SOPs, routine surrogate control limits do not apply and recoveries are not evaluated. This should be noted in the final report. The recovery is calculated as follows:

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$$\text{Surrogate Percent Recovery} = \frac{X}{t} \times 100$$

Where: $X$ = observed concentration
$t$ = concentration of surrogate added

4.5.2 Corrective Action

4.5.2.1 Surrogate Failures in MB, LCS, or LCSD

- check calculation and instrument performance,
- reanalyze QC sample and/or reanalyze all samples in the QC batch.

Note: Unless otherwise specified by the client, it may be possible to report qualified results if method QC surrogate recoveries are biased high and analytes were not detected in the field samples. However, all other QC requirements would have to be met and the failure would have to be noted in the final report.

4.5.2.2 Surrogate Failures in Field Samples or MS/MSD

- check calculation and instrument performance;
- evaluate objective evidence of matrix interference (e.g. heterogeneous sample, interfering compounds seen on chromatograms, or interference demonstrated by prior analyses);
- document the failure and note it on the final report;

Note: Some client programs require reanalysis to confirm matrix interferences. Check special project instructions for this corrective action.

4.6 Matrix Spike and Matrix Spike Duplicates (MS/MSD) Evaluation (also see Figure 4)

4.6.1 Acceptance Criteria
MS and MSD recoveries and RPD should be within established control limits. If MS or MSD samples require dilutions beyond the threshold stated in the analytical SOPs, routine control limits do not apply and recoveries are not evaluated, but this should be noted in the final report. The MS and MSD recoveries are calculated as follows:

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$$\text{MS or MSD Percent Recovery} = \left[\frac{X_s - X}{t}\right] \times 100$$

Where: $X$ = observed concentration in unspiked sample
$X_s$ = observed concentration in spiked sample
$t$ = concentration of spike added

Notes: 1. If sample result is ND, $X = 0$ when no values reported below RL. If sample result is reported as a value <RL, $X$ = reported value.
2. CLP forms software uses observed recovery, not concentrations.

RPD is defined in Section 4.4.1.

4.6.2 Corrective Action for MS/MSD or MS/MSD RPD Failure (assuming that the LCS is in control)

- check calculation and instrument performance,
- consider objective evidence of matrix interference (e.g. heterogeneous sample, interfering compounds seen on chromatograms, or interference demonstrated by prior analyses);
- document the failure and note on final report;

Note: Some client programs require reanalysis to confirm matrix interferences. Check special project requirements for this corrective action.

4.7 Sample Duplicate (DU)

4.7.1 Acceptance Criteria
The RPD for the sample and its duplicate must be within established control limits. The RPD is the same as for the MS/MSD (see 4.6.1 above).

4.7.2 Corrective Action for DU Failure

- check calculation and instrument performance,
- document the QC failure and note on the final report.

## 5.0 Establishing QC Acceptance Limits

5.1 Selecting the Data Set
For new procedures, published method limits can be used until sufficient QC data are acquired (minimum of 20 to 30 data points recommended). However, the published limits may not be appropriate if they are based on a single-operator or single-laboratory study. In this case, the QA Manager may establish default limits until enough data is collected for laboratory established limits to be determined. For existing procedures, data collected

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over several months to a year or more can be used. Control tables or control charts are used together with the calculated mean and standard deviation to determine if the data set being considered are free of trends and are representative. If it appears that the data include gross outliers, outlier tests such as the Grubbs Test, Dixon Test (for 20 or fewer data points), or Rule-of-Huge-Error Test can be used to justify eliminating individual data points. Laboratory established limits must be reevaluated at least annually.

5.2 Calculating Laboratory Statistical Performance

*Accuracy:* mean recovery $\pm 3s$
*Precision:* zero to (mean RPD + 3s)

Where: $s$ = standard deviation

If there are insufficient MS/MSD data available to calculate limits, LCS/LCSD limits may be used. If there are insufficient sample surrogate recovery data available to calculate limits, method limits may be used, if available. For methods, matrices, and/or analytes with very limited data, interim limits should be established using available data or by analogy to similar methods or matrices.

5.3 Setting Control Limits

The working control limits to be used by the laboratory are based on evaluation of the calculated laboratory statistical performance and available interlaboratory limits provided in the reference methods. Note that some SW-846 methods only supply single-operator or single-laboratory method performance data, which should be used for guidance only and may not be appropriate for routine lab operation.

The control limits should be evaluated for systematic trends and consistency of the performance of the analytical procedure at least annually or whenever new patterns of performance are observed in the laboratory data (i.e. new methods, equipment, etc.). When evaluating current "laboratory-generated limits" against historical "laboratory-generated limits", the laboratory QA manager should investigate any significant changes in "laboratory-generated mean" and "laboratory-generated range" and should attempt to identify the cause before making any changes to the laboratory limits. If the recalculated limits are consistent with the historical limits, the historical limits may remain unchanged.

Notes:
1. Laboratory-generated mean = statistical mean (i.e. $\Sigma x_i / n$)
   Laboratory-generated range = statistical ranges indicated in the previous section
2. If the laboratory-generated mean is within ± 10% of the historical mean, the two means are not significantly different and no investigation of cause of change would be necessary.
3. If the in-house calculated data lead to limits that are significantly tighter than both the guidance limits and/or the calibration acceptance criteria for the method, the laboratory

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can default to using the laboratory-generated mean ± calibration acceptance limit. Unreasonably tight statistical limits can result from the exclusion of unacceptable results from the database. If investigation demonstrates that this is happening, the laboratory's data entry systems should be improved. The lab should employ a statistical test for outlier values before excluding data points. (Reiterations of outlier tests lead to narrower limits and should be used with caution.)

4. If the decision is to use guidance limits from the method, the laboratory should investigate procedural improvements leading to better performance.

## 6.0 Reporting QC Data

The QC data routinely reported includes the LCS, method blank and surrogate standards. Matrix QC are reported on a project or client basis, and clients are encouraged to identify on the custody forms specific samples to be used for matrix spiking. Client reporting requirements are negotiated and documented as part of the project records. Ultimately, all reporting decisions should accommodate the client's requirements.

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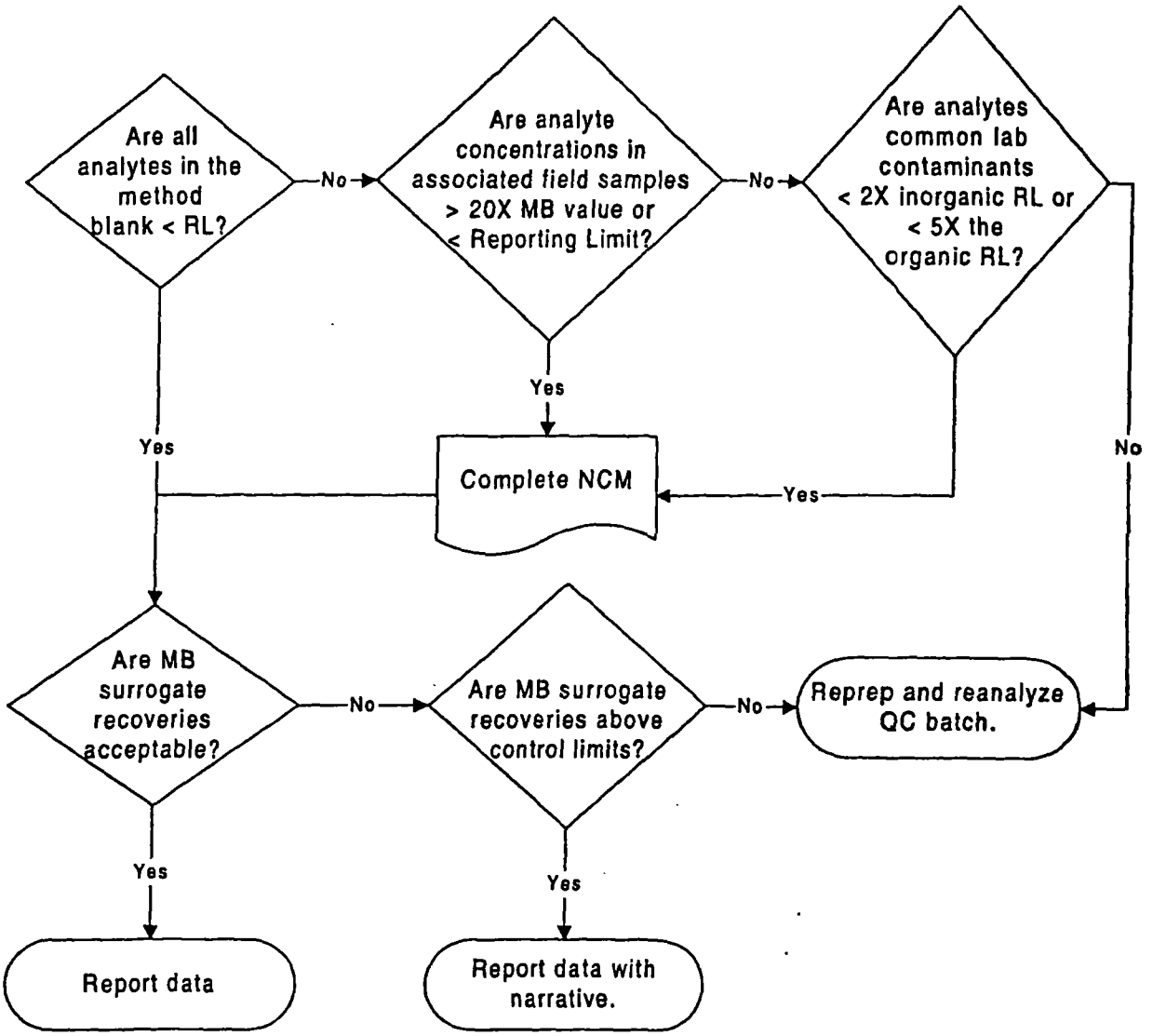
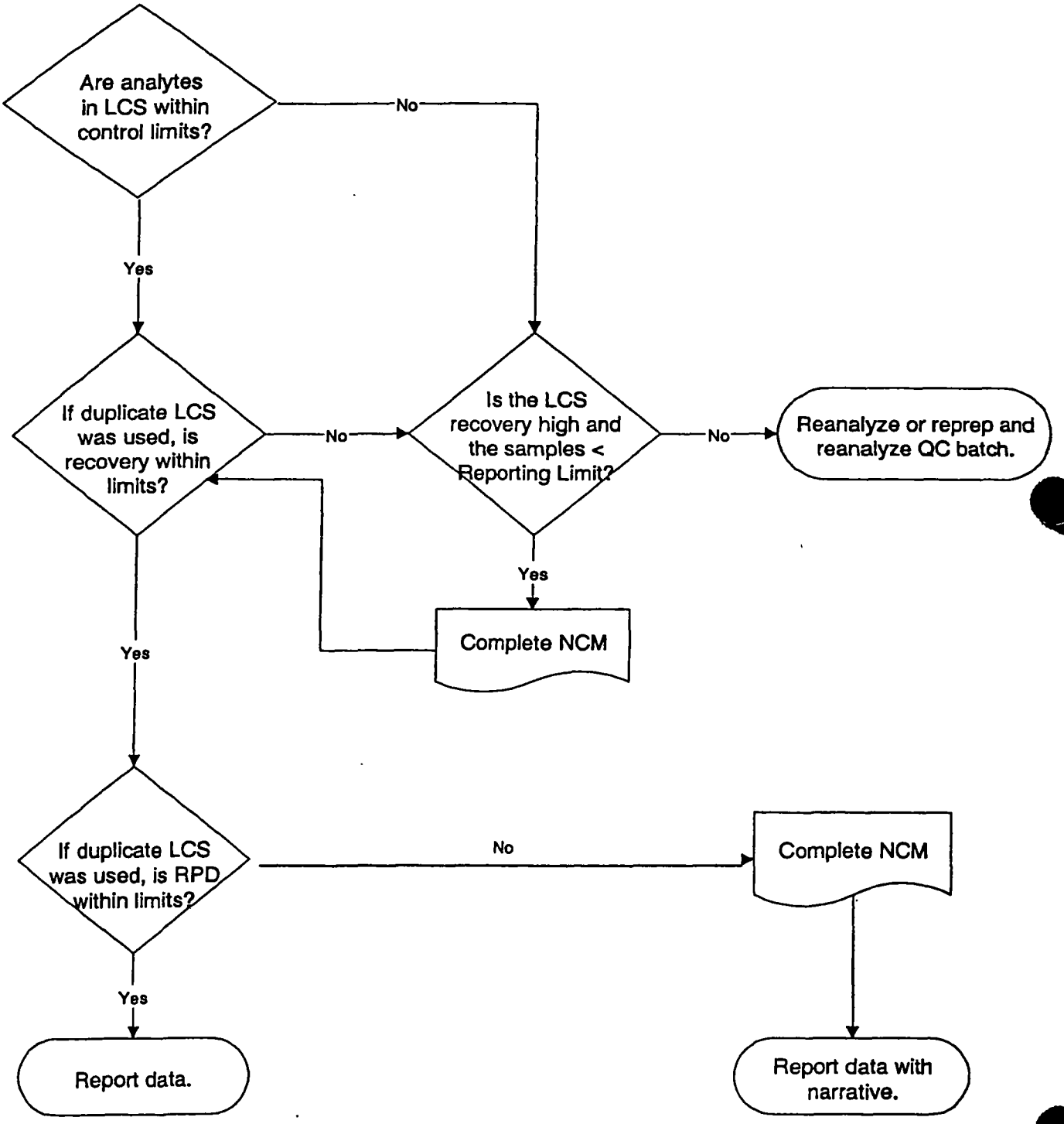
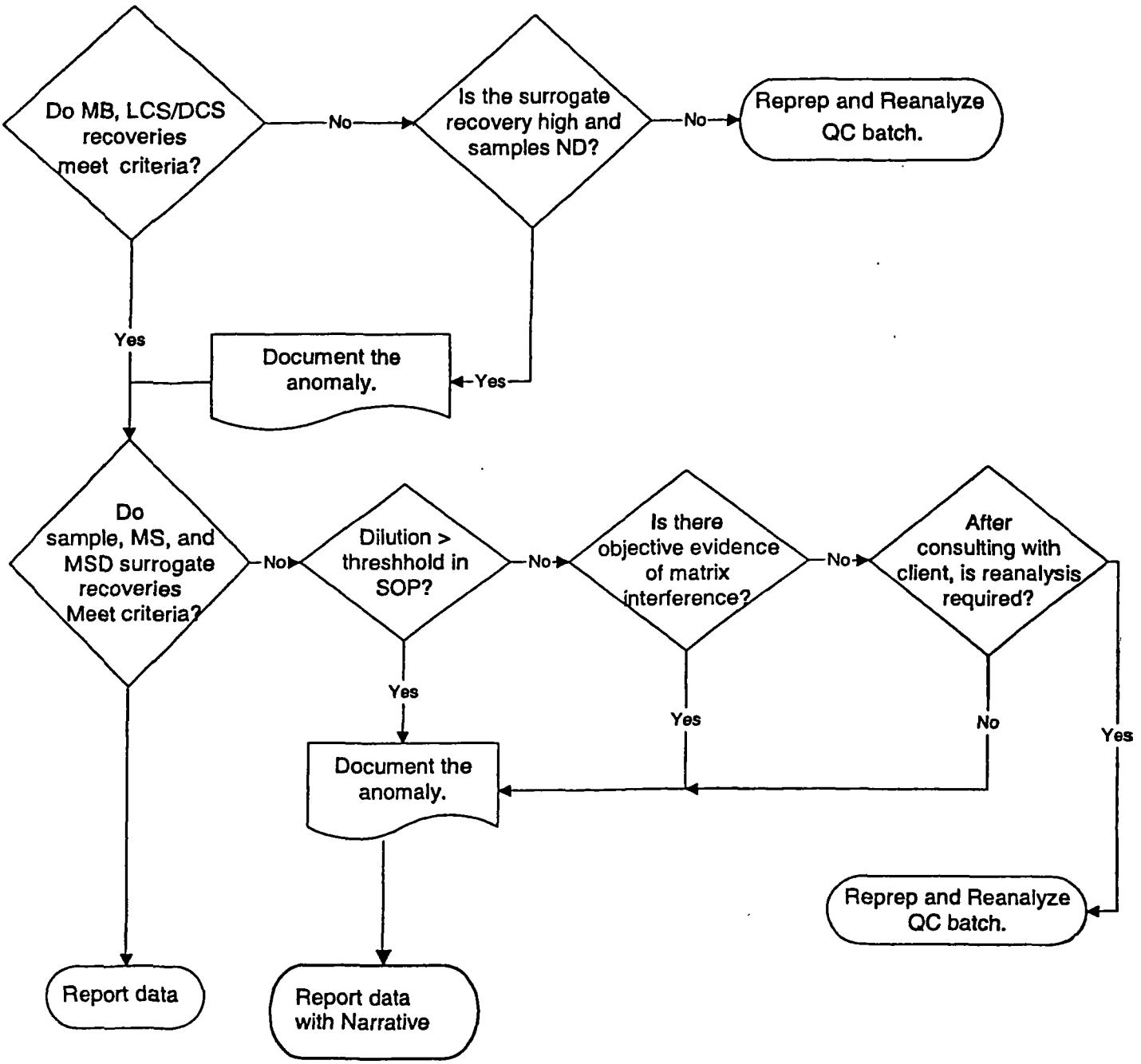
## Figure 1 - Method Blank Evaluation



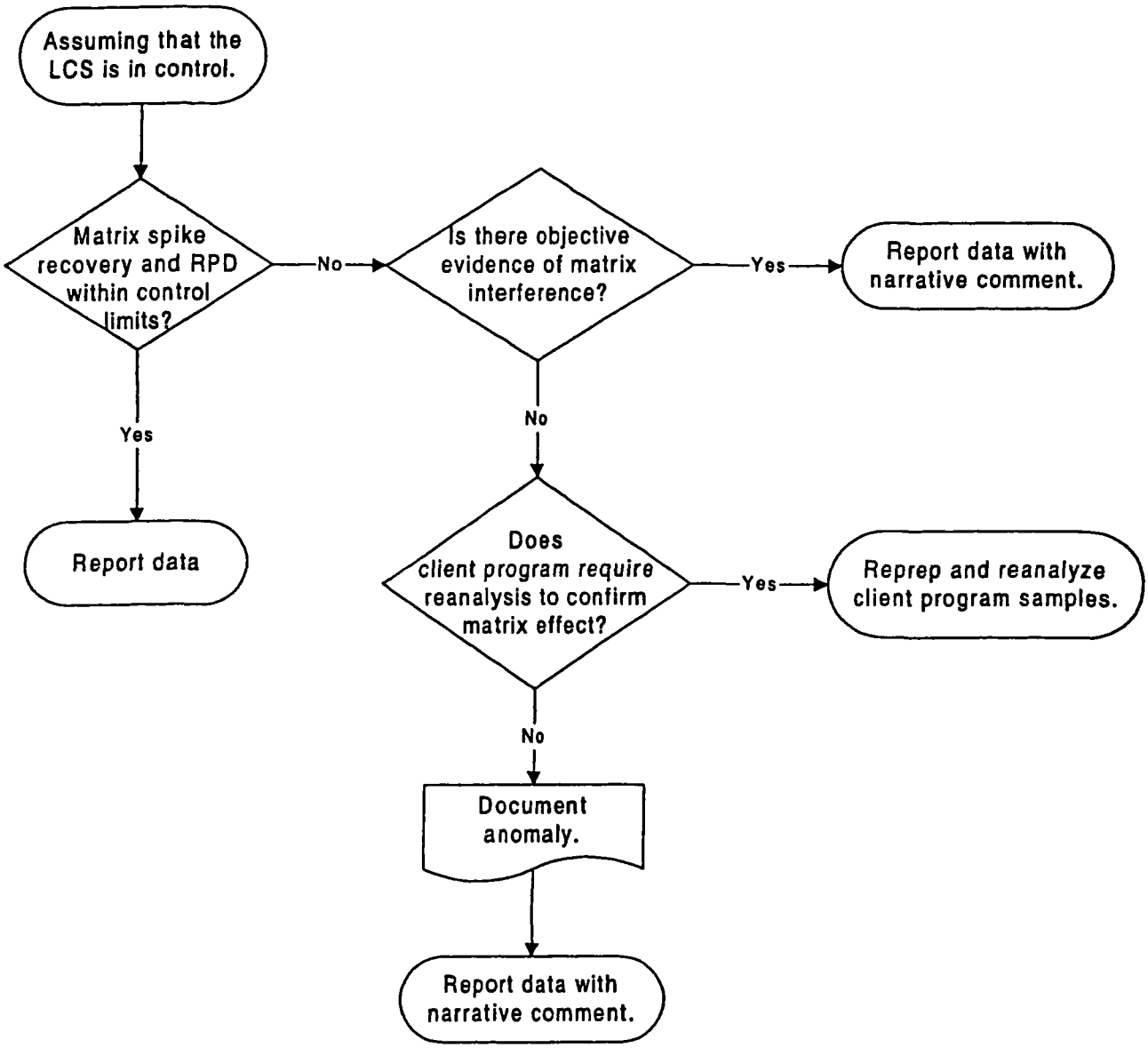
## Figure 2 - LCS/LCSD Evaluation



## Figure 3 - Surrogate Evaluation



## Figure 4 - Matrix Spike/Matrix Spike Duplicate Evaluation



# ATTACHMENT 2
# QUANTERRA® RADIOCHEMISTRY QUALITY CONTROL PROGRAM

## 1.0 Introduction

This Attachment describes the general quality control (QC) program in place to support radiochemical analyses performed in Quanterra® laboratories. Due to the lack of a national QC program which has been deemed to be the industry standard for radiochemistry, individual procedures may vary in their requirements. The program defined here should be taken as the minimum QC program. The details of the implementation and acceptability of the program are described in laboratory SOPs. The requirements of this Attachment may be superseded by a project Scope of work or QA program.

All data produced by the Quanterra® radiochemistry laboratories shall be reviewed by procedures described in the Quanterra® QAMP and facility SOPs. The review will be documented using a data review check list.

## 2.0 Quality Control Samples

2.1 Sample batches (defined in Attachment 1 of this policy) will be accompanied by laboratory prepared QC samples. The minimum QC samples required in a batch are as follows:

2.1.1 Method Blanks: carried through the entire preparation and analysis procedure, one for each batch.

2.1.2 Laboratory Control Samples: prepared and/or analyzed with the samples, one for each batch.

2.1.3 Sample Duplicates: one for each batch, assuming sufficient sample is received.

2.2 Additional Quality Control Samples may include matrix spikes and matrix spike duplicates (matrix spike duplicates will replace sample duplicates) which are performed when contractually required. Matrix spikes are not prepared for samples which are counted directly and are subject to homogenization restrictions, such as solid samples for gamma or alpha/beta analysis.

2.3 Tracers and carriers are added to every sample, blank, and QC sample when required by the analytical method. Tracers are radioisotopes usually with the same atomic number as the target analytes, when available. Carriers are non-radioactive compounds added to assist in isolation of the target analyte(s). Both tracers and carriers, when standardized can be used to correct counting results for actual recovery of the analyte when available radioactive tracers are NIST traceable.

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## 3.0 Acceptability Criteria/Corrective Action

3.1 In the absence of specific client instructions, the following criteria apply. However, individual cases allow for exceptions as stated below:

3.1.1 Re-counts - Client and/or QC samples are recounted if the acceptance criteria have not been met as indicated on the Data Review Checklist and as deemed necessary by the team leader/designee. Additionally, any blank, spike or client sample may be recounted to verify a result. If the re-count result is found to be within limits, the Data Reviewer accepts the re-count data. If the re-count result is found not to be within limits, the affected samples may need to be reanalyzed.

3.1.2 Reanalysis - If sample reanalysis is necessary and/or the client provides permission, the affected samples and associated quality control samples shall be reanalyzed providing sufficient sample is available. The data of the reanalysis set shall be reviewed using the same criteria as the original data set.

3.2 Method Blank: In general, method blanks may not contain concentrations of the analyte(s) of interest above the Reporting Limit (RL) or Client-Required Detection Limit (CRDL). Specific client requirements may require other criteria for the method blank. The occurrence of an unacceptable method blank requires investigation into the source of the contamination, followed by reanalysis of the associated batch of samples with an acceptable method blank unless the activity levels of the samples are significantly higher than the blank and or the MDA or MDC. The method blank may be water for all matrices unless client requirements specify otherwise

3.3 Yield Monitors: - For QC and sample data where gravimetric (chemical) or tracer recoveries are used for yield correction, the yield of the sample must meet, in the absence of specific limits, a yield monitor recovery greater than or equal to 20% and less than or equal to 115%. Unacceptable yields for method blanks or LCS require investigation and reanalysis of the associated sample batch with acceptable QC sample yields. Unacceptable yields for a sample require reanalysis of the sample in a batch with acceptable QC sample yields. Samples may be reported with unacceptable yield only if repeat analyses indicate that a matrix effect exists that prevents acceptable yield.

3.4 Laboratory Control Sample: Criteria for acceptability of Laboratory Control Samples are set by each procedure, and may utilize historical LCS recovery data. The occurrence of an unacceptable LCS requires investigation into the source of the nonconformance, followed by reanalysis of the associated batch of samples with an acceptable LCS.

3.5 Duplicate Samples: Acceptability criteria for duplicate sample results are stated in laboratory Standard Operating Procedures, and may utilize historical duplicate RPD data. Data associated with duplicate analyses that exceed the RPD criteria are evaluated for usability, and if reported without corrective action, are flagged and noted in client reports.

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3.6 Matrix Spike Recoveries: Acceptable matrix spike recovery is determined from laboratory historical data. Control limits are established for acceptability for each method and matrix at least annually. Samples with unacceptable matrix spike recoveries are flagged and noted in client reports unless the recovery can be shown to be due to laboratory error.

## 4.0 MDAs/MDCs

4.1 All radiochemical results are reported with both a sample-specific Minimum Detectable Activity (MDA) or Minimum Detectable Concentration (MDC) and an associated error. Formulas for calculating the MDA or MDC and the error are given in the Standard Operating Procedures. If the sample MDA/MDC is greater than the RL or CRDL, the Data Reviewer shall examine the sample volume/weight, counting time, and detector efficiency. The Data Reviewer shall decide if the sample should be recounted, reanalyzed, or the data accepted. If the sample activity exceeds the achieved MDA/MDC, no further action is necessary.

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**STL STANDARD OPERATING PROCEDURE**

**TITLE: STATISTICAL EVALUATION OF DATA AND DEVELOPMENT OF CONTROL CHARTS**

**(SUPERSEDES: REVISION NO. 3)**

| | | |
|---|---|---|
| Reviewed by: | Brenda R. Pietsay-Kravetz | 06/20/00 Date |
| Reviewed by: | Technology Specialist | 6/20/00 Date |
| Approved by: | Quality Assurance Manager | 6/19/00 Date |
| Approved by: | Stacy D. Campbell for Steve Jackson<br>Environmental Health and Safety Coordinator | 6/20/00 Date |
| Approved by: | Laboratory Director | 6/21/00 Date |

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## 1. PURPOSE

1.1. The purpose of this SOP is to describe the requirements for: (1) statistically establishing QC acceptance criteria and (2) long-term trend analysis of QC data using control charts at the STL-North Canton Laboratory.

1.2. The control chart is an effective tool for long-term trending because it records in real time the accuracy (bias) and precision of the appropriate parts of the measurement process. The control chart provides the means to demonstrate statistical control.

1.3. This document accurately reflects current standard operating procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary by the laboratory QA department.

## 2. RESPONSIBILITIES

2.1. Analyst

2.1.1. All non-CLP QC data is entered into the Laboratory Information Management System (LIMS) for statistical evaluation for the generation of control charts. (Data entry may be automated or may be completed from the report generation software as part of the report or review group activities.)

2.1.2. Monitor method performance using established limits and identify any out-of-control situation. Respond to out-of-control conditions. QC Data results are considered out of control when recoveries exceed established control limits.

2.2. Group Leader/Supervisor

2.2.1. Respond to out-of-control conditions.

2.3. QA Department Staff

2.3.1. For analytical methods, coordinate updating of control limits annually. During this process, review control charts to detect any trends in routine analytical procedures.

2.3.2. Archive control charts and statistically derived QC acceptance data.

2.3.3. Each year at a minimum, publish statistically derived QC acceptance criteria.

2.3.4. Provide guidance in the development of control charts and in the application of QC samples and acceptance data.

2.3.5. With the Laboratory Director, ensure that Operations staff conforms to the requirements provided in this SOP.

2.4. Project Manager

2.4.1. Incorporate updated limits into project-specific QAPPs.

2.4.2. Submit project-specific control charts to the requesting client.

## 3. SAFETY

3.1. Procedures shall be carried out in a manner that protects the health and safety of all STL associates.

3.2. Normal office dependent safety precautions must be taken in performing this SOP. If personnel are required to perform any portion of the procedure in the laboratory area, appropriate personal protective equipment and precautions must be utilized.

3.3. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL associate. The situation must be reported **immediately** to a laboratory supervisor.

## 4. PROCEDURE

4.1. Empirical Establishment of QC Acceptance Limits

4.1.1. The assessment of QC sample data shall be performed by comparing precision and accuracy results against control limits. As defined in the following subsections, the control limits used for this comparison shall be either in-house (statistically generated using historical data) control limits or published limits from methods, contracts, or project QA plans.

4.1.2. In-house limits for all QC data must be determined and compared to those limits published in the methods for applicable matrices. Method limits will be employed until sufficient QC data are acquired. A minimum of 20 to 30 of the most recent data points should be used to establish in-house limits based on historical performance data for each major method. Periodically, QC data may need to be reviewed and house limits reestablished whenever a significant change in an analytical process occurs.

4.1.3. Control limits shall be generated for each matrix (i.e., aqueous and soil) for each preparative method using data from at least 20-30 of the most recent data points.

4.1.4. In-house control limits shall be established for the following samples:

4.1.4.1. Laboratory control sample (LCS) spike recoveries for method required analytes list.

4.1.4.2. Matrix Spike and Matrix Spike Duplicate (MS/MSD) spike recoveries for method required analytes list.

4.1.4.3. Surrogate spike recoveries in LCSs for organic analyses only.

4.1.5. Control limits shall be established for all methods except for CLP. For CLP-related projects, the acceptance criteria specified in the most current SOW shall be followed in evaluating data quality. CLP SOWs do not specify the generation of control charts.

4.1.6. The calculations used to generate the control limits for accuracy (%R) are described in the following subsections.

4.1.6.1. The %R is defined as the observed concentration in LCS divided by the theoretical concentration of the spike or LCS, times 100:

$$\%R = \frac{Found}{True} \times 100$$

4.1.6.2. The mean percent recovery and standard deviation is calculated using the following formulas:

$$\overline{\%R} = \frac{\sum_{i=1}^{n} \%R_i}{n}$$

$$S = \sqrt{\frac{\sum_{i=1}^{n}\left(\%R_i - \overline{\%R}\right)^2}{n-1}}$$

where:

| | | |
|---|---|---|
| %R | = | the mean percent recovery |
| $\%R_i$ | = | the percent recovery of an LCS |
| n | = | the number of data points |
| $S$ | = | the standard deviation of the data set of percent recoveries |

4.1.6.3.The warning (95% or 2-sigma) and control limits (99% or 3-sigma) are then calculated from the following equations:

| | | |
|---|---|---|
| Upper Control Limit | = | $\overline{\%R} + 3\,s$ |
| Lower Control Limit | = | $\overline{\%R} - 3\,s$ |
| Upper Warning Limit | = | $\overline{\%R} + 2\,s$ |
| Lower Warning Limit | = | $\overline{\%R} - 2\,s$ |

where:

| | | |
|---|---|---|
| $\overline{\%R}$ | = | the mean percent recovery |
| $S$ | = | the standard deviation of the data set |

4.1.7. Control limits will be recalculated after excluding the following points from the calculations:

4.1.7.1. Samples with values outside control limits due to assignable cause.

4.1.7.2. True outliers as defined in the Grubbs test.

4.1.7.3. The LIMS is equipped to perform a Grubbs outlier test used to generate the control charts.

4.2. Monthly Trend Control Charts (Navy Only)

4.2.1. Control charts are required for LCSs only.

4.2.2. Control charts will be generated and reviewed on a monthly basis to keep current assessment of laboratory performance. Charts generated on a monthly basis will include a subset of parameters spiked as indicated in Table 4-1.

**Table 4-1**

| Analyte | Analytical Method | Analyte | Analytical Method |
|---|---|---|---|
| Cyanide | Manual distillation/ automated analysis | Aluminum and Cadmium | Total Prep/ Inductively Coupled Plasma |
| Thallium | Total Prep, Graphite Furnace Atomic Absorption | Mercury | Manual digestion/ automated CVAA |
| Trichloroethene | Purge & Trap/ GC Volatile Hall | Toluene | Purge & Trap/ GC Volatile - PID |
| 1,1-Dichloroethene, Benzene | Purge & Trap, GC Mass Spec Volatiles | 1,2,4-Trichlorobenzene, 4-Nitrophenol | Liq/Liq, GC Mass Spec Semivolatile |
| Aldrin, Endrin | Liq/Liq, GC ECD | Aroclor 1016, Aroclor 1260 | Liq/Liq, GC ECD |
| TCMX | Liq/Liq, GC ECD | | |

4.2.3. A control chart (X chart) is generated using the LIMS or a commercially available software to monitor accuracy and precision by plotting the LCS %R data in a graphical format as follows:

4.2.3.1. The average of the %R determinations for the original data set is established as the midpoint on the Y axis of the graph.

4.2.3.2. The upper and lower warning and control limits are plotted as solid horizontal lines across the graph at their respective points on the Y axis.

4.2.3.3. The calculated %R of each spiked sample is plotted chronologically on the graph to determine whether the recovery is within the warning and control limits of the control chart.

4.2.4. Control charts can be generated from any networked system (see network administrator) as follows:

4.2.4.1. From the Desktop, TraQAr double click the "Control limit " icon button.

4.2.4.2. Select "On-line Control Charts"

4.2.4.3. Select "QC Type"

4.2.4.4. Select "QuantIMS Method"

4.2.4.5. Select "QC Program" and write down spike list number

4.2.4.6. Select "Close Form"

4.2.4.7. Select QA Access button to create control charts and limits.

4.2.4.8. Select "location" (North Canton), "QC Type" (LCS/DCS, MS/MSD, LCS/DCS Surrogates, MS/MSD Surrogates, All Surrogates), "Start and End Date", "spike form" and then spike number.

4.2.4.9. Select "Collect Data" this screen will run and then the Control Limits Review screen comes up.

4.2.5. Control Limits Review screen

4.2.5.1. A "Grubbs test complete" sign comes up, select OK

4.2.5.2. A minimum of 20 - 30 points are required. If points are below 20 - 30 select close form and increase the start and end date to no more than one year.

4.2.5.3. If points are at least 30, select individual matrix.

4.2.5.4. Select "Grubbs Test"

4.2.5.5. A "Grubbs test complete" sign comes up, select OK

4.2.5.6. Select "Control Limits Rpt". Right click on report and select print.

4.2.5.7. Select "Control Charts Rpt". Right click on report and select print.

4.2.5.8. Close form and repeat 4.2.5.3. through 4.2.5.7.

4.2.5.9. This procedure can be used to demonstrate both "before" and "after" data sets used for control charts generation. An evaluation of the data excluded by a student-t test is useful to reveal existing problems (high volume of unused analyses, etc.).

4.2.6. The following information must be present on the control charts or in an associated table:

4.2.6.1. Parameter, Analytical Method and preparation procedure

4.2.6.2. LCS Batch ID allowing cross-reference to LIMS containing all analytical information.

4.2.6.3. Matrix

4.2.6.4. Number of points used

4.2.6.5. Mean

4.2.6.6. Standard Deviation

4.2.6.7. Percent recoveries

4.2.6.8. Upper and Lower warning and Control limits

4.2.6.9. Chart generation date.

4.2.6.10. An example of the Excel workbook output is provided in **Appendix A.**

4.3. Evaluation of Control Charts

4.3.1. When method, contract, or project plan requirements stipulate control limits which are more stringent than the laboratory generated limits, the more stringent limits shall be used to evaluate the quality control sample data.

4.3.2. If the laboratory-generated limits are more stringent than the method, contract, or project specific limits, the laboratory-generated limits shall be used to evaluate QC samples.

4.3.3. Criteria for an Out-of-Control Conditions

4.3.3.1. The causes for a shift or a trend in control charts could result from (1) incorrect preparation of a standard or a reagent, (2) sample contamination, (3) improper storage or preservation, (4) incorrect instrument calibration, (5) poor analytical technique, and (6) deviation from the analytical method. A measurement process for a particular analyte will be considered out-of-statistical-control when one of the following conditions occur:

4.3.3.1.1. A single point outside 3-sigma control limits

4.3.3.1.2. A series of eight consecutive points on the same side of the central line.

4.3.3.1.3. A series of three consecutive points between the warning limits and control limits.

4.3.3.1.4. A series of six consecutively increasing or decreasing points on the same side of the centerline.

4.3.3.1.5. A cyclic pattern of control values.

4.3.3.1.6. These conditions may indicate that the measurement system is out of statistical control. When this situation occurs, the data must be evaluated thoroughly to identify the most appropriate corrective action to be implemented. The problem and its solution may be documented through a Nonconformance Memo as appropriate. Exceeding warning limits will only require a close observation of the measurement system. In reviewing control charts, any significant changes in key analysts, instrumentation, standard

reference materials, or processes must be kept in mind to explain potential out-of-control situations. After thorough evaluation of the data and documentation of corrective actions taken, the QA Department must determine if the defensiveness of analytical results generated during the out of control situation has been jeopardized. If it is determined that data defensiveness has been compromised, the client will be notified of the out of control situation.

4.4. Setting Control Limits

4.4.1. The working control limits to be used by the laboratory are based on evaluation of the calculated laboratory statistical performance and available interlaboratory limits provided in the reference methods. Note that some SW-846 methods only supply single-operator or single-laboratory method performance data, which may not be appropriate.

Accuracy Evaluation

| Lower Limit Evaluation | Upper Limit Evaluation | Accuracy Decision |
|---|---|---|
| Laboratory-generated Lower Limit > Guidance Limit | Laboratory-generated Upper Limit > Guidance Limit | Use laboratory-gen. Lower Limit & Guidance Upper Limit |
| Laboratory-generated Lower Limit > Guidance Limit | Laboratory-generated Upper Limit < Guidance Limit | Use laboratory-gen. Lower Limit & laboratory-generated Upper Limit |
| Laboratory-generated Lower Limit < Guidance Limit | Laboratory-generated Upper Limit > Guidance limit | Use guidance Lower Limit & guidance Upper Limit |
| Laboratory-generated Lower Limit < Guidance Limit | Laboratory-generated Upper Limit < Guidance limit | Use guidance Lower Limit & laboratory-generated Upper Limit |

Precision Evaluation

| Range Evaluation | Precision Decision |
|---|---|
| Laboratory-generated precision value > Guidance precision | Use guidance precision |

| | |
|---|---|
| Laboratory-generated precision < Guidance precision | Use laboratory-generated precision |

Notes: If the decision is to use guidance limits from the method, the laboratory should investigate procedural improvements leading to better performance.

The following outlines other criteria:

| Min/Max | Limit | Percentage | Inorganics | Organics |
|---|---|---|---|---|
| Minimum | LCL | 10% | √ | √ |
| Maximum | LCL | 90% | √ | √ |
| Minimum | UCL | 110% | √ | √ |
| Maximum | UCL | 200% | √ | √ |
| Minimum | RPD | 20% | √ | |
| Maximum | RPD | 99% | √ | √ |
| Maximum | RPD | 30% | | √ |

NOTE: Best Practice limits may be utilized for a particular method/parameter based on laboratory and client approval. Best Practice limits combines the data from a group of laboratories (Knoxville, North Canton and Pittsburgh) to generate limits that are used between the laboratories. This allows for the ease in transfer of work between the laboratories including sharing large projects.

## 5. DEFINITIONS

5.1. Control Chart - A graphical QC tool to monitor method performance over time and to establish acceptance limits.

5.2. Relative Percent Difference (RPD) - a measure of intra-lab precision based on a duplicate sample analyses.

5.3. Grubbs Test – extension of sample sizes and percentage points for significant tests of outlying observations - a statistical outlier test.

5.4. Percent Recovery (%R) or Recovery - a measure of the accuracy (bias) of the measurement process based on a comparison of a measured value for a fortified (spiked) QC sample against the known spiked values.

5.5. Precision - a measure of mutual agreement (or variability) among individual measurements of the same property, usually under prescribed similar conditions.

5.6. Accuracy - the degree of agreement of a measurement (or an average of measurements of the same thing) with an accepted reference or true value. Accuracy is the measure of bias inherent in the system.

5.7. Bias - a systematic (consistent) error in test results. The difference between the population mean and the true or reference value, or as estimated from sample statistics; the difference between the sample average and the reference value.

5.8. X-chart - a control chart that plots a single measurement of a property (e.g., percent recovery) of quality control samples over time. The chart consists of a single line that is the mean of the statistic, warning limits at ± two standard deviations, and control limits at ± 3 sigma.

5.9. Assignable cause - a known reason for an outlying result (e.g., no spike added).

5.10. Duplicate: A second aliquot of a sample that is treated the same as the original sample in order to determine the precision of the method.

5.11. Laboratory Control Sample (LCS):

5.11.1. Organics: A LCS is a volume of deionized laboratory water (for water samples) or a suitable solid material (e.g., clean sand) (for soil/sediment samples) which is spiked with compounds of interest and subjected to the entire analytical procedure in order to estimate the accuracy of the method via percent spike recovery.

5.11.2. Inorganics: A well characterized liquid or solid sample which is prepared, digested or extracted along with each analytical batch of samples.

## 6. REFERENCES

6.1. STL Quality Management Plan, current revision.

6.1.1. STL Quality Management Plan, current revision.

6.1.2. Control Chart Generation SOP, NC-QA-0024

6.1.3. HAZWRAP Requirements for Quality Control of Analytical Data DOE/HWP-65/R1, July, 1990 or current revision.

6.1.4. Navy Installation Restoration Laboratory Quality Assurance Guide (Interim Guidance Document), February 1996.

6.1.5. Handbook for Analytical Quality Control in Water and Wastewater Laboratories, EMSL, US EPA, March 1977.

6.1.6. Test Methods for Evaluating Solid Waste, Third Edition, SW-846, US EPA, Final Update II, September 1994.

# APPENDIX A

(Examples of Control Charts)

## *Calculated Control Limits*

SEVERN TRENT SERVICES

*North Canton*
*Spike List: 928: NC: 8082 Best Practice -LCS*

*QC Type: LCS/DCS*
*Analysis Dates: 05/25/2000 - 06/07/2000*

*Associated SACs:*

| *QC* | *Method* | *Prep* |
|---|---|---|
| 01 | MY | 10 |
| 01 | MY | 2M |
| 01 | MY | 57 |
| 01 | MY | 60 |
| 01 | MY | 61 |
| 01 | MY | 63 |
| 01 | MY | 7C |
| 01 | OH | |
| 2U | MY | 41 |
| 30 | OH | |
| 72 | OH | |

*Aqueous*

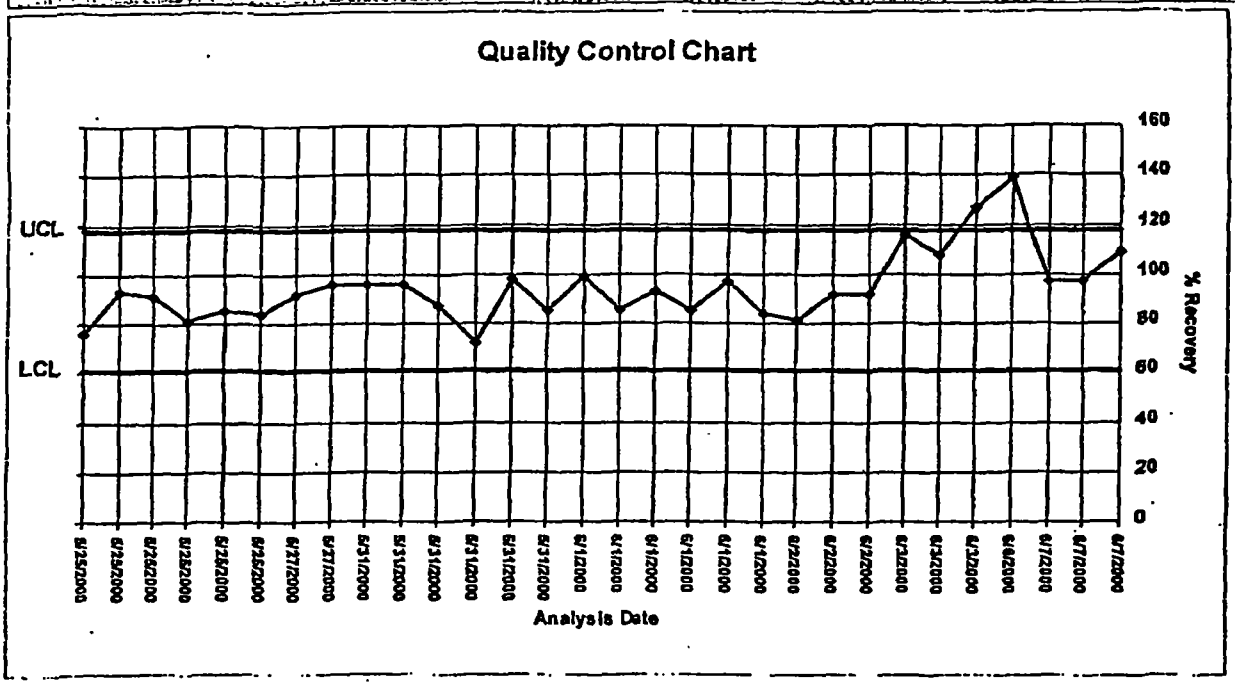
| *Constituent* | *Spike Level* | *Units* | *N* | *Mean* | *Std. Dev.* | *QuantIMS LCL* | *QuantIMS UCL* | *QuantIMS RPD* | *Calculated LCL* | *Calculated UCL* | *Calculated RPD* |
|---|---|---|---|---|---|---|---|---|---|---|---|
| PCB-1016 | 10 | ug/L | 29 | 92.90 | 11.62 | 61 | 118 | 20 | 58 | 128 | 33 |
| PCB-1260 | 10 | ug/L | 30 | 91.20 | 17.69 | 61 | 124 | 27 | 38 | 144 | 53 |

## PCB-1016 · Laboratory Control Sample · Aqueous

**QuantIMS Spike List:** 928 (NC: 8082 Best Practice -LCS)

**Analysis Dates:** 05/25/2000 - 06/07/200

| Method | Method Description | Extraction |
|---|---|---|
| 8081 | Pesticides/PCBs (8081) | EXTRACTION, SOLID/SOLVENT (Auto shaker) w/ACID STRIP (P |
| 8081 | Pesticides/PCBs (8081) | LIQ/LIQ, ACCEL ONE STEP w/ACID STRIP (PCB) - Nominal |
| 8081 | Pesticides/PCBs (8081) | LIQ/LIQ, CONT w/ACID STRIP (PCB) - Nominal |
| 8081 | Pesticides/PCBs (8081) | LIQ/LIQ, SEP FUNNEL w/ACID STRIP (PCB) - Nominal |
| 8081 | Pesticides/PCBs (8081) | SONICATION w/ACID STRIP (PCB) |
| 8081 | Pesticides/PCBs (8081) | SOXHLET (Na2SO4) w/ACID STRIP (PCB) |
| 8081 | Pesticides/PCBs (8081) | WASTE DILUTION w/ACID STRIP (PCB) |
| 8082 | PCBs (8082) | Not specified |




**Statistical Calculations**

| | |
|---|---|
| N | 28 |
| Mean %R: | 92.897 |
| Std. Dev.: | 11.620 |
| Spike Level: | 10 |
| Spike Units: | ug/L |
| QIMS LCL | [illegible] |
| QIMS UCL | [illegible] |
| CALC LWL | 74 |
| CALC UWL | 118 |
| CALC LCL | 58 |
| CALC UCL | 128 |
| N RPD | 11 |
| QIMS RPD | 20 |
| Calc RPD | 0-310 |

Rejected data points are charted

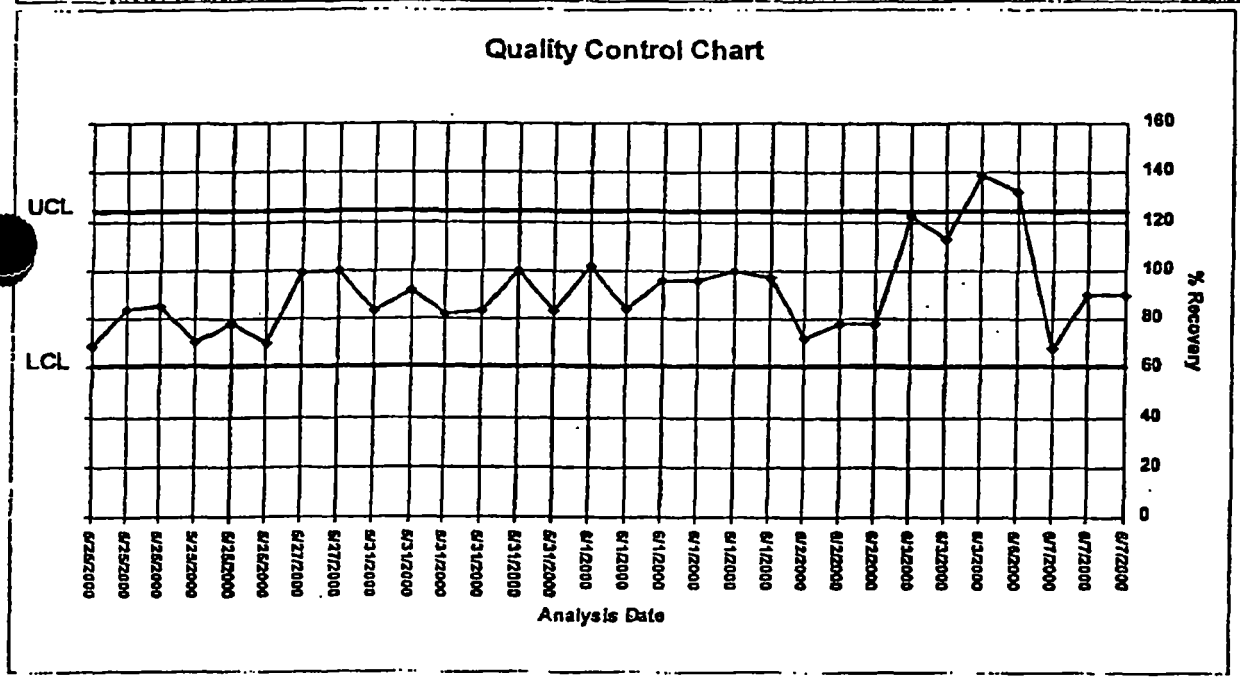
Generated: 6/19/2000

## PCB-1260 — Laboratory Control Sample — Aqueous

**QuantIMS Spike List:** 928 (NC: 8082 Best Practice -LCS)

**Analysis Dates:** 05/25/2000 - 06/07/2000

| Method | Method Description | Extraction |
|---|---|---|
| 8081 | Pesticides/PCBs (8081) | EXTRACTION, SOLID/SOLVENT (Auto shaker) w/ACID STRIP (P |
| 8081 | Pesticides/PCBs (8081) | LIQ/LIQ, ACCEL ONE STEP w/ACID STRIP (PCB) - Nominal |
| 8081 | Pesticides/PCBs (8081) | LIQ/LIQ, CONT w/ACID STRIP (PCB) - Nominal |
| 8081 | Pesticides/PCBs (8081) | LIQ/LIQ, SEP FUNNEL w/ACID STRIP (PCB) - Nominal |
| 8081 | Pesticides/PCBs (8081) | SONICATION w/ACID STRIP (PCB) |
| 8081 | Pesticides/PCBs (8081) | SOXHLET (Na2SO4) w/ACID STRIP (PCB) |
| 8081 | Pesticides/PCBs (8081) | WASTE DILUTION w/ACID STRIP (PCB) |
| 8082 | PCBs (8082) | Not specified |




**Statistical Calculations**

| | |
|---|---|
| N | 30 |
| Mean %R: | 91.2 |
| Std. Dev.: | 17.69 |
| Spike Level: | 10 |
| Spike Units: | ug/L |
| QIMS LCL | 61 |
| QIMS UCL | 124 |
| CALC LWL | 56 |
| CALC UWL | 127 |
| CALC LCL | 38 |
| CALC UCL | 144 |
| N RPD | 12 |
| QIMS RPD | 27 |
| Calc RPD | 53.324 |

Rejected data points are charted

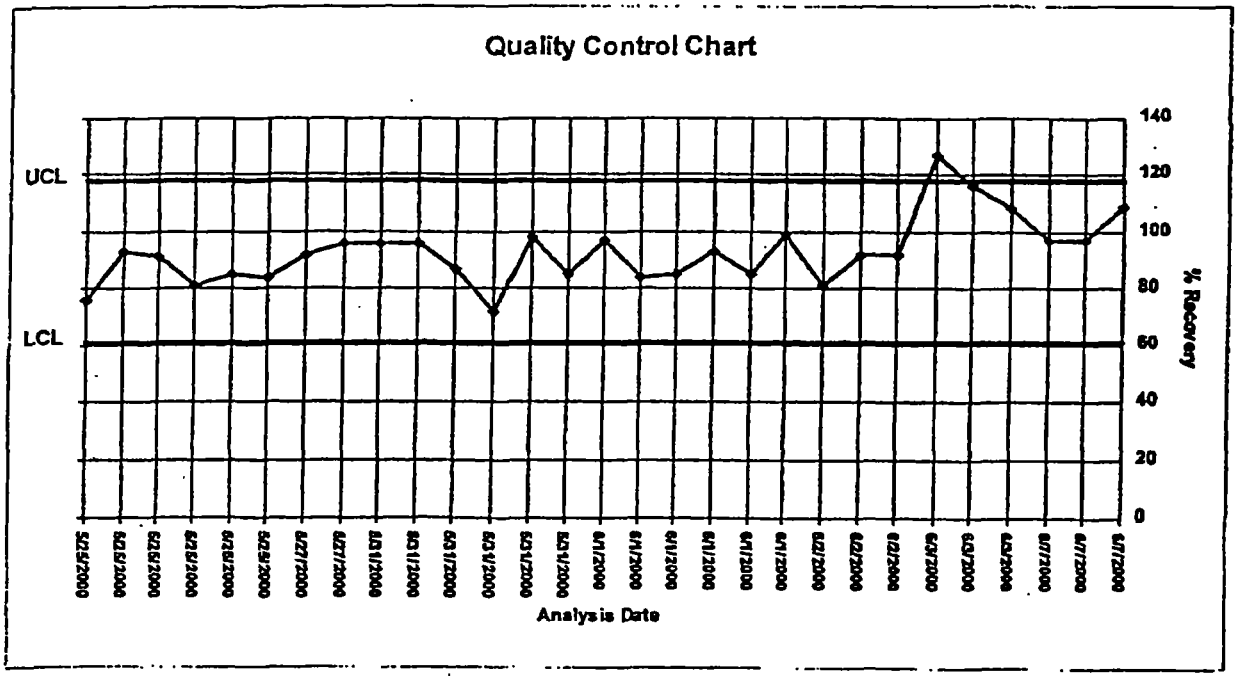
*Generated: 6/19/2000*

## PCB-1016 — Laboratory Control Sample — Aqueous

**QuantIMS Spike List:** 928 (NC: 8082 Best Practice -LCS)

**Analysis Dates:** 05/25/2000 - 06/07/2000

| Method | Method Description | Extraction |
|---|---|---|
| 8081 | Pesticides/PCBs (8081) | EXTRACTION, SOLID/SOLVENT (Auto Shaker) w/ACID STRIP (P |
| 8081 | Pesticides/PCBs (8081) | LIQ/LIQ, ACCEL ONE STEP w/ACID STRIP (PCB) - Nominal |
| 8081 | Pesticides/PCBs (8081) | LIQ/LIQ, CONT w/ACID STRIP (PCB) - Nominal |
| 8081 | Pesticides/PCBs (8081) | LIQ/LIQ, SEP FUNNEL w/ACID STRIP (PCB) - Nominal |
| 8081 | Pesticides/PCBs (8081) | SONICATION w/ACID STRIP (PCB) |
| 8081 | Pesticides/PCBs (8081) | SOXHLET (Na2SO4) w/ACID STRIP (PCB) |
| 8081 | Pesticides/PCBs (8081) | WASTE DILUTION w/ACID STRIP (PCB) |
| 8082 | PCBs (8082) | Not specified |




**Statistical Calculations**

| | |
|---|---|
| N | 29 |
| Mean %R: | 92.897 |
| Std. Dev.: | 11.620 |
| Spike Level: | |
| Spike Units: | |
| QIMS LCL | 61 |
| QIMS UCL | 118 |
| CALC LWL | 70 |
| CALC UWL | 116 |
| CALC LCL | 58 |
| CALC UCL | 128 |
| N RPD | 11 |
| QIMS RPD | 20 |
| Calc RPD | 33.5 |

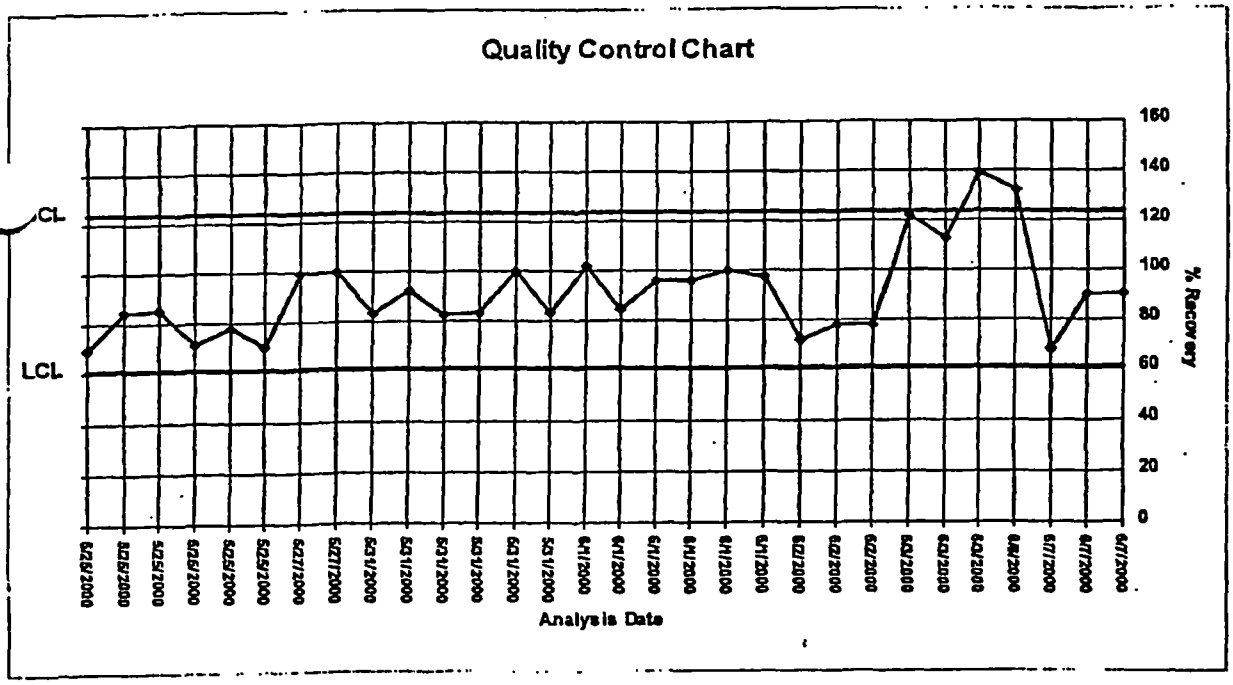
Rejected data points are not charted

## PCB-1260 — Laboratory Control Sample — Aqueous

**QuantIMS Spike List:** 928 (NC: 8082 Best Practice -LCS)

**Analysis Dates:** 05/25/2000 - 06/07/2000

| Method | Method Description | Extraction |
|---|---|---|
| 8081 | Pesticides/PCBs (8081) | EXTRACTION, SOLID/SOLVENT (Auto shaker) w/ACID STRIP (P |
| 8081 | Pesticides/PCBs (8081) | LIQ/LIQ, ACCEL ONE STEP w/ACID STRIP (PCB) - Nominal |
| 8081 | Pesticides/PCBs (8081) | LIQ/LIQ, CONT w/ACID STRIP (PCB) - Nominal |
| 8081 | Pesticides/PCBs (8081) | LIQ/LIQ, SEP FUNNEL w/ACID STRIP (PCB) - Nominal |
| 8081 | Pesticides/PCBs (8081) | SONICATION w/ACID STRIP (PCB) |
| 8081 | Pesticides/PCBs (8081) | SOXHLET (Na2SO4) w/ACID STRIP (PCB) |
| 8081 | Pesticides/PCBs (8081) | WASTE DILUTION w/ACID STRIP (PCB) |
| 8082 | PCBs (8082) | Not specified |




**Statistical Calculations**

| | |
|---|---|
| N | 30 |
| Mean %R: | 91.2 |
| Std. Dev.: | 17.69 |
| Spike Level: | 10 |
| Spike Units: | ug/L |
| QIMS LCL | 61 |
| QIMS UCL | 124 |
| CALC LWL | 66 |
| CALC UWL | 127 |
| CALC LCL | 36 |
| CALC UCL | 144 |
| N RPD | 12 |
| QIMS RPD | 27 |
| Calc RPD | 63.324 |

Rejected data points are not charted

Controlled Copy
Copy No. _____
Implementation Date: _____

SOP No. CORP-IP-0002NC
Revision No. 2.2
Revision Date: 09/25/01


# STL NORTH CANTON STANDARD OPERATING PROCEDURE

## TITLE: ACID DIGESTION OF SOILS, SW846 METHOD 3050B

(SUPERSEDES: REVISION 2.1 DATE 02/11/00)

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Corporate Technology Date

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# 1. SCOPE AND APPLICATION

1.1. This procedure describes the preparation of soil samples for the analysis of certain metals by Graphite Furnace Atomic Absorption (GFAA), Flame Atomic Absorption

(FLAA), Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP), and Inductively Coupled Plasma-Mass Spectrometry (ICP/MS) as specified in SW846 Method 3050B.

1.2. Samples prepared by the protocols detailed in this SOP may be analyzed by ICP, ICP/MS, FLAA or GFAA for the elements listed in Table I (Appendix A). Other elements and matrices may be analyzed following digestion by these protocols provided that the method performance criteria specified in Section 13.0 of this SOP are met.

1.3. This method is not a total digestion, but will dissolve almost all metals that could become "environmentally available". By design, metals bound in silicate structures are not dissolved by this procedure, as they are not usually mobile in the environment. This SOP can be applied to metals in solids, sludges, wastes and sediments.

1.4. This document accurately reflects current laboratory standard operating procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary.

## 2. SUMMARY OF METHOD

A representative 1 gram (wet weight) portion of sample is digested in nitric acid and hydrogen peroxide. The digestate is refluxed with hydrochloric acid for ICP, FLAA or antimony by GFAA analysis. The digestates are then filtered and diluted to 100 mL/100 g.

## 3. DEFINITIONS

3.1. Refer to the glossary in the Laboratory Quality Manual (LQM), latest version.

3.2. Total Metals: The concentration determined on an unfiltered sample following digestion. Note that this method is designed to determine the total *environmentally available* metals.

## 4. INTERFERENCES

4.1. There are numerous routes by which samples may become contaminated. Potential sources of trace metals contamination include: metallic or metal-containing labware (e.g., talc gloves which contain high levels of zinc), containers, impure reagents, dirty glassware, improper sample transfers, dirty work areas, atmospheric inputs such as dirt and dust, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them.

4.2. The entire work area, including the bench top and fume hood, should be thoroughly cleaned on a routine schedule in order to minimize the potential for environmental contamination.

4.3. Boron and silica from the glassware will grow into the sample solution during and following sample processing. For critical low level determinations of boron and silica, only quartz and/or plastic labware should be used.

4.4. Physical interference effects may contribute to inaccuracies in the determinations of trace elements. Oils, solvents and other matrices may not be digested using these methods if they are not soluble with acids. If physical interferences are present, they should be documented.

4.5. Visual interferences or anomalies (such as foaming, emulsions, precipitates, etc.) must be documented.

4.6. Allowing samples to boil or go dry during digestion may result in the loss of volatile metals. If this occurs the sample must be reprepared. Antimony is easily lost by volatilization from hydrochloric media.

4.7. Specific analytical interferences are discussed in each of the determinative methods.

## 5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all STL North Canton associates.

5.2. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately

5.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory. The following specific hazards are known:

5.3.1. The following materials are known to be **corrosive:**

Hydrochloric acid and nitric acid.

5.3.2. The following materials are known to be **oxidizing agents**:

Nitric acid and hydrogen peroxide.

5.3.3. All heating of samples must be carried out in a fume hood.

5.4. The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. Acidification of samples should be done in a fume hood. The analyst should also be aware of the potential for a vigorous reaction.

5.5. Exposure to chemicals must be maintained **as low as reasonably achievable.** Therefore, unless they are known to be non-hazardous, all samples should be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.6. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit or under other means of mechanical ventilation.

5.7. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL North Canton associate. The situation must be reported **immediately** to a laboratory supervisor.

5.8. Always carry bulk concentrated acid bottles in appropriate impact proof containers.

5.9. Acid/peroxide spills must be neutralized immediately, flushed with water and cleaned up using appropriate spill kits.

5.10. Discard chipped or broken beakers to prevent injury. Chipped glassware may be fire polished as an alternative to disposal.

5.11. Any and all accidents and spills must be reported to the lab supervisor or EH&S coordinator.

## 6. EQUIPMENT AND SUPPLIES

6.1. Hot plate, digestion block, steam bath or other heating source capable of maintaining a temperature of 90-99°C.

6.2. Calibrated thermometer that covers a temperature range of 0-200°C.

6.3. Griffin beakers of assorted sizes or equivalent.

6.4. Vapor recovery device (Watch glasses, ribbed or other device).

6.5. Whatman No. 41 filter paper or equivalent.

6.6. Funnels or equivalent filtration apparatus.

6.7. Centrifugation equipment (if desired method of removing particulates is centrifugation).

6.8. Graduated cylinder or equivalent capable of measuring 100 mL within 3% accuracy.

6.9. Analytical balance capable of accurately weighing to the nearest 0.01 grams.

6.10. Repippetors or suitable reagent dispensers.

6.11. Calibrated automatic pipettes with corresponding pipette tips or Class A glass volumetric pipettes.

6.12. Class A volumetric flasks.

6.13. pH indicator strips (pH range 0 - 6).

6.14. Plastic bottles.

## 7. REAGENTS AND STANDARDS

7.1. Reagent water must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks as defined in the determinative SOPs.

7.2. Laboratory Control Sample (LCS) and matrix spike (MS) solutions are purchased as custom STL North Canton solutions. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem.

7.3. Working ICP LCS/MS spike solution: Prepare the ICP LCS/MS working spike solutions from custom stock standards to the final concentration listed in Table II. The

working spike must be prepared in a matrix of 5% $HNO_3$. This acid (5 mL of concentrated $HNO_3$ per 100 mL) must be added to the volumetric flask before the addition of the stock standard aliquot. The working ICP LCS solution must be made fresh every three months.

7.4. Working GFAA LCS/MS spike solution: Prepare the GFAA working LCS/MS spike solutions by diluting the custom stock solution (7.2) 200x. The working spike solution must be prepared in a matrix of 5% $HNO_3$. This acid (5 mL of concentrated $HNO_3$ per 100 mL) must be added to the volumetric flask before the addition of the stock standard aliquot. The working GFAA LCS/MS solution must be made fresh every three months.

7.5. The LCS and MS samples must contain all the elements designated for analysis in each batch of samples. If a non-routine element is required that is not contained in the custom STL North Canton solution, the individual facility must purchase a solution from the designated vendor that will cover the additional analyte(s) of interest and provide for a final spike concentration that is appropriate to the determinative method.

7.6. Aqueous laboratory control samples (LCSW) and matrix spike samples are prepared as described in Sections 9.5 and 9.6. Refer to Tables II and III (Appendix A) for details regarding the stock, working standard and final digestate spike concentrations for ICP and GFAA LCS and matrix spike preparations.

7.7. Nitric acid ($HNO_3$), concentrated, trace metal grade or better.

7.8. Nitric acid, 1:1 - dilute concentrated $HNO_3$ with an equal volume of reagent water.

**Note:** When preparing diluted acids always add acid to water. If the water is added to the acid a violent reaction may occur.

7.9. Hydrochloric acid (HCl), concentrated, trace metal grade or better.

7.10. Hydrochloric acid, 1:1 - dilute concentrated HCl with an equal volume of reagent water.

**Note:** When preparing diluted acids always add acid to water. If the water is added to the acid a violent reaction may occur.

7.11. 30% Hydrogen peroxide ($H_2O_2$), reagent grade.

## 8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Sample holding time for metals included under the scope of this SOP is 180 days from the date of collection to the date of analysis.

8.2. Soil samples do not require preservation but must be stored at 4 °C ± 2 °C until the time of analysis.

## 9. QUALITY CONTROL

Table IV (Appendix A) provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.

9.1. Initial Demonstration of Capability

Prior to analysis of any analyte using Method 3050B the following requirements must be met.

9.1.1. Method Detection Limit (MDL) - An MDL must be determined for each analyte/matrix prior to the analysis of any samples. The MDL is determined using seven replicates of reagent water, spiked with all the analytes of interest, that have been carried through the entire analytical procedure. MDLs must be redetermined on an annual basis in accordance with 40 CFR Part 136 Appendix B requirements or verified as detailed in STL North Canton QA Policy QA-005. The spike level must be between the calculated MDL and 10X the MDL to be valid. The result of the MDL determination must be below the STL North Canton reporting limit.

9.1.2. Initial Demonstration Study- this requires the analysis of four QC check samples. The QC check sample is a well characterized laboratory generated sample used to monitor method performance, which should contain all the analytes of interest. The results of the initial demonstration study must be acceptable before analysis of samples may begin. The results of the initial demonstration study may be used to extend a method for the analysis of other elements provided all acceptance criteria are met.

9.1.2.1. Four aliquots of the check sample (LCS) are prepared and analyzed using the procedures detailed in this SOP and the determinative SOPs.

9.1.2.2. Calculations and acceptance criteria for QC check samples are given in the determinative SOPs (CORP-MT-0001, CORP-MT-0003).

9.2. Preparation Batch - A group of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The preparation batch must contain a method blank, a LCS and a matrix spike/matrix spike duplicate. In some cases, at client request, it may be appropriate to process a matrix spike and sample duplicate in place of the MS/MSD. If clients specify specific samples for MS/MSD, the batch may contain multiple MS/MSD pairs.

9.3. Sample Count - Laboratory generated QC samples (method blanks, LCS, MS/MSD) are not counted towards the maximum 20 samples in a batch. Field QC samples are included in the batch count.

9.4. Method Blank (MB) - One method blank must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. Criteria for the acceptance of blanks are contained within the individual analytical method SOP's. If the method blank does not meet the criteria contained within the analytical method SOPs, the blank and all associated samples in the batch must be redigested.

9.5. Laboratory Control Sample (LCS) - One aqueous LCS must be processed with each preparation batch. The LCS must contain all analytes of interest and must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. On going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. Criteria for the acceptance of LCS results are contained within the individual analytical method SOP's. Corrective action when LCS results fail to meet control limits will be repreparation and reanalysis of the batch. Tables II and III provide the details regarding the stock, working standards and final spike concentrations for ICP and GFAA. Refer to Section 7.3 or 7.4 for instructions on preparation of the aqueous LCS.

9.5.1. The LCS is prepared by spiking a 1mL or 1 g aliquot of reagent water with 2 mL of the working LCS/MS spike solution (7.3 or 7.4). The LCS is then processed as described in either Section 11.10.

9.6. Matrix Spike/Matrix Spike Duplicate (MS/MSD) - One MS/MSD pair must be processed for each preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in

addition to MS/MSD's. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Samples identified as field blanks cannot be used for MS/MSD analysis. If any analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch. Corrective action when MS results fail to meet control limits does not include repreparation of samples unless the results indicate that a spiking error may have occurred. Tables II and III provide the details regarding the stock, working standards and final matrix spike concentrations for ICP and GFAA. Refer to Sections 7.3 and 7.4 for instructions on preparation of the working matrix spike solutions.

9.6.1. The soil matrix spike sample is prepared by spiking a 1 g aliquot of a sample with 2mL of the working LCS/MS spike solution (7.3 or 7.4). The matrix spike sample is then processed as described in either Section 11.10.

9.7. Quality Assurance Summaries - Certain clients may require specific project or program QC which may supersede the SOP requirements. Quality Assurance Summaries (QAS) should be developed to address these requirements.

## 10. CALIBRATION AND STANDARDIZATION

10.1. Hotplate or block temperature must be verified daily for each unit used and must be recorded on either the metals preparation log or in a hotplate temperature logbook. The hotplate temperature should be verified by measuring the temperature of a beaker of reagent water placed on each hotplate. For block digestors, use a tube containing water.

## 11. PROCEDURE

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.3. The heating procedures are carried out in a properly functioning hood.

11.4. All samples are to be checked out of sample control with the chain of custody documentation filled out completely.

11.5. Proper sample identification is extremely important in any preparation procedure. Labeling of beakers and bottles must be done in a manner to ensure connection with the proper sample. The use of automatic label printing programs is recommended to reduce transcription errors (QuantIMS option).

11.6. Samples are typically logged in as either waters or soils. Wastes such as organic liquids or sludges and tissues (animal/vegetable) are usually logged in with solid test codes. When initiating prep, examine the sample to see if the sample matches the matrix designation. If the sample is logged in as aqueous but it appears more like a waste (biphasic, sludge like, organic liquid, lots of sediment etc.) contact the lab supervisor or project administrator for further instructions. In some cases it may be more appropriate to process these samples as solids.

11.7. If possible prepare all the samples of a project at the same time to minimize the QC required and streamline the flow of the project through the lab and reporting group.

11.8. In some cases, both AA and ICP digests are required on each sample. It is recommended that both aliquots be weighed out and processed at the same time.

11.9. Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards.

11.10. Preparation of Soils, Sediments and Sludges for Analysis by GFAA, ICP, ICP/MS and FLAA.

11.10.1. Mix sample thoroughly by stirring with a clean plastic or wooden spoon or spatula.

11.10.2. For each digestion procedure required (i.e., ICP or GFAA), weigh a 1.0 portion of solid and record the exact weight to the nearest 0.01 g. A 2 g sample size may also be used if needed to meet the reporting limits.

11.10.3. Measure additional aliquots of the designated samples for the MS and MSD analyses.

11.10.4. Spike each of the MS and MSD aliquots with 2 mL of the working LCS/MS spiking solution (7.3 or 7.4).

11.10.5. Prepare a beaker for the method blank.

11.10.6. Prepare a beaker for the LCS. Add 2 mL of the working LCS/MS spiking solution (7.3 or 7.5).

11.10.7. Add 10 mL of 1:1 $HNO_3$ and mix the sample.

11.10.8. Heat sample to 95° ±4° C and reflux for 10 minutes without boiling, using a vapor recovery device.

**Note: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY during any part of the digestion.** Doing so will result in the loss of analyte and the sample must be reprepared.

11.10.9. Allow sample to cool, if necessary.

11.10.10. Add 5 mL of concentrated $HNO_3$ and replace vapor recovery device.

11.10.11. Reflux at 95° ±4° C for 30 minutes. (Add reagent water as needed to ensure that the volume of solution is not reduced to less than 5 mL.)

11.10.12. If brown fumes are observed, repeat step 11.10.10 until no more fumes are evolved.

11.10.13. Allow the samples to cool, if necessary.

11.10.14. Add approximately 2 mL of reagent water and 1 mL of 30 % $H_2O_2$. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence.

11.10.15. Replace the vapor recovery device and heat sample until effervescence subsides.

11.10.16. Allow the sample to cool, if necessary.

11.10.17. Continue adding 30% $H_2O_2$ in 1 mL aliquots with warming until effervescence is minimal or sample appearance is unchanged.

**Note:** Do not add more than a total of 10 mL of 30 % $H_2O_2$.

11.10.18. Continue heating at 95° ±4° C for 75 minutes until the volume is reduced to approximately 5-10 mL. Alternatively the sample may be heated for 2 hours.

11.10.19. If the sample is being prepared for ICP or FLAA analyses add 10 mL of concentrated HCl and reflux for an additional 10 minutes without boiling. This step is omitted for analysis by ICP-MS and GFAA

**Note:** Antimony and silver have poor solubility in dilute nitric acid solution. Therefore it is strongly recommended that these elements are determined by the ICP procedure that includes HCl as the final digestion acid.

11.10.20. Allow the sample to cool.

11.10.21. Wash down beaker walls and vapor recovery device with reagent water.

11.10.22. Filter sample through Whatman 41 filter paper or equivalent into a graduated cylinder or equivalent or a pre-weighed bottle. Other measuring bottles (for example, Corning Snap Seals™) may be used if their accuracy is documented and is better than ± 2%. Rinse beaker and filter paper with reagent water to ensure complete sample transfer.

**Note:** In place of filtering, the samples, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material

11.10.23. Dilute sample to 100 mL or 100g with reagent water. The sample is now ready for analysis.

**Note:** This SOP allows for samples to be weighed instead of measured volumetrically. This assumes the density of the diluted sample is close to 1.0 g/mL (See Section 17.1.2).

## 12. DATA ANALYSIS AND CALCULATIONS

Not Applicable.

## 13. METHOD PERFORMANCE

13.1. Method performance is determined by the analysis of matrix spike and matrix spike duplicate samples as well as method blanks and laboratory control samples. In general, the matrix spike recovery should fall within +/- 20 % and the matrix spike duplicates should compare within 20% RPD. Method blanks must meet the criteria specified in the determinative SOPs. The laboratory control samples should recover within 20% of the true value until in house control limits are established. Acceptance criteria are given in the determinative SOPs.

13.2. The initial demonstration study as detailed in Section 9.1.2 must be acceptable before the analysis of field samples under this SOP may begin. The results of the initial demonstration study may be used to extend a method for the analysis of other elements provided all acceptance criteria are met.

13.3. Training Qualification:

The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

## 14. POLLUTION PREVENTION

14.1. This method does not contain any specific modifications that serve to minimize or prevent pollution.

## 15. WASTE MANAGEMENT

15.1. Waste generated in the procedure must be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

15.2. Standards should be purchased and prepared in volumes consistent with laboratory use to minimize the volume of expired standards to be disposed.

## 16. REFERENCES

16.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update III, December 1996. Method 3050B.

16.2. CORP-MT-0001, Inductively Coupled Plasma-Atomic Emission Spectroscopy, Spectrometric Method for Trace Element Analysis of Water and Wastes, Method 6010B and Method 200.7.

16.3. CORP-MT-0003, Graphite Furnace Atomic Absorption Spectroscopy, SW846 Method 7000A and MCAWW 200 Series Methods.

16.4. NC-MT-0002, Inductively Coupled Plasma-Mass Spectrometry, EPA Methods 6020 and 200.8.

16.5. QA-003, STL North Canton QC Program.

16.6. QA-004, Rounding and Significant Figures.

16.7. QA-005, Method Detection Limits.

## 17. MISCELLANEOUS (TABLES, APPENDICES, ETC. . . )

17.1. Modifications/Interpretations from reference method.

17.1.1. Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit. Common lab contaminants, as defined in the determinative SOPs, are allowed up to two times the reporting limit in the blank following consultation with the client.

17.1.2. This SOP allows for aqueous samples to be weighed instead of measured volumetrically. This assumes the density of the sample is close to 1.0 g/mL. Samples with large amounts of sediment or suspended solids, sludges, non-aqueous liquids must be processed volumetrically. Weighing samples directly into the digestion vessel minimizes the potential for cross contamination, offers improved accuracy over the use of graduated cylinders (comparable to volumetric flask accuracy), uses less glassware and is more efficient.

17.2. Modifications from previous SOP

17.2.1. ICP/MS has been added as an appropriate determinative technique.

17.2.2. The approved analyte list may be modified provided that additional elements meet the requirements in section 13.

17.2.3. Directions for digestion for set time periods rather than reduction to set volumes have been added.

17.2.4. The order of two steps in the digestion has been changed. (See section 11.10.20)

17.2.5. Definition of the method as determining total environmentally available metals has been added.

17.3. Facility Specific SOPs

Each facility shall attach a list of facility specific SOPs or approved attachments (if applicable) which are required to implement this SOP or which are used in conjunction with this SOP. If no facility specific SOPs or amendments are to be attached, a statement must be attached specifying that there are none. Refer to the Appendices for any facility specific information required supporting this SOP.

17.4. Documentation and Record Management

The preparation benchsheet should, at a minimum, include the following information:

- Preparation date, analyst initials, matrix, prep type (ICP or GFAA), SOP reference.
- Sample ID; initial weight/volume and final weight/volume.
- Standards Documentation (source, lot, prep date, volume added).
- Analyst Signature.
- Reviewer's Signature and date.

**Figure 1. Soil Sample Preparation (Section 11.10)**

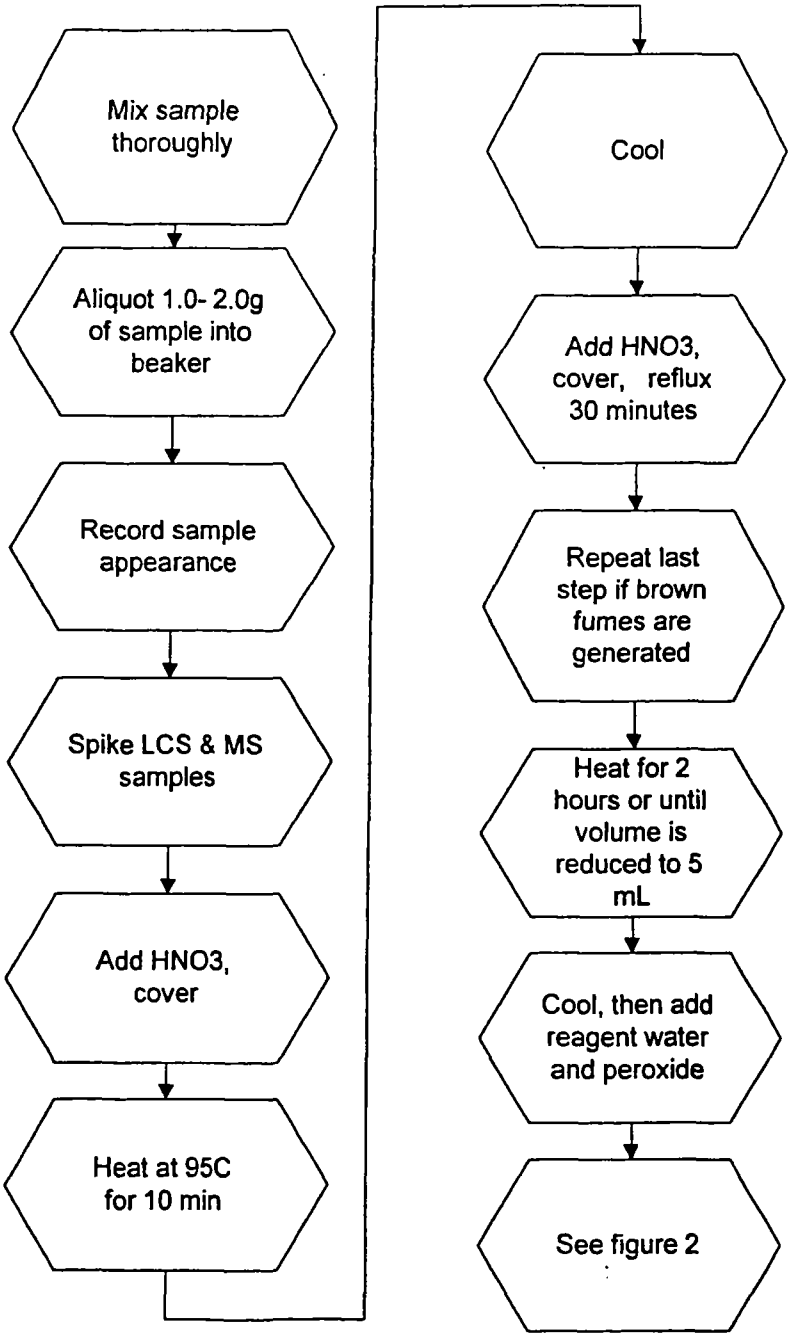
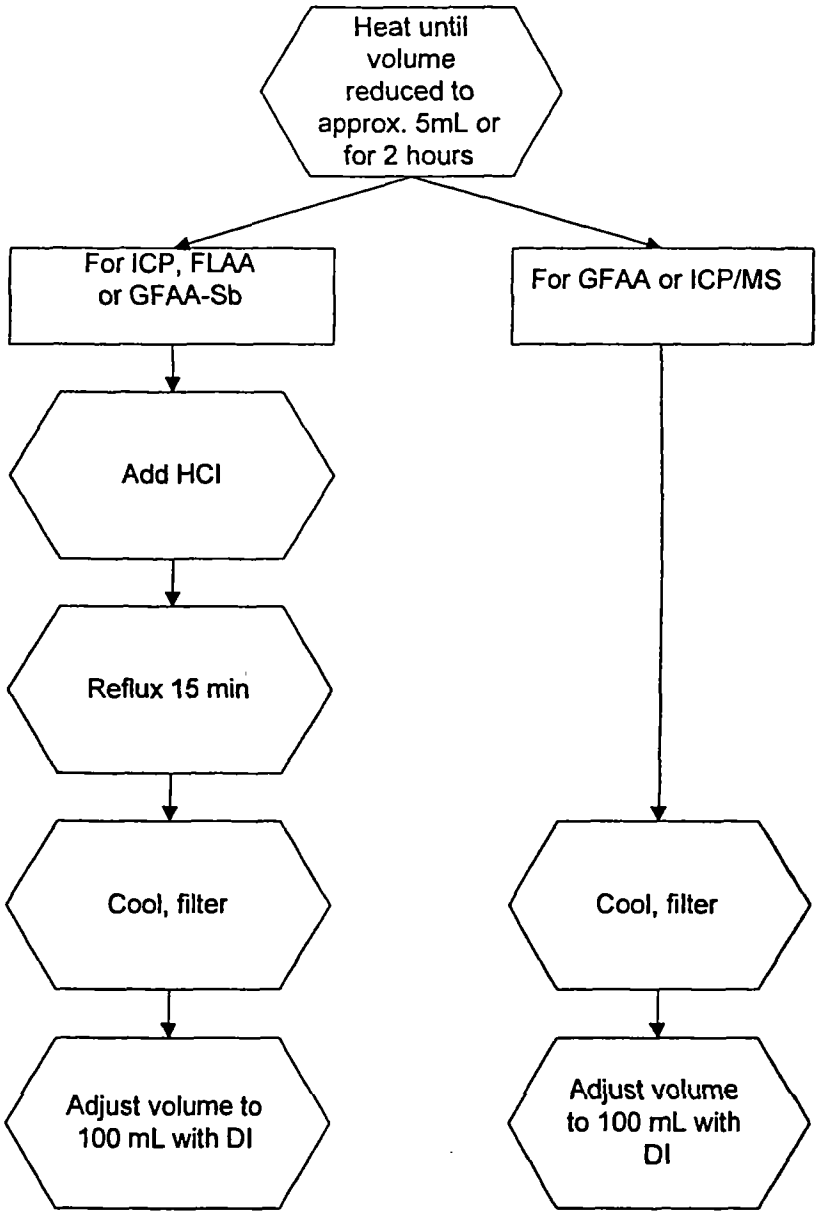


**Figure 2. Soil Sample Preparation (continued)**



# APPENDIX A

# TABLES

**TABLE I. Method 3050A Approved Analyte List**

| ELEMENT | Symbol | CAS Number |
|---|---|---|
| Aluminum | Al | 7429-90-5 |
| Antimony | Sb | 7440-36-0 |
| Arsenic | As | 7440-38-2 |
| Barium | Ba | 7440-39-3 |
| Beryllium | Be | 7440-41-7 |
| Cadmium | Cd | 7440-43-9 |
| Calcium | Ca | 7440-70-2 |
| Chromium | Cr | 7440-47-3 |
| Cobalt | Co | 7440-48-4 |
| Copper | Cu | 7440-50-8 |
| Iron | Fe | 7439-89-6 |
| Lead | Pb | 7439-92-1 |
| Magnesium | Mg | 7439-95-4 |
| Manganese | Mn | 7439-96-5 |
| Molybdenum | Mo | 7439-98-7 |
| Nickel | Ni | 7440-02-0 |
| Potassium | K | 7440-09-7 |
| Selenium | Se | 7782-49-2 |
| Silver | Ag | 7440-22-4 |
| Sodium | Na | 7440-23-5 |
| Thallium | Tl | 7440-28-0 |
| Vanadium | V | 7440-62-2 |
| Zinc | Zn | 7440-66-6 |

## TABLE II. ICP and FLAA Soil Matrix Spike and Aqueous LCS Levels

| ELEMENT | Working LCS/MS Standard (mg/L) | Aqueous LCS/MS Level* (ug/L) | Soil MS Level ** (mg/Kg) |
|---|---|---|---|
| Aluminum | 100 | 2000 | 200 |
| Antimony | 25 | 500 | 50 |
| Arsenic | 100 | 2000 | 200 |
| Barium | 100 | 2000 | 200 |
| Beryllium | 2.5 | 50 | 5 |
| Cadmium | 2.5 | 50 | 5 |
| Calcium | 2500 | 50000 | 5000 |
| Chromium | 10 | 200 | 20 |
| Cobalt | 25 | 500 | 50 |
| Copper | 12.5 | 250 | 25 |
| Iron | 50 | 1000 | 100 |
| Lead | 25 | 500 | 50 |
| Lithium | 50 | 1000 | 100 |
| Magnesium | 2500 | 50000 | 5000 |
| Manganese | 25 | 500 | 50 |
| Molybdenum | 50 | 1000 | 100 |
| Nickel | 25 | 500 | 50 |
| Potassium | 2500 | 50000 | 5000 |
| Selenium | 100 | 2000 | 200 |
| Silver | 2.5 | 50 | 5 |
| Sodium | 2500 | 50000 | 5000 |
| Strontium | 50 | 1000 | 100 |
| Thallium | 100 | 2000 | 200 |
| Vanadium | 25 | 500 | 50 |
| Zinc | 25 | 500 | 50 |
| Boron | 50 | 1000 | 100 |
| Tin | 100 | 2000 | 200 |
| Titanium | 50 | 1000 | 100 |

* Levels shown indicate the spike concentration in the final digestate of the aqueous LCS or matrix spike based on the addition of 2.0 mL working spike (7.3) to 100 mL of sample.

** Final soil spike concentration based on the addition of 2.0 mL working spike (7.3) to 1.0 g of sample/100 mL final volume (assumes 100% solids).

## TABLE III. ICPMS Soil Matrix Spike and Aqueous LCS Levels

| ELEMENT | Working LCS/MS Standard (mg/L) | Aqueous LCS/MS Level* (ug/L) | Soil MS Level ** (mg/Kg) |
|---|---|---|---|
| Aluminum | 10 | 1000 | 100 |
| Antimony | 10 | 100 | 10 |
| Arsenic | 10 | 100 | 10 |
| Barium | 10 | 100 | 10 |
| Beryllium | 10 | 100 | 10 |
| Cadmium | 10 | 100 | 10 |
| Calcium | 100 | 1000 | 100 |
| Chromium | 10 | 100 | 10 |
| Cobalt | 10 | 100 | 10 |
| Copper | 10 | 100 | 10 |
| Iron | 100 | 1000 | 100 |
| Lead | 10 | 100 | 10 |
| Magnesium | 100 | 1000 | 100 |
| Manganese | 10 | 100 | 10 |
| Molybdenum | 10 | 100 | 10 |
| Nickel | 10 | 100 | 10 |
| Potassium | 100 | 1000 | 100 |
| Selenium | 10 | 100 | 10 |
| Silver | 10 | 100 | 10 |
| Sodium | 100 | 1000 | 100 |
| Strontium | 10 | 100 | 10 |
| Thallium | 10 | 100 | 10 |
| Vanadium | 10 | 100 | 10 |
| Zinc | 10 | 100 | 10 |
| Boron | 10 | 100 | 10 |
| Tin | 10 | 100 | 10 |
| Titanium | 10 | 100 | 10 |
| Zirconium | 10 | 100 | 10 |

* Levels shown indicate the spike concentration in the final digestate of the aqueous LCS or matrix spike based on the addition of 1.0 mL working spike (7.4) to 100 mL of sample.

** Final soil spike concentration based on the addition of 1.0 mL working spike (7.4) to 1.0 g of sample/100 mL final volume (assumes 100% solids).

**TABLE IV. GFAA Soil Matrix Spike and Aqueous LCS Spike Levels**

| ELEMENT | Stock LCS/MS Standard (mg/L) | Working LCS/MS Standard (ug/L) | Aqueous LCS/ MS Level * (ug/L) | Soil MS Level** (mg/Kg) |
|---|---|---|---|---|
| Arsenic | 400 | 2000 | 40 | 4 |
| Selenium | 400 | 2000 | 40 | 4 |
| Lead | 400 | 2000 | 40 | 4 |
| Thallium | 400 | 2000 | 40 | 4 |
| Antimony | 400 | 2000 | 40 | 4 |
| Cadmium | 40 | 200 | 4 | 0.4 |
| Chromium | 100 | 500 | 10 | 1 |
| Silver | 50 | 250 | 5 | 0.5 |

* Levels shown indicate the spike concentration in the final digestate of the aqueous LCS or matrix spike based on the addition of 1.0 mL working spike (7.5) to 50 mL of sample.

** Final soil spike concentration based on the addition of 2.0 mL working spike (7.5) to 1.0 g of sample/100 mL final volume (assumes 100% solids).

**TABLE V. Summary of Quality Control Requirements**

| QC PARAMETER | FREQUENCY | ACCEPTANCE CRITERIA | CORRECTIVE ACTION |
|---|---|---|---|
| Method Blank | One per sample preparation batch of up to 20 samples. | Refer to determinative SOPs:<br><br>CORP-MT-0001<br>CORP-MT-0003 | Redigest and reanalyze samples. |
| Laboratory Control Sample (LCS) | One per sample preparation batch of up to 20 samples. | Refer to determinative SOPs:<br><br>CORP-MT-0001<br>CORP-MT-0003 | Redigest and reanalyze all samples associated with the LCS. |
| Matrix Spike | One per sample preparation batch of up to 20 samples. | Refer to determinative SOPs:<br><br>CORP-MT-0001<br>CORP-MT-0003 | Reprep not required unless preparation error suspected. |
| Matrix Spike Duplicate | See Matrix Spike | Refer to determinative SOPs:<br><br>CORP-MT-0001<br>CORP-MT-0003 | See Corrective Action for Matrix Spike. |

# APPENDIX B

# CONTAMINATION CONTROL GUIDELINES

## APPENDIX B. CONTAMINATION CONTROL GUIDELINES

**The following procedures are strongly recommended to prevent contamination:**

All work areas used to prepare standards and spikes should be cleaned before and after each use.

All glassware should be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered or latex gloves must not be used in the metals laboratory since the powder contains silica and zinc, as well as other metallic analytes. Only vinyl or nitrile gloves should be used in the metals laboratory.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

**The following are helpful hints in the identification of the source of contaminants:**

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Separate glassware if an unusually high sample is analyzed and soak with sulfuric acid prior to routine cleaning.

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Copy No. _____
Implementation Date: 4/25/03

SOP No. CORP-IP-0003NC
Revision No. 1.4
Revision Date: 02/19/03


# STL STANDARD OPERATING PROCEDURE

## TITLE: ACID DIGESTION OF AQUEOUS SAMPLES BY SW846 AND MCAWW 200 SERIES METHODS

**(Supersedes: Revision 1.3 Dated 09/25/01)**

Prepared by: Lisa McGall 4.25.03
Date

Reviewed by: Patrick [illegible] 3/21/03
Technology Specialist Date

Reviewed by: Beth Lambert 3/4/03
Quality Assurance Manager Date

Reviewed by: Deborah Budde 3/31/03
Environmental Health and Safety Date

Reviewed by: [illegible] 4/1/03
Laboratory Director Date

Reviewed by: Mark Brenner 4/1/03
~~Corporate~~ Technical Director Technology

Date

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# STL STANDARD OPERATING PROCEDURE

## TITLE: ACID DIGESTION OF AQUEOUS SAMPLES BY SW846 AND MCAWW 200 SERIES METHODS

**(Supersedes: Revision 1.3 Dated 09/25/01)**

Prepared by: _____
Date

Reviewed by: _____
Technology Specialist Date

Reviewed by: _____
Quality Assurance Manager Date

Reviewed by: _____
Environmental Health and Safety Date

Reviewed by: _____
Laboratory Director Date

Reviewed by: _____
Corporate Technology Date

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## 1. SCOPE AND APPLICATION

1.1. This procedure describes the preparation of aqueous samples for the analysis of certain metals by Graphite Furnace Atomic Absorption (GFAA), Flame Atomic Absorption (FLAA), Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP), and Inductively Coupled Plasma-Mass Spectrometry (ICP/MS) using the MCAWW 200 series methods (NPDES) and SW846 Methods 3005A, 3010A, 3020A and 7060A/7740 (RCRA).

1.2. The applicability of each of these preparation protocols to specific analytes is detailed in Tables I and II (Appendix A) and the applicable determinative methods are illustrated by Figures 6 and 7 (Section 17). Additional elements may be analyzed following digestion by these protocols provided that the method performance criteria specified in Section 13.0 of this SOP are met.

1.3. This SOP provides procedures applicable to the preparation of dissolved, suspended, total recoverable and total elements in ground water, aqueous samples, certain aqueous sludges, wastes, and biological tissues, and leachates/extracts.

1.4. SW-846 Method 3005A is used to prepare surface and groundwater samples for total recoverable and dissolved metals determination by FLAA, ICP and GFAA (antimony only).

1.5. MCAWW Method 200.7 Section 9.4 is used to prepare surface water, domestic and industrial waste samples for total recoverable and dissolved metals determination by ICP.

1.6. SW-846 Method 3010A is used to prepare aqueous samples, EP and mobility-procedure extracts, and wastes that contain suspended solids for total metals analysis by FLAA or ICP.

1.7. MCAWW Method 200.7 Section 9.3 is used to prepare surface water and wastes that contain suspended solids for total metals analysis by ICP.

1.8. SW-846 Method 3020A is used to prepare aqueous samples, EP and mobility-procedure extracts, and wastes that contain suspended solids for total metals by GFAA, or ICP/MS.

1.9. MCAWW Method 200.0 Section 4.1.3 is used to prepare surface water and wastes that contain suspended solids for total metals analysis by GFAA.

1.10. MCAWW Method 200.0 Section 4.1.4 is used to surface water, domestic and industrial waste samples for total recoverable and dissolved metals determination by GFAA.

1.11. SW-846 Methods 7060A and 7740, respectively, contain the procedure for the preparation of aqueous samples for arsenic and selenium.

1.12. MCAWW Methods 206.2 and 270.2, respectively, contain the procedure for the preparation of aqueous samples for arsenic and selenium.

1.13. All matrices require digestion prior to analysis with the exception of analyses for dissolved metals in filtered and acidified aqueous samples. Although digestion is not specifically required by the method, some clients and regulators do require digestion of dissolved samples and this must be clarified before project initiation.

## 2. SUMMARY OF METHOD

2.1. Method 3005A / Method 200.7 Section 9.4 - Preparation for Total Recoverable or Dissolved Metals Analysis by FLAA or ICP Spectroscopy

2.1.1. A representative aliquot of sample is heated with nitric and hydrochloric acids and substantially reduced in volume. The digestate is filtered (if necessary) and diluted to volume.

2.2. Method 3010A / Method 200.7 Section 9.3 - Preparation for Total Metals Analysis by FLAA or ICP Spectroscopy

2.2.1. A representative aliquot of sample is refluxed with nitric acid. After the digestate has been reduced to a low volume, it is refluxed with hydrochloric acid, filtered (if necessary) and brought up to volume.

2.3. Method 3020A / Method 200.0 Section 4.1.3 - Preparation for Total Metals for Analysis by GFAA Spectroscopy and ICP/MS.

2.3.1. A representative aliquot of sample is refluxed with nitric acid. After the digestate has been reduced to a low volume, it is cooled, filtered (if necessary) and brought up to volume.

2.4. Methods 7060A/206.2 and Methods 7740/270.2 - Preparation for Arsenic/Selenium Analysis by GFAA

2.4.1. A representative aliquot of sample is heated with nitric acid and peroxide until the digestate has been reduced to a low volume. The sample is cooled, filtered (if necessary) and brought up to volume.

2.5. Method 200.0 Section 4.1.4 - Total Recoverable GFAA Preparation (NPDES)

2.5.1. A representative aliquot of sample is heated with nitric acid and until the digestate has been reduced to a low volume. The sample is cooled, filtered (if necessary) and brought up to volume.

## 3. DEFINITIONS

Additional definitions of terms used in this SOP may be found in the glossary of the LQM.

3.1. Dissolved Metals: Those elements which pass through a 0.45 um membrane. (Sample is acidified after filtration).

3.2. Suspended Metals: Those elements which are retained by a 0.45 um membrane.

3.3. Total Metals: The concentration determined on an unfiltered sample following digestion.

3.4. Total Recoverable Metals: The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid.

## 4. INTERFERENCES

4.1. There are numerous routes by which samples may become contaminated. Potential sources of trace metals contamination include: metallic or metal-containing labware (e.g., talc gloves which contain high levels of zinc), containers, impure reagents, dirty glassware, improper sample transfers, dirty work areas, atmospheric inputs such as dirt and dust, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them.

4.2. The entire work area, including the bench top and fume hood, should be thoroughly cleaned on a routine schedule in order to minimize the potential for environmental contamination. Refer to Appendix B for additional contamination control guidelines.

4.3. Boron and silica from the glassware will migrate into the sample solution during and following sample processing. For critical low level determinations of boron and silica, only quartz and/or plastic labware should be used.

4.4. Physical interference effects may contribute to inaccuracies in the determinations of trace elements. Oils, solvents and other matrices may not be digested using these methods if they are not soluble with acids. If physical interferences are present, they should be documented.

4.5. Visual interferences or anomalies (such as foaming, emulsions, precipitates, etc.) must be documented.

4.6. Allowing samples to boil or go dry during digestion may result in the loss of volatile metals. If this occurs the sample must be reprepared. Antimony is easily lost by volatilization from hydrochloric acid media.

4.7. Precipitation of silver chloride (AgCl) may occur when chloride ions and high concentrations of silver (i.e., greater than 1 mg/L) are present in the sample.

4.8. Specific analytical interferences are discussed in each of the determinative methods.

## 5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all STL associates.

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory. The following specific hazards are known:

5.3.1. The following materials are known to be **corrosive:**

hydrochloric acid and nitric acid.

5.3.2. The following materials are known to be **oxidizing agents**:

nitric acid and hydrogen peroxide.

5.3.3. All sample digestions, including cooling of digestates, must be carried out in a fume hood.

5.4. The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. Acidification of samples should be done in a fume hood. The analyst should also be aware of the potential for a vigorous reaction.

5.5. Exposure to chemicals must be maintained **as low as reasonably achievable.** Therefore, unless they are known to be non-hazardous, all samples should be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.6. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL associate. The situation must be reported **immediately** to a laboratory supervisor.

5.7. Always carry bulk concentrated acid bottles in appropriate impact proof containers.

5.8. Acid/peroxide spills must be neutralized immediately, flushed with water and cleaned up using appropriate spill kits.

5.9. Discard chipped or broken beakers to prevent injury. Chipped glassware may be fire polished as an alternative to disposal.

5.10. Any and all accidents and spills must be reported to the lab supervisor or EH&S coordinator.

## 6. EQUIPMENT AND SUPPLIES

6.1. Hot plate, digestion block or other adjustable heating source capable of maintaining a temperature of 95°C (± 4).

6.2. Calibrated thermometer that covers a temperature range of 0-200°C.

6.3. Griffin beakers of assorted sizes or equivalent.

6.4. Watch glasses, ribbed or equivalent.

6.5. Whatman No. 4 filter paper or equivalent.

6.6. Funnels or equivalent filtration apparatus.

6.7. Centrifugation equipment (if desired method of removing particulates is centrifugation).

6.8. Graduated cylinder or equivalent capable of measuring 50 mL within 3% accuracy.

6.9. Analytical balance capable of accurately weighing to the nearest 0.01 grams.

6.10. Repipetors or suitable reagent dispensers.

6.11. Calibrated automatic pipettes with corresponding pipette tips or Class A glass volumetric pipettes.

6.12. Class A volumetric flasks.

6.13. pH indicator strips (pH range 0 - 6).

6.14. Plastic digestate storage bottles.

## 7. REAGENTS AND STANDARDS

7.1. Reagent water must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks as defined in the determinative SOPs.

7.2. Laboratory Control Sample (LCS) and matrix spike (MS) solutions are purchased as custom STL solutions. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem.

7.3. Working ICP LCS/MS spike solution: Prepare the ICP LCS/MS working spike solution from custom stock standards to the final concentration listed in Table III. The working spike must be prepared in a matrix of 5% $HNO_3$. This acid (5 mL of concentrated $HNO_3$ per 100 mL) must be added to the volumetric flask before the addition of the stock standard aliquot. The working ICP LCS solution must be made fresh every three months.

7.4. Working GFAA LCS/MS spike solution: Prepare the GFAA working LCS spike solution by diluting the custom stock solution (7.2) 200x. The working spike solution must be prepared in a matrix of 5% $HNO_3$. This acid (5 mL of concentrated $HNO_3$ per 100 mL) must be added to the volumetric flask before the addition of the stock standard aliquot. The working GFAA LCS solution must be made fresh every three months.

7.5. The TCLP MS working spike solution is provided directly by the vendor, no further standard preparation is necessary.

7.6. The LCS and MS samples must contain all the elements designated for analysis in each batch of samples. If a non-routine element is required that is not contained in the custom STL solution, the individual facility must purchase a solution from the designated vendor that will cover the additional analyte(s) of interest and provide for a final spike concentration that is appropriate to the determinative method.

7.7. Aqueous laboratory control samples (LCSW) and matrix spike samples are prepared as described in Sections 9.5 and 9.6. Refer to Tables III and IV(Appendix A) for details regarding the stock, working standard and final digestate spike concentrations for ICP and GFAA LCS and matrix spike preparations.

7.8. Nitric acid ($HNO_3$), concentrated, trace metal grade or better.

7.9. Nitric acid, 1:1 - dilute concentrated $HNO_3$ with an equal volume of reagent water.

**Note**: When preparing diluted acids always add acid to water. If the water is added to the acid a violent reaction may occur.

7.10. Hydrochloric acid (HCl), concentrated, trace metal grade or better.

7.11. Hydrochloric acid, 1:1 - dilute concentrated HCl with an equal volume of reagent water.

**Note**: When preparing diluted acids <u>always</u> add acid to water. If the water is added to the acid a violent reaction may occur.

7.12. 30% Hydrogen peroxide ($H_2O_2$), reagent grade.

## 8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Sample holding time for metals included under the scope of this SOP is 180 days from the date of collection to the date of analysis.

8.2. Aqueous samples are preserved with nitric acid to a pH of <2 and may be stored in either plastic or glass. If boron or silica are to be determined, plastic containers are preferred. Refrigeration is not required. Preservation must be verified prior to analysis.

8.3. For dissolved metals analysis, the samples should be filtered through a 0.45 um filter prior to preservation. Filtration must be done in the field or within 24 hours of collection.

**Note**: If a sample being analyzed for dissolved metals is found to contain sediment the analyst should contact their supervisor or group leader. The client should be notified of the problem to decide how to treat the sample.

## 9. QUALITY CONTROL

Table VI (Appendix A) provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.

9.1. Initial Demonstration of Capability

Prior to analysis of any analyte using any method contained within this SOP the following requirements must be met:

9.1.1. Method Detection Limit (MDL) - An MDL must be determined for each analyte/matrix prior to the analysis of any samples. The MDL is determined using seven replicates of reagent water, spiked with all the analytes of interest, that have been carried through the entire analytical procedure. MDL's must be redetermined on an annual basis in accordance with 40 CFR Part 136 Appendix B requirements as detailed in STL QA Policy QA-005. The spike level must be between the calculated MDL and 10X the MDL to be valid. The result of the MDL determination must be below the STL reporting limit.

9.1.2. Initial Demonstration Study - This requires the analysis of four QC check samples. The QC check sample is a well-characterized laboratory generated

sample used to monitor method performance, which should contain all the analytes of interest. The results of the initial demonstration study must be acceptable before analysis of samples may begin. The results of the initial demonstration study may be used to extend a method for the analysis of other elements provided all acceptance criteria are met.

9.1.2.1. Four aliquots of the check sample (LCS) are prepared and analyzed using the procedures detailed in this SOP and the determinative SOPs.

9.1.2.2. Calculations and acceptance criteria for QC check samples are given in the determinative SOPs (CORP-MT-0001, CORP-MT-0003).

9.2. Preparation Batch - A group of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The preparation batch must contain a method blank, a LCS and a matrix spike/matrix spike duplicate. In some cases, at client request, it may be appropriate to process a matrix spike and sample duplicate in place of the MS/MSD. If clients specify specific samples for MS/MSD, the batch may contain multiple MS/MSD pairs.

9.3. Sample Count - Laboratory generated QC samples (method blanks, LCS) are not included in the sample count for determining the size of a preparation batch. MS/MSD are not included in the sample count unless there are multiple sets of MS/MSD per batch. In other words, the first MS/MSD are not counted; all additional MS and MSDs are counted as samples.

9.4. Method Blank (MB) - One method blank must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. Criteria for the acceptance of blanks are contained within the individual analytical method SOP's. If the method blank does not meet the criteria contained within the analytical method SOPs; the blank and all associated samples in the batch must be redigested.

9.4.1. Aqueous method blanks are prepared by taking 50 mL or 50 g of reagent water through the appropriate procedure as described in Section 11.

9.4.2. TCLP method blanks are prepared by taking 50 mL or 50 g of leachate fluid through the appropriate procedure as described in Section 11.

9.5. Laboratory Control Sample (LCS) - One aqueous LCS must be processed with each preparation batch. The LCS must contain all analytes of interest and must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. On going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. Criteria for the acceptance of LCS results are contained within the individual analytical method SOP's. Corrective action when LCS results fail to meet control limits will be repreparation and reanalysis of the batch. Refer to Section 7.3 and 7.4 for instructions on preparation of the aqueous LCS spike solution.

9.5.1. The aqueous LCS is prepared by spiking a 50 mL aliquot of reagent water with 1.0 mL of the working LCS/MS spike solution (7.3 or 7.4). The LCS is then processed through the appropriate procedure as described in Section 11.

9.6. Matrix Spike/Matrix Spike Duplicate (MS/MSD) - One MS/MSD pair must be processed for each preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MSD's. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Samples identified as field blanks cannot be used for MS/MSD analysis. If any analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch. Corrective action when MS results fail to meet control limits does not include repreparation of samples unless the results indicate that a spiking error may have occurred.

9.6.1. The aqueous matrix spike sample is prepared by spiking a 50 mL aliquot of a sample with 1.0 mL of the working LCS/MS spike solution (7.3 or 7.4). The matrix spike sample is then processed as described in Section 11.

9.6.2. The TCLP matrix spike sample is prepared by spiking a 50 mL aliquot of a leachate with 0.5 mL of the working TCLP spike solution (7.5). The matrix spike sample is then processed as described in Section 11.

NOTE: The TCLP matrix spike must be added prior to preservation of the leachate.

9.6.3. If insufficient sample is available to process a MS/MSD, then a second LCS must be processed. The LCS pair is then evaluated according to the MS/MSD criteria.

9.7. Quality Assurance Summaries - Certain clients may require specific project or program QC that may supersede the SOP requirements. Quality Assurance Summaries (QAS) should be developed to address these requirements.

## 10. CALIBRATION AND STANDARDIZATION

10.1 Hotplate temperature must be verified daily for each hotplate used and must be recorded on either the metals preparation log or in a hotplate temperature logbook. The hotplate temperature should be verified by measuring the temperature of a beaker of reagent water placed on each hotplate.

## 11. PROCEDURE

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.3. All digestion procedures must be carried out in a properly functioning hood.

11.4. All samples are to be checked out of sample control with the chain of custody documentation filled out completely.

11.5. Proper sample identification is extremely important in any preparation procedure. Labeling of beakers and bottles must be done in a manner to ensure connection with the proper sample.

11.6. Samples are typically logged in as either waters or soils. Wastes such as organic liquids or sludges and tissues (animal/vegetable) are usually logged in with solid test codes. When initiating prep, examine the sample to see if the sample matches the matrix designation. If the sample is logged in as aqueous but it appears more like a waste (biphasic, sludge like, organic liquid, lots of sediment etc.) contact the lab

supervisor or project manager for further instructions. In some cases it may be more appropriate to process these samples as solids.

11.7. If possible prepare all the samples of a project at the same time to minimize the QC required and streamline the flow of the project through the lab and reporting group.

11.8. In most cases, both AA and ICP digests are required on each sample. It is recommended that both aliquots be measured out and processed at the same time.

11.9. Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards.

11.10. The following procedure must be followed for all aqueous sample preparations:

11.10.1. Measure sample pH with pH paper on a separate aliquot of sample.

**Note**: If the sample pH is > 2 pH units, the client must be notified of the anomaly.

**Note**: If sample pH has already been verified and documented in sample receipt this step may be omitted.

11.10.2. Mix sample by shaking the container.

11.10.3. Measure and transfer 50 mL or 50 g of the sample into a beaker.

**Note**: This SOP allows for samples to be weighed instead of measured volumetrically.

11.10.4. Measure two extra aliquots of sample selected for the MS/MSD analysis. Spike each aliquot with the appropriate spiking solutions (7.3-7.5,9.6).

11.10.5. Measure and transfer 50 mL of reagent water into a beaker for the method blank.

11.10.6. Measure and transfer 50 mL of reagent water into a beaker for the LCS and add the appropriate spiking solutions (7.3-7.5,9.6).

11.11. Proceed to the appropriate Section for the desired method as follows:

| | |
|---|---|
| Method 3005A or Method 200.7 Section 9.4 | 11.12 |
| Method 3010A or Method 200.7 Section 9.3 | 11.13 |
| Method 3020A or Method 200.0 Section 4.1.3 | 11.14 |
| Method 7060A/7740 or Method 206.2/270.2 | 11.15 |
| Method 200.0 Section 4.1.4 | 11.16 |

11.12. **Method 3005A / Method 200.7 Section 9.4 - Preparation for Total Recoverable or Dissolved Metals Analysis by FLAA or ICP (See Figures 1, 6 and 7)**

11.12.1. To the sample beaker, add 1 mL of concentrated $HNO_3$ and 2.5 mL of concentrated HCl.

11.12.2. Cover with ribbed watch glass.

11.12.3. Heat at 95°C (± 4) until volume is reduced to between 15 and 20 mL.

**NOTE: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY.** Doing so will result in the loss of analyte and the sample must be reprepared.

11.12.4. Cool the beaker in a fume hood.

11.12.5. Wash down beaker walls and watch glass with reagent water.

11.12.6. Filter sample, if insoluble materials are present, through Whatman 4 filter paper that has been pre-rinsed with dilute nitric acid.

**Note**: If any samples in a preparation batch are filtered, the method blank and LCS associated with that batch must also be filtered.

**Note:** In place of filtering, the samples, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

11.12.7. Rinse beaker and filter paper with reagent water to ensure complete sample transfer.

11.12.8. Adjust the final volume/mass to 50 mL or 50 g with reagent water. The sample is now ready for analysis

11.13. **Method 3010A / Method 200.7 Section 9.3 - Preparation for Total Metals Analysis by FLAA or ICP Spectroscopy (See Figures 2, 6 and 7)**

11.13.1. To the sample beaker, add 3.0mL of concentrated $HNO_3$.

11.13.2. Cover with ribbed watch glass.

11.13.3. Place beaker on hotplate 95°C (± 4) and evaporate for 4-5 hours or to low volume of 15-20 mL while ensuring that no portion of the bottom of the beaker is allowed to go dry.

**NOTE: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY.** Doing so will result in the loss of analyte and the sample must be reprepared.

11.13.4. If necessary, add another 1.5 ml portion of concentrated $HNO_3$ and re-cover the beaker. Reflux 15 minutes.

11.13.5. Add 5 mL of 1:1 HCl.

11.13.6. Cover and reflux for an additional 15 minutes to dissolve precipitate or residue. Cool in a fume hood.

11.13.7. Wash down beaker walls and watch glass with reagent water.

11.13.8. Filter sample, if insoluble materials are present, through Whatman 4 filter paper.

**Note**: If any samples in the QC batch are filtered the method blank and LCS associated with that batch must also be filtered.

**Note:** In place of filtering, the samples, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

11.13.9. Rinse beaker and filter paper with reagent water to ensure complete sample transfer.

11.13.10. Adjust final volume/mass to 50 mL or 50 g with reagent water. The sample is now ready for analysis.

11.14. **Method 3020A / Method 200.0 Section 4.1.3 - Preparation for Total Metals Analysis by GFAA or Total Recoverable Metals by ICPMS (See Figures 3, 6 and 7)**

11.14.1. To the sample beaker, add 1.5 mL of concentrated $HNO_3$.

11.14.2. Cover with ribbed watch glass.

11.14.3. Place beaker on hotplate 95°C (± 4) and evaporate to low volume of 15-20 mL while ensuring that no portion of the bottom of the beaker is allowed to go dry.

**NOTE: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY.** Doing so will result in the loss of analyte and the sample must be reprepared.

11.14.4. If necessary, add another 1.5 mL portion of concentrated $HNO_3$. Recover, and reflux 15 minutes. Cool the beaker in a fume hood.

11.14.5. Filter sample, if insoluble materials are present, through Whatman 4 filter paper.

**Note**: If any samples in the QC batch are filtered the method blank and LCS associated with that batch must also be filtered.

**Note:** In place of filtering, the samples, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

11.14.6. Rinse beaker and filter paper with reagent water to ensure complete sample transfer.

11.14.7. Adjust final volume to 50 mL with reagent water. The sample is now ready for analysis.

11.15. **Method 7060A/7740 and Method 206.2/270.2 - Preparation for Arsenic and Selenium Analysis by GFAA (See Figures 4, 6 and 7)**

11.15.1. To the sample beaker, add 1 mL of 30 % $H_2O_2$ and 1.0 mL of 1:1 $HNO_3$.

11.15.2. Heat, until the digestion is complete, at 95°C (± 4) or until the volume has been reduced to 15-20 mL.

11.15.3. Cool beaker.

11.15.4. Filter sample, if insoluble materials are present, through Whatman 4 filter paper that has been pre-rinsed with dilute nitric acid.

**Note**: If any samples in the QC batch are filtered the method blank and LCS associated with that batch must also be filtered.

**Note:** In place of filtering, the samples, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

11.15.5. Rinse beaker and filter paper with reagent water to ensure complete sample transfer.

11.15.6. Adjust final volume to 50 mL with reagent water. The sample is now ready for analysis.

11.16. **Method 200.0 Section 4.1.4 - Preparation for Total Recoverable GFAA Analyses. (See Figures 5 and 7)**

11.16.1. To the sample beaker, add 1.0 mL of 1:1 $HNO_3$.

11.16.2. Heat, until the digestion is complete, at 95°C (± 4) or until the volume has been reduced to 15 - 20 mL.

11.16.3. Cool beaker.

11.16.4. Filter sample, if insoluble materials are present, though Whatman 4 filter paper.

**Note**: If any samples in the QC batch are filtered the method blank and LCS associated with that batch must also be filtered.

**Note:** In place of filtering, the samples, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

11.16.5. Rinse beaker and filter paper with reagent water to ensure complete sample transfer.

11.16.6. Adjust final volume to 50 mL with reagent water. The sample is now ready for analysis.

## 12. DATA ANALYSIS AND CALCULATIONS

Not Applicable.

## 13. METHOD PERFORMANCE

13.1. Method performance is determined by the analysis of matrix spike and matrix spike duplicate samples as well as method blanks and laboratory control samples. In general, the matrix spike recovery should fall within +/- 20 % and the matrix spike duplicates should compare within 20% RPD. Method blanks must meet the criteria specified in determinative SOPs. The laboratory control samples should recover within 20% of the true value until in house control limits are established. Acceptance criteria are given in the determinative SOPs.

13.2. The initial demonstration study as detailed in Section 9.1.2 must be acceptable before the analysis of field samples under this SOP may begin. The results of the initial demonstration study may be used to extend a method for the analysis of other elements provided all acceptance criteria are met.

13.3. Training Qualification:

The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

## 14. POLLUTION PREVENTION

14.1. This method allows for the proportional reduction of sample and reagent volumes to decrease waste generation.

## 15. WASTE MANAGEMENT

15.1. Waste generated in the procedure must be segregated and disposed according to the facility hazardous waste procedures. The facility EH & S coordinator should be contacted if additional information is required.

15.2. Standards should be purchased and prepared in volumes consistent with laboratory use to minimize the volume of expired standards to be disposed.

## 16. REFERENCES

16.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update I, Revision 1, July 1992. Methods 3005A, 3010A, 3020A, 7060A and 7740A.

16.2. Methods for the Chemical Analysis of Water and Waste (MCAWW), 1983.

16.3. CORP-MT-0001, Inductively Coupled Plasma-Atomic Emission Spectroscopy, Spectrometric Method for Trace Element Analysis of Water and Wastes, Method 6010A and Method 200.7.

16.4. CORP-MT-0003, Graphite Furnace Atomic Absorption Spectroscopy, SW846 Method 7000A and MCAWW 200 Series Methods.

16.5. QA-003, STL QC Program.

16.6. QA-004, Rounding and Significant Figures.

16.7. QA-005, Method Detection Limits.

## 17. MISCELLANEOUS (TABLES, APPENDICES, ETC. . . )

17.1. Modifications/Interpretations from reference methods.

17.1.1. Modifications applicable to SW-846 reference methods.

17.1.1.1. Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit. Common lab contaminants are allowed up to two times the reporting limit in the blank following consultation with the client.

17.1.1.2. The referenced methods as well as Table 3-1 of SW-846 refer to the use of a 100 mL aliquot for digestion. This SOP requires the use of a 50 mL sample size to reduce waste generation. The use of reduced sample volumes are supported in EPA's document "Response to Public Comments Background Document,

Promulgation of the Second Update to SW-846, Third Edition" dated November 3, 1994. This document stated "flexibility to alter digestion volumes is addressed and "allowed" by the table (3-1) and is also inherently allowed by specific digestion methods. Table 3-1 is only to be used as guidance when collecting samples..." EMSL-Ci has also taken the stance that "reduction in sample size and appropriate corresponding reduction in sample volume is not considered a significant change in the methodology." Additionally, in written correspondence from the Office of Solid Waste, Olliver Fordham stated " As a "representative sample" can be assured, scaling causes no loss of precision and accuracy in the analysis."

17.1.2. Modifications Specific to Method 3010A

17.1.2.1. Section 11.13.7 of this SOP requires the sample be reduced to a volume of 15 - 20 mL. Section 7.2 of Method 3010A states the volume should be reduced to 3 mL but also states that no portion of the bottom of the beaker should go dry. The SOP required volume is a closer approximation of the volume required to provide an adequate covering of the beaker so as to prevent the loss of critical analytes through volatilization.

17.1.2.2. The scope of 3010A has been expanded to include silver based on comparison studies with 7760A. Method 3010A consistently demonstrated improved accuracy and precision over Method 7760A in the matrices tested (reagent water, surface water and TCLP leachate) up to a concentration of 1 ppm silver.

17.1.3. Modifications Specific to Method 3020A

17.1.3.1. Section 11.14.3 of this SOP requires the sample be reduced to a volume of 15 - 20 mL. Section 7.2 of Method 3010A states the volume should be reduced to 3 mL but also states that no portion of the bottom of the beaker should go dry. The SOP required volume is a closer approximation of the volume required to provide an adequate covering of the beaker so as to prevent the loss of critical analytes through volatilization.

17.1.4. Modifications Specific to Method 7060A/7740

17.1.4.1. Methods 7060A and 7740A incorporate the use of a two step dilution to accommodate the addition of a nickel nitrate modifier.

This SOP performs the dilution directly in one step and omits the addition of the modifier. The modifier is added automatically at the instrument by direct injection into the furnace.

17.1.5. Modifications Specific to MCAWW Methods

It was determined by technical review that several of the MCAWW methods were equivalent to the SW-846 methods and therefore were combined under the scope of this SOP as described in Section 11.0. The nature of the differences were deemed insignificant in regards to the amount of acid added and the evaporative volume based on the flexibility allowed by the methods (i.e., add additional acid as required) and the subjective wording of the methods (i.e., evaporate to near dryness vs. an exact volume).

17.2. Modifications from previous SOP

17.2.1. Added ICP/MS to the digestion procedures.

17.3. Facility Specific SOPs

Each facility shall attach a list of facility specific SOPs or approved attachments (if applicable) which are required to implement this SOP or which are used in conjunction with this SOP. If no facility specific SOPs or amendments are to be attached, a statement must be attached specifying that there are none. Refer to the Appendices for any facility specific information required to support this SOP.

17.4. Documentation and Record Management

The preparation benchsheet should, at a minimum, include the following information:

- Preparation date, analyst name, matrix, prep type (ICP or GFAA), SOP reference.
- Sample ID; initial weight/volume and final weight/volume.
- Standards Documentation (source, lot, prep date, volume added).
- Analyst Signature.
- Reviewer's Signature and date.

**Figure 1. Method 3005A / Method 200.7 Section 9.4 (Section 11.12)**

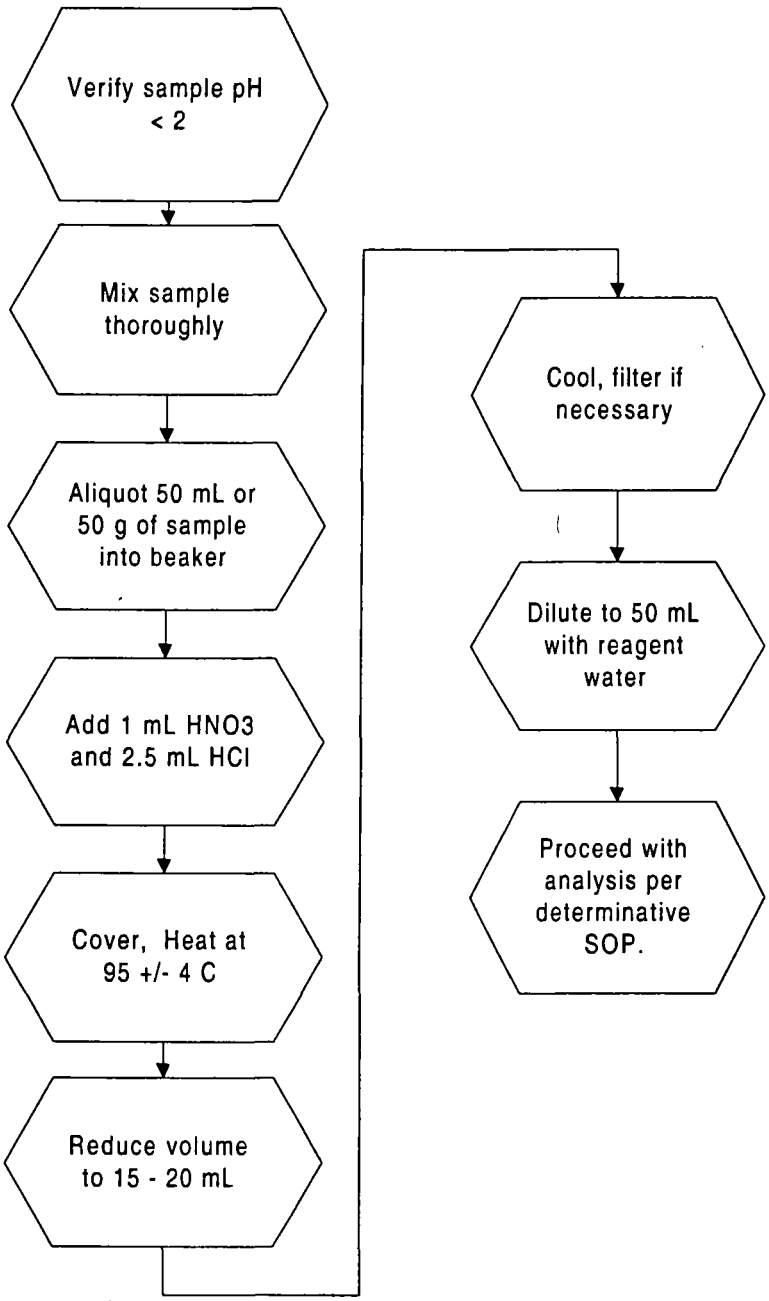


**Figure 2. Method 3010A / Method 200.7 Section 9.3 (Section 11.13)**

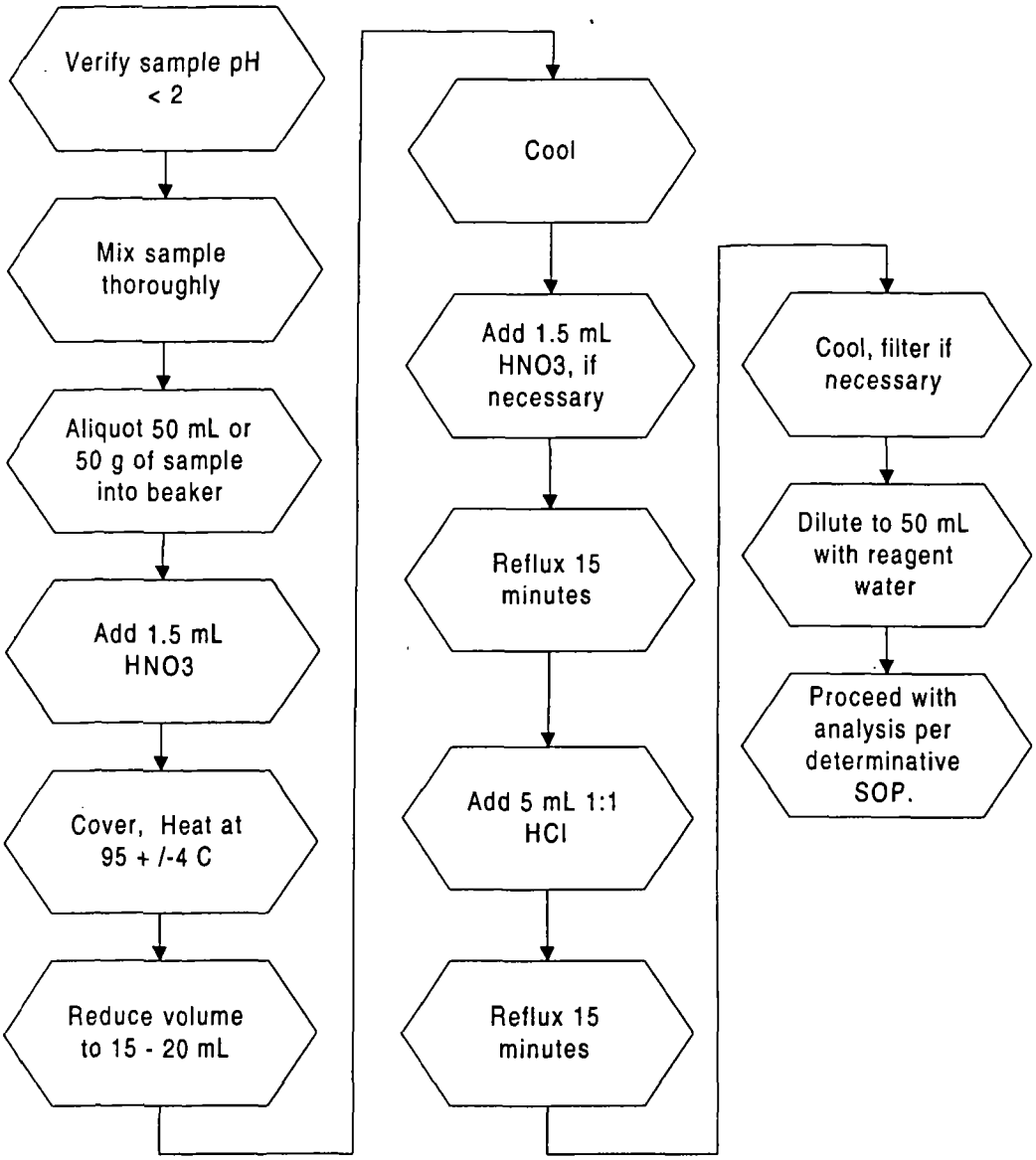


**Figure 3. Method 3020A / Method 200.0 Section 4.1.3 (Section 11.14)**

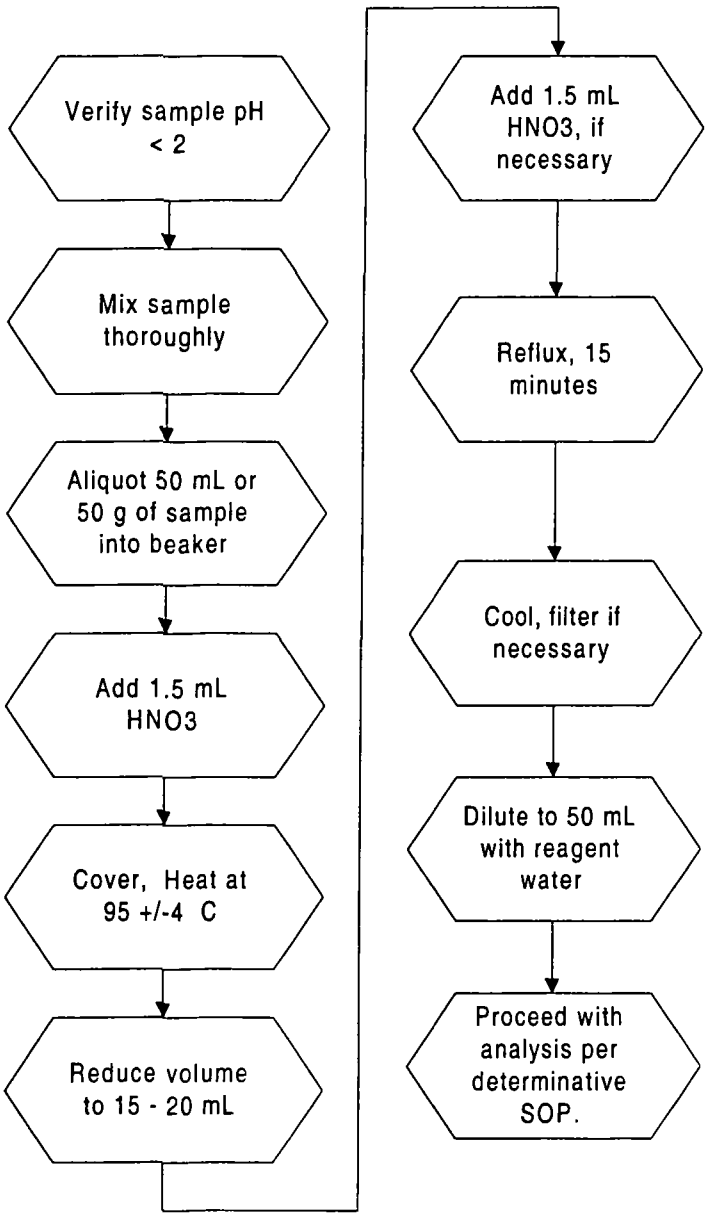


**Figure 4. Method 7060A/7740A and Method 206.2/270.2 (Section 11.15)**

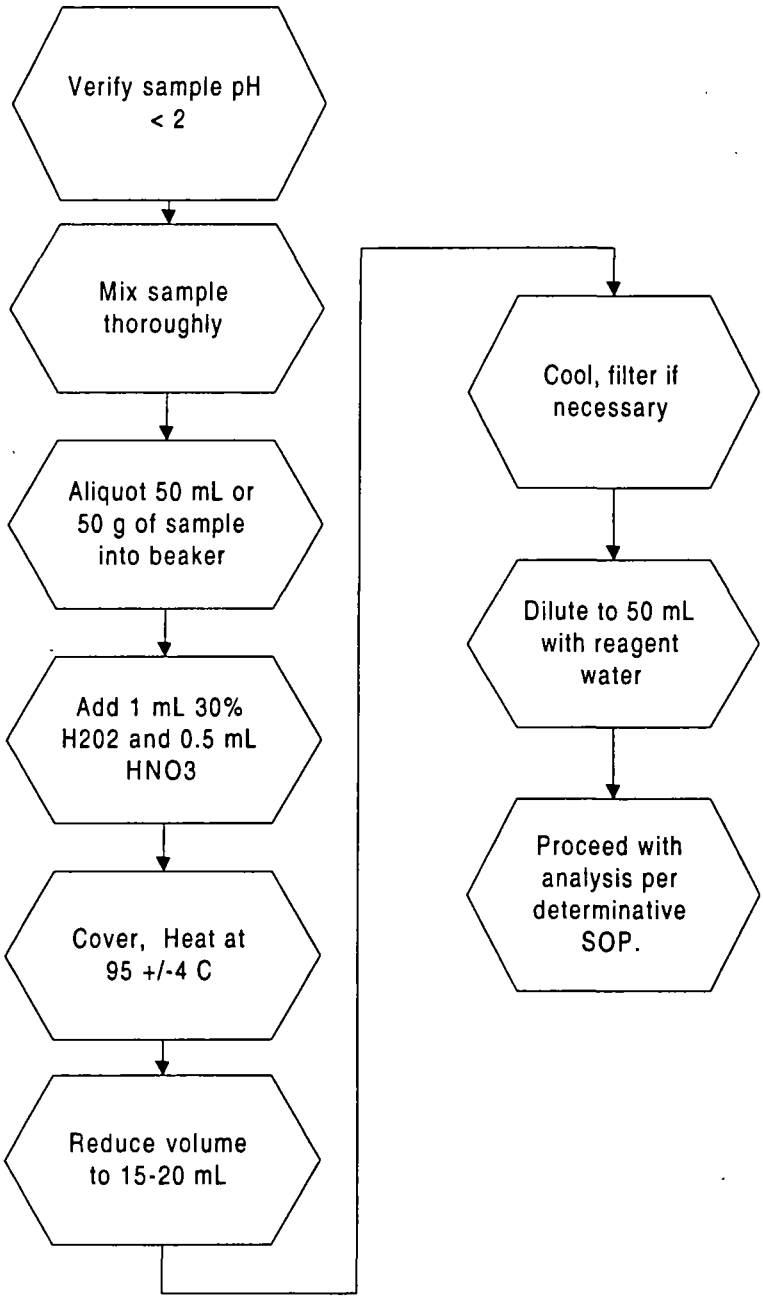


**Figure 5. Method 200.0 Section 4.1.4 (Section 11.16)**

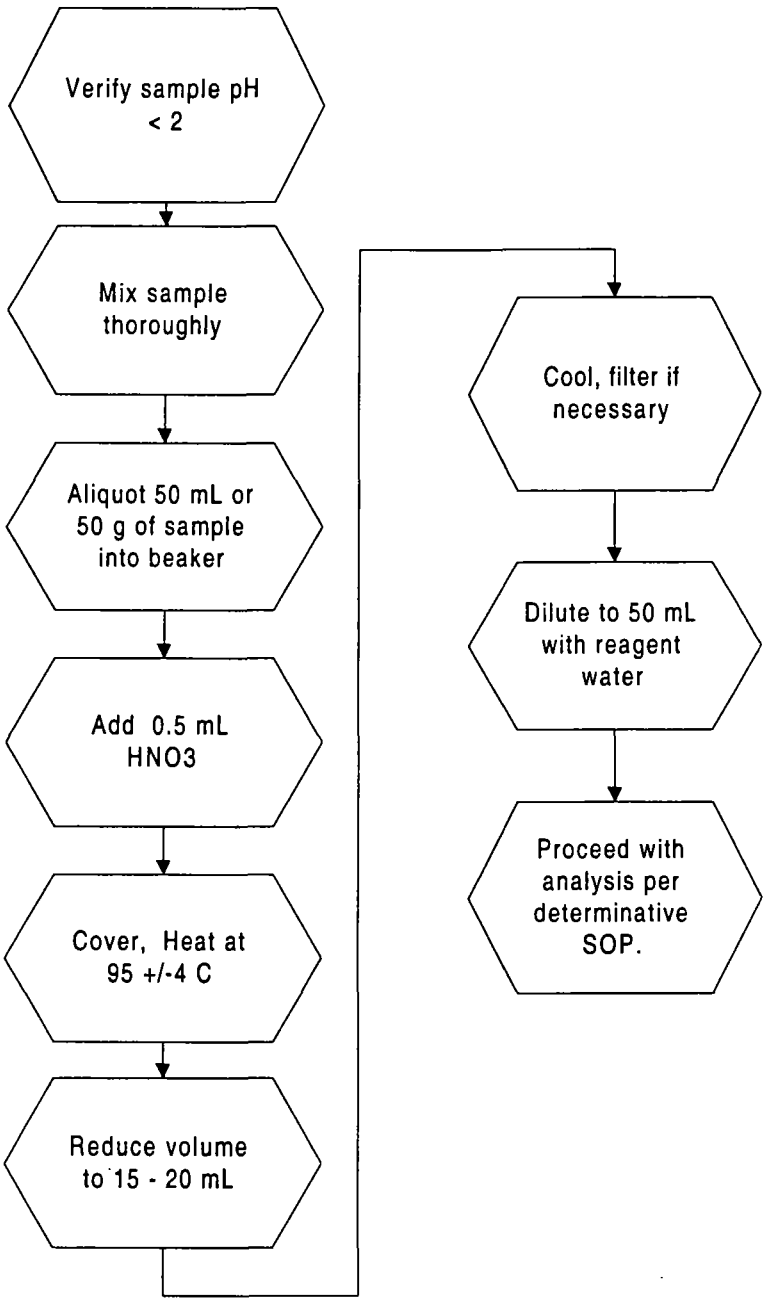
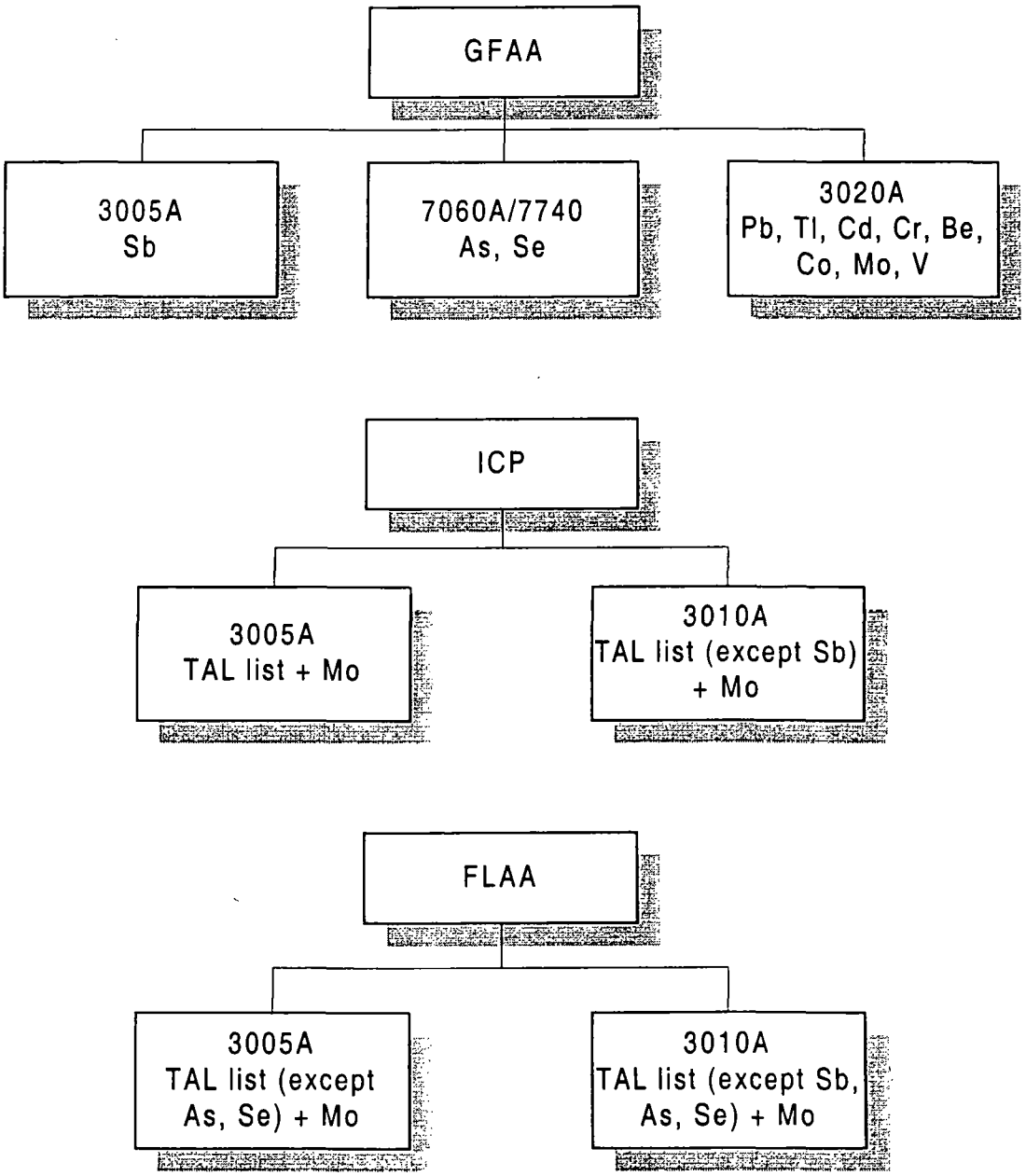
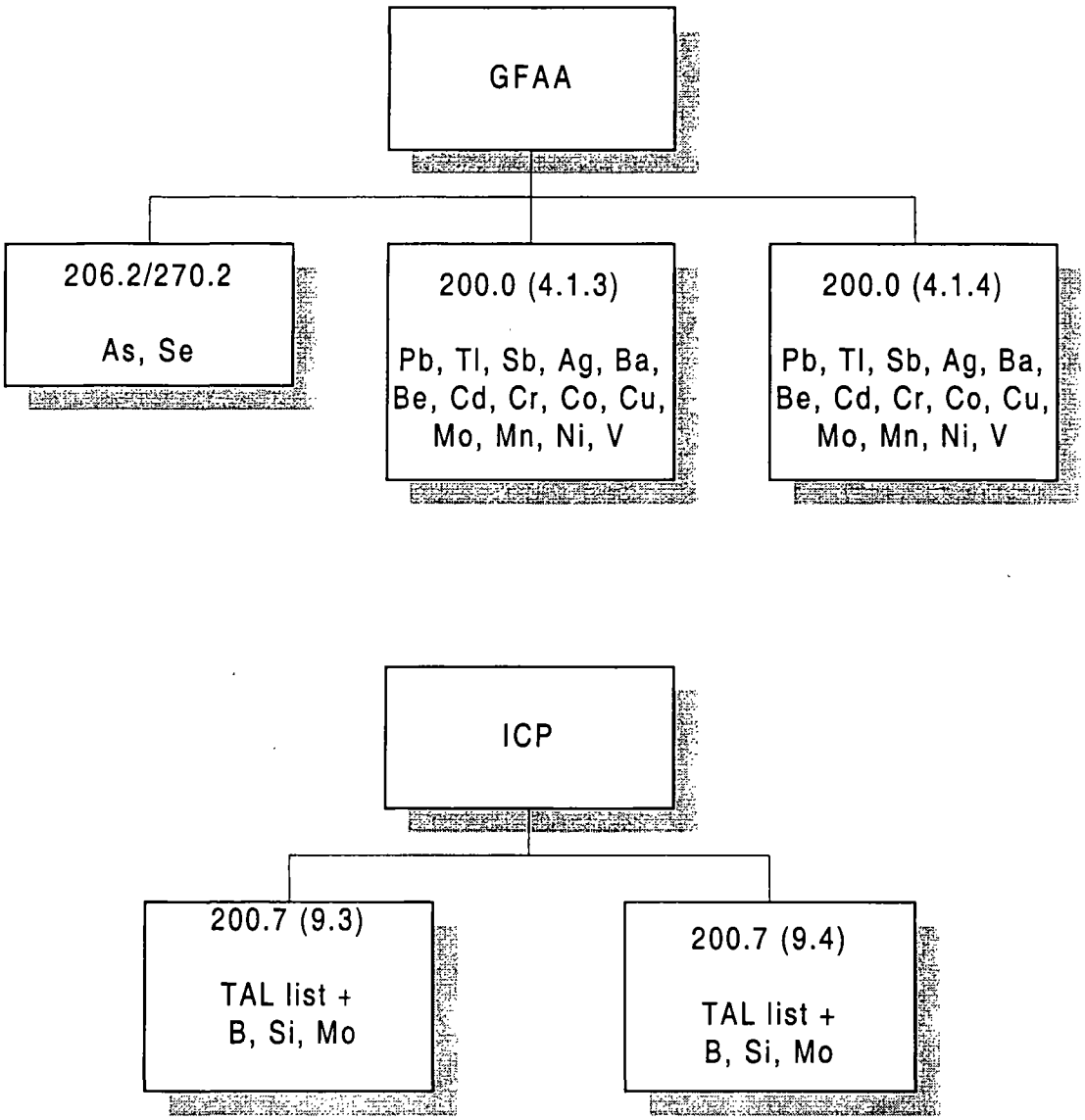


**Figure 6. Overview of SW846 Aqueous Preparation Methods by Determinative Method**




TAL list: Al, Sb, As, Ba, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, K, Se, Ag, Na, Tl, V, Zn

**Figure 7. Overview of MCAWW Aqueous Preparation Methods by Determinative Technique**




TAL list: Al, Sb, As, Ba, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, K, Se, Ag, Na, Tl, V, Zn

# APPENDIX A

# TABLES

**TABLE I. Approved Preparation Method Analytes - SW846**

| ELEMENT | Symbol | CAS Number | 3005A | 3010 A | 3020 A | 7060 A 7740 |
|---|---|---|---|---|---|---|
| Aluminum | Al | 7429-90-5 | X | X | | |
| Antimony | Sb | 7440-36-0 | X | | | |
| Arsenic | As | 7440-38-2 | X | X | | X |
| Barium | Ba | 7440-39-3 | X | X | | |
| Beryllium | Be | 7440-41-7 | X | X | X | |
| Cadmium | Cd | 7440-43-9 | X | X | X | |
| Calcium | Ca | 7440-70-2 | X | X | | |
| Chromium | Cr | 7440-47-3 | X | X | X | |
| Cobalt | Co | 7440-48-4 | X | X | X | |
| Copper | Cu | 7440-50-8 | X | X | | |
| Iron | Fe | 7439-89-6 | X | X | | |
| Lead | Pb | 7439-92-1 | X | X | X | |
| Magnesium | Mg | 7439-95-4 | X | X | | |
| Manganese | Mn | 7439-96-5 | X | X | | |
| Molybdenum | Mo | 7439-98-7 | X | X | X | |
| Nickel | Ni | 7440-02-0 | X | X | | |
| Potassium | K | 7440-09-7 | X | X | | |
| Selenium | Se | 7782-49-2 | X | X | | X |
| Silver | Ag | 7440-22-4 | X | X | | |
| Sodium | Na | 7440-23-5 | X | X | | |
| Thallium | Tl | 7440-28-0 | X | X | X | |
| Vanadium | V | 7440-62-2 | X | X | X | |
| Zinc | Zn | 7440-66-6 | X | X | | |

X - Designates that the preparation method is approved for an element

**Note:** Additional elements may be analyzed following digestion by these protocols provided the method performance criteria specified in Section 13.0 of the SOP are met.

**TABLE II. Approved Preparation Method Analytes - NPDES**

| ELEMENT | Symbol | CAS Number | 200.7 (9.4) | 200.7 (9.3) | 200.0 (4.1.4) | 200.0 (4.1.3) | 206.2 270.2 |
|---|---|---|---|---|---|---|---|
| Aluminum | Al | 7429-90-5 | X | X | | | |
| Antimony | Sb | 7440-36-0 | X | X | X | X | |
| Arsenic | As | 7440-38-2 | X | X | | | X |
| Boron | B | 7440-42-8 | X | X | | | |
| Barium | Ba | 7440-39-3 | X | X | X | X | |
| Beryllium | Be | 7440-41-7 | X | X | X | X | |
| Cadmium | Cd | 7440-43-9 | X | X | X | X | |
| Calcium | Ca | 7440-70-2 | X | X | | | |
| Chromium | Cr | 7440-47-3 | X | X | X | X | |
| Cobalt | Co | 7440-48-4 | X | X | X | X | |
| Copper | Cu | 7440-50-8 | X | X | X | X | |
| Iron | Fe | 7439-89-6 | X | X | X | X | |
| Lead | Pb | 7439-92-1 | X | X | X | X | |
| Magnesium | Mg | 7439-95-4 | X | X | | | |
| Manganese | Mn | 7439-96-5 | X | X | X | X | |
| Molybdenum | Mo | 7439-98-7 | X | X | X | X | |
| Nickel | Ni | 7440-02-0 | X | X | X | X | |
| Potassium | K | 7440-09-7 | X | X | | | |
| Selenium | Se | 7782-49-2 | X | X | | | X |
| Silicon | Si | 7631-86-9 | X | X | | | |
| Silver | Ag | 7440-22-4 | X | X | X | X | |
| Sodium | Na | 7440-23-5 | X | X | | | |
| Thallium | Tl | 7440-28-0 | X | X | X | X | |
| Vanadium | V | 7440-62-2 | X | X | X | X | |
| Zinc | Zn | 7440-66-6 | X | X | | | |

X - Designates that the preparation method is approved for an element

**Note:** Additional elements may be analyzed following digestion by these protocols provided the method performance criteria specified in Section 13.0 of the SOP are met.

**TABLE III. ICP and FLAA Matrix Spike and Aqueous Laboratory Control Sample Levels**

| ELEMENT | Working LCS/MS Standard (mg/L) | Aqueous LCS/ MS Level * (ug/l) |
|---|---|---|
| Aluminum | 100 | 2000 |
| Antimony | 25 | 500 |
| Arsenic | 100 | 2000 |
| Barium | 100 | 2000 |
| Beryllium | 2.5 | 50 |
| Cadmium | 2.5 | 50 |
| Calcium | 2500 | 50000 |
| Chromium | 10 | 200 |
| Cobalt | 25 | 500 |
| Copper | 12.5 | 250 |
| Iron | 50 | 1000 |
| Lead | 50 | 500 |
| Magnesium | 2500 | 50000 |
| Manganese | 25 | 500 |
| Molybdenum | 50 | 1000 |
| Nickel | 25 | 500 |
| Phosphorous | 500 | 10000 |
| Potassium | 2500 | 50000 |
| Selenium | 100 | 2000 |
| Silver | 2.5 | 50 |
| Sodium | 2500 | 50000 |
| Thallium | 100 | 2000 |
| Vanadium | 25 | 500 |
| Zinc | 25 | 500 |
| Boron | 50 | 1000 |
| Tin | 100 | 2000 |
| Titanium | 50 | 1000 |

* Levels shown indicate the spike concentration in the final digestate of the aqueous LCS or matrix spike based on the addition of 1.0 mL working spike (7.3) to 50 mL of sample.

**TABLE IV. GFAA Matrix Spike and Aqueous LCS Spike Levels**

| ELEMENT | Stock LCS/MS Standard (mg/L) | Working LCS/MS Standard (ug/L) | Aqueous LCS/ MS Level * (ug/l) |
|---|---|---|---|
| Arsenic | 400 | 2000 | 40 |
| Selenium | 400 | 2000 | 40 |
| Lead | 400 | 2000 | 40 |
| Thallium | 400 | 2000 | 40 |
| Antimony | 400 | 2000 | 40 |
| Cadmium | 40 | 200 | 4 |
| Chromium | 100 | 500 | 10 |
| Silver | 50 | 250 | 5 |

* Levels shown indicate the spike concentration in the final digestate of the aqueous LCS or matrix spike based on the addition of 1.0 mL working spike (7.4) to 50 mL of sample.

**TABLE V. TCLP Reporting Limits, Regulatory Limits and Matrix Spike Levels**

| ELEMENT | RL (ug/L) | Regulatory Limit (ug/L) | Spike Level (ug/L)* |
|---|---|---|---|
| Arsenic | 500 | 5000 | 5000 |
| Barium | 10000 | 100000 | 50000 |
| Cadmium | 100 | 1000 | 1000 |
| Chromium | 500 | 5000 | 5000 |
| Lead | 500 | 5000 | 5000 |
| Selenium | 250 | 1000 | 1000 |
| Silver | 500 | 5000 | 1000 |

* Levels shown indicate the spike concentration in the final digestate of the aqueous LCS or matrix spike based on the addition of 0.5 mL working spike (7.4) to 50 mL of sample.

**TABLE VI. Summary of Quality Control Requirements**

| QC PARAMETER | FREQUENCY | ACCEPTANCE CRITERIA | CORRECTIVE ACTION |
|---|---|---|---|
| Method Blank | One per sample preparation batch of up to 20 samples. | Refer to determinative SOPs:<br>NC-MT-0002<br>CORP-MT-0001<br>CORP-MT-0003 | Redigest and reanalyze samples associated with the method blank. |
| Laboratory Control Sample (LCS) | One per sample preparation batch of up to 20 samples. | Refer to determinative SOPs:<br>NC-MT-0002<br>CORP-MT-0001<br>CORP-MT-0003 | Redigest and reanalyze all samples associated with the LCS. |
| Matrix Spike | One per sample preparation batch of up to 20 samples. | Refer to determinative SOPs:<br>NC-MT-0002<br>CORP-MT-0001<br>CORP-MT-0003 | Reprep not required unless preparation error suspected. |
| Matrix Spike Duplicate | See Matrix Spike | Refer to determinative SOPs:<br>NC-MT-0002<br>CORP-MT-0001<br>CORP-MT-0003 | See Corrective Action for Matrix Spike. |

# APPENDIX B

# CONTAMINATION CONTROL GUIDELINES

## APPENDIX B. CONTAMINATION CONTROL GUIDELINES

**The following procedures are strongly recommended to prevent contamination:**

All work areas used to prepare standards and spikes should be cleaned before and after each use.

All glassware should be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered or Latex Gloves must not be used in the metals laboratory since the powder contains silica and zinc, as well as other metallic analytes. Only vinyl or nitrile gloves should be used in the metals laboratory.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

**The following are helpful hints in the identification of the source of contaminants:**

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Separate glassware if an unusually high sample is analyzed and soak with sulfuric acid prior to routine cleaning.

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Implementation Date:_____

SOP No. CORP-MT-0001NC
Revision No. 3.3
Revision Date: 12/05/01
Page 1 of 57

## STL NORTH CANTON STANDARD OPERATING PROCEDURE

## TITLE: INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROSCOPY, SPECTROMETRIC METHOD FOR TRACE ELEMENT ANALYSES, SW-846 METHOD 6010B AND EPA METHOD 200.7

**(SUPERSEDES: REVISION 3.2, REVISION DATE 01/19/01)**

Approved by: _____ 12/6/01
Date

Approved by: Karen L. Counts 12/6/01
Technical Specialist Date

Approved by: _____ 12/10/01
Quality Assurance Manager Date

Approved by: _____ 12-10-01
Environmental, Health and Safety Coordinator Date

Approved by: _____ 12-10-01
Laboratory Manager Date

Approved by: _____ 1/30/01
Corporate Technology Date

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## 1. SCOPE AND APPLICATION

1.1. This procedure describes the analysis of trace elements including metals in solution by Inductively Coupled Plasma -Atomic Emission Spectroscopy (ICP-AES) using SW-846 Method 6010B and EPA Method 200.7 . Table I of Appendix A lists the elements appropriate for analysis by Methods 6010B and 200.7. Additional elements may be analyzed under Methods 6010B and 200.7 provided that the method performance criteria presented in Section 13.0 are met.

1.2. ICP analysis provides for the determination of metal concentrations over several orders of magnitude. Detection limits, sensitivity and optimum concentration ranges of the metals will vary with the matrices and instrumentation used. For instance, in comparison to conventional ICP technique, ICP-Trace can achieve detection levels comparable to those determined using the graphite furnace atomic absorption spectroscopy (GFAAS) technique.

1.3. Method 6010B is applicable to the determination of dissolved, suspended, total recoverable and total elements in ground water, aqueous samples, soils, sludges, wastes, sediments, and TCLP, EP and other leachates/extracts. All matrices require digestion prior to analysis with the exception of analyses for dissolved metals in filtered and acidified aqueous samples. Although digestion is not specifically required by the method, some clients and regulators may require digestion of **dissolved samples** and this must be clarified and documented before project initiation. Silver concentrations must be below 2.0 mg/L in aqueous samples and 100 mg/kg in solid matrix samples. Precipitation may occur in samples where silver concentrations exceed these levels and lead to the generation of erroneous data.

1.4. Method 200.7 is applicable to the determination of dissolved, suspended, total recoverable, and total elements in water, waste water, and solid wastes. All matrices require digestion prior to analysis with the exception of analyses for dissolved metals in filtered and acidified aqueous samples if the criteria in Section 11.1 are met. Silver concentrations must be below 0.1 mg/L in aqueous samples and 50 mg/kg in solid matrix samples.

1.5. State-specific requirements may take precedence over this SOP for drinking water sample analyses.

1.6. The applicable LIMS method codes are QO (6010B), QM (6010B Trace), AS (200.7), JI (200.7 Trace).

## 2. SUMMARY OF METHOD

2.1. This method describes a technique for the determination of multi elements in solution using sequential or simultaneous optical systems and axial or radial viewing of the plasma. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by a radio frequency inductively coupled plasma (ICP). The spectra are dispersed by a grating spectrometer and the intensities of the emission lines are monitored by photomultiplier tubes. The photocurrents from the photomultiplier tubes are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background must be measured adjacent to analyte lines during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interferences and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences should also be recognized and appropriate actions taken. Alternatively, multivariate calibration methods may be chosen for which point selection for background correction is superfluous since whole spectral regions are processed.

2.2. Refer to the appropriate SOPs for details on sample preparation methods.

## 3. DEFINITIONS

3.1. Dissolved Metals: Those elements which pass through a 0.45 um membrane. (Sample is acidified <u>after</u> filtration).

3.2. Suspended Metals: Those elements which are retained by a 0.45 um membrane.

3.3. Total Metals: The concentration determined on an unfiltered sample following vigorous digestion.

3.4. Total Recoverable Metals: The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid.

## 4. INTERFERENCES

4.1. Spectral, physical and chemical interference effects may contribute to inaccuracies in the determinations of trace elements by ICP. Spectral interferences are caused by:

- Overlap of a spectral line from another element.
- Unresolved overlap of molecular band spectra.
- Background contribution from continuous or recombination phenomena.
- Stray light from the line emission of high concentration elements.

4.1.1. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background correction is not required in cases where a background corrective measurement would actually degrade the analytical result.

4.1.2. Inter-element correction factors (IECs) are necessary to compensate for spectral overlap. Inter-element interferences occur when elements in the sample emit radiation at wavelengths so close to that of the analyte that they contribute significant intensity to the analyte channel. If such conditions exist, the intensity contributed by the matrix elements will cause an excessively high (or sometimes low) concentration to be reported for the analyte. Inter-element corrections IECs must be applied to the analyte to remove the effects of these unwanted emissions.

4.1.3. Physical interferences are generally considered to be effects associated with sample transport, nebulization and conversion within the plasma. These interferences may result in differences between instrument responses for the sample and the calibration standards. Physical interferences may occur in the transfer of solution to the nebulizer (e.g., viscosity effects), at the point of aerosol formation and transport to the plasma (e.g., surface tension) or during excitation and ionization processes within the plasma itself. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, dilution of the sample, use of a peristaltic pump, mass flow controller, use of an internal standard and/or use of a high solids nebulizer can reduce the effect.

4.1.4. Chemical interferences are characterized by molecular compound formation, ionization effects and solute vaporization effects. Normally these effects are not significant with the ICP technique but if observed can be minimized by buffering the sample, matrix matching or standard addition procedures.

## 5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all STL North Canton associates.

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory.

5.3.1. The following materials are known to be **corrosive**:

sulfuric acid, hydrochloric acid, nitric acid and hydrofluoric acid. (NOTE: sulfuric and hydrofluoric acids are used in cleaning the ICP torch and hydrofluoric acid is also commonly used in air toxics preparations.)

5.3.2. The following materials are known to be **oxidizing agents**:

nitric acid and hydrogen peroxide.

5.3.3. The plasma emits strong UV light and is harmful to vision. **NOTE: AVOID looking directly at the plasma.**

5.3.4. The RF generator produces strong radio frequency waves, most of which are unshielded. People with pacemakers should not go near the instrument while in operation.

5.4. Exposure to chemicals must be maintained **as low as reasonably achievable,** therefore, unless they are known to be non-hazardous, all samples should be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Metals digestates can be processed outside of a fume hood. Solvent and waste containers will be kept closed unless transfers are being made.

5.5. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL North Canton associate. The situation must be reported **immediately** to a laboratory supervisor.

5.6. The use of hydrofluoric acid requires special safety precautions. Consult the facility EH&S Manager and laboratory supervisor for guidance.

## 6. EQUIPMENT AND SUPPLIES

6.1. Inductively Coupled Plasma Atomic Emission Spectrometer equipped with autosampler and background correction.

6.2. Radio Frequency Generator.

6.3. Argon gas supply, welding grade or equivalent.

6.4. Coolflow or appropriate water cooling device.

6.5. Peristaltic Pump.

6.6. Calibrated automatic pipettes or Class A glass volumetric pipettes.

6.7. Class A volumetric flasks.

6.8. Autosampler tubes.

## 7. REAGENTS AND STANDARDS

7.1. Intermediate standards are purchased as custom STL North Canton multi-element mixes or as single-element solutions. All standards must be stored in FEP

fluorocarbon or unused polyethylene or polypropylene bottles. Intermediate standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the intermediate solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem. Expiration dates can be extended provided that the acceptance criteria described in laboratory-specific SOPs are met.

7.2. Working calibration and calibration verification solutions may be used for up to 3 months and must be replaced sooner if verification from an independent source indicates a problem. Standards should be prepared in a matrix of 5% hydrochloric and 5% nitric acids. An exception to this is in the event the Trace ICP is utilized without the internal standard. In this case, the standard acid matrix must be matched to the final preparation matrix as listed in Section 11.9.

7.3. Refer to Tables III, IV, IVA, V and VI (Appendix A) for details regarding the working standard concentrations for calibration, calibration verification, interference correction and spiking solutions.

7.4. Concentrated nitric acid ($HNO_3$), trace metal grade or better.

7.5. Concentrated hydrochloric acid (HCl), trace metal grade or better.

7.6. Reagent water must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

## 8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Sample holding times for metals are six months from time of collection to the time of analysis.

8.2. Aqueous samples are preserved with nitric acid to a pH of <2 and may be stored in either plastic or glass. If boron or silica are to be determined, plastic containers are preferred. Refrigeration is not required. Preservation must be verified prior to analysis.

8.3. Soil samples do not require preservation but must be stored at 4°C ± 2° until the time of preparation .

## 9. QUALITY CONTROL

Table VII (Appendix A) provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.

9.1. Initial Demonstration of Capability

Prior to analysis of any analyte using either Method 200.7 or Method 6010B, the following requirements must be met.

Instrument Detection Limit (IDL) - The IDL for each analyte must be determined for each analyte wavelength used least each instrument. The IDL must be determined annually. If the instrument is adjusted in anyway that may affect the IDL, the IDL for that instrument must be redetermined. The IDL shall be determined by multiplying by 3, the standard deviation obtained from the analysis of a standard solution (each analyte in reagent water) at a concentration 3x - 5x the previously determined IDL, with seven consecutive measurements. Each measurement must be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure performed between the analysis of separate samples). The result of the IDL determination must be below the STL North Canton reporting limit. The CLP IDL procedure can be used for this method.

9.1.1. Method Detection Limit (MDL) - An MDL must be determined for each analyte prior to the analysis of any client samples. Refer to STL North Canton SOP NC-QA-0021 for details on MDL analysis and criteria.

9.1.2. Linear Range Verification (LR) - The linear range must be determined on at least an annual basis for each analyte wavelength used on each instrument. The linear range is the concentration above which results cannot be reported without dilution of the sample. The standards used to verify the linear range limit must be analyzed during a routine analytical run and must read within 5% of the expected value.

For the **initial** determination of the upper limit of the linear dynamic range (LDR) for each wavelength, determine the signal responses from a minimum of three to five different concentration standards across the estimated range. One standard should be near the upper limit of the estimated range. The concentration measured at the LDR must be no more than 10% less than the expected level extrapolated from lower standards. If the instrument is adjusted in any way that may affect the LRs, new dynamic ranges must be determined. The LR data must be documented and kept on file.

9.1.3. Background Correction Points - To determine the appropriate location for off-line background correction when establishing methods, the user must scan the area on either side adjacent to the wavelength and record the apparent emission intensity from all other method analytes. This spectral information must be documented and kept on file. The location selected for background correction must be either free of off-line interelement spectral interference or a computer routine must be used for automatic correction on all determinations. Tests to determine spectral interference must be done using analyte concentrations that will adequately describe the interference. Background correction points must be set prior to determining IECs. Refer to the facility-

specific instrument operation SOP and ICP instrument manual for specific procedures to be used in setting background correction points.

9.1.4. Inter-element Corrections (IECs) - ICP interelement correction factors must be determined prior to the analysis of samples and every six months thereafter. If the instrument is adjusted in any way that may affect the IECs, the IECs must be redetermined. When initially determining IECs for an instrument, wavelength scans must be performed to ensure that solutions in use are free from contaminants. If an IEC varies significantly from the previously determined IEC then the possibility of contamination should be investigated. The purity of the IEC check solution can be verified by using a standard from a second source or an alternate method (i.e., GFAA or ICP-MS). Published wavelength tables ( e.g. MIT tables, Inductively Coupled Plasma-Atomic Spectroscopy: Prominent Lines) can also be consulted to evaluate the validity of the IECs. Refer to the facility specific instrument operation SOP and instrument manufacturer's recommendations for specific procedures to be used in setting IECs. An IEC must be established to compensate for any interelement interference which results in a false analyte signal greater than ± the RL as defined in Tables I, IA or II. To determine IECs, run a single element standard at the established linear range. To calculate an IEC, divide the observed concentration of the analyte by the actual concentration of the "interfering element."

Note: Trace ICP IECs are more sensitive to small changes in the plasma and instrument setup conditions. Adjustments in the IECs will be required on a more frequent basis for the Trace as reflected by the ICSA response. Additional spectral interference is present from easily ionizable elements such as potassium and sodium in axial viewing instruments.

9.1.5. Rinse Time Determination - Rinse times must be determined upon initial set-up of an ICP instrument. To determine the appropriate rinse time for a particular ICP system, the linear range verification standard (see 9.1.3) should be aspirated as a regular sample followed by the analysis of a series of rinse blanks. The length of time required to reduce the analyte signals to < RL will define the rinse time for a particular ICP system. For some analytes it may be impractical to set the rinse time based on the linear range standard result (i.e., analyte not typically detected in environmental samples at that level and an excessive rinse time would be required at the linear range level). Until the required rinse time is established, the method recommends a rinse period of at least 60 seconds between samples and standards. If a memory effect is suspected, the sample must be reanalyzed after a rinse period of sufficient length. Rinse time studies can be conducted at additional concentration levels. These additional studies must be documented and kept on file, if a concentration other than the linear range level is used to set the rinse time. The

concentration levels used to establish the rinse time must be taken into consideration when reviewing the data.

9.2. Method Blank (MB) - One method blank must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest at or above the reporting limit (exception: common laboratory contaminants, see below) or at or above 5% of the measured concentration of that analyte in associated samples, whichever is higher (sample result must be a minimum of 20x higher than the blank contamination level).

- If the analyte is a common laboratory contaminant (copper, iron, lead (Trace only) or zinc) the data may be reported with qualifiers if the concentration of the analyte in the method blank is less than two times the RL. **Such action must be taken in consultation with the client and must be addressed in the project narrative.**

- Repreparation and reanalysis of all samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples (see exception noted above).

- If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. **Such action must be taken in consultation with the client and must be addressed in the project narrative.**

- If the above criteria are not met and reanalysis is not possible, then the sample data must be qualified. **This anomaly must be addressed in the project narrative and the client must be notified.**

- For dissolved metals samples which have not been digested, a CCB result is reported as the method blank. The CCB run immediately prior to the start of the dissolved sample analyses must be used for this purpose. No more than 20 samples can be associated with one CCB.

9.3. Laboratory Control Sample (LCS) - One aqueous LCS must be processed with each preparation batch. The LCS must contain all analytes of interest and must be carried through the entire analytical procedure. Aqueous LCS spike levels are provided in Table III (Appendix A). The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

- If any analyte is outside established control limits the system is out of control and corrective action must occur. Unless in-house control limits are established, a control limit of 80 - 120% recovery must be applied.

- In the event that an MS/MSD analysis is not possible a Laboratory Control Sample Duplicate (LCSD) must be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

- In the instance where the LCS recovery is greater than 120% and the sample results are < RL, the data may be reported with qualifiers. **Such action must be taken in consultation with the client and must be addressed in the report narrative.**

- Corrective action will be repreparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable.

- For dissolved metals samples which have not been digested, a CCV result is reported as the LCS. The CCV run immediately prior to the start of the dissolved sample analyses must be used for this purpose. No more than 20 samples can be associated with one CCV.

9.4. Matrix Spike/Matrix Spike Duplicate (MS/MSD) - One MS/MSD pair must be processed for each preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MSDs. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis. Spiking levels are provided in Tables III and VI (Appendix A).

- If any analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. For both methods 200.7 and 6010B, control limits of 75-125% recovery and 20% RPD or historical acceptance criteria must be applied to the MS/MSD. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch. MS/MSD results which fall outside the control limits must be addressed in the narrative.

- If the native analyte concentration in the MS/MSD exceeds 4x the spike level for that analyte, the recovery data are reported as NC, MSB (i.e., not calculated). If

the reporting software does not have the ability to report NC, MSB then the actual recovery must be reported and narrated as follows: "Results outside of limits do not necessarily reflect poor method performance in the matrix due to high analyte concentrations in the sample relative to the spike level." Two other narrative notes for metals analyses: Matrix spike/spike duplicate spike recovery/recoveries was/were outside the acceptance limits of some analytes. The acceptable LCS analysis data indicated that the analytical system was operating within control and this condition is most likely due to matrix interference. See the Matrix Spike Report for the affected analytes which will be flagged with N. Matrix spike/spike duplicate relative percent difference (RPD) exceeded the acceptance limits for some analytes. The imprecision may be attributed to sample heterogeneity. See the Matrix Spike Report for the affected analytes, which will be flagged with *.

- If an MS/MSD is not possible due to limited sample volume then a laboratory control sample duplicate (LCSD) should be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

- For dissolved metals samples which have not been digested, a MS/MSD must be performed per batch of up to 20 samples by spiking two aliquots of the sample at the levels specified in Table III (Appendix A).

9.5. Dilution test – A dilution test is performed to determine whether significant physical or chemical interferences exist due to the sample matrix. One sample per preparation batch must be processed as a dilution test. The test is performed by running a sample at a 5x (1:4) dilution. Samples identified as field blanks cannot be used for dilution tests. The results of the diluted sample, after correction for dilution, should agree within 10% of the original sample determination when the original sample concentration is greater than 50x the IDL. If the results are not within 10%, the possibility of chemical or physical interference exists.

9.6. Initial Calibration Verification (ICV/ICB) - Calibration accuracy is verified by analyzing a second source standard (ICV). For analyses conducted under Method 200.7, the ICV result must fall within 5% of the true value for that solution with relative standard deviation <3% from replicate (minimum of two) exposures. For Method 6010B, the ICV must fall within 10% of the true value for that solution with relative standard deviation <5% from replicate (minimum of two) exposures. An ICB is analyzed immediately following the ICV to monitor low level accuracy and system cleanliness. The ICB result must fall within +/- the RL from zero. If either the ICV or ICB fail to meet criteria, the analysis should be terminated, the problem corrected, the instrument recalibrated and the calibration reverified. (See Section 11.10 or 11.13 for required run sequence).

9.7. Continuing Calibration Verification (CCV/CCB) - Calibration accuracy is monitored throughout the analytical run through the analysis of a known standard after every 10 samples. The CCV is be a mid-range standard made from a dilution of the

calibration standard. The CCV for both methods must fall within 10% of the true value for that solution with relative standard deviation <5% from replicate (minimum of two) exposures. A CCB is analyzed immediately following each CCV. (See Section 11.10 or 11.13 for required run sequence.) The CCB result must fall within +/- RL from zero. If the blank is less than 1/10 the concentration of the action level of interest, and no sample is within 10% of the action limit, reanalysis and recalibration are not required before continuation of the run. Sample results may only be reported when bracketed by valid CCV/CCB pairs. If a mid-run CCV or CCB fails, the analysis for the affected element must be terminated, the problem corrected, the instrument recalibrated, the calibration verified and the affected samples reanalyzed. (Refer to Section 11.13 for an illustration of the appropriate rerun sequence).

9.8. Interference Check Analysis (ICSA/ICSAB) - The validity of the interelement correction factors is demonstrated through the successful analysis of interference check solutions. The ICSA contains only interfering elements, the ICSAB contains analytes and interferents. Refer to Table V (Appendix A) for the details of ICSA and ICSAB composition. Custom STL North Canton multielement ICS solutions must be used. All analytes should be spiked into the ICSAB solution, therefore, if a non-routine analyte is required then it should be manually spiked into the ICSAB using a certified ultra high purity single element solution or custom lab-specific mix. If the ICP will display overcorrection as a negative number then the non-routine elements can be controlled from the ICSA as described in section 9.8.3. Elements known to be interferents on a required analyte must be included in the ICP run when that analyte is determined. Aluminum, iron, calcium and magnesium must always be included in all ICP runs.

9.8.1. The ICSA and ICSAB solutions must be run at the beginning of the run. (See Section 11.10 or 11.13 for required run sequence.)

9.8.2. The ICSAB results for the interferents must fall within 80 - 120% of the true value. If any ICSAB interferent result fails criteria, the analysis should be terminated, the problem corrected, the instrument recalibrated and the samples rerun.

9.8.3. ICSA results for the non-interfering elements with reporting limits ≤ 10 ug/L must fall within the STL North Canton guidelines of ± 2x RL from zero. ICSA results for the non-interfering elements with RLs> 10 µg/L must fall within the STL North Canton guidelines of ± 1x RL from zero. If the ICSA results for the non-interfering elements do not fall within +/- 2x RL (RL ≤10) or ± 1xRL (RL>10) from zero the field sample data must be evaluated as follows:

- If the non-interfering element concentration in the ICSA is the result of contamination versus a spectral interference, and this reason is documented, the field sample data can be accepted.

- If the affected element was not required then the sample data can be accepted.

- If the interfering elements are not present in the field sample at a concentration which would result in a false positive or negative result greater than +/- 2x RL from zero then the field sample data can be accepted.

- If the interfering element is present in the field sample at a level which would result in a false analyte signal greater than ± 2x RL from zero, the data can be accepted only if the concentration of the affected analyte in the field sample is more than 10x the analyte signal in the ICSA.

- If the data does not meet the above conditions then the IECs must be re-evaluated and corrected if necessary and the affected samples reanalyzed or the sample results manually corrected through application of the new IEC to the raw results. If the results are recalculated manually the calculations must be clearly documented on the raw data.

9.9. CRI - To verify linearity near the RL for ICP analysis, a CRI standard is run at the beginning of each sample analysis run. Additionally, some projects may require CRI analysis at the end of the run. (See Section 11.10 or 11.13 for required run sequence.) Evaluate associated samples based upon advisory limits of +/- 50% of true value.

Note: The custom STL North Canton CRI mix contains most analytes at a level near the standard lab reporting limit.

9.10. Method of Standard Addition (MSA) -This technique involves adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample interferent that may enhance or depress the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift. Refer to Section 11.17 for additional information on when MSA is required as well as Appendix D for specific MSA requirements.

9.11. Quality Assurance/Project Summaries - Certain clients may require project- or program-specific QC which may supersede this SOP requirements. Quality Assurance Summaries (QASs) or equivalent documents providing project-specific requirements should be developed so that project staff clearly understand the special project requirements.

## 10. CALIBRATION AND STANDARDIZATION

10.1. Set up the instrument with the operating parameters recommended by the manufacturer. Allow the instrument to become thermally stable before beginning calibration (approximately 30 minutes of warm-up is required).

10.2. Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures. Flush the system with the calibration blank between each standard or as the manufacturer recommends. The calibration curve must consist of a minimum of a blank and a standard. Refer to the facility-specific instrument SOP or ICP instrument manual for a detailed set up and operation protocols.

10.3. Calibration must be performed daily and each time the instrument is set up. Instrument runs may be continued over periods exceeding 24 hours as long as all calibration verification (CCV) and interference check QC criteria are met. The instrument standardization date and time must be included in the raw data.

10.4. Refer to Section 9.0 for calibration verification procedures, acceptance criteria and corresponding corrective actions.

## 11. PROCEDURE

11.1. For 200.7 analyses, dissolved (preserved) samples must be digested unless it can be documented that the sample meets all of the following criteria:

A. Visibly transparent with a turbidity measurement of 1 NTU or less.

B. Is of one liquid phase and free of particulate or suspended matter following acidification.

C. Is NOT being analyzed for silver.

11.2. A minimum of <u>two</u> <u>exposures</u> for each standard, field sample and QC sample is required. The average of the exposures is reported. For Trace ICP analyses, the results of the sum channel must be used for reporting.

11.3. Prior to calibration and between each sample/standard the system is rinsed with the calibration blank solution. The minimum rinse time between analytical samples is 60 seconds unless following the protocol outlined in 9.1.6 it can be demonstrated that a shorter rinse time may be used. Triton-X can be added to the rinse solution to facilitate the rinse process.

11.4. The use of an autosampler for all runs is strongly recommended.

11.5. The use of automated QC checks through the instrument software is highly recommended for all calibration verification samples (ICV,CCV), blanks

(ICB,CCB,PB), interference checks (ICSA,ICSAB) and field samples (linear range) to improve the data review process.

11.6. To facilitate the early identification of QC failures and samples requiring rerun it is strongly recommended that sample data be reviewed periodically throughout the run.

11.7. To facilitate the data review and reporting processes it is strongly recommended that all necessary dilutions be performed before closing out the instrument run.

11.8. The use of an internal standard is recommended on the conventional, non-Trace ICPs as an alternative to using the method of standard additions. This technique is useful in overcoming matrix interferences especially in high solids matrices. However, for conventional ICP techniques, internal standards may not be necessary provided that one of the following is performed to minimize physical interferences: (1) peristaltic pump is used, (2) high solids nebulizer is used, or (3) high solids samples are diluted and reanalyzed.

11.9. The use of an internal standard is **required** on the Trace ICP unless the calibration and QC standards are matrix matched to each digestion procedure used as follows:

| Preparation Method | % $HNO_3$ | % HCl |
|---|---|---|
| CLP Aqueous | 1 | 5 |
| CLP Soil | 5 | 2.5 |
| SW846 3050 | 10 | 10 |
| SW846 3005 | 2 | 5 |
| SW846 3010 | 6 | 5 |

The following procedural guidelines must be followed when using an internal standard:

11.9.1. Typically used internal standards are: yttrium or scandium. (Note: Any element can be used that is not typically found in environmental samples at a high rate of occurrence.)

11.9.2. The internal standard (IS) must be added to every sample and standard at the same concentration. It is recommended that the IS be added to each analytical sample automatically through use of a third pump channel and mixing coil. Internal standards should be added to blanks, samples and

standards in a like manner, so that dilution effects resulting from the addition may be disregarded.

11.9.3. The concentration of the internal standard should be sufficiently high to obtain good precision in the measurement of the IS analyte used for data correction and to minimize the possibility of correction errors if the IS analyte is naturally present in the sample.

11.9.4. The internal standard raw intensity counts must be printed on the raw data.

11.9.5. The analyst must monitor the response of the internal standard throughout the sample analysis run. This information is used to detect potential problems and identify possible background contributions from the sample (i.e., natural occurrence of IS analyte). The instrument automatically adjusts sample results based on comparison of the internal standard intensity in the sample to the internal standard intensity at calibration.

11.9.5.1. If the internal standard counts fall within ±30% of the counts observed in the ICB then the data is acceptable.

11.9.5.2. If the internal standard counts in the field samples are more than ±30% higher than the expected level, the field samples must then be:

(1) Diluted and reanalyzed;

(2) The IS concentrations must be raised; or

(3) A different internal standard must be used.

11.10. The following analytical sequence must be used for Methods 6010B and 200.7:

Instrument Calibration
ICV
ICB
CRI
ICSA
ICSAB
7 samples
CCV
CCB
10 samples
CCV
CCB
Repeat sequence of up to 10 samples between CCV/CCB pairs as required to complete run

CRI (The CRI counts as a sample analysis.)
CCV
CCB

Refer to Quality Control Section 9.0 and Table VII (Appendix A) for Method 6010B and 200.7 quality control criteria.

11.11. Additional quality control analyses are necessary for analysis under the Contract Laboratory Program (CLP). If these are included then CLP, 6010 and 200.7 samples can be included in the same sequence. Refer to CORP-MT-0002NC for details.

11.12. Full method required QC must be available for each wavelength used in determining reported analyte results.

11.13. The following run sequence provides an illustration of a mid-run CCV or CCB failure and the appropriate corrective action run sequence as described in Section 9.7:

<u>Original Run</u>: Instrument Calibration

ICV

ICB

CRI

ICSA

ICSAB

7 samples

CCV1

CCB1

10 samples

CCV2

CCB2

10 samples **

CCV3 * * Failure occurs at CCV3/CCB3

CCB3 * **Samples requiring rerun for affected analytes

10 samples **

CCV4

CCB4

10 samples

CCV5

CCB5

Reanalysis: Recalibrate

ICV

ICB

CRI

ICSA

ICSAB

CCV2

CCB2

10 samples

CCV3

CCB3

10 samples

CCV4

CCB4

Notes:

Samples between CCV4 and CCV5 do not require reanalysis as they were bracketed by compliant QC samples.

See CORP-MT-0002NC for the appropriate reanalysis sequence if CLP requirements must also be met.

11.14 The instrument may be reprofiled between CCV/CCB pairs to correct for environment induced drift.

11.15 Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards, preventive maintenance and troubleshooting.

11.16 All measurements must fall within the defined linear range where spectral interference correction factors are valid. Dilute and reanalyze all samples for required analytes that exceed the linear range or use an alternate wavelength for which QC data are established. If an interelement correction exists for an analyte which exceeds the linear range, the IEC may be inaccurately applied. Therefore, even if an overrange analyte may not be required to be reported for a sample, if that analyte is a interferent for any requested analyte in that sample, the sample must be diluted. Acid strength must be maintained in the dilution of samples.

11.17 For TCLP samples, full four-point MSA will be required if all of the following conditions are met:

1) recovery of the analyte in the matrix spike is not at least 50%,

2) the concentration of the analyte does not exceed the regulatory level, and,

3) the concentration of the analyte is within 20% of the regulatory level.

The reporting and regulatory limits for TCLP analyses as well as matrix spike levels are detailed in Table VI (Appendix A). Appendix E provides guidance on performing MSA analyses.

11.18 Any variation in procedure shall be completely documented using instrument run logs, maintenance logs, report narratives, a Nonconformance Memo, or an anomaly report and is approved by a Supervisor/Group Leader and QA Manager. If contractually required, the client shall be notified by the Project Manager.

11.19 Nonconformance documentation shall be filed in the project file.

11.20 Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

## 12 DATA ANALYSIS AND CALCULATIONS

12.1ICV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(ICV)}{True(ICV)}\right)$$

12.2CCV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(CCV)}{True(CCV)}\right)$$

12.3Matrix Spike Recoveries are calculated according to the following equation:

$$\%R = 100\left(\frac{SSR - SR}{SA}\right)$$

Where:
SSR = Spike Sample Result
SR = Sample Result
SA = Spike Added

12.4The relative percent difference (RPD) of matrix spike/matrix spike duplicates are calculated according to the following equations:

$$RPD = 100\left[\frac{|MSD - MS|}{\left(\frac{MSD + MS}{2}\right)}\right]$$

Where:
MS = determined spiked sample concentration
MSD = determined matrix spike duplicate concentration

12.5The final concentration for a digested aqueous sample is calculated as follows:

$$mg/L = \frac{C \times V1 \times D}{V2}$$

Where:
C = Concentration (mg/L) from instrument readout
D = Instrument dilution factor
V1 = Final volume in liters after sample preparation
V2 = Initial volume of sample digested in liters

12.6 The final concentration determined in digested solid samples when reported on a dry weight basis is calculated as follows:

$$mg / Kg, dry\ weight = \frac{C \times V \times D}{W \times S}$$

Where:
C = Concentration (mg/L) from instrument readout
D = Instrument dilution factor
V = Final volume in liters after sample preparation
W = Weight in Kg of wet sample digested
S = Percent solids/100

Note: A Percent Solids determination must be performed on a separate aliquot when dry weight concentrations are to be reported. If the results are to be reported on wet weight basis the "S" factor should be omitted from the above equation.

12.7 The LCS percent recovery is calculated according to the following equation:

$$\%R = 100\left(\frac{Found(LCS)}{True(LCS)}\right)$$

12.8 The dilution test percent difference for each component is calculated as follows:

$$\%Difference = \frac{|I - S|}{I} \times 100$$

Where:
I = Sample result (Instrument reading)
S = Dilution test result (Instrument reading × 5)

12.9 Appropriate factors must be applied to sample values if dilutions are performed.

12.10 Sample results should be reported with up to three significant figures in accordance with the STL North Canton significant figure policy.

## 13 METHOD PERFORMANCE

13.1 Each laboratory must have initial demonstration of performance data on file for each analyte of interest as described in Section 9.0.

13.2 Refer to Tables I, IA & II in Appendix A for the list of Method 6010B and 200.7 analytes as well as additional analytes that may be analyzed using this SOP.

13.3 Method performance is determined by the analysis of MS and MSD samples as well as method blanks and laboratory control samples. The MS or MSD recovery should fall within +/- 25 % and the MS/MSD should compare within 20% RPD or within the laboratory's historical acceptance limits. These criteria apply to analyte concentrations greater than or equal to 10xIDL. Method blanks must meet the criteria specified in Section 9.2. The laboratory control samples should recover within 20% of the true value or within the laboratory's historical acceptance limits.

13.4 Training Qualification:

The group/team leader or the supervisor has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

## 14 POLLUTION PREVENTION

14.1 This method does not contain any specific modifications that serve to minimize or prevent pollution.

## 15 WASTE MANAGEMENT

15.1 Waste generated in the procedure must be segregated and disposed of according to the facility hazardous waste procedures and per the local, state, and federal regulations. The Environmental Health and Safety Director should be contacted, if additional information is required.

15.2 Standards should be purchased and prepared in volumes consistent with laboratory use to minimize the volume of expired standards to be disposed.

## 16 REFERENCES

16.1 40 CFR Part 136, Appendix B, 7-5-95, Determination of Method Detection Limits.

16.2 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update III, Revision 2, December 1996. Method 6010B.

16.3 Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry, Revision 4.4, May 1994. Method 200.7.

16.4 CORP-MT-0002NC, Inductively Coupled Plasma-Atomic Emission Spectroscopy, Method 200.7 & CLP-M, SOW ILMO3.0 and ILMO4.0).

16.5QA-003, STL North Canton QC Program.

16.6QA-004, Rounding and Significant Figures.

16.7QA-005, Method Detection Limits.

## 17 MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1Modifications/Interpretations from reference method

17.1.1 Modifications/interpretations from both Methods 6010B and 200.7.

17.1.1.1 STL North Canton laboratories use mixed calibration standard solutions purchased from approved vendors instead of using individual mixes prepared in house as recommended by the subject methods.

17.1.1.2 Methods 200.7 and 6010B state that if the correction routine is operating properly, the determined apparent analyte(s) concentration from analysis of each interference solution should fall within a specific concentration range around the calibration blank. In determining IECs, because of lack of definition clarification for "concentration range around the calibration blank," STL North Canton has adopted the procedure in EPA CLP ILMO4.0.

17.1.1.3 Section 8.5 of Method 6010B and Section 9.5 of Method 200.7 recommend that whenever a new or unusual matrix is encountered, a series of tests be performed prior to reporting concentration data for that analyte. The dilution test helps determine if a chemical or physical interference exists. Because STL North Canton laboratories receive no prior information from clients regarding when to expect a new or unusual matrix, STL North Canton may select to perform a dilution test on one sample in each prep batch. According to the method, the post digestion spike (PDS) determines any potential matrix interferences. At STL North Canton LABS, matrix interference is determined by evaluating data for the LCS and MS/MSD. STL North Canton REQUIRES documented, clear guidance when a new or unusual matrix will be received for a project and a request to perform the dilution test or PDS on a client-identified sample.

17.1.2 Modifications from Method 200.7.

17.1.2.1 Method 200.7 defines the IDL as the concentration equivalent to a signal, due to the analyte, which is equal to three times the standard deviation of a series of ten replicate measurements of the calibration blank signal at the same wavelength. STL North Canton labs utilize the CLP IDL definition as defined in Section 9.1.1 of this SOP.

17.1.2.2 The calibration blank is prepared in an acid matrix of 5% $HNO_3$/5% HCl instead of the specified 2% $HNO_3$/10% HCl matrix as the former matrix provides for improved performance relative to the wide variety of digestate acid matrices which result from the various EPA preparation protocols applied.

17.1.2.3 Method section 9.3.4 specifies that "Analysis of the IPC (ICSA/AB) solution immediately following calibration must verify that the instrument is within ± 5% of calibration with a relative standard deviation <3% from replicate integrations ≥ 4." STL North Canton uses a minimum of two exposures.

17.1.2.4 Section 7.12 of 200.7 indicates that the QCS (ICV) should be prepared at a concentration near 1 ppm. The ICV specified in this SOP accommodates the 1 ppm criteria for the majority of analytes. For the remaining analytes, this SOP specifies ICV concentrations which are appropriate to the range of calibration. The intent of the ICV, verification of calibration standard accuracy, is independent of the ICV concentration used.

17.1.2.5 The ICS criteria applied by this SOP differ from those stated in the method. Method 200.7 section 10.4 states that results should fall within the established control limits of 3 times the standard deviation of the calibration blank for that analyte. The control limits listed in this SOP are those applicable to the EPA designed solution.

17.1.2.6 Method 200.7 section 9.3.4 states the CCB should be less than the IDL, but > the lower 3-sigma control limit of the calibration blank. The intent of this requirement is to ensure that the calibration is not drifting at the low end. STL North Canton has adopted an absolute control limit of +/- RL from zero for calibration blank criteria. SOP section 9.7 provides the detailed corrective action criteria that must be followed.

17.1.3 Modifications from Method 6010B.

17.1.3.1 Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit. Common lab contaminants are allowed up to two times the reporting limit in the blank following consultation with the client.

17.1.3.2 Method 6010B section 8.6.1.3 states that the results of the calibration blank are to agree within 3x the IDL. If not, repeat the analysis two or more times and average the results. If the average is not within three standard deviations of the background mean, terminate the analysis, correct the problem, recalibrate, and reanalyze the previous 10 samples. The intent of this requirement is to ensure that the calibration is not drifting at the low end. STL North Canton has adopted an absolute control limit of +/- RL from zero for calibration blank criteria. See SOP Section 9.7 for a detailed description of the required corrective action procedures.

17.2Modifications from previous SOP

Refer to revision 2 of this SOP.

17.3Facility-Specific SOPs

Each facility shall review and revise as appropriate this SOP to reflect any facility-specific requirements. If no facility-specific amendments are required, the SOP can be adopted as is.

17.4Documentation and Record Management

The following documentation comprises a complete ICP raw data package:

- Raw data (direct instrument printout).
- Relevant sample preparation benchsheets.
- Run log printout from instrument software where this option is available (TJA) or manually generated run log (i.e., Ward WSL printout).
- Data review checklist - See Appendix B.
- Standards documentation (including prep and expiration dates, source, and lot #).
- Nonconformance/anomaly documentation (if applicable).

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SOP No. CORP-MT-0001NC
Revision No. 3.3
Revision Date: 12/05/01
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## STL NORTH CANTON STANDARD OPERATING PROCEDURE

## TITLE: INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROSCOPY, SPECTROMETRIC METHOD FOR TRACE ELEMENT ANALYSES, SW-846 METHOD 6010B AND EPA METHOD 200.7

(SUPERSEDES: REVISION 3.2, REVISION DATE 01/19/01)

| | | |
|---|---|---|
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## 1. SCOPE AND APPLICATION

1.1. This procedure describes the analysis of trace elements including metals in solution by Inductively Coupled Plasma -Atomic Emission Spectroscopy (ICP-AES) using SW-846 Method 6010B and EPA Method 200.7 . Table I of Appendix A lists the elements appropriate for analysis by Methods 6010B and 200.7. Additional elements may be analyzed under Methods 6010B and 200.7 provided that the method performance criteria presented in Section 13.0 are met.

1.2. ICP analysis provides for the determination of metal concentrations over several orders of magnitude. Detection limits, sensitivity and optimum concentration ranges of the metals will vary with the matrices and instrumentation used. For instance, in comparison to conventional ICP technique, ICP-Trace can achieve detection levels comparable to those determined using the graphite furnace atomic absorption spectroscopy (GFAAS) technique.

1.3. Method 6010B is applicable to the determination of dissolved, suspended, total recoverable and total elements in ground water, aqueous samples, soils, sludges, wastes, sediments, and TCLP, EP and other leachates/extracts. All matrices require digestion prior to analysis with the exception of analyses for dissolved metals in filtered and acidified aqueous samples. Although digestion is not specifically required by the method, some clients and regulators may require digestion of **dissolved samples** and this must be clarified and documented before project initiation. Silver concentrations must be below 2.0 mg/L in aqueous samples and 100 mg/kg in solid matrix samples. Precipitation may occur in samples where silver concentrations exceed these levels and lead to the generation of erroneous data.

1.4. Method 200.7 is applicable to the determination of dissolved, suspended, total recoverable, and total elements in water, waste water, and solid wastes. All matrices require digestion prior to analysis with the exception of analyses for dissolved metals in filtered and acidified aqueous samples if the criteria in Section 11.1 are met. Silver concentrations must be below 0.1 mg/L in aqueous samples and 50 mg/kg in solid matrix samples.

1.5. State-specific requirements may take precedence over this SOP for drinking water sample analyses.

1.6. The applicable LIMS method codes are QO (6010B), QM (6010B Trace), AS (200.7), JI (200.7 Trace).

## 2. SUMMARY OF METHOD

2.1. This method describes a technique for the determination of multi elements in solution using sequential or simultaneous optical systems and axial or radial viewing of the plasma. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by a radio frequency inductively coupled plasma (ICP). The spectra are dispersed by a grating spectrometer and the intensities of the emission lines are monitored by photomultiplier tubes. The photocurrents from the photomultiplier tubes are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background must be measured adjacent to analyte lines during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interferences and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences should also be recognized and appropriate actions taken. Alternatively, multivariate calibration methods may be chosen for which point selection for background correction is superfluous since whole spectral regions are processed.

2.2. Refer to the appropriate SOPs for details on sample preparation methods.

## 3. DEFINITIONS

3.1. Dissolved Metals: Those elements which pass through a 0.45 um membrane. (Sample is acidified <u>after</u> filtration).

3.2. Suspended Metals: Those elements which are retained by a 0.45 um membrane.

3.3. Total Metals: The concentration determined on an unfiltered sample following vigorous digestion.

3.4. Total Recoverable Metals: The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid.

## 4. INTERFERENCES

4.1. Spectral, physical and chemical interference effects may contribute to inaccuracies in the determinations of trace elements by ICP. Spectral interferences are caused by:

- Overlap of a spectral line from another element.
- Unresolved overlap of molecular band spectra.
- Background contribution from continuous or recombination phenomena.
- Stray light from the line emission of high concentration elements.

4.1.1. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background correction is not required in cases where a background corrective measurement would actually degrade the analytical result.

4.1.2. Inter-element correction factors (IECs) are necessary to compensate for spectral overlap. Inter-element interferences occur when elements in the sample emit radiation at wavelengths so close to that of the analyte that they contribute significant intensity to the analyte channel. If such conditions exist, the intensity contributed by the matrix elements will cause an excessively high (or sometimes low) concentration to be reported for the analyte. Inter-element corrections IECs must be applied to the analyte to remove the effects of these unwanted emissions.

4.1.3. Physical interferences are generally considered to be effects associated with sample transport, nebulization and conversion within the plasma. These interferences may result in differences between instrument responses for the sample and the calibration standards. Physical interferences may occur in the transfer of solution to the nebulizer (e.g., viscosity effects), at the point of aerosol formation and transport to the plasma (e.g., surface tension) or during excitation and ionization processes within the plasma itself. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, dilution of the sample, use of a peristaltic pump, mass flow controller, use of an internal standard and/or use of a high solids nebulizer can reduce the effect.

4.1.4. Chemical interferences are characterized by molecular compound formation, ionization effects and solute vaporization effects. Normally these effects are not significant with the ICP technique but if observed can be minimized by buffering the sample, matrix matching or standard addition procedures.

## 5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all STL North Canton associates.

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory.

5.3.1. The following materials are known to be **corrosive**:

sulfuric acid, hydrochloric acid, nitric acid and hydrofluoric acid. (NOTE: sulfuric and hydrofluoric acids are used in cleaning the ICP torch and hydrofluoric acid is also commonly used in air toxics preparations.)

5.3.2. The following materials are known to be **oxidizing agents**:

nitric acid and hydrogen peroxide.

5.3.3. The plasma emits strong UV light and is harmful to vision. **NOTE: AVOID looking directly at the plasma.**

5.3.4. The RF generator produces strong radio frequency waves, most of which are unshielded. People with pacemakers should not go near the instrument while in operation.

5.4. Exposure to chemicals must be maintained **as low as reasonably achievable,** therefore, unless they are known to be non-hazardous, all samples should be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Metals digestates can be processed outside of a fume hood. Solvent and waste containers will be kept closed unless transfers are being made.

5.5. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL North Canton associate. The situation must be reported **immediately** to a laboratory supervisor.

5.6. The use of hydrofluoric acid requires special safety precautions. Consult the facility EH&S Manager and laboratory supervisor for guidance.

## 6. EQUIPMENT AND SUPPLIES

6.1. Inductively Coupled Plasma Atomic Emission Spectrometer equipped with autosampler and background correction.

6.2. Radio Frequency Generator.

6.3. Argon gas supply, welding grade or equivalent.

6.4. Coolflow or appropriate water cooling device.

6.5. Peristaltic Pump.

6.6. Calibrated automatic pipettes or Class A glass volumetric pipettes.

6.7. Class A volumetric flasks.

6.8. Autosampler tubes.

## 7. REAGENTS AND STANDARDS

7.1. Intermediate standards are purchased as custom STL North Canton multi-element mixes or as single-element solutions. All standards must be stored in FEP

fluorocarbon or unused polyethylene or polypropylene bottles. Intermediate standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the intermediate solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem. Expiration dates can be extended provided that the acceptance criteria described in laboratory-specific SOPs are met.

7.2. Working calibration and calibration verification solutions may be used for up to 3 months and must be replaced sooner if verification from an independent source indicates a problem. Standards should be prepared in a matrix of 5% hydrochloric and 5% nitric acids. An exception to this is in the event the Trace ICP is utilized without the internal standard. In this case, the standard acid matrix must be matched to the final preparation matrix as listed in Section 11.9.

7.3. Refer to Tables III, IV, IVA, V and VI (Appendix A) for details regarding the working standard concentrations for calibration, calibration verification, interference correction and spiking solutions.

7.4. Concentrated nitric acid ($HNO_3$), trace metal grade or better.

7.5. Concentrated hydrochloric acid (HCl), trace metal grade or better.

7.6. Reagent water must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

## 8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Sample holding times for metals are six months from time of collection to the time of analysis.

8.2. Aqueous samples are preserved with nitric acid to a pH of <2 and may be stored in either plastic or glass. If boron or silica are to be determined, plastic containers are preferred. Refrigeration is not required. Preservation must be verified prior to analysis.

8.3. Soil samples do not require preservation but must be stored at 4°C ± 2° until the time of preparation .

## 9. QUALITY CONTROL

Table VII (Appendix A) provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.

9.1. Initial Demonstration of Capability

Prior to analysis of any analyte using either Method 200.7 or Method 6010B, the following requirements must be met.

Instrument Detection Limit (IDL) - The IDL for each analyte must be determined for each analyte wavelength used least each instrument. The IDL must be determined annually. If the instrument is adjusted in anyway that may affect the IDL, the IDL for that instrument must be redetermined. The IDL shall be determined by multiplying by 3, the standard deviation obtained from the analysis of a standard solution (each analyte in reagent water) at a concentration 3x - 5x the previously determined IDL, with seven consecutive measurements. Each measurement must be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure performed between the analysis of separate samples). The result of the IDL determination must be below the STL North Canton reporting limit. The CLP IDL procedure can be used for this method.

9.1.1. Method Detection Limit (MDL) - An MDL must be determined for each analyte prior to the analysis of any client samples. Refer to STL North Canton SOP NC-QA-0021 for details on MDL analysis and criteria.

9.1.2. Linear Range Verification (LR) - The linear range must be determined on at least an annual basis for each analyte wavelength used on each instrument. The linear range is the concentration above which results cannot be reported without dilution of the sample. The standards used to verify the linear range limit must be analyzed during a routine analytical run and must read within 5% of the expected value.

For the **initial** determination of the upper limit of the linear dynamic range (LDR) for each wavelength, determine the signal responses from a minimum of three to five different concentration standards across the estimated range. One standard should be near the upper limit of the estimated range. The concentration measured at the LDR must be no more than 10% less than the expected level extrapolated from lower standards. If the instrument is adjusted in any way that may affect the LRs, new dynamic ranges must be determined. The LR data must be documented and kept on file.

9.1.3. Background Correction Points - To determine the appropriate location for off-line background correction when establishing methods, the user must scan the area on either side adjacent to the wavelength and record the apparent emission intensity from all other method analytes. This spectral information must be documented and kept on file. The location selected for background correction must be either free of off-line interelement spectral interference or a computer routine must be used for automatic correction on all determinations. Tests to determine spectral interference must be done using analyte concentrations that will adequately describe the interference. Background correction points must be set prior to determining IECs. Refer to the facility-

specific instrument operation SOP and ICP instrument manual for specific procedures to be used in setting background correction points.

9.1.4. Inter-element Corrections (IECs) - ICP interelement correction factors must be determined prior to the analysis of samples and every six months thereafter. If the instrument is adjusted in any way that may affect the IECs, the IECs must be redetermined. When initially determining IECs for an instrument, wavelength scans must be performed to ensure that solutions in use are free from contaminants. If an IEC varies significantly from the previously determined IEC then the possibility of contamination should be investigated. The purity of the IEC check solution can be verified by using a standard from a second source or an alternate method (i.e., GFAA or ICP-MS). Published wavelength tables ( e.g. MIT tables, Inductively Coupled Plasma-Atomic Spectroscopy: Prominent Lines) can also be consulted to evaluate the validity of the IECs. Refer to the facility specific instrument operation SOP and instrument manufacturer's recommendations for specific procedures to be used in setting IECs. An IEC must be established to compensate for any interelement interference which results in a false analyte signal greater than ± the RL as defined in Tables I, IA or II. To determine IECs, run a single element standard at the established linear range. To calculate an IEC, divide the observed concentration of the analyte by the actual concentration of the "interfering element."

Note: Trace ICP IECs are more sensitive to small changes in the plasma and instrument setup conditions. Adjustments in the IECs will be required on a more frequent basis for the Trace as reflected by the ICSA response. Additional spectral interference is present from easily ionizable elements such as potassium and sodium in axial viewing instruments.

9.1.5. Rinse Time Determination - Rinse times must be determined upon initial set-up of an ICP instrument. To determine the appropriate rinse time for a particular ICP system, the linear range verification standard (see 9.1.3) should be aspirated as a regular sample followed by the analysis of a series of rinse blanks. The length of time required to reduce the analyte signals to < RL will define the rinse time for a particular ICP system. For some analytes it may be impractical to set the rinse time based on the linear range standard result (i.e., analyte not typically detected in environmental samples at that level and an excessive rinse time would be required at the linear range level). Until the required rinse time is established, the method recommends a rinse period of at least 60 seconds between samples and standards. If a memory effect is suspected, the sample must be reanalyzed after a rinse period of sufficient length. Rinse time studies can be conducted at additional concentration levels. These additional studies must be documented and kept on file, if a concentration other than the linear range level is used to set the rinse time. The

concentration levels used to establish the rinse time must be taken into consideration when reviewing the data.

9.2. Method Blank (MB) - One method blank must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest at or above the reporting limit (exception: common laboratory contaminants, see below) or at or above 5% of the measured concentration of that analyte in associated samples, whichever is higher (sample result must be a minimum of 20x higher than the blank contamination level).

- If the analyte is a common laboratory contaminant (copper, iron, lead (Trace only) or zinc) the data may be reported with qualifiers if the concentration of the analyte in the method blank is less than two times the RL. **Such action must be taken in consultation with the client and must be addressed in the project narrative.**

- Repreparation and reanalysis of all samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples (see exception noted above).

- If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. **Such action must be taken in consultation with the client and must be addressed in the project narrative.**

- If the above criteria are not met and reanalysis is not possible, then the sample data must be qualified. **This anomaly must be addressed in the project narrative and the client must be notified.**

- For dissolved metals samples which have not been digested, a CCB result is reported as the method blank. The CCB run immediately prior to the start of the dissolved sample analyses must be used for this purpose. No more than 20 samples can be associated with one CCB.

9.3. Laboratory Control Sample (LCS) - One aqueous LCS must be processed with each preparation batch. The LCS must contain all analytes of interest and must be carried through the entire analytical procedure. Aqueous LCS spike levels are provided in Table III (Appendix A). The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

- If any analyte is outside established control limits the system is out of control and corrective action must occur. Unless in-house control limits are established, a control limit of 80 - 120% recovery must be applied.

- In the event that an MS/MSD analysis is not possible a Laboratory Control Sample Duplicate (LCSD) must be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

- In the instance where the LCS recovery is greater than 120% and the sample results are < RL, the data may be reported with qualifiers. **Such action must be taken in consultation with the client and must be addressed in the report narrative.**

- Corrective action will be repreparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable.

- For dissolved metals samples which have not been digested, a CCV result is reported as the LCS. The CCV run immediately prior to the start of the dissolved sample analyses must be used for this purpose. No more than 20 samples can be associated with one CCV.

9.4. Matrix Spike/Matrix Spike Duplicate (MS/MSD) - One MS/MSD pair must be processed for each preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MSDs. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis. Spiking levels are provided in Tables III and VI (Appendix A).

- If any analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. For both methods 200.7 and 6010B, control limits of 75-125% recovery and 20% RPD or historical acceptance criteria must be applied to the MS/MSD. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch. MS/MSD results which fall outside the control limits must be addressed in the narrative.

- If the native analyte concentration in the MS/MSD exceeds 4x the spike level for that analyte, the recovery data are reported as NC, MSB (i.e., not calculated). If

the reporting software does not have the ability to report NC, MSB then the actual recovery must be reported and narrated as follows: "Results outside of limits do not necessarily reflect poor method performance in the matrix due to high analyte concentrations in the sample relative to the spike level." Two other narrative notes for metals analyses: Matrix spike/spike duplicate spike recovery/recoveries was/were outside the acceptance limits of some analytes. The acceptable LCS analysis data indicated that the analytical system was operating within control and this condition is most likely due to matrix interference. See the Matrix Spike Report for the affected analytes which will be flagged with N. Matrix spike/spike duplicate relative percent difference (RPD) exceeded the acceptance limits for some analytes. The imprecision may be attributed to sample heterogeneity. See the Matrix Spike Report for the affected analytes, which will be flagged with *.

- If an MS/MSD is not possible due to limited sample volume then a laboratory control sample duplicate (LCSD) should be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

- For dissolved metals samples which have not been digested, a MS/MSD must be performed per batch of up to 20 samples by spiking two aliquots of the sample at the levels specified in Table III (Appendix A).

9.5. Dilution test – A dilution test is performed to determine whether significant physical or chemical interferences exist due to the sample matrix. One sample per preparation batch must be processed as a dilution test. The test is performed by running a sample at a 5x (1:4) dilution. Samples identified as field blanks cannot be used for dilution tests. The results of the diluted sample, after correction for dilution, should agree within 10% of the original sample determination when the original sample concentration is greater than 50x the IDL. If the results are not within 10%, the possibility of chemical or physical interference exists.

9.6. Initial Calibration Verification (ICV/ICB) - Calibration accuracy is verified by analyzing a second source standard (ICV). For analyses conducted under Method 200.7, the ICV result must fall within 5% of the true value for that solution with relative standard deviation <3% from replicate (minimum of two) exposures. For Method 6010B, the ICV must fall within 10% of the true value for that solution with relative standard deviation <5% from replicate (minimum of two) exposures. An ICB is analyzed immediately following the ICV to monitor low level accuracy and system cleanliness. The ICB result must fall within +/- the RL from zero. If either the ICV or ICB fail to meet criteria, the analysis should be terminated, the problem corrected, the instrument recalibrated and the calibration reverified. (See Section 11.10 or 11.13 for required run sequence).

9.7. Continuing Calibration Verification (CCV/CCB) - Calibration accuracy is monitored throughout the analytical run through the analysis of a known standard after every 10 samples. The CCV is be a mid-range standard made from a dilution of the

calibration standard. The CCV for both methods must fall within 10% of the true value for that solution with relative standard deviation <5% from replicate (minimum of two) exposures. A CCB is analyzed immediately following each CCV. (See Section 11.10 or 11.13 for required run sequence.) The CCB result must fall within +/- RL from zero. If the blank is less than 1/10 the concentration of the action level of interest, and no sample is within 10% of the action limit, reanalysis and recalibration are not required before continuation of the run. Sample results may only be reported when bracketed by valid CCV/CCB pairs. If a mid-run CCV or CCB fails, the analysis for the affected element must be terminated, the problem corrected, the instrument recalibrated, the calibration verified and the affected samples reanalyzed. (Refer to Section 11.13 for an illustration of the appropriate rerun sequence).

9.8. Interference Check Analysis (ICSA/ICSAB) - The validity of the interelement correction factors is demonstrated through the successful analysis of interference check solutions. The ICSA contains only interfering elements, the ICSAB contains analytes and interferents. Refer to Table V (Appendix A) for the details of ICSA and ICSAB composition. Custom STL North Canton multielement ICS solutions must be used. All analytes should be spiked into the ICSAB solution, therefore, if a non-routine analyte is required then it should be manually spiked into the ICSAB using a certified ultra high purity single element solution or custom lab-specific mix. If the ICP will display overcorrection as a negative number then the non-routine elements can be controlled from the ICSA as described in section 9.8.3. Elements known to be interferents on a required analyte must be included in the ICP run when that analyte is determined. Aluminum, iron, calcium and magnesium must always be included in all ICP runs.

9.8.1. The ICSA and ICSAB solutions must be run at the beginning of the run. (See Section 11.10 or 11.13 for required run sequence.)

9.8.2. The ICSAB results for the interferents must fall within 80 - 120% of the true value. If any ICSAB interferent result fails criteria, the analysis should be terminated, the problem corrected, the instrument recalibrated and the samples rerun.

9.8.3. ICSA results for the non-interfering elements with reporting limits ≤ 10 ug/L must fall within the STL North Canton guidelines of ± 2x RL from zero. ICSA results for the non-interfering elements with RLs> 10 µg/L must fall within the STL North Canton guidelines of ± 1x RL from zero. If the ICSA results for the non-interfering elements do not fall within +/- 2x RL (RL ≤10) or ± 1xRL (RL>10) from zero the field sample data must be evaluated as follows:

- If the non-interfering element concentration in the ICSA is the result of contamination versus a spectral interference, and this reason is documented, the field sample data can be accepted.

- If the affected element was not required then the sample data can be accepted.

- If the interfering elements are not present in the field sample at a concentration which would result in a false positive or negative result greater than +/- 2x RL from zero then the field sample data can be accepted.

- If the interfering element is present in the field sample at a level which would result in a false analyte signal greater than ± 2x RL from zero, the data can be accepted only if the concentration of the affected analyte in the field sample is more than 10x the analyte signal in the ICSA.

- If the data does not meet the above conditions then the IECs must be re-evaluated and corrected if necessary and the affected samples reanalyzed or the sample results manually corrected through application of the new IEC to the raw results. If the results are recalculated manually the calculations must be clearly documented on the raw data.

9.9. CRI - To verify linearity near the RL for ICP analysis, a CRI standard is run at the beginning of each sample analysis run. Additionally, some projects may require CRI analysis at the end of the run. (See Section 11.10 or 11.13 for required run sequence.) Evaluate associated samples based upon advisory limits of +/- 50% of true value.

Note: The custom STL North Canton CRI mix contains most analytes at a level near the standard lab reporting limit.

9.10. Method of Standard Addition (MSA) -This technique involves adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample interferent that may enhance or depress the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift. Refer to Section 11.17 for additional information on when MSA is required as well as Appendix D for specific MSA requirements.

9.11. Quality Assurance/Project Summaries - Certain clients may require project- or program-specific QC which may supersede this SOP requirements. Quality Assurance Summaries (QASs) or equivalent documents providing project-specific requirements should be developed so that project staff clearly understand the special project requirements.

## 10. CALIBRATION AND STANDARDIZATION

10.1. Set up the instrument with the operating parameters recommended by the manufacturer. Allow the instrument to become thermally stable before beginning calibration (approximately 30 minutes of warm-up is required).

10.2. Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures. Flush the system with the calibration blank between each standard or as the manufacturer recommends. The calibration curve must consist of a minimum of a blank and a standard. Refer to the facility-specific instrument SOP or ICP instrument manual for a detailed set up and operation protocols.

10.3. Calibration must be performed daily and each time the instrument is set up. Instrument runs may be continued over periods exceeding 24 hours as long as all calibration verification (CCV) and interference check QC criteria are met. The instrument standardization date and time must be included in the raw data.

10.4. Refer to Section 9.0 for calibration verification procedures, acceptance criteria and corresponding corrective actions.

## 11. PROCEDURE

11.1. For 200.7 analyses, dissolved (preserved) samples must be digested unless it can be documented that the sample meets all of the following criteria:

A. Visibly transparent with a turbidity measurement of 1 NTU or less.

B. Is of one liquid phase and free of particulate or suspended matter following acidification.

C. Is NOT being analyzed for silver.

11.2. A minimum of <u>two</u> <u>exposures</u> for each standard, field sample and QC sample is required. The average of the exposures is reported. For Trace ICP analyses, the results of the sum channel must be used for reporting.

11.3. Prior to calibration and between each sample/standard the system is rinsed with the calibration blank solution. The minimum rinse time between analytical samples is 60 seconds unless following the protocol outlined in 9.1.6 it can be demonstrated that a shorter rinse time may be used. Triton-X can be added to the rinse solution to facilitate the rinse process.

11.4. The use of an autosampler for all runs is strongly recommended.

11.5. The use of automated QC checks through the instrument software is highly recommended for all calibration verification samples (ICV,CCV), blanks

(ICB,CCB,PB), interference checks (ICSA,ICSAB) and field samples (linear range) to improve the data review process.

11.6. To facilitate the early identification of QC failures and samples requiring rerun it is strongly recommended that sample data be reviewed periodically throughout the run.

11.7. To facilitate the data review and reporting processes it is strongly recommended that all necessary dilutions be performed before closing out the instrument run.

11.8. The use of an internal standard is recommended on the conventional, non-Trace ICPs as an alternative to using the method of standard additions. This technique is useful in overcoming matrix interferences especially in high solids matrices. However, for conventional ICP techniques, internal standards may not be necessary provided that one of the following is performed to minimize physical interferences: (1) peristaltic pump is used, (2) high solids nebulizer is used, or (3) high solids samples are diluted and reanalyzed.

11.9. The use of an internal standard is **required** on the Trace ICP unless the calibration and QC standards are matrix matched to each digestion procedure used as follows:

| Preparation Method | % $HNO_3$ | % HCl |
|---|---|---|
| CLP Aqueous | 1 | 5 |
| CLP Soil | 5 | 2.5 |
| SW846 3050 | 10 | 10 |
| SW846 3005 | 2 | 5 |
| SW846 3010 | 6 | 5 |

The following procedural guidelines must be followed when using an internal standard:

11.9.1. Typically used internal standards are: yttrium or scandium. (Note: Any element can be used that is not typically found in environmental samples at a high rate of occurrence.)

11.9.2. The internal standard (IS) must be added to every sample and standard at the same concentration. It is recommended that the IS be added to each analytical sample automatically through use of a third pump channel and mixing coil. Internal standards should be added to blanks, samples and

standards in a like manner, so that dilution effects resulting from the addition may be disregarded.

11.9.3. The concentration of the internal standard should be sufficiently high to obtain good precision in the measurement of the IS analyte used for data correction and to minimize the possibility of correction errors if the IS analyte is naturally present in the sample.

11.9.4. The internal standard raw intensity counts must be printed on the raw data.

11.9.5. The analyst must monitor the response of the internal standard throughout the sample analysis run. This information is used to detect potential problems and identify possible background contributions from the sample (i.e., natural occurrence of IS analyte). The instrument automatically adjusts sample results based on comparison of the internal standard intensity in the sample to the internal standard intensity at calibration.

11.9.5.1. If the internal standard counts fall within ±30% of the counts observed in the ICB then the data is acceptable.

11.9.5.2. If the internal standard counts in the field samples are more than ±30% higher than the expected level, the field samples must then be:

(1) Diluted and reanalyzed;

(2) The IS concentrations must be raised; or

(3) A different internal standard must be used.

11.10. The following analytical sequence must be used for Methods 6010B and 200.7:

Instrument Calibration
ICV
ICB
CRI
ICSA
ICSAB
7 samples
CCV
CCB
10 samples
CCV
CCB
Repeat sequence of up to 10 samples between CCV/CCB pairs as required to complete run

CRI (The CRI counts as a sample analysis.)
CCV
CCB

Refer to Quality Control Section 9.0 and Table VII (Appendix A) for Method 6010B and 200.7 quality control criteria.

11.11. Additional quality control analyses are necessary for analysis under the Contract Laboratory Program (CLP). If these are included then CLP, 6010 and 200.7 samples can be included in the same sequence. Refer to CORP-MT-0002NC for details.

11.12. Full method required QC must be available for each wavelength used in determining reported analyte results.

11.13. The following run sequence provides an illustration of a mid-run CCV or CCB failure and the appropriate corrective action run sequence as described in Section 9.7:

<u>Original Run</u>: Instrument Calibration

ICV

ICB

CRI

ICSA

ICSAB

7 samples

CCV1

CCB1

10 samples

CCV2

CCB2

10 samples **

CCV3 * * Failure occurs at CCV3/CCB3

CCB3 * **Samples requiring rerun for affected analytes

10 samples **

CCV4

CCB4

10 samples

CCV5

CCB5

Reanalysis: Recalibrate

ICV

ICB

CRI

ICSA

ICSAB

CCV2

CCB2

10 samples

CCV3

CCB3

10 samples

CCV4

CCB4

Notes:

Samples between CCV4 and CCV5 do not require reanalysis as they were bracketed by compliant QC samples.

See CORP-MT-0002NC for the appropriate reanalysis sequence if CLP requirements must also be met.

11.14 The instrument may be reprofiled between CCV/CCB pairs to correct for environment induced drift.

11.15 Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards, preventive maintenance and troubleshooting.

11.16 All measurements must fall within the defined linear range where spectral interference correction factors are valid. Dilute and reanalyze all samples for required analytes that exceed the linear range or use an alternate wavelength for which QC data are established. If an interelement correction exists for an analyte which exceeds the linear range, the IEC may be inaccurately applied. Therefore, even if an overrange analyte may not be required to be reported for a sample, if that analyte is a interferent for any requested analyte in that sample, the sample must be diluted. Acid strength must be maintained in the dilution of samples.

11.17 For TCLP samples, full four-point MSA will be required if all of the following conditions are met:

1) recovery of the analyte in the matrix spike is not at least 50%,

2) the concentration of the analyte does not exceed the regulatory level, and,

3) the concentration of the analyte is within 20% of the regulatory level.

The reporting and regulatory limits for TCLP analyses as well as matrix spike levels are detailed in Table VI (Appendix A). Appendix E provides guidance on performing MSA analyses.

11.18 Any variation in procedure shall be completely documented using instrument run logs, maintenance logs, report narratives, a Nonconformance Memo, or an anomaly report and is approved by a Supervisor/Group Leader and QA Manager. If contractually required, the client shall be notified by the Project Manager.

11.19 Nonconformance documentation shall be filed in the project file.

11.20 Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

## 12 DATA ANALYSIS AND CALCULATIONS

12.1ICV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(ICV)}{True(ICV)}\right)$$

12.2CCV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(CCV)}{True(CCV)}\right)$$

12.3Matrix Spike Recoveries are calculated according to the following equation:

$$\%R = 100\left(\frac{SSR - SR}{SA}\right)$$

Where:
SSR = Spike Sample Result
SR = Sample Result
SA = Spike Added

12.4The relative percent difference (RPD) of matrix spike/matrix spike duplicates are calculated according to the following equations:

$$RPD = 100\left[\frac{|MSD - MS|}{\left(\frac{MSD + MS}{2}\right)}\right]$$

Where:
MS = determined spiked sample concentration
MSD = determined matrix spike duplicate concentration

12.5The final concentration for a digested aqueous sample is calculated as follows:

$$mg/L = \frac{C \times V1 \times D}{V2}$$

Where:
C = Concentration (mg/L) from instrument readout
D = Instrument dilution factor
V1 = Final volume in liters after sample preparation
V2 = Initial volume of sample digested in liters

12.6 The final concentration determined in digested solid samples when reported on a dry weight basis is calculated as follows:

$$mg / Kg, dry\ weight = \frac{C \times V \times D}{W \times S}$$

Where:
C = Concentration (mg/L) from instrument readout
D = Instrument dilution factor
V = Final volume in liters after sample preparation
W = Weight in Kg of wet sample digested
S = Percent solids/100

Note: A Percent Solids determination must be performed on a separate aliquot when dry weight concentrations are to be reported. If the results are to be reported on wet weight basis the "S" factor should be omitted from the above equation.

12.7 The LCS percent recovery is calculated according to the following equation:

$$\%R = 100\left(\frac{Found(LCS)}{True(LCS)}\right)$$

12.8 The dilution test percent difference for each component is calculated as follows:

$$\%Difference = \frac{|I - S|}{I} \times 100$$

Where:
I = Sample result (Instrument reading)
S = Dilution test result (Instrument reading × 5)

12.9 Appropriate factors must be applied to sample values if dilutions are performed.

12.10 Sample results should be reported with up to three significant figures in accordance with the STL North Canton significant figure policy.

## 13 METHOD PERFORMANCE

13.1 Each laboratory must have initial demonstration of performance data on file for each analyte of interest as described in Section 9.0.

13.2 Refer to Tables I, IA & II in Appendix A for the list of Method 6010B and 200.7 analytes as well as additional analytes that may be analyzed using this SOP.

13.3 Method performance is determined by the analysis of MS and MSD samples as well as method blanks and laboratory control samples. The MS or MSD recovery should fall within +/- 25 % and the MS/MSD should compare within 20% RPD or within the laboratory's historical acceptance limits. These criteria apply to analyte concentrations greater than or equal to 10xIDL. Method blanks must meet the criteria specified in Section 9.2. The laboratory control samples should recover within 20% of the true value or within the laboratory's historical acceptance limits.

13.4 Training Qualification:

The group/team leader or the supervisor has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

## 14 POLLUTION PREVENTION

14.1 This method does not contain any specific modifications that serve to minimize or prevent pollution.

## 15 WASTE MANAGEMENT

15.1 Waste generated in the procedure must be segregated and disposed of according to the facility hazardous waste procedures and per the local, state, and federal regulations. The Environmental Health and Safety Director should be contacted, if additional information is required.

15.2 Standards should be purchased and prepared in volumes consistent with laboratory use to minimize the volume of expired standards to be disposed.

## 16 REFERENCES

16.1 40 CFR Part 136, Appendix B, 7-5-95, Determination of Method Detection Limits.

16.2 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update III, Revision 2, December 1996. Method 6010B.

16.3 Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry, Revision 4.4, May 1994. Method 200.7.

16.4 CORP-MT-0002NC, Inductively Coupled Plasma-Atomic Emission Spectroscopy, Method 200.7 & CLP-M, SOW ILMO3.0 and ILMO4.0).

16.5QA-003, STL North Canton QC Program.

16.6QA-004, Rounding and Significant Figures.

16.7QA-005, Method Detection Limits.

## 17 MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1Modifications/Interpretations from reference method

17.1.1 Modifications/interpretations from both Methods 6010B and 200.7.

17.1.1.1 STL North Canton laboratories use mixed calibration standard solutions purchased from approved vendors instead of using individual mixes prepared in house as recommended by the subject methods.

17.1.1.2 Methods 200.7 and 6010B state that if the correction routine is operating properly, the determined apparent analyte(s) concentration from analysis of each interference solution should fall within a specific concentration range around the calibration blank. In determining IECs, because of lack of definition clarification for "concentration range around the calibration blank," STL North Canton has adopted the procedure in EPA CLP ILMO4.0.

17.1.1.3 Section 8.5 of Method 6010B and Section 9.5 of Method 200.7 recommend that whenever a new or unusual matrix is encountered, a series of tests be performed prior to reporting concentration data for that analyte. The dilution test helps determine if a chemical or physical interference exists. Because STL North Canton laboratories receive no prior information from clients regarding when to expect a new or unusual matrix, STL North Canton may select to perform a dilution test on one sample in each prep batch. According to the method, the post digestion spike (PDS) determines any potential matrix interferences. At STL North Canton LABS, matrix interference is determined by evaluating data for the LCS and MS/MSD. STL North Canton REQUIRES documented, clear guidance when a new or unusual matrix will be received for a project and a request to perform the dilution test or PDS on a client-identified sample.

17.1.2 Modifications from Method 200.7.

17.1.2.1 Method 200.7 defines the IDL as the concentration equivalent to a signal, due to the analyte, which is equal to three times the standard deviation of a series of ten replicate measurements of the calibration blank signal at the same wavelength. STL North Canton labs utilize the CLP IDL definition as defined in Section 9.1.1 of this SOP.

17.1.2.2 The calibration blank is prepared in an acid matrix of 5% $HNO_3$/5% HCl instead of the specified 2% $HNO_3$/10% HCl matrix as the former matrix provides for improved performance relative to the wide variety of digestate acid matrices which result from the various EPA preparation protocols applied.

17.1.2.3 Method section 9.3.4 specifies that "Analysis of the IPC (ICSA/AB) solution immediately following calibration must verify that the instrument is within ± 5% of calibration with a relative standard deviation <3% from replicate integrations ≥ 4." STL North Canton uses a minimum of two exposures.

17.1.2.4 Section 7.12 of 200.7 indicates that the QCS (ICV) should be prepared at a concentration near 1 ppm. The ICV specified in this SOP accommodates the 1 ppm criteria for the majority of analytes. For the remaining analytes, this SOP specifies ICV concentrations which are appropriate to the range of calibration. The intent of the ICV, verification of calibration standard accuracy, is independent of the ICV concentration used.

17.1.2.5 The ICS criteria applied by this SOP differ from those stated in the method. Method 200.7 section 10.4 states that results should fall within the established control limits of 3 times the standard deviation of the calibration blank for that analyte. The control limits listed in this SOP are those applicable to the EPA designed solution.

17.1.2.6 Method 200.7 section 9.3.4 states the CCB should be less than the IDL, but > the lower 3-sigma control limit of the calibration blank. The intent of this requirement is to ensure that the calibration is not drifting at the low end. STL North Canton has adopted an absolute control limit of +/- RL from zero for calibration blank criteria. SOP section 9.7 provides the detailed corrective action criteria that must be followed.

17.1.3 Modifications from Method 6010B.

17.1.3.1 Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit. Common lab contaminants are allowed up to two times the reporting limit in the blank following consultation with the client.

17.1.3.2 Method 6010B section 8.6.1.3 states that the results of the calibration blank are to agree within 3x the IDL. If not, repeat the analysis two or more times and average the results. If the average is not within three standard deviations of the background mean, terminate the analysis, correct the problem, recalibrate, and reanalyze the previous 10 samples. The intent of this requirement is to ensure that the calibration is not drifting at the low end. STL North Canton has adopted an absolute control limit of +/- RL from zero for calibration blank criteria. See SOP Section 9.7 for a detailed description of the required corrective action procedures.

17.2Modifications from previous SOP

Refer to revision 2 of this SOP.

17.3Facility-Specific SOPs

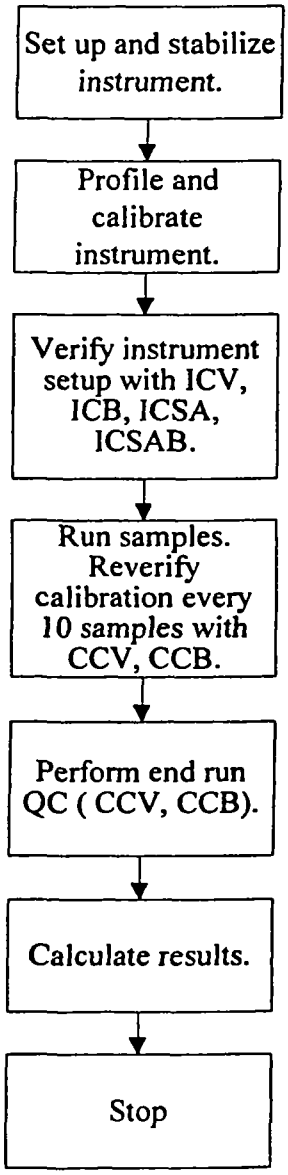
Each facility shall review and revise as appropriate this SOP to reflect any facility-specific requirements. If no facility-specific amendments are required, the SOP can be adopted as is.

17.4Documentation and Record Management

The following documentation comprises a complete ICP raw data package:

- Raw data (direct instrument printout).
- Relevant sample preparation benchsheets.
- Run log printout from instrument software where this option is available (TJA) or manually generated run log (i.e., Ward WSL printout).
- Data review checklist - See Appendix B.
- Standards documentation (including prep and expiration dates, source, and lot #).
- Nonconformance/anomaly documentation (if applicable).

17.5Flow Diagram



# APPENDIX A

# TABLES

**TABLE I. Method 200.7 and 6010B Target Analyte List**

| ELEMENT | Symbol | CAS # | 6010B analyte | 200.7 analyte | Reporting Limit (ug/L) Water | Reporting Limit (mg/kg) Soil |
|---|---|---|---|---|---|---|
| Aluminum | Al | 7429-90-5 | X | X | 200 | 20 |
| Antimony | Sb | 7440-36-0 | X | X | 60 | 6 |
| Arsenic | As | 7440-38-2 | X | X | 300 | 30 |
| Barium | Ba | 7440-39-3 | X | X | 200 | 20 |
| Beryllium | Be | 7440-41-7 | X | X | 5.0 | 0.5 |
| Boron | B | 7440-42-8 | | X | 200 | 20 |
| Cadmium | Cd | 7440-43-9 | X | X | 5.0 | 0.5 |
| Calcium | Ca | 7440-70-2 | X | X | 5000 | 500 |
| Chromium | Cr | 7440-47-3 | X | X | 10 | 1 |
| Cobalt | Co | 7440-48-4 | X | X | 50 | 5 |
| Copper | Cu | 7440-50-8 | X | X | 25 | 2.5 |
| Iron | Fe | 7439-89-6 | X | X | 100 | 10 |
| Lead | Pb | 7439-92-1 | X | X | 100 | 10 |
| Magnesium | Mg | 7439-95-4 | X | X | 5000 | 500 |
| Manganese | Mn | 7439-96-5 | X | X | 15 | 1.5 |
| Molybdenum | Mo | 7439-98-7 | X | X | 40 | 4 |
| Nickel | Ni | 7440-02-0 | X | X | 40 | 4 |
| Potassium | K | 7440-09-7 | X | X | 5000 | 500 |
| Selenium | Se | 7782-49-2 | X | X | 250 | 25 |
| Silver | Ag | 7440-22-4 | X | X | 10 | 1 |
| Sodium | Na | 7440-23-5 | X | X | 5000 | 500 |
| Thallium | Tl | 7440-28-0 | X | X | 2000 | 200 |
| Vanadium | V | 7440-62-2 | X | X | 50 | 5 |
| Zinc | Zn | 7440-66-6 | X | X | 20 | 2 |

**TABLE IA. Method 200.7 and 6010B Trace ICP Target Analyte List**

| ELEMENT | Symbol | CAS # | Reporting Limit (ug/L) Water | Reporting Limit (mg/kg) Soil |
|---|---|---|---|---|
| Arsenic | As | 7440-38-2 | 10 | 1.0 |
| Lead | Pb | 7439-92-1 | 3.0 | 0.3 |
| Selenium | Se | 7782-49-2 | 5.0 | 0.5 |
| Thallium | Tl | 7440-28-0 | 10 | 1.0 |
| Antimony | Sb | 7440-36-0 | 10 | 1.0 |
| Cadmium | Cd | 7440-43-9 | 2.0 | 0.2 |
| Silver | Ag | 7440-22-4 | 5.0 | 0.5 |
| Chromium | Cr | 7440-47-3 | 5.0 | 0.5 |

**TABLE II. Non-Routine Analyte List**

| ELEMENT | Symbol | CAS # | Reporting Limit (ug/L) Water | Reporting Limit (mg/kg) Soil |
|---|---|---|---|---|
| Tin | Sn | 7440-31-5 | 100 | 10 |
| Titanium | Ti | 7440-32-6 | 50 | 5 |

**TABLE III. Matrix Spike and Aqueous Laboratory Control Sample Levels**

| ELEMENT | LCS Level (ug/L) | Matrix Spike Level (ug/L) |
|---|---|---|
| Aluminum | 2000 | 2000 |
| Antimony | 500 | 500 |
| Arsenic | 2000 | 2000 |
| Barium | 2000 | 2000 |
| Beryllium | 50 | 50 |
| Cadmium | 50 | 50 |
| Calcium | 50000 | 50000 |
| Chromium | 200 | 200 |
| Cobalt | 500 | 500 |
| Copper | 250 | 250 |
| Iron | 1000 | 1000 |
| Lead | 500 | 500 |
| Magnesium | 50000 | 50000 |
| Manganese | 500 | 500 |
| Molybdenum | 1000 | 1000 |
| Nickel | 500 | 500 |
| Potassium | 50000 | 50000 |
| Selenium | 2000 | 2000 |
| Silver | 50 | 50 |
| Sodium | 50000 | 50000 |
| Thallium | 2000 | 2000 |
| Vanadium | 500 | 500 |
| Zinc | 500 | 500 |
| Boron | 1000 | 1000 |
| Tin | 2000 | 2000 |
| Titanium | 1000 | 1000 |

**TABLE IV. ICP Calibration and Calibration Verification Standards**

| Element | Calibration Level | RL (ug/L) | ICV (ug/L) | CCV (ug/L) |
|---|---|---|---|---|
| Aluminum | 100000 | 200 | 25000 | 50000 |
| Antimony | 10000 | 60 | 1000 | 5000 |
| Arsenic | 10000 | 300 | 1000 | 5000 |
| Barium | 10000 | 200 | 1000 | 5000 |
| Beryllium | 10000 | 5 | 1000 | 5000 |
| Cadmium | 10000 | 5 | 1000 | 5000 |
| Calcium | 100000 | 5000 | 25000 | 50000 |
| Chromium | 10000 | 10 | 1000 | 5000 |
| Cobalt | 10000 | 50 | 1000 | 5000 |
| Copper | 10000 | 25 | 1000 | 5000 |
| Iron | 100000 | 100 | 25000 | 50000 |
| Lead | 10000 | 100 | 1000 | 5000 |
| Magnesium | 100000 | 5000 | 25000 | 50000 |
| Manganese | 10000 | 15 | 1000 | 5000 |
| Molybdenum | 10000 | 40 | 1000 | 5000 |
| Nickel | 10000 | 40 | 1000 | 5000 |
| Potassium | 100000 | 5000 | 25000 | 50000 |
| Selenium | 10000 | 250 | 1000 | 5000 |
| Silver | 2000 | 10 | 500 | 1000 |
| Sodium | 100000 | 5000 | 25000 | 50000 |
| Thallium | 20000 | 2000 | 5000 | 10000 |
| Vanadium | 10000 | 50 | 1000 | 5000 |
| Zinc | 10000 | 20 | 1000 | 5000 |
| Boron | 10000 | 200 | 1000 | 5000 |
| Tin | 10000 | 100 | 1000 | 5000 |
| Titanium | 10000 | 50 | 1000 | 5000 |

**TABLE IVA. Trace ICP Calibration and Calibration Verification Standards**

| Element | Calibration Level | RL (ug/L) | ICV (ug/L) | CCV (ug/L) |
|---|---|---|---|---|
| Aluminum | 50000 | 200 | 12500 | 25000 |
| Antimony | 1000 | 10 | 250 | 500 |
| Arsenic | 1000 | 10 | 250 | 500 |
| Barium | 4000 | 10 | 1000 | 2000 |
| Beryllium | 4000 | 5 | 1000 | 2000 |
| Cadmium | 1000 | 2 | 250 | 500 |
| Calcium | 100000 | 5000 | 25000 | 50000 |
| Chromium | 4000 | 5 | 1000 | 2000 |
| Cobalt | 4000 | 50 | 1000 | 2000 |
| Copper | 4000 | 25 | 1000 | 2000 |
| Iron | 50000 | 100 | 12500 | 25000 |
| Lead | 1000 | 3 | 250 | 500 |
| Magnesium | 100000 | 5000 | 25000 | 50000 |
| Manganese | 4000 | 15 | 1000 | 2000 |
| Molybdenum | 4000 | 40 | 1000 | 2000 |
| Nickel | 4000 | 40 | 1000 | 2000 |
| Potassium | 100000 | 5000 | 25000 | 50000 |
| Selenium | 1000 | 5 | 250 | 500 |
| Silver | 2000 | 5 | 500 | 1000 |
| Sodium | 100000 | 5000 | 25000 | 50000 |
| Thallium | 2000 | 10 | 500 | 1000 |
| Vanadium | 4000 | 50 | 1000 | 2000 |
| Zinc | 4000 | 20 | 1000 | 2000 |

**TABLE V. Interference Check Sample Concentrations***

| Element | ICSA (ug/L) | ICSAB (ug/L) |
|---|---|---|
| Aluminum | 500000 | 500000 |
| Antimony | - | 1000 |
| Arsenic | - | 1000 |
| Barium | - | 500 |
| Beryllium | - | 500 |
| Cadmium | - | 1000 |
| Calcium | 500000 | 500000 |
| Chromium | - | 500 |
| Cobalt | - | 500 |
| Copper | - | 500 |
| Iron | 200000 | 200000 |
| Lead | - | 1000 |
| Magnesium | 500000 | 500000 |
| Manganese | - | 500 |
| Molybdenum | - | 1000 |
| Nickel | - | 1000 |
| Potassium | - | 10000 |
| Selenium | - | 1000 |
| Silver | - | 1000 |
| Sodium | - | 10000 |
| Thallium | - | 10000** |
| Vanadium | - | 500 |
| Zinc | - | 1000 |
| Tin | - | 1000 |
| Boron | | 1000 |
| Titanium | | 1000 |

* Custom STL North Canton solutions contain analytes common to all STL North Canton facilities. Non-routine elements not listed above should be spiked into the ICSAB at 1000 ug/L.

** Thallium level for Trace ICP should be at 1000 ug/L.

**TABLE VI. TCLP Reporting Limits, Regulatory Limits and Matrix Spike Levels**

| ELEMENT | Reporting Level (ug/L) | Regulatory Limit (ug/L) | Spike Level (ug/L) |
|---|---|---|---|
| Arsenic | 500 | 5000 | 5000 |
| Barium | 10000 | 100000 | 50000 |
| Cadmium | 100 | 1000 | 1000 |
| Chromium | 500 | 5000 | 5000 |
| Lead | 500 | 5000 | 5000 |
| Selenium | 250 | 1000 | 1000 |
| Silver | 500 | 5000 | 1000 |

**TABLE VII. Summary Of Quality Control Requirements**

| QC PARAMETER | FREQUENCY | ACCEPTANCE CRITERIA | CORRECTIVE ACTION |
|---|---|---|---|
| Two-point Initial Calibration | Beginning of every analytical run, every 24 hours, whenever instrument is modified, or CCV criterion is not met | | Terminate analysis; Correct the problem; Prepare new standards; Recalibrate following system performance. |
| ICV | Beginning of every analytical run. | Method 200.7: 95 - 105 % recovery. RSD dupl. exp < 3%<br><br>Method 6010B: 90 - 110 % recovery. RSD dupl. exp < 5% | Terminate analysis; Correct the problem; Recalibrate. |
| ICB | Beginning of every analytical run, immediately following the ICV. | The result must be within +/- RL from zero. | Terminate analysis; Correct the problem; Recalibrate. |
| CCV | Every 10 samples and at the end of the run. | Method 200.7 & 6010B: 90 - 110 % recovery. RSD dupl. exp < 5% | Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCV. |
| CCB | Immediately following each CCV. | The result must be within +/- RL from zero. | Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCB. |
| CRI | Beginning of every run | 50-150% recovery (advisory) | Evaluate associated samples. |
| ICSA | Beginning of every run | See Section 9.8.3 | See Section 9.8.3 |
| ICSAB | Immediately following each ICSA. | Results must be within 80 - 120% recovery. | See Section 9.8.2. |

* See Sections 11.10 and 11.13 for exact run sequence to be followed.

**TABLE VII. Summary of Quality Control Requirements (Continued)**

| QC PARAMETER | FREQUENCY | ACCEPTANCE CRITERIA | CORRECTIVE ACTION |
|---|---|---|---|
| Dilution Test | One per prep batch. | For samples > 50x IDL, dilutions must agree within 10%. | Narrate the possibility of physical or chemical interference per client request. |
| Method Blank | One per sample preparation batch of up to 20 samples. | The result must be less than or equal to the RL.<br><br>Common lab contaminants may be accepted up to 2x the RL after consultation with the client (See 9.2).<br><br>Sample results greater than 10x the blank concentration are acceptable.<br><br>Samples for which the contaminant is < RL may not require redigestion or reanalysis (see Section 9.2). | Redigest and reanalyze samples.<br><br>Note exceptions under criteria section.<br><br>See Section 9.2 for additional requirements. |
| Laboratory Control Sample (LCS) | One per sample preparation batch of up to 20 samples. | Aqueous LCS must be within 80 - 120% recovery or in-house control limits.<br><br>Samples for which the contaminant is < RL and the LCS results are > 120% may not require redigestion or reanalysis (see Section 9.3) | Terminate analysis; Correct the problem; Redigest and reanalyze all samples associated with the LCS. |

**TABLE VII. Summary of Quality Control Requirements (Continued)**

| QC PARAMETER | FREQUENCY | ACCEPTANCE CRITERIA | CORRECTIVE ACTION |
|---|---|---|---|
| Matrix Spike | One per sample preparation batch of up to 20 samples. | 75 - 125 % recovery or in-house control limits. For TCLP See Section 11.17. | In the absence of client specific requirements, flag the data; no flag required if the sample level is > 4x the spike added. For TCLP see Section 11.17. |
| Matrix Spike Duplicate | See Matrix Spike | 75 - 125 % recovery; RPD ≤ 20% . | See Corrective Action for Matrix Spike. |

# APPENDIX B

## STL NORTH CANTON ICP DATA REVIEW CHECKLIST

## (EXAMPLE)

SCAL STD_____ ICSA STD_____ SCAL2 STD_____ ICSAB STD_____

CRI STD_____ ICV STD_____ CLP CRI STD_____ CCV STD_____

**(Example)**

## STL North Canton ICP Data Review Checklist

**Run/Project Information:**

**Run Date:** _____ **Analyst:**_____ **Instrument:**_____

**Prep Batches Run:**_____

**Cu/MnRatio:**_____

**Circle Methods used:** **6010B / 200.7: CORP-MT-0001 Rev 2 CLP ILM03.0: CORP-MT-0002 Rev 1**

**6010A/200.7: CORP-MT-0001NC, Rev 2**

**Review Items**

| A. Calibration/Instrument Run QC | Yes | No | N/A | 2nd Level |
|---|---|---|---|---|
| 1. Instrument calibrated per manufacturer's instructions and at SOP specified levels ? | | | | |
| 2. ICV/CCV analyzed at appropriate frequency and within control limits ? (*ICV:* 6010B, CLP = 90 - 110%, 200.7 = 95 -105%) *(CCV: 90 - 110%)* | | | | |
| 3. ICB/CCB analyzed at appropriate frequency and within +/- RL or +/- CRDL (CLP) ? | | | | |
| 4. High Std. (HCAL) reanalyzed before samples and recovered within QC limits ? (6010A/200.7 95-105%, CLP- N/A) | | | | |
| 5. CRI run and recovered within QC limits ? (+/- 50% for non-CLP - 6010A only) | | | | |
| 6. ICSA/ICSAB run at required frequency and within SOP limits ? | | | | |
| **B. Sample Results** | | | | |
| 1. Were samples with concentrations > the linear range for any parameter diluted and reanalyzed ? | | | | |
| 2. All reported results bracketed by in control QC ? | | | | |
| 3. Sample analyses done within holding time ? | | | | |
| **C. Preparation/Matrix QC** | | | | |
| 1. LCS done per prep batch and within QC limits ? | | | | |
| 2. Method blank done per prep batch and < RL or CRDL (CLP) ? | | | | |
| 3. MS/MSD run at required frequency and within limits ? | | | | |

| | | | | |
|---|---|---|---|---|
| 4. MSD or DU run at required frequency and RPD within SOP limits ? | | | | |
| 5. Serial dilution done per prep batch (or per SDG for CLP) ? | | | | |
| 6. Post digest spike analyzed if required (CLP only) ? | | | | |
| D. Other | | | | |
| 1. Are all nonconformances documented appropriately ? | | | | |
| 2. Current IDL/LR/IEC data on file ? | | | | |
| 3. Calculations checked for error ? | | | | |
| 4. Transcriptions checked for error ? | | | | |
| 5. All client/project specific requirements met ? | | | | |
| 6. Date/time of analysis verified as correct ? | | | | |

**Level I Analyst:**_____ **Date:**_____ **Time:**_____

**Comments:**_____

**Level II Reviewer:**_____ **Date:**_____ **Time:**_____

# APPENDIX C

## CROSS REFERENCE OF TERMS USED IN METHODS 6010B, 200.7, AND BY STL NORTH CANTON

## CROSS REFERENCE OF TERMS COMMONLY USED IN METHODS EPA 200.7, SW6010B, AND STL NORTH CANTON INC. SOP

| EPA 200.7 | SW6010B | STL North Canton Inc. SOP |
|---|---|---|
| Calibration blank (CB) | Calibration blank | Initial and continuing calibration blanks (ICB/CCB) |
| Dilution test | Dilution test | Dilution Test |
| Instrument detection limit (IDL) | Instrument detection limit (IDL) | Instrument detection limit (IDL) |
| Instrument performance check (IPC) | Continuing calibration verification (CCV) | Continuing calibration verification (CCV) |
| Internal standard | Internal standard | Internal standard (IS) |
| Laboratory duplicates | n/a | n/a |
| Laboratory fortified blank (LFB) | n/a | Laboratory control sample (LCS) |
| Laboratory fortified sample matrix (LFM) | Matrix spike and matrix spike duplicate (MS/MSD) | Matrix spike and matrix spike duplicate (MS/MSD) |
| Laboratory reagent blank (LRB) | Method blank | Method or Prep blank (MB) |
| Linear dynamic range (LDR) | Linear dynamic range (LDR) | Linear dynamic range (LDR) |
| Method detection limit (MDL) | Method detection limit (MDL) | Method detection limit (MDL) |
| Quality control sample (QCS) | Check standard or Initial calibration verification (ICV) | Initial calibration verification (ICV) |
| Spectral interference check solution (SIC) | Interference check solution (ICS) | Interference check solution (ICSA/ICSAB) |

# APPENDIX D

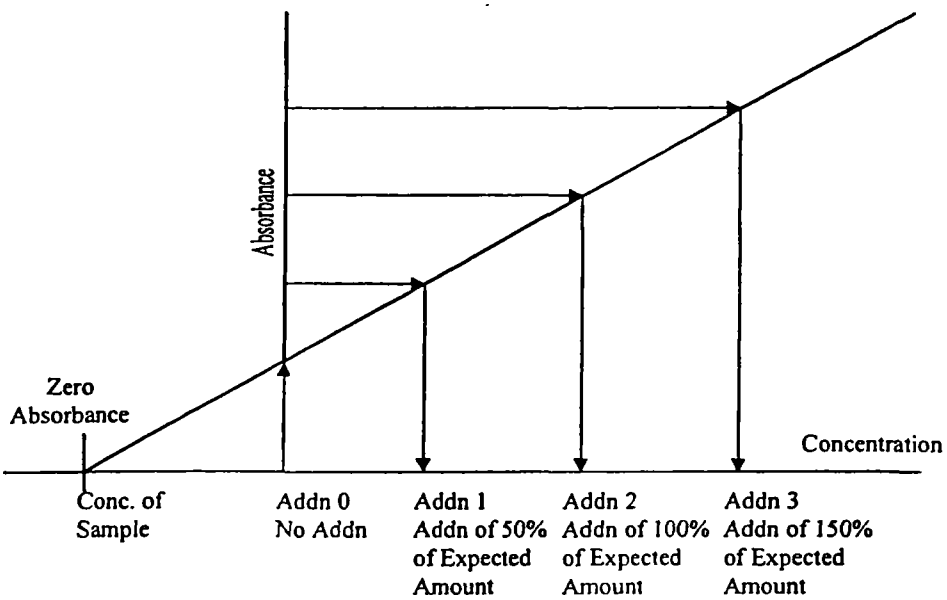
# MSA GUIDANCE

## Appendix D. MSA Guidance

### Method of Standard Addition

Four equal volume aliquots of sample are measured and known amounts of standards are added to three aliquots. The fourth aliquot is the unknown and no standard is added to it. The concentration of standard added to the first aliquot should be 50% of the expected concentration. The concentration of standard added to the second aliquot should be 100% of the expected concentration and the concentration of standard added to the third aliquot should be 150% of the expected concentration. The volume of the unspiked and spiked standard should be the same.

In order to determine the concentration of analyte in the sample, the analytical value of each solution is determined and a plot or linear regression performed. On the vertical axis the analytical value is plotted versus the concentrations of the standards on the horizontal axis. An example plot is shown in Figure 1. When the resulting line is extrapolated back to zero absorbance, the point of interception of the horizontal axis is the concentration of the unknown.




For the method of standard additions to be correctly applied, the following limitations must be taken into consideration:

- The plot of the sample and standards must be linear over the concentration range of concern. For best results, the slope of the curve should be similar to that of a plot of the aqueous standard curve.
- The effect of the interference should not vary as the ratio of the standard added to the sample matrix changes.

# APPENDIX E

# TROUBLESHOOTING GUIDE

## APPENDIX E. TROUBLESHOOTING GUIDE

| Problem | Possible Cause/ Solution |
|---|---|
| High Blanks | Increase rinse time<br>Clean or replace tip<br>Clean or replace torch<br>Clean or replace sample tubing<br>Clean or replace nebulizer<br>Clean or replace mixing chamber<br>Lower Torch |
| Instrument Drift | RF not cooling properly<br>Vacuum level is too low<br>Replace torch (Crack)<br>Clean or replace nebulizer (blockage)<br>Check room temperature (changing)<br>Replace pump tubing<br>Room humidity too high<br>Clean torch tip (salt buildup)<br>Check for argon leaks<br>Adjust sample carrier gas<br>Reprofile Horizontal Mirror<br>Replace PA tube |
| Erratic Readings,<br>Flickering Torch or<br>High RSD | Check for argon leaks<br>Adjust sample carrier gas<br>Replace tubing (clogged)<br>Check drainage(back pressure changing)<br>Increase uptake time (too short)<br>Increase flush time (too short)<br>Clean nebulizer, torch or spray chamber<br>Increase sample volume introduced<br>Check that autosampler tubes are full<br>Sample or dilution of sample not mixed<br>Increase integration time (too short)<br>Realign torch<br>Reduce amount of tubing connectors |
| Cu/Mn Ratio Outside Limits or<br>Low Sensitivity | Plasma conditions changed<br>Clean nebulizer, torch or spray chamber<br>Replace tubing (clogged)<br>Realign torch<br>Check IECs |
| Standards reading twice normal<br>absorbance or concentration | Incorrect standard used<br>Incorrect dilution performed |

# APPENDIX F

# CONTAMINATION CONTROL GUIDELINES

## APPENDIX F. CONTAMINATION CONTROL GUIDELINES

**The following procedures are strongly recommended to prevent contamination:**

All work areas used to prepare standards and spikes should be cleaned before and after each use.

All glassware should be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered or Latex Gloves must not be used in the metals laboratory since the powder contains silica and zinc as well as other metallic analytes. Only vinyl or nitrile gloves should be used in the metals laboratory.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

**The following are helpful hints in the identification of the source of contaminants:**

Yellow pipet tips and volumetric caps can sometimes contain cadmium.

Some sample cups have been found to contain lead.

The markings on glass beakers have been found to contain lead. If acid baths are in use for glassware cleaning, they should be periodically checked for contaminants since contaminant concentrations will increase over time.

New glassware especially beakers can be a source of silica and boron.

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Latex gloves contain over 500 ppb of zinc.

# APPENDIX G

# PREVENTIVE MAINTENANCE

## APPENDIX G. PREVENTIVE MAINTENANCE

A maintenance log is used to record when maintenance is performed on instruments. When an instrument problem occurs indicate the date, time and instrument number, then identify the problem and corrective action in the maintenance log.

**The following procedures are required to ensure that that the instrument is fully operational.**

| | |
|---|---|
| **Daily** | Change sample pump tubing and pump windings<br>Check argon gas supply level<br>Check rinse solution and fill if needed<br>Check waste containers and empty if needed<br>Check sample capillary tubing is clean and in good condition<br>Check droplet size to verify nebulizer is not clogged.<br>Check sample flow for cross flow nebulizer<br>Check Cu/Mn ratio-should be 30% of value at date that IECs were performed<br>Check pressure for vacuum systems |
| **As Needed** | Clean plasma torch assembly to remove accumulated deposits<br>Clean nebulizer and drain chamber; keep free-flowing to maintain optimum performance<br>Replace peristaltic pump tubing, sample capillary tubing and autosampler sipper probe |
| **Weekly** | Apply silicon spray on autosampler tracks<br>Check water level in coolflow |
| **Monthly** | Clean air filters on back of power unit to remove dust<br>Check D mirror for air instruments |
| **Bi-yearly** | Change oil for vacuum systems<br>Replace coolant water filter (may require more or less frequently depending on quality of cooling water) |

# APPENDIX H

# ICP OPERATING INSTRUCTIONS

# ICP Analysis (TJA 61E)

(Example)

## 1. SETUP

a. Plasma Control Panel (enter)

b. (F1)-Startup

c. (F9)-Continue

d. (F2)-Levels

1. Change auxiliary gas to low – use space bar to toggle
2. Change nebulizer gas flow to 0.5 L/min.
3. Change pump rate to 130
4. Esc
5. Allow instrument to warm up approximately 30 minutes.

## 2. DEVELOPMENT

a. Methods (enter)

b. Enter method name

c. (F3)-Method Info.

d. Change file name

e. (F9)-Done

f. (F9)-Done/Keep

## 18 OPERATION

a. Analysis (enter)

b. (F5)-Profile

1. (F3)-Automatic
2. (F1)-Run
3. If peak position is greater than +/- .05 units from the center peak position, you must adjust the profile. If it is within +/- .05 units, press (F9)-done.
4. To adjust select (F1)-CalcSS and enter current vernier position. (enter)
5. Adjust to new vernier position(F9)-done
6. Rerun profile until peak position is +/- .05 units.
7. (F9)-Done

c. Autosampler (F9)

1. Enter method name (enter)
2. Enter autosampler table name (enter)
3. (F1)-Run

# STL NORTH CANTON STANDARD OPERATING PROCEDURE

**TITLE:** **EXTRACTION AND CLEANUP OF ORGANIC COMPOUNDS FROM WATERS AND SOILS, BASED ON SW-846 3500 SERIES, 3600 SERIES, 8151A AND 600 SERIES METHODS.**

**(SUPERSEDES: Revision 3.8 (Dated 05/23/01)**

Prepared by: _____ Date

Reviewed by: _____
Technology Specialist Date

Approved by: _____
Quality Assurance Manager Date

Approved by: _____
Environmental Health and Safety Coordinator Date

Approved by: _____
Laboratory Director Date

Approved by: _____ 5/20/2002
Corporate Technology Date

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**(SUPERSEDES: Revision 3.8 (Dated 05/23/01)**

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Reviewed by: 5/7/02
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Approved by: 5/7/02
Quality Assurance Manager Date

Approved by: 5-7-02
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Approved by: 5-13-02
Laboratory Director Date

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## 1. SCOPE AND APPLICATION

This SOP describes procedures for preparation (extraction and cleanup) of semivolatile organic analytes in aqueous, TCLP leachate, and soil matrices for analysis by Gas Chromatography (GC) and Gas Chromatography / Mass Spectrometry (GC/MS). The procedures are based on SW-846 and 600 series methodology and are applicable for measurements made to comply with the Resource Conservation and Recovery Act (RCRA) and for wastewater testing.

1.1. Extraction procedures for the following determinative methods are covered: 8081A, 8082, 8141A, 8151B, 8270C, 8310, 8015B, 8100, 608, 610, and 625

1.2. The extraction procedures here may be appropriate for other determinative methods when appropriate spiking mixtures are used.

1.3. Other extraction procedures (PFE, SPE, accelerated Soxhlet, etc.) may be used but are not currently covered in this SOP.

1.4. The applicable LIMS method codes are: P2 (8141A), QJ (8081A), QS (8151A), QL (8270C), SG (8310), DM (608), VT (610), DP (625), A1 (8100), HS (8015B)

## 2. SUMMARY OF METHOD

2.1. Separatory Funnel Extraction

A measured volume of sample, typically 1 liter, is adjusted, if necessary, to a specified pH and serially extracted with methylene chloride using a separatory funnel.

2.2. Continuous Liquid/Liquid Extraction

A measured volume of sample, typically 1 liter, is placed into a continuous liquid/liquid extractor, adjusted, if necessary, to a specific pH and extracted with methylene chloride for 18-24 hours.

2.3. Sonication Extraction

A measured weight of sample, typically 30 g, is mixed with anhydrous sodium sulfate to form a free flowing powder. This is solvent extracted three times using an ultrasonic horn.

2.4. Soxhlet Extraction

A 30 g sample is mixed with anhydrous sodium sulfate to form a free flowing powder. This is extracted with refluxing solvent.

2.5. Cleanup and Concentration

Procedures are presented for removing interferents from sample extracts, and for drying and concentration of the extract to final volume for analysis.

2.6. Phenoxy acid herbicide extractions

Procedures for the extraction and cleanup of phenoxy acid herbicides are presented in Appendix A.

## 3. DEFINITIONS

Definitions of terms used in this SOP may be found in the glossary of the STL North Canton Laboratory Quality Manual (LQM), current version .

## 4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus. All these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2. Visual interferences or anomalies (such as foaming, emulsions, odor, etc.) must be documented.

## 5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all STL North Canton associates. The following requirements must be met:

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat and appropriate gloves must be worn while samples, standards, solvents and reagents are being handled. Disposable gloves that have become contaminated will be removed and discarded, other gloves will be cleaned immediately. Viton gloves may be worn when halogenated solvents are used for extractions or sample preparation. Nitrile gloves may be used when other solvents are handled. [Note: VITON is readily degraded by acetone]. When good manual dexterity is needed, for example, when handling small quantities/containers, disposable gloves (such as latex or N-DEX®) shall be used. While these gloves protect against splashes, they give little or no protection against contact with large quantities of solvent, and no protection against spills or immersion.

5.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the MSDS files maintained in the laboratory. The following specific hazards are known:

Chemicals that have been classified as **carcinogens** or **potential carcinogens** under OSHA include methylene chloride, PCBs, certain pesticides.

The following materials are known to be **corrosive**: Concentrated sulfuric acid, sodium hydroxide, 1N nitric acid.

Sulfuric acid cleanup must not be performed on any matrix that may have water present as a violent reaction between the acid and water may result in acid exploding out of the vessel.

Chemicals known to be **flammable** are: Diethyl ether, acetone, hexane, 2-propanol.
Mercury is a highly toxic compound that must be handled with care. The analyst must be aware of the appropriate handling and clean-up techniques before handling this material.

5.4. Exposure to hazardous chemicals must be maintained **as low as reasonably achievable**, therefore, unless they are known to be non-hazardous, all samples should be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.5. The preparation of standards and reagents and glassware cleaning procedures that involve solvents such as methylene chloride will be conducted in a fume hood with the sash closed as far as the operations will permit. Use of methylene chloride for glassware cleaning should be avoided as far as possible. If more than 500 mL of Methylene chloride is spilled, evacuate the area until the area has been cleaned by a Hazardous Material Team.

5.6. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL North Canton associate. The situation must be reported **immediately** to a laboratory supervisor.

## 6. EQUIPMENT AND SUPPLIES

6.1. Glassware should be cleaned with soap and water, rinsed with water and dried in an oven at 400°C for at least 2 hours. Alternatively the glassware can be solvent rinsed with acetone or methanol followed by methylene chloride after the water rinse.

6.2. Equipment and supplies for extraction procedures

| EQUIPMENT AND SUPPLIES | Sep fun. | CLLE | Soni | Sox | Conc |
|---|---|---|---|---|---|
| Separatory Funnel: 2 L | √ | | | | |
| Separatory Funnel Rack | √ | | | | |
| Balance: >1400 g capacity, accurate ±1 g | √ | √ | | | |
| pH indicator paper, wide-range: covers extraction pH | √ | √ | | | |
| Graduated cylinder: 1 liter. (other sizes may be used) | √ | √ | | | |
| Erlenmeyer Flask or Fleaker: 125 & 300 mL (other sizes optional) | √ | | √ | | |
| Centrifuge | √ | | | | |
| Auto-Shaker | √ | | | | |
| Methylene Chloride Collection Tank | √ | √ | | | |

| EQUIPMENT AND SUPPLIES | Sep fun. | CLLE | Soni | Sox | Conc |
|---|---|---|---|---|---|
| Solvent Dispenser Pump or 100 mL Graduated Cylinder | √ | | √ | | |
| Continuous Liquid/Liquid Extractor | | √ | | | |
| Round or flat Bottom: 250, 500 mL or 1 L | | √ | | | |
| Boiling Chips: Contaminant free, approximately 10/40 mesh (Teflon® PTFE, carbide or equivalent). | | √ | | √ | √ |
| Cooling Condensers | | √ | | √ | |
| Heating Mantle: Rheostat controlled | | √ | | √ | |
| Auto-timer for heating mantle | | √ | | √ | |
| Beakers: 250 & 400 mL, graduated | | | √ | | |
| Balance: >100 g capacity, accurate ±0.1 g | | | √ | √ | |
| Soxhlet Extractor | | | | √ | |
| Sonicator (at least 300 watts) | | | √ | | |
| Sonicator horn, 3/4 inch | | | √ | | |
| Kuderna-Danish (K-D) Apparatus: 500 mL | | | | | √ |
| Concentrator Tube: 10 mL, attached to K-D with clips | | | | | √ |
| Supply Manifold: Heated, capable of temperature control (± 5°C) up to 95°C. | | | | | √ |
| MegaCT: 150 ml | | | | | √ |
| Snyder Column: Three-ball macro | | | | | √ |
| Water Bath: Heated, with concentric ring cover, capable of temperature control (± 5°C) up to 95°C. The bath must be used in a hood or with a solvent recovery system. | | | | | √ |
| Vials: Glass, 2 mL, 4 mL, and 10 mL capacity with Teflon®-lined screw-cap | | | | | √ |
| Nitrogen Blowdown Apparatus | | | | | √ |
| Nitrogen: reagent grade. | | | | | √ |
| Culture tubes: 10 mL, 16 mmx100 mm | | | | | √ |
| Syringe: 1 mL | √ | √ | √ | √ | |
| Phase Separation Paper | √ | √ | √ | √ | |
| Glass Wool | √ | √ | √ | √ | |
| Glass Funnel: 75 X 75 mm | √ | √ | √ | √ | √ |
| Disposable Pipets | √ | √ | √ | √ | √ |
| Aluminum foil | √ | √ | √ | √ | √ |
| Paper Towels | √ | √ | √ | √ | √ |
| Wrist Shaker | | | | | |

6.3.Equipment and Supplies for Cleanup Procedures

| EQUIPMENT AND SUPPLIES | GPC | Florisil | Sulfur | Acid | A/B | *FC* |
|---|---|---|---|---|---|---|
| Gel permeation chromatography system (GPC Autoprep Model 1002A or 1002B Analytical Biochemical Laboratories, Inc. or Zymark Benchmate or equivalent). | √ | | | | | |
| Bio Beads: (S-X3) -200-400 mesh, 70 gm (Bio-Rad Laboratories, | √ | | | | | |

| EQUIPMENT AND SUPPLIES | GPC | Florisil | Sulfur | Acid | A/B | FC |
|---|---|---|---|---|---|---|
| Richmond, CA, Catalog 152-2750 or equivalent). | | | | | | |
| Chromatographic column: 700 mm x 25 mm ID glass column. Flow is upward. | √ | | | | | |
| Ultraviolet detector: Fixed wavelength (254 nm) and a semi-prep flow-through cell. | √ | | | | | |
| Strip chart recorder, recording integrator, or laboratory data system. | √ | | | | | |
| Syringe: 10 mL with Luerlok fitting. | √ | | | | | |
| Syringe filter assembly, with disposable 5 um filter discs, Millipore No. LSWP 01300 or equivalent. | √ | | | | | |
| Chromatographic column: 250 mm long x 10 mm ID; with Pyrex glass wool at the bottom and a Teflon stopcock (for silica gel cleanup). | √ | | | | | |
| Vacuum system for eluting multiple cleanup cartridges. Vac Elute Manifold - Analytichem International, J.T. Baker, or Supelco (or equivalent). The manifold design must ensure that there is no contact between plastics containing phthalates and sample extracts. | | √ | | | | |
| Vacuum trap made from a 500 mL sidearm flask fitted with a one-hole stopper and glass tubing. | | √ | | | | |
| Vacuum pressure gauge. | | √ | | | | |
| Rack for holding 10 mL volumetric flasks in the manifold. | | √ | | | | |
| Mechanical shaker or mixer: Vortex Genie or equivalent. | | | √ | √ | | |
| Separatory Funnels with Ground-Glass Stoppers: 250 mL | | | | | √ | |
| Erlenmeyer Flasks: 125 mL | | | | | √ | |
| Disposable Pipets | | √ | √ | √ | √ | √ |
| Culture tubes: 10 mL, 16 mmx100 mm | √ | √ | √ | √ | √ | √ |

## 7. REAGENTS AND STANDARDS

### 7.1. Reagents for Extraction Procedures

All reagents must be ACS reagent grade or better unless otherwise specified.

| REAGENTS | Sep fun. | CLLE | Soni | Sox | Conc |
|---|---|---|---|---|---|
| Sodium hydroxide (NaOH), Pellets: Reagent Grade | √ | √ | | | |
| Sodium hydroxide solution, 10 N: Dissolve 40 g of NaOH in reagent water and dilute to 100 mL. | √ | √ | | | |
| Sulfuric acid ($H_2SO_4$), Concentrated: Reagent Grade | √ | √ | | | |
| Sulfuric acid (1:1): Carefully add 500 mL of $H_2SO_4$ to 500 mL of reagent water. Mix well. | √ | √ | | | |
| Hydrochloric Acid (HCl) | | | | | |
| Organic free reagent water. | √ | √ | | | |
| Sodium sulfate ($Na_2SO_4$), Granular, Anhydrous: Purify by heating at 400°C a minimum of two hours. | √ | √ | √ | √ | √ |

| REAGENTS | Sep fun. | CLLE | Soni | Sox | Conc |
|---|---|---|---|---|---|
| Extraction/Exchange Solvents: Methylene chloride, hexane, acetonitrile, acetone, pesticide quality or equivalent | √ | √ | √ | √ | √ |
| Acetone: Used for cleaning | √ | √ | √ | √ | √ |

7.2. Reagents for Cleanup Procedures

| REAGENTS | GPC | Florisil | Sulfur | Acid | A/B | *FC* |
|---|---|---|---|---|---|---|
| Florisil: 500 mg or 1 g cartridges with stainless steel or Teflon frits (calalog 694-313, Analytichem, 24201 Frampton Ave., Harbor City, CA, or equivalent.) | | √ | | | | |
| Mercury: triple distilled | | | √ | | | |
| Tetrabutylammonium hydrogen sulfate | | | √ | | | |
| Sodium sulfite | | | √ | | | |
| Tetrabutylammonium (TBA) sulfite reagent: Prepare reagent by dissolving 3.39 g of Tetrabutylammonium hydrogen sulfate in 100 mL organic-free reagent water. Extract this solution 3 times with 20 mL portions of hexane. Discard the hexane extracts. Add 25 g sodium sulfite to the water solution. | | | √ | | | |
| 2-Propanol | | | √ | | | |
| Nitric acid: 1N | | | √ | | | |
| Copper powder: remove oxides (if powder is dark) by treating with 1N nitric acid, rinse with organic-free reagent water to remove all traces of acid, rinse with acetone, and dry under a stream of nitrogen. | | | √ | | | |
| Sulfuric acid, Concentrated | | | | √ | | |
| Sodium hydroxide, Pellets | | | | | √ | |
| Sodium hydroxide, 10N: Dissolve 40 g of NaOH in 100 mL of reagent water | | | | | √ | |
| Sulfuric acid ($H_2SO_4$), Concentrated: Reagent Grade | | | | | √ | |
| Sulfuric acid (1:1): Carefully add 500 mL of $H_2SO_4$ to 500 mL of reagent water. Mix well. | | | | | √ | |
| *Fluorocarbon: PF-5080, 3M* | | | | | | √ |

7.3. Standards

7.3.1. Stock Standards

Stock standards are purchased as certified solutions or prepared from neats. Semivolatile stock standards are stored at $\leq 6^{o}C$. All stock standards must be protected from light. Stock standard solutions must be replaced after one year (from the time of preparation, if prepared in house, or from the time the ampoule is opened if purchased.) Standards must be allowed to come to room temperature before use.

7.3.2. Surrogate Spiking Standards

Prepare or purchase surrogate spiking standards at the concentrations listed in Table 5. Surrogate spiking standards are purchased or prepared as dilutions of the

stock standards. Surrogate spiking solutions must be refrigerated and protected from light. The standards must be replaced at least every six months or sooner if there is reason to believe that the standard has degraded or concentrated.

7.3.3. Matrix Spiking and Laboratory Control Spiking Standards.

The same spiking solution is used for the matrix spike and the Laboratory Control Sample. Prepare MS/LCS spiking standards at the concentrations listed in Table 6. Spiking standards are purchased or prepared as dilutions of the stock standards. Spiking solutions must be refrigerated and protected from light. The standards must be replaced at least every six months or sooner if there is reason to believe that the standard has degraded or concentrated.

7.3.4. GPC calibration solution - prepare or purchase a solution in methylene chloride that contains the following analytes in the concentrations listed below:

| Analyte | mg/mL |
|---|---|
| Corn Oil | 25.0 |
| Bis (2-ethylhexyl) phthalate | 1.0 |
| Methoxychlor | 0.2 |
| Perylene | 0.02 |
| Sulfur | 0.08 |

NOTE: Sulfur is not very soluble in methylene chloride, however, it is soluble in warm corn oil. Therefore, one approach is to weigh out the corn oil, warm it, and transfer the weighed amount of sulfur into the warm corn oil. Mix it and then transfer into a volumetric flask with methylene chloride, along with the other calibration compounds. This standard has a lifetime of 6 months.

## 8. SAMPLE COLLECTION PRESERVATION AND STORAGE

8.1. Samples are not chemically preserved.

8.2. Samples are stored at 4°C ± 2°C in glass containers with Teflon®-lined caps.

8.3. Holding Times

8.3.1 Extraction is initiated within 7 days of the sampling date for aqueous samples, 14 days for solid and waste samples.

8.3.2 For TCLP leachates, extraction is initiated within seven days from when the TCLP Leach tumbling has been completed, excluding the filtration step. If the filtration step requires extended times, this time counts as part of the seven day holding time.

8.3.3. Analysis of the extracts is completed within forty days of extraction.

## 9. QUALITY CONTROL

9.1. Quality Control Batch

The batch is a set of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The batch must contain a method blank, an LCS and a matrix spike / matrix spike duplicate. (In some cases, at client request, it may be appropriate to process a matrix spike and sample duplicate in place of the MS / MSD). If clients specify specific samples for MS/MSD, the batch may contain multiple MS/MSD. See policy QA-003 for further definition of the batch.

9.2. Definition of matrix

The possible matrix types are aqueous, soil, waste and TCLP leachate.

9.3. Insufficient Sample

If insufficient sample is available to process a MS/MSD, then a second LCS must be processed. The LCS pair is then evaluated according to the MS/MSD criteria. Use of a LCS pair in place of a MS/MSD must be documented.

9.4. Sample count

Laboratory generated QC samples (method blanks, LCS, MS/MSD) are not included in the sample count. Field samples are included.

9.5. Method Blank

A method blank consisting of all reagents added to the samples must be prepared and analyzed with each batch of samples. Surrogates are spiked into the method blank at the same level as the samples. The method blank is used to identify any background interference or contamination of the analytical system which may lead to the reporting of elevated concentration levels or false positive data.

9.5.1. Aqueous Method Blanks use 1000 mL of reagent water spiked with the surrogates. The method blank goes through the entire analytical procedure, including any cleanup steps.

9.5.2. Solid method blanks use 30 g of sodium sulfate spiked with the surrogates. The method blank goes through the entire analytical procedure, including any cleanup steps.

9.5.3. TCLP method blanks use 250 mL of leachate fluid (100 mL for herbicides) spiked with the surrogates. The leachate may optionally be diluted to 1000 mL with reagent water. The method blank goes through the entire analytical procedure, including any cleanup steps.

9.6. Laboratory Control Sample (LCS)

Laboratory Control Samples are well-characterized, laboratory generated samples used to monitor the laboratory's day to day performance of routine analytical methods. The LCS, spiked with a group of target compounds representative of the method analytes, is used to monitor the accuracy of the analytical process, independent of matrix effects. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within accepted QC guidelines for accuracy and precision. The LCS goes through the entire analytical procedure, including any cleanup steps.

9.6.1. The LCS is made up in the same way as the method blank (See sections 9.5.1 - 9.5.3) but spiked with the LCS standard and the surrogates.

9.7. Surrogates

9.7.1. Surrogates are organic compounds which are similar to the target analyte(s) in chemical composition and behavior in the analytical process, but which are not normally found in environmental samples.

9.7.2. Each applicable sample, blank, LCS and MS/MSD is spiked with surrogate standards. Surrogate spike recoveries must be evaluated by determining whether the concentration (measured as percent recovery) falls within the required recovery limits.

9.8. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

A matrix spike is an environmental sample to which known concentrations of target analytes have been added. A matrix spike duplicate is a second spiked aliquot of the same sample which is prepared and analyzed along with the sample and matrix spike.

9.9. Initial Demonstration of Capability

The initial demonstration and method detection limit studies described in section 13 must be acceptable before analysis of samples may begin.

9.10. Quality Assurance Summaries

Certain clients may require specific project or program QC which may supersede these method requirements. Quality Assurance Summaries (QAS) should be developed to address these requirements.

9.11. STL North Canton QC Program

Further details of QC and corrective action guidelines are presented in the STL North Canton QC Program document (QA-003). Refer to this document if in doubt regarding corrective actions.

## 10. CALIBRATION AND STANDARDIZATION

10.1. On a weekly basis, measure 1.0 mL of solvent into an autovial using a gastight syringe that is manufactured to a certified volume delivery tolerance of ±0.01 mL

(1mL total volume). The "standard" autovial is sealed and the top and bottom of the meniscus are marked. The autovials containing the sample extracts are then compared against the "standard" vial to ensure that the final volume is consistently 1.0 ± 0.01mL. If a new box of autovials are used, then the steps are repeated to further ensure that variations due to vial size and shape are minimized. A log is kept of the lot number of the vials and the day the vials were prepared.

10.2. Refer to section 11.8.1.2. for calibration of the GPC. Otherwise this section is not applicable.

## 11. PROCEDURE

Procedures for separatory funnel liquid/liquid extraction (11.2), continuous liquid/liquid extraction (11.3), sonication extraction (11.4), soxhlet extraction (11.5), waste dilution (11.6), extract concentration (11.7), and extract cleanup (11.8) are presented in this section.

11.1. Procedural Variations

Procedural variations are allowed only if deemed necessary in the professional judgment of the supervisor to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance memo and approved by a supervisor and QA/QC manager. If contractually required, the client will be notified. The Nonconformance memo will be filed in the project file.

Any deviations from this procedure identified after the work has been completed must be documented as a nonconformance, with a cause and corrective action described. A Nonconformance memo shall be used for this documentation.

11.2. Separatory Funnel Liquid/Liquid Extraction of Water Samples.

A flow chart for this procedure is included in Section 17.

11.2.1. Measure the initial sample pH with wide-range pH paper and record on the extraction benchsheet. If sample is a leachate (e.g. TCLP), compare the current pH against leachate log, note on the benchsheet if there is any discrepancy.

11.2.2. The normal sample volume is 1 liter. Other sample volumes may be used to obtain specific reporting limits, and reduced sample volumes, diluted to 1 liter with reagent water, may be used for very dirty samples.

11.2.3. Weigh the sample container on a balance (± 1 g). taring the sample and container. Transfer the sample to the separatory funnel. . Add the appropriate volume of surrogate spiking solution (see Table 3). Also add appropriate volume of matrix spiking solution to any matrix spike / matrix spike duplicate samples (see.Table 4) Mix well. If the sample is a 600 series analysis or BP GCLN sample rinse the sample bottle with 60 mL methylene chloride and transfer to the separatory funnel. Reweigh the container. Assume a density of 1 g/mL and record the difference as the sample volume on the benchsheet to the nearest milliliter.

Note: Aqueous samples must be determined volumetrically for Ohio VAP samples.

**Warning:** Dichloromethane creates excessive pressure very rapidly! Therefore, initial venting should be done immediately after the sample container has been sealed and inverted. Vent into hood away from analysts and other samples.

11.2.3.1. If the entire sample bottle will not be used, transfer the aliquot to the separatory funnel, then add the spiking solutions to the sample in the separatory funnel.

**Note:** Alternative methods of measurement of sample volume include a) transferring the sample to a measuring cylinder and b) marking a meniscus on the sample bottle and then measuring the volume of water required to fill the bottle to the meniscus after the sample is transferred. The former method is not recommended because of the risk of cross contamination while the latter is not recommended because of poor accuracy. However, either method may be necessary for specific client programs.

11.2.4. Prepare a method blank, LCS and MS/MSD for each batch as specified in section 9 of this SOP. Use 1 L of reagent water for method blanks and LCS. The LCS is spiked with the surrogate and matrix spike solutions, the method blank only with the surrogates.

11.2.5. Use 250 mL of leachate for TCLP pesticides and TCLP semivolatiles, measured in a graduated cylinder. An alternative method would be to tare 400ml beaker on the balance and then add 250g to the beaker. Assume a density of 1g/mL and record the volume on the benchsheet. The leachate may be made up to 1 L in volume with reagent water.

11.2.6. For a TCLP method blank,LCS and LCS Dup measure 250 mL of the buffer solution used in the leaching procedure and transfer to the separatory funnel. Add 60 mL of methylene chloride to the separatory funnel. The TCLP leachate may be diluted to approximately 1 liter before extraction if desired.

11.2.7. Adjust sample pH as indicated in Table 1 for the initial extraction. Use the minimum amount of 1:1 $H_2SO_4$ or 10 N NaOH necessary. Recheck the sample with pH paper by dipping a disposable pipette into the sample and wetting the pH paper. Record adjusted pH, spiking volumes and standard numbers on the benchsheet. Return spiking solutions to the refrigerator as soon as possible.

11.2.8. Seal and shake or rotate the separatory funnel vigorously for 2 minutes with periodic venting to release excess pressure. An autoshaker may be used to shake and rotate the separatory funnel.

**Warning:** Dichloromethane creates excessive pressure very rapidly! Therefore, initial venting should be done immediately after the separatory funnel has been sealed and inverted. Vent into hood away from analysts and other samples.

11.2.9. Allow the organic layer to separate from the water phase until complete visible separation has been achieved (approximately 10 minutes). If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. If the emulsion cannot be broken (recovery of <80% of the methylene chloride*), transfer the sample, solvent, and emulsion into the extraction chamber of a continuous extractor and proceed as described in continuous liquid-liquid extraction (Section 11.2.). If this is done, the sample must be extracted as part of a valid CLLE batch.

*Note: 15 - 20 mL of methylene chloride is expected to dissolve in 1 L of water. Thus, solvent recovery could be as low as 35 mL from the first shake and still be acceptable. Subsequent shakes should recover at least 50 mL of solvent.

11.2.10. Fill a funnel with 10-20 g of anhydrous sodium sulfate. The funnel can be plugged with glass wool or filter paper may be used to hold the sodium sulfate. Drain the solvent extract from the separatory funnel through the prepared filtration funnel into a clean glass container. The extract may be drained directly into the KD flask. Close the stopcock just before the water level begins draining out of the separatory funnel. If the sodium sulfate becomes saturated with water add more to the funnel or replace the existing sodium sulfate with fresh drying agent.

11.2.11. Repeat the extraction process two more times using fresh 60 mL portions of solvent, combining the three solvent extracts in the collection container.

11.2.12. If extraction at a secondary pH is required, adjust the pH of the sample in the separatory funnel to the pH indicated in Table 1 with a minimum amount of 10 N NaOH or 1:1 $H_2SO_4$. Measure with pH paper and record the adjusted pH on the benchsheet. Serially extract with three 60 mL portions of methylene chloride, as outlined in Steps 11.1.7 to 11.1.9. Collect these three extracts in the same container used for the previous fraction.

11.2.13. Rinse the extract residue from the sodium sulfate by pouring 20-30 mL of clean methylene chloride through the funnel and into the collection container.

11.2.14. Dispose of solvent and water remaining in the extractor into the appropriate waste container.

11.2.15. Cover with aluminum foil if the extract is not concentrated immediately. Refer to Section 11.8 for concentration and Section 11.9 for cleanup.

11.3 Short-Term Continuous Liquid-Liquid Extraction

11.3.1 Extraction personnel must first determine if one liter of sample exists in the sample bottle.

11.3.2 Mark the meniscus on the side of the sample bottle for later determination of sample volume.

11.3.3 Add 225 mL methylene chloride to the extractor, turn stopcock to the open position. Connect extractor to a 250 ml boiling flask with boiling chips.

11.3.4 Check the pH of the sample and adjust, if necessary, using 1:1 H2SO4 or 10N sodium hydroxide. Quantitatively transfer the sample from the sample bottle to the extractor. *Rinse the sample bottle with 25-ml of methylene chloride for BP samples. Pour the rinsate from the sample bottle into the continuous extractor.

11.3.5 Adjust the volume of solvent in the boiling flask by adding reagent water to the extractor, if necessary.

11.3.6 Next, fill the sample bottle to the mark with reagent water. Pour the reagent water into a graduated cylinder. Measure the reagent water to ± 10 ml and document this sample volume on the extraction benchsheet.

11.3.7 Add the appropriate volume of surrogate to each sample and spiking solutions to the MS, MSD, LCS, and/or LCSD in the extractor and mix well.

11.3.8 Extract samples for 12 hours. 8270 extractions will still be performed in two pH extraction steps. Each step will run 6 hours, however, where timing is a factor the samples may be left to extract for longer than 12 hours.

11.3.9 Turn stopcocks to the closed position.

11.3.10 Allow the extractors to run another 5 minutes, then turn off the rheostats and mantles.

11.3.11 The samples will macro concentrate in the CLLE. After the flasks have cooled, continue to concentrate the extracts by KD or QES methodology.

11.3.12 This method of extraction **cannot** be used for method 625, 610 or 608.

11.4 Continuous Liquid/Liquid Extraction from Water Samples.

A flow chart for this procedure is included in Section 17.

11.4.1. Assemble the apparatus. Add 250-400mL of methylene chloride to the extractor body. Add 3 to 5 boiling chips to the round-bottom distilling flask.

11.4.2. Measure the initial sample pH with wide-range pH paper and record on the extraction benchsheet. If sample is a leachate (e.g. TCLP), compare the current pH against leachate log, note on the benchsheet if there is any discrepancy.

11.4.3. Weigh the sample container on a balance (± 1 g), taring the sample and container. Transfer the sample to the continuous liquid/liquid extractor . Add the appropriate volume of surrogate spiking solution (see Table 3). Also add appropriate volume of matrix spiking solution to any matrix spike / matrix spike duplicate samples (see.Table 4) Mix well. If the sample is a 600 series analysis or BP GCLN sample rinse the sample bottle with 60 mL methylene chloride and transfer to the continuous liquid/liquid extractor. Reweigh the container. Assume a density of 1 g/mL and record the difference as the sample volume on the benchsheet to the nearest milliliter.

Note: Aqueous samples must be determined volumetrically for Ohio VAP samples.

**Warning:** Dichloromethane creates excessive pressure very rapidly! Therefore, during the rinse for 600 series methodology venting should be done immediately after the sample container has been sealed and inverted. Vent into hood away from analysts and other samples.

11.4.3.1. If the entire sample bottle will not be used, transfer the aliquot to the extractor, then add the spiking solutions to the sample in the extractor.

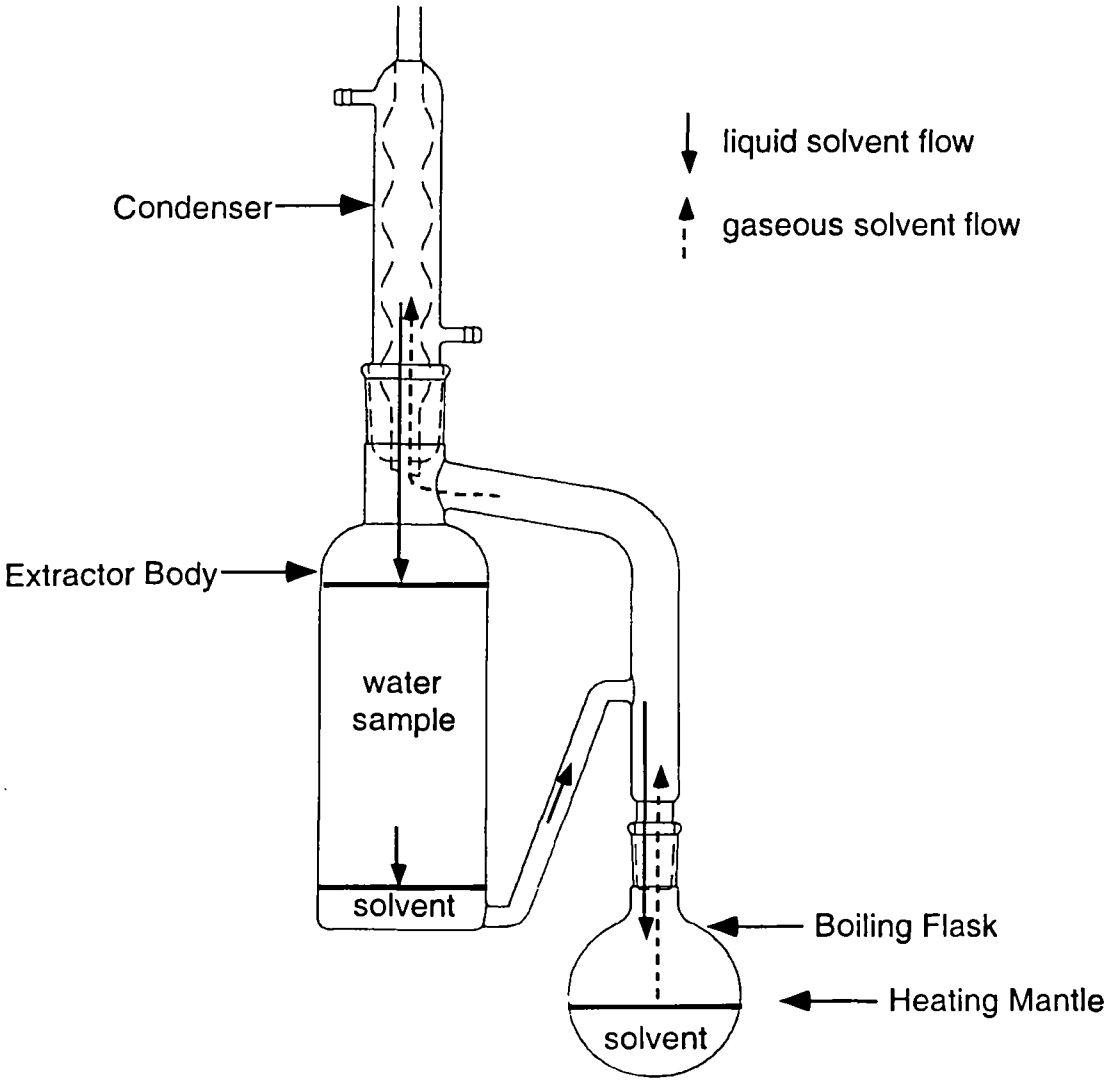
**Note**: Alternative methods of measurement of sample volume include: a.) transferring the sample to a measuring cylinder and b.) marking a meniscus on the sample bottle and then measuring the volume of water required to fill the bottle to the meniscus after the sample is transferred. The former method is not recommended because of the risk of cross contamination while the latter is not recommended because of poor accuracy. However, either method may be necessary for specific client programs.

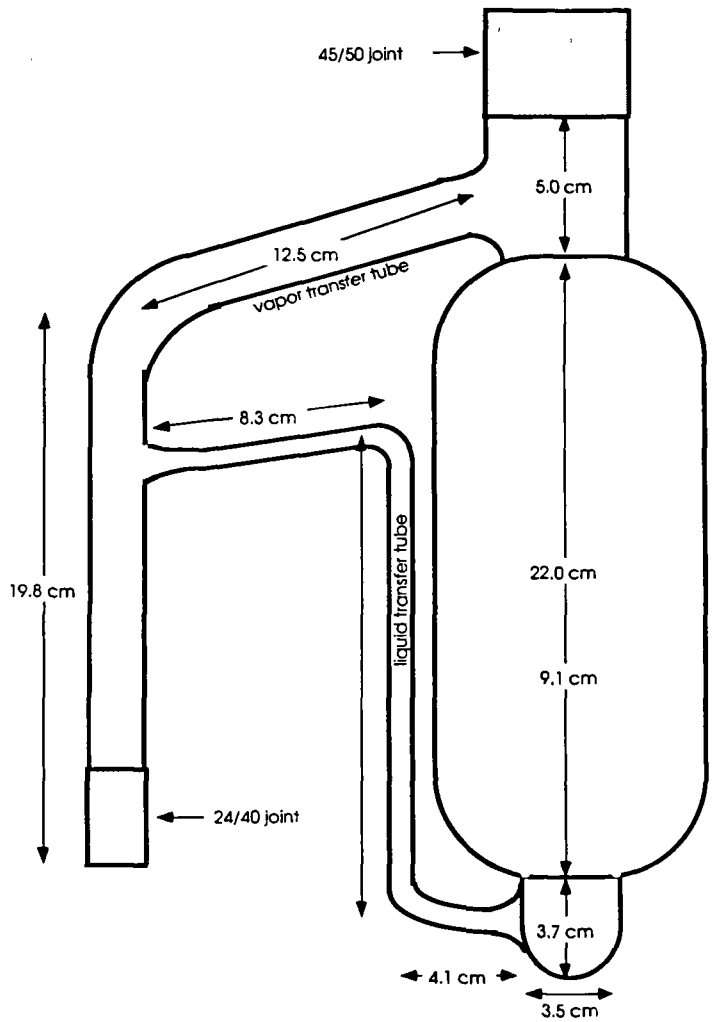
11.4.3.2. Prepare a method blank, LCS and MS/MSD for each batch as specified in section 9 of this SOP. Use 1 L of reagent water for method blanks and LCS. The method blank is spiked with the surrogates, the LCS and matrix spikes with the surrogates and matrix spiking solutions.

11.4.3.3. Use 250mL of leachate for TCLP for TCLP semivolatiles and TCLP pesticides measured in a graduated cylinder. An alternative method would be to tare 400ml beaker on the balance and then add 250g to the beaker. Assume a density of 1g/mL and record the volume on the benchsheet. Dilute to about 1 liter with reagent water.

11.4.3.4. For a TCLP method blank, LCS and LCS Dup measure 250 mL of the buffer solution used in the leaching procedure and transfer to the separatory funnel. Dilute to about 1 liter with reagent water.

11.4.3.5. Less than one liter of sample may be used, for highly contaminated samples, or if the reporting limit can be achieved with less than one liter of sample. In this event dilute the sample to about 1 liter with reagent water.


liquid solvent flow
gaseous solvent flow
Condenser
Extractor Body
water sample
solvent
Boiling Flask
Heating Mantle
solvent




11.4.4. Adjust sample pH as indicated in Table 1 for the initial extraction. Use the minimum amount of 1:1 $H_2SO_4$ or 10 N NaOH necessary. Recheck the sample with pH paper. Record adjusted pH, spiking volumes and standard numbers on the benchsheet. Return spiking solutions to the refrigerator as soon as possible.

11.4.5. Add reagent water to the extractor body until approximately 250 mL of methylene chloride is pushed over into the round-bottomed flask to ensure proper operation and solvent cycling. Attach cold condenser (about 10°C). Turn on heating mantle. Inspect joints for leaks once solvent has begun cycling. Extract for 18-24 hours. (24 hours required for 600 series)

11.4.6. If extraction at a secondary pH is required, (see Table 1) turn off the heating mantle and allow the extractor to cool. Detach the condenser and adjust the pH of the sample in the extractor body to the pH indicated in Table 1 with a minimum amount of 10 N NaOH or 1:1 $H_2SO_4$. Measure with pH paper and record the adjusted pH on the benchsheet. Reattach the condenser and turn on heating mantle. Extract for 18-24 hours.

11.4.7. Turn off the heating mantle and allow the extractor to cool.

11.4.8. Place a funnel containing 10-20 g of anhydrous sodium sulfate on the Kuderna-Danish (K-D) apparatus or other glass container. The funnel can be plugged with glass wool enabling it to hold the granular anhydrous sodium sulfate or phase separation filter paper may be used.

11.4.9. Dry the extract in the round bottom flask by filtering it through the sodium sulfate filled funnel. Note that it is not necessary or advisable to attempt to add the solvent remaining in the continuous extractor body to the extract.

11.4.10. Collect the dried extract in a K-D or other glass container. Rinse the flask which contained the solvent extract with 20-30 mL of methylene chloride and add it to the funnel to complete the quantitative transfer. Dispose of solvent and water remaining in the extractor in the appropriate waste container.

*Note:* Some types of CLLE apparatus have built in drying columns. If this type of apparatus is used then a drying step subsequent to the extraction may not be necessary.

11.4.11. Cover with aluminum foil if the extract is not concentrated immediately. Refer to Section 11.8 for concentration and Section 11.9 for cleanup.

11.5. Sonication

A flow chart for this procedure is included in Section 17.

11.5.1. Determination of percent moisture (Optional - if a different group performs this test, refer to the facility SOP.)

In some cases, sample results are needed on a dry weight basis. If this is the case, weigh 5-10 g of sample into a suitable tared container (typically an aluminum weigh pan. Determine the % moisture by drying overnight (at least 12 hours) at 105°C. Allow to cool in a desiccator before weighing.

$$\% \text{ Moisture} = \frac{(\text{weight of wet sample} - \text{weight of dry sample})}{\text{weight of wet sample}} \times 100$$

11.5.2. Determination of pH (Optional - if a different group performs this test, refer to the facility SOP.)

If pH determination is required, transfer 10 g of soil to a beaker. Add 10 mL of water. Stir for five minutes then let stand for 1 hour. Determine the pH of the sample with a glass electrode and pH meter.

11.5.3. Decant and discard any water layer on a sediment/soil sample. Record and document if a water layer was discarded on the benchsheet. Homogenize the sample by mixing it thoroughly in the container. If this is not possible place the sample in clean beaker and homogenize. Upon completion of homogenization in beaker return sample to original container. Discard foreign objects such as sticks, leaves and rocks, unless extraction of this material is required by client. If the sample consists primarily of foreign materials consult with the client (via the Project Manager or Administrator).

11.5.4. Remove surrogate and matrix spiking solutions from refrigerator and allow to warm to room temperature.

11.5.5. Weigh 30 g of sample ± 0.2g into a 250 or 400 mL beaker. Record the weight to the nearest 0.01 g in the appropriate column on the benchsheet. Use 30 g of sodium sulfate for the method blank and 30 g of sodium sulfate with 30 g of reagent sand for the LCS.

11.5.6. Mix weighed sample with a spatula adding enough anhydrous sodium sulfate (approximately 30 g ) to be free flowing. (If the sample is not free flowing extraction efficiency may be reduced)

11.5.7. Prepare a method blank, LCS and MS/MSD for each batch as specified in section 9 of this SOP.

11.5.8. Add the appropriate volume of surrogate spiking solution (see Table 3). Also add appropriate volume of matrix spiking solution to any matrix spike / matrix spike duplicate samples (see.Table 4) Add 1 mL of the surrogate spiking solution to each sample, method blank, Laboratory Control Sample (LCS), and matrix spikes. Refer to Table 6 for details of the surrogate spiking solutions. Add 1 mL of the appropriate matrix spiking solution to each Matrix Spike/Matrix Spike Duplicate (MS/MSD) and LCS. Refer to Tables 3 and 5 for details of the spiking solutions. Record spiking volumes and standard numbers on the benchsheet. Return spiking solutions promptly to refrigerator.

**Note:** The same volume of surrogate and matrix spiking solution is used if GPC is indicated since the final volume would be reduced to compensate for loss of extract during the GPC procedure.

11.5.9. Immediately add a minimum of 100 mL of solvent to the beaker.

Solvents:

| | |
|---|---|
| Semivolatile GC/MS, TPH, Organochlorine pesticides and PCBs | 1:1 Methylene Chloride / Acetone |

**Note:** Steps 11.5.5 - 11.5.9 should be performed rapidly to avoid loss of the more volatile extractables.

11.5.10. Place the bottom surface of the appropriate disrupter horn tip approximately ½ inch below the surface of the solvent, but above the sediment layer.

11.5.11. Sonicate for 3 minutes, making sure the entire sample is agitated. If the W-380 or W-385 sonicator is used the output should be set at 6 for the 3/4 inch high gain (Q) horn or 10 for the 3/4 inch standard horn. with mode switch on pulse, and percent-duty cycle knob set at 50%.

**Note:** Do ***not*** use ***Microtip*** probe.

11.5.12. Loosely plug the stem of a 75 mm x 75 mm glass funnel with glass wool and/or line the funnel with filter paper. Add 10-20 g of anhydrous sodium sulfate to the funnel cup.

11.5.13. Place the prepared funnel on a collection apparatus (beaker or K-D Apparatus.

11.5.14. Decant and filter extracts through the prepared funnel into a clean beaker or K-D Apparatus.

11.5.15. Repeat the extraction two more times with additional 100 mL minimum portions of solvent each time. Decant off extraction solvent after each sonication. On the final sonication pour the entire sample (sediment and solvent) into the funnel and rinse with an additional 10 mL-20 mL of the methylene chloride/acetone appropriate solvent (Refer to Table in 11.5.9).

Note: Alternatively, the three extracts may be collected together and then filtered through the sodium sulfate.

11.5.16. Cover with aluminum foil if the extract is not concentrated immediately. Refer to Section 11.8 for concentration and Section 11.9 for cleanup.

11.5.17. Sonicator Tuning.

11.5.17.1. Tune the sonicator according to manufacturer's instructions. The sonicator must be tuned at least every time a new horn is installed.

11.6. Soxhlet

11.6.1. Determination of % moisture

In some cases, sample results are needed on a dry weight basis. If this is the case, weigh 5-10 g of sample into a suitable tared container (typically an aluminum weigh pan. Determine the % moisture by drying overnight at 105°C. Allow to cool in a desiccator before weighing.

$$\% \text{ Moisture} = \frac{(\text{weight of wet sample} - \text{weight of dry sample})}{\text{weight of wet sample}} \times 100$$

11.6.2. Determination of pH

If pH determination is required, transfer 10 g of soil to a beaker. Add 10 mL of water. Stir for 1 hour. Determine the pH of the sample with a glass electrode and pH meter.

11.6.3. Decant and discard any water layer on a sediment/soil sample. Record and document if a water layer was discarded on the benchsheet. Homogenize the sample by mixing it thoroughly in the container. If this is not possible place the sample in clean beaker and homogenize. Upon completion of homogenization in beaker return sample to original container. Discard foreign objects such as sticks, leaves and rocks, unless extraction of this material is required by client. If the sample consists primarily of foreign materials consult with the client (via the Project Manager or Administrator).

11.6.4. Remove surrogate and matrix spiking solutions from refrigerator and allow to warm to room temperature.

11.6.5. Weigh 30 g of sample ± 0.2g into a beaker, recording the weight to the nearest 0.01 g on the benchsheet.. Use 30 g of sodium sulfate for the method blank and LCS. Add 30 g of anhydrous sodium sulfate and mix well. The mixture should have a free flowing texture. If not, add more sodium sulfate. Add the sample/sodium sulfate mixture to a soxhlet thimble, but do not pack the thimble tightly. The extraction thimble must drain freely for the duration of the extraction period. A glass wool plug above and below the sample in the soxhlet extractor is an acceptable alternative for the thimble.

11.6.6. Add the appropriate amount of surrogate and matrix spiking solution as indicated in Tables 3, 4, 5, and 6.

Sample weights less than 30 g but over 5 g may be used if the appropriate reporting limits can be met.

11.6.7. Prepare a method blank, LCS and MS/MSD for each batch as specified in section 9 of this SOP, using sodium sulfate as the matrix. The weight of sodium sulfate used should be approximately the weight of soil used in each sample.

11.6.8. Place approximately 200mL of solvent into a 250 mL flat bottom flask containing one or two clean boiling chips. Attach the flask to the extractor and extract the sample for 16-24 hours at 4-6 cycles per hour. Check the system for leaks at the ground glass joints after it has warmed up.

NOTE: If a reduced quantity of sample is extracted, it is usually necessary to increase the amount of sodium sulfate added or increase the solvent boiling rate to properly set the cycling rate.

Solvents:

| | |
|---|---|
| Semivolatile GC/MS, OPP, PAH, TPH Organochlorine pesticides and PCBs | 1:1 Methylene Chloride / Acetone |

11.6.9. Allow the extract to cool after the extraction is complete, then disassemble by gently twisting the soxhlet from the flask. Dry the extract in the flask by filtering it through a sodium sulfate filled funnel.

11.6.10. Collect the dried extract in a K-D or other glass container. Rinse the flask which contained the solvent extract with 20-30 mL of methylene chloride and add it to the funnel to complete the quantitative transfer.

11.6.11. Cover with aluminum foil if the extract is not concentrated immediately. Refer to Section 11.8 for concentration and Section 11.9 for cleanup.

11.7. Waste Dilution

11.7.1. This method is used for materials that are soluble in an organic solvent.

11.7.2. Transfer 10 mL of the solvent to be used for dilution into a Teflon capped vial. Mark the meniscus on the vial, then discard the solvent.

11.7.3. Tare the vial, then transfer approximately 1g of sample to the vial. Record the weight to the nearest 0.01 g.

11.7.4. Add appropriate volume of surrogate and spike solutions (Table 3).

11.7.5. Dilute to 10 mL with the appropriate solvent. (Methylene Chloride for GC/MS-BNA and GCS-TPH. Add 10 mL of appropriate solvent (Hexane) for GCS-pesticide and/or PCB analysis.

11.7.6. Add 2 g + 0.1 g sodium sulfate to the sample. Cap and shake or vortex each extract for 2 minutes.

11.7.7. If H2O is still present, add 4-5 g sodium sulfate to a small pipette funnel. The funnel can be plugged with glass wool or phase separation filter paper may be used to hold the sodium sulfate.

11.7.8. Pour the sample through the funnel, collecting as much as possible in a clean vial. Do NOT rinse the funnel with additional solvent, and do NOT concentrate the sample. The final volume is defined as 10 mL.

11.7.9. Label the sample, which is now ready for cleanup or analysis.

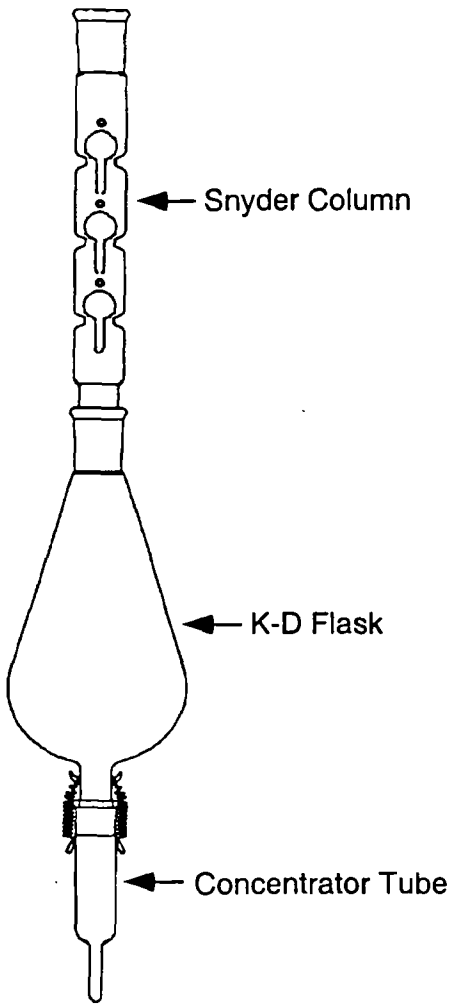
11.8. Concentration

According to the type of sample and any cleanup procedures needed, different final solvents and volumes will be required. Refer to Table 2 for the appropriate final volumes and concentrations.

11.8.1. Kuderna-Danish (KD) Method:

11.8.1.1. Assemble a Kuderna-Danish concentrator by attaching a 10 mL concentrator tube to the 500 mL KD flask. Transfer the sample to the K-D flask.

11.8.1.2. Add one or two clean boiling chips and the extract to be concentrated to the KD flask and attach a three ball Snyder Column. Add approximately 1 mL of clean methylene chloride to the top of the Snyder column (this is important to ensure that the balls are not stuck and that the column will work properly).




11.8.1.3. Place the KD apparatus on a water bath (90-98°C) so that the tip of the concentrator tube is submerged. The water level should not reach the joint between the concentrator and the KD flask. At the proper rate of distillation, the balls will actively chatter but the chambers should not flood.

11.8.1.4. Concentrate to 5-15 mL. If the determinative method requires a solvent exchange add the appropriate exchange solvent (50 mL hexane, 20 ml hexane/acetone, or 4 mL acetonitrile,4mL toluene (Herbicide TCLP), or 10 mL toluene) to the top of the Snyder Column, and then continue the water bath

concentration back down to 1-4 mL. Refer to Table 2 for details of exchange solvents and final volumes. The Snyder column may be insulated if necessary to maintain the correct rate of distillation.

*Note:* Add an additional boiling chip with the addition of exchange solvent. An alternative technique for solvent exchange is to replace the macro Snyder column and KD flask with a micro Snyder column, concentrate to approximately 1 mL, add the appropriate solvent, and concentrate back down to 1 mL. The extract must be cool before the macro Snyder assembly is removed.

*Note:* It is very important not to concentrate to dryness as analytes will be lost.

11.8.1.5. Remove the KD apparatus from the water bath and allow to cool for a minimum of 10 minutes. If the level of the extract is above the level of the concentrator tube joint, continue to distill the solvent as necessary. Again, allow the KD flask to cool for a minimum of 10 minutes.

11.8.1.6. If the final volume is 5 or 10 mL the extract may be made up to volume in the graduated KD tube or transferred to a 12 mL vial previously marked at the appropriate volume level. Document the final volume. Otherwise proceed to section 11.8.2

11.8.2. Nitrogen Evaporation to Final Concentration

11.8.2.1. Transfer the entire extract to a calibrated evaporation tube. Rinse the concentrator tube with 1-2 mL of the appropriate solvent and transfer the solvent rinsate to the evaporation tube.

11.8.2.2. Place the tube in a warm water bath that is at least 5°C below the boiling temperature of the solvent being evaporated and evaporate the solvent using a gentle stream of nitrogen. The nitrogen flow will form a slight depression on the surface of the solvent, but should not create splattering of the extract.

Boiling points of commonly used solvents are:

| | |
|---|---|
| Methylene chloride | 40°C |
| Acetone | 56°C |
| Hexane | 69°C |
| Acetonitrile | 82°C |
| Toluene | 111°C |

11.8.2.3. During the course of the evaporation rinse the sides of the evaporation tube twice with approximately 1 mL of clean solvent. The first rinse should be about half way through he process, with the second rinse when the solvent volume gets close to 1 mL. Concentrate the solvent accurately to the calibrated volume line and transfer the extract to the appropriate storage vial.

*Note:* It is very important not to concentrate to dryness as analytes will be lost.

An alternative technique is to follow the previous steps concentrating the solvent to slightly below the required final volume and then drawing the extract into a syringe. Rinse the evaporation tube with a small amount of solvent and draw additional solvent into the syringe to make up the accurate final volume.

*Note:* It is very important not to concentrate to dryness as analytes will be lost.

*Note:* The final concentration and volume measurement steps are critical. Use care when concentrating and make certain that the final volume measurement is accurate.

Alternative QES Concentration Method:

*This concentration method uses a hot water jacketed concentrator tube (CT) instead of the hot water bath and concentrator tube used in Section 11.8.1.1. The construction of the jacketed concentrator tube reduces the tendency of the extract to evaporate to dryness. Thus, low boiling analytes are retained in the extract better with less analyst monitoring of the concentration process.*

*Assemble the jacketed concentrator tube, KD body and hot water hoses. Add 1mL of exchange solvent (if needed) and one large, clean boiling chip.*

*NOTE: The boiling chips used in the jacketed concentrator tube must be large enough to prevent them falling down into the tip of the CT. If the boiling chip is not in the proper position, the extract may superheat and bump vigorously if the extract solvent warms up slowly.*

*Pour the extract to be concentrated into the KD flask, and attach a three-ball Snyder column.*

*Turn on the hot (95°C) water flow to the jacketed concentrator tube.*

*Concentrate to 1 mL. If the determinative method requires a solvent exchange, add the appropriate exchange solvent (5-10 mL hexane, 1 mL acetonitrile, 4 mL acetone/hexane) to the top of the Snyder column. Continue to concentrate until the Snyder column balls stop chattering.*

*Cool the jacketed concentrator tube until it is cold to the touch.*

*Quantitatively transfer the extract and dilute to final volume, or continue concentration with nitrogen evaporation (section 11.8.2).*

11.8.3. Turbovap Method

11.8.3.1. Turn on the Turbovap and adjust the water temperature to 5-10°C less than the boiling point of the solvent to be evaporated.

11.8.3.2. Switch all endpoint sensors to the "NO" position.

11.8.3.3. Adjust the water bath level

11.8.3.4. Adjust the nitrogen gas pressure to approximately 12 psi.

11.8.3.5. Transfer the extract into the Turbovap tube and load into the Turbovap. Do not fill the Turbovap tubes over approximately 3/4 full.

11.8.3.6. Reset the sensor and close the lid.

*Note:* If the extract splashes when the nitrogen flow starts, reduce the nitrogen flow or transfer a portion of the extract back into the original extract container.

11.8.3.7. As the extract concentrates, transfer the remainder of the extract into the appropriate Turbovap tube. After all of the extract has been transferred, rinse the flask with a few mL of methylene chloride and add to the Turbovap tube.

11.8.3.8. During the concentration rinse the Turbovap tube walls with a few mL of solvent 1 or 2 times.

11.8.3.9. Concentrate the extract to slightly less than the required final volume.

11.8.3.10. If solvent exchange is required, concentrate to 1-4 mL and add 50 mL of the exchange solvent. Concentrate back down to the appropriate volume. Refer to Table 2 for details of exchange solvents and final volumes.

11.8.3.11. Transfer the concentrated extract to volumetric glassware for adjustment of final volume, using a small amount of solvent to rinse the tube and complete the transfer.

*Note:* Water contamination from condensation during concentration is not acceptable. If water is present, remove the Turbovap tube and filter the extract through sodium sulfate. Transfer to a clean Turbovap tube and continue the concentration.

*Note 2*: Dark, opaque or turbid samples may not concentrate. If this occurs, set the concentrator sensor to dryness and supervise the entire concentration procedure.

11.9. Cleanup Techniques

The following techniques may be used to remove interfering peaks, and /or to remove materials that may cause column deterioration and/ or loss of detector sensitivity.
*Gel Permeation Chromatography* (Section 11.9.1) is a generally applicable technique which can be used to prepare extracts for Semivolatiles (8270), and pesticides (8081) analysis. It is capable of separating high molecular weight material from the sample analytes, and so is particularly useful if tissue or vegetable matter is part of the sample, and for many soil samples.
Note: GPC used only for CLP Projects

*Florisil column cleanup* (Section 11.9.2) is particularly useful for cleanup of pesticides for analysis by method 8081 and should normally be applied to these samples unless the matrix is clean. It separates compounds with a different polarity from the target analytes.
Note: GPC used only for CLP Projects
Gel Permeation Chromatography and Florisil column cleanup may both be applied to samples for analysis by method 8081/8082. In this case the GPC should be performed first.

*Sulfur cleanup* (Section 11.9.3) is generally applied to samples for analysis by method 8081/8082, since the Electron Capture Detector responds strongly to sulfur. It is performed after GPC and Florisil cleanup.

*Sulfuric acid cleanup* (Section 11.9.4) is applied to samples requiring analysis for Polychlorinated Biphenyls (PCBs) only. Most organic matter is destroyed by the sulfuric acid.
WARNING: Sulfuric acid cleanup must not be performed on any matrix that may have water present as a violent reaction between the acid and water may result in acid exploding out of the vessel.

*Acid Base Partition Cleanup* (Section 11.9.5) is useful for separating organic acids and phenols from basic and neutral organics.

*Fluorocarbon cleanup (Section 11.9.7) is used to remove hydrocarbons from water samples to be analyzed for water soluble alcohols.*

11.9.1. Gel Permeation Chromatography (GPC)

Note: GPC systems include the GPC Autoprep Model 1002A or 1002B Analytical Biochemical Laboratories, Inc., Zymark Benchmate, or equivalent.

11.9.1.1. GPC Column Preparation

11.9.1.1.1. Weigh out 70 g of Bio Beads (SX-3) into a 400-mL beaker.

11.9.1.1.2. Add approximately 300 mL of methylene chloride and stir gently.

11.9.1.1.3. Cover with aluminum foil and allow the beads to swell for a minimum of two hours. Maintain enough solvent to sufficiently cover the beads at all times.

11.9.1.1.4. Position and tighten the outlet bed support (top) plunger assembly in the tube by inserting the plunger and turning it clockwise until snug. Install the plunger near the column end but no closer than 5 cm (measured from the gel packing to the collar).

11.9.1.1.5. Turn the column upside down from its normal position with the open end up. Place the tubing from the top plunger assembly into a waste beaker below the column.

11.9.1.1.6. Swirl the bead/solvent slurry to get a homogeneous mixture and pour the mixture into the open end of the column. Transfer as much as possible with one continuous pour trying to minimize bubble formation. Pour enough to fill the column. Wait for the excess solvent to drain out before pouring in the rest. Add additional methylene chloride to transfer the remaining beads and to rinse the beaker and the sides of the column. If the top of the gel begins to look dry, add more methylene chloride to rewet the beads.

11.9.1.1.7. Wipe any remaining beads and solvent from the inner walls of the column with a laboratory tissue. Loosen the seal slightly on the other plunger assembly (long plunger) and insert it into the column. Make the seal just tight enough so that any beads on the glass surface will be pushed forward, but loose enough so that the plunger can be pushed forward.

**CAUTION**: Do not tighten the seal if beads are between the seal and the glass surface because this can damage the seal and cause leakage.

11.9.1.1.8. Push the plunger until it meets the gel, then compress the column bed about 4 cm.

11.9.1.1.9. Connect the column inlet to the solvent reservoir and place the column outlet tube in a waste container. Pump methylene chloride through the column at a rate of 5 mL/min. for one hour.

11.9.1.1.10. After washing the column for at least one hour, connect the column outlet tube to the inlet side of the UV detector. Connect the system outlet to the outlet side of the UV detector. Placing a restrictor (made from a piece of capillary tubing of 1/16"OD x 10/1000"ID x 2") in the outlet tube from the UV detector will prevent bubble formation which causes a noisy UV baseline. The restrictor will not effect the flow rate. After pumping methylene chloride through the column for an additional 1-2

hours, adjust the inlet bed support plunger until approximately 6-10 psi back-pressure is achieved. Push the plunger in to increase pressure or slowly pull outward to reduce pressure.

11.9.1.1.11. When the GPC column is not to be used for several days, connect the column inlet and outlet lines to prevent column drying and/or channeling. If channeling occurs, the gel must be removed from the column, re-swelled, and re-poured as described above. If drying occurs, pump methylene chloride through the column until the observed column pressure is constant and the column appears wet. Always recalibrate after column drying has occurred to verify that retention volumes have not changed.

11.9.1.2. Initial Calibration of the GPC Column

11.9.1.2.1. Before use, the GPC must be calibrated based on monitoring the elution of standards with a UV detector connected to the GPC column.

11.9.1.2.2. Pump solvent through the GPC column for 2 hours. Verify that the flow rate is 4.5-5.5 mL/min. Corrective action must be taken if the flow rate is outside this range. Record the column pressure (should be 6-10 psi) and room temperature (22°C is ideal).

Note: Changes in pressure, solvent flow rate, and temperature conditions can affect analyte retention times and must be monitored. If the flow rate and/or column pressure do not fall within the above ranges, a new column should be prepared.

11.9.1.2.3. Inject the calibration solution and retain a UV trace that meets the following requirements (See resolution calculation in section 11.9.1.6):

- Peaks must be observed and should be symmetrical for all compounds in the calibration solution.
- Corn oil and phthalate peaks must exhibit >85% resolution.
- Phthalate and methoxychlor peaks must exhibit >85% resolution.
- Methoxychlor and perylene peaks must exhibit >85% resolution.
- Perylene and sulfur peaks must not be saturated and must exhibit >90% baseline resolution.

11.9.1.2.4. A UV trace that does not meet the criteria in paragraph 11.9.1.2.3 indicates the need for system maintenance and/or the need for a new column.

11.9.1.2.5. Determine appropriate collect and dump cycles.

11.9.1.2.6. The calibrated GPC program for pesticides/PCB should dump >85% of the phthalate and should collect >95% of the methoxychlor and perylene. Use a wash time of 10 minutes.

11.9.1.2.7. For semivolatile extracts, initiate a column eluate collection just before the elution of bis (2-ethylhexyl) phthalate and after the elution of the corn oil. Stop eluate collection shortly after the elution of perylene. Stop collection before sulfur elutes. Use a wash time of 10 minutes after the elution of sulfur.

11.9.1.2.8. Reinject the calibration solution after appropriate dump and collect cycles have been set.

11.9.1.2.9. Measure and record the volume of collected GPC eluate in a graduated cylinder.

11.9.1.2.10. The retention times for both bis(2-ethylhexyl) phthalate and perylene must not vary more than +/- 5% between calibrations.

11.9.1.3. GPC calibration check

Check the calibration of the GPC immediately after the initial calibration and at least every 7 days thereafter, while the column is in use.

11.9.1.3.1. Inject the calibration solution, and obtain a UV trace. If the retention times of bis(2-ethylhexyl)phthalate or perylene have changed by more than ± 5% use this run as the start of a new initial calibration. Otherwise, proceed with the recovery check. Excessive retention time shifts may be caused by poor laboratory temperature control or system leaks, an unstabilized column, or high laboratory temperature causing outgassing of methylene chloride. Pump methylene chloride through the system and check the retention times each day until stabilized.

11.9.1.4. GPC Recovery Check for Pesticides/ PCBs

11.9.1.4.1. The recovery from the GPC must be verified immediately after the initial calibration and at least every 7 days, when the instrument is in use. Two recovery check solutions are used. The first mixture is prepared by diluting 1.0 2.0 mL of the pesticide matrix spiking solution (Table 6) to 10 mL in methylene chloride. The second mixture is prepared by diluting 12.0 mL of the PCB only matrix spiking solution (Table 6) to 10 mL with methylene chloride.

11.9.1.4.2. Load the pesticide matrix spike mixture, the PCB mixture, and a methylene chloride blank onto the GPC using the GC dump and collect values.

**Note**: If the analysis is for PCBs only, then the pesticide recovery check is not necessary.

11.9.1.4.3. After collecting the GPC calibration check fraction, concentrate, solvent exchanging to hexane. Adjust the final volume to 5.0 mL, and analyze by GC/EC. Refer to concentration, section 11.8.

11.9.1.4.4. The methylene chloride blank may not exceed more than one half the reporting limit of any analyte. And if the recovery of each of the single component analytes is 80-10120% and if the Aroclor pattern is the same as previously run standards, then the analyst may use the column. If the above criteria are not met, there may be a need for system maintenance.

11.9.1.5. GPC Blank for Semivolatiles

11.9.1.5.1. The recovery from the GPC must be verified immediately after the initial calibration and at least every 7 days, when the instrument is in use.

11.9.1.5.2. Load a methylene chloride blank onto the GPC using the semivolatiles dump and collect values.

11.9.1.5.3. After collecting the GPC recovery check fraction, concentrate, and analyze by GC/MS. Refer to the concentration section 11.8.

The blank should not contain any analytes at or above the reporting limit. If these conditions are met the column may be used for sample analysis. Otherwise correct the contamination problem, or extend the collect time to improve recovery of target analytes.

11.9.1.6. Sample Extract Cleanup

11.9.1.6.1. Reduce the sample extract volume to 1-2 mL, then adjust to 10 mL with methylene chloride prior to cleanup. This reduces the amount of acetone in the extract. Refer to section 11.8.

11.9.1.6.2. Start the pump and let the flow stabilize for 2 hours. The solvent flow rate should be 4.5-5.5 mL/min. The ideal laboratory temperature to prevent outgassing of the methylene chloride is 22°C. The normal backpressure is 6-10 psi.

11.9.1.6.3. In order to prevent overloading of the GPC column, highly viscous sample extracts must be diluted prior to cleanup. Any sample extract with a viscosity greater than that of a 1:1 glycerol:water solution (by visual comparison) must be diluted and loaded into several loops.

11.9.1.6.4. Samples being loaded onto the GPC should be filtered with a 5 micron (or less) filter disk. Attach a filter to a 10 mL Luerlok syringe and filter the 10 mL sample extract into the sample tube.

**Note:** The Zymark Benchmate automatically filters the sample extracts, but manual prefiltration of very dirty extracts may be necessary.

11.9.1.6.5. Load the filtered (or unfiltered if using the Benchmate) samples into the proper sample tubes and place on the GPC.

**Note:** For the GPC Autoprep Model 1002A, wash the loading port with methylene chloride after loading each sample loop in order to minimize cross contamination. This step is automated on the GPC Autoprep 1002B and on the Benchmate.

11.9.1.6.6. Set the collect, dump, and wash times determined by the calibration procedure.

11.9.1.6.7. Switch to the run mode and start the automated sequence. Process each sample using the collect and dump cycle times established by the calibration procedure.

11.9.1.6.8. Collect each sample in a suitable glass container. Monitor sample volumes collected.

11.9.1.6.9. Any samples that were loaded into 2 or more positions must be recombined.

11.9.1.6.10. Concentrate semivolatile sample extracts to 0.5 mL in methylene chloride. Refer to the concentration section 11.8.

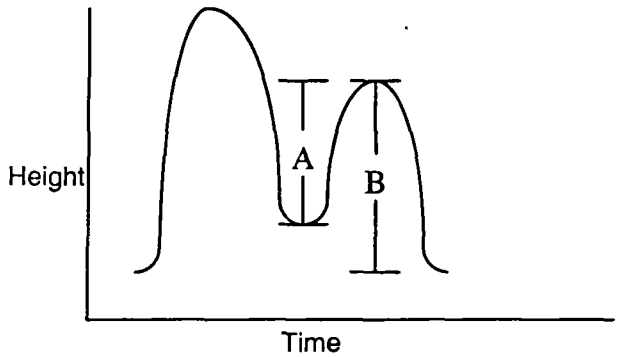
11.9.1.6.11. Solvent exchange pesticide/PCB sample extracts into hexane and concentrate to 5.0 mL. Refer to the concentration section 11.8.

11.9.1.7. Calculations

11.9.1.7.1. Resolution

To calculate the resolution between two peaks on a chromatograph, divide the depth of the valley between the peaks by the peak height of the smaller peak being resolved and multiply by 100.

Resolution Calculation




$$\% \text{ Resolution } = \frac{A}{B} \times 100$$

Where: A = depth of valley to height of smaller peak
B = peak height of smaller peak

11.9.1.7.2. Dump Time

Mark on the chromatograph the point where collection is to begin. Measure the distance from the injection point. Divide the distance by the chart speed. Alternatively the collect and dump times may be measured by means of an integrator or data system.

$$\text{Dump time (min)} = \frac{\text{Distance (cm) from injection to collection start}}{\text{Chart speed (cm / min)}}$$

11.9.1.7.3. Collection Time

$$\text{Collection time (min)} = \frac{\text{Distance (cm) between collection start and stop}}{\text{Chart speed (cm / min)}}$$

11.9.2. Florisil Cartridge Cleanup

***Florisil cleanup is generally used for organochlorine pesticides, although it may be applied to other analytes. Sections 11.9.8.2.1 through 11.9.8.2.8 outline the procedure for organochlorine pesticides, while section 11.9.2.9 outlines modifications required for other analytes.***

*Note 1:* Systems for eluting multiple cleanup cartridges include the Supelco, Inc. Solid Phase Extraction (SPE) assemblyor equivalent.

*Note 2:* Follow the lab specific procedure when using ABC Model 1002B.

11.9.2.1. Before Florisil cleanup sample volume must be reduced to 10 mL (5 mL if GPC cleanup was used) and the solvent must be hexane. Refer to Section 11.8 for details of concentration.

11.9.2.2. Attach a vacuum manifold to a vacuum pump or water aspirator with a trap installed between the manifold and the vacuum. Adjust the vacuum in the manifold to 5-10 psi.

11.9.2.3. Place one Florisil cartridge into the vacuum manifold for each sample extract. Prior to cleanup of samples, pre-elute each cartridge with 5 mL of hexane/acetone (9:1). Adjust the vacuum applied to each cartridge so that the flow through each cartridge is approximately 2 mL/min. Do not allow the cartridges to go dry.

11.9.2.4. Just before the cartridges go dry, release the vacuum to the manifold and remove the manifold top.

11.9.2.5. Place a rack of clean labeled 12 mL concentrator tubes into the manifold and replace the manifold top. Make sure that the solvent line from each cartridge is placed inside the appropriate tube.

11.9.2.6. After the clean tubes are in place, vacuum to the manifold is restored and 2.0 mL of the extract is added to the appropriate Florisil cartridge.

11.9.2.7. The pesticides/aroclors in the extract concentrates are then eluted through the column with 8 mL of hexane/acetone (90:10) and are collected into the 10 mL culture tube or concentrator tube held in the rack inside the vacuum manifold.

11.9.2.8. Transfer the extract to a graduated concentrator tube and concentrate the extract to 2 mL. Refer to the concentration section. (11.8)

*Note 1:* A cartridge performance standard must be run with each lot of Florisil cartridges.

*Note 2:* Florisil cartridge performance check--every lot number of Florisil must be tested before use. Add 0.5 ug/mL of 2,4,5-trichlorophenol solution and 0.5 mL of GC Standard Mix A (midpoint concentration) to 4 mL hexane. Reduce volume to 0.5 mL. Add the concentrate to a pre-washed Florisil cartridge and elute with 9 mL hexane/acetone [(90:10)(v/v)]. Rinse cartridge with 1.0 mL hexane two additional times. Concentrate eluate to 1.0 mL final volume and transfer to vial. Analyze the solution by GC/EC. The test sample must show 80 to 120% recovery of all pesticide analytes with <5% trichlorophenol recovery, and no peaks interfering with target compounds can

be detected. This standard has a lifetime of six months. Alternatively, this standard may be purchased as a stock solution.

11.9.2.9. Modifications for other analyte classes

11.9.2.9.1. PCBs

Pre-elute the cartridge with 4 mL hexane. Add 2 mL of the sample extract and elute with 3 mL hexane. The eluant will contain the PCBs together with any heptachlor, aldrin, 4,4'DDE and part of any 4,4'DDT. Any BHC isomers, heptachlor epoxide, chlordane, endosulfan I and II, endrin aldehyde and endrin sulfate and methoxychlor will be retained on the column and can be eluted in a separate fraction with 8 mL 90:10 hexane:acetone if required.

11.9.3. Sulfur Removal

11.9.3.1. Sulfur can be removed by one of three methods: mercury, copper, or tetrabutylammonium sulfite (TBA) according to laboratory preference. If the sulfur concentration is such that crystallization occurs in the concentrated extract, centrifuge the extract to settle the crystals, and carefully draw off the sample extract with a disposable pipet, leaving the excess sulfur in the centrifuge tube. Transfer the extract to a clean concentrator tube before proceeding with further sulfur cleanup.

11.9.3.2. Sulfur Removal with Elemental Mercury

**Note**: Use Mercury sparingly in order to minimize exposure and disposal costs.

11.9.3.2.1. Transfer 2 mL of sample extract into a clean concentrator tube or Teflon sealed vial.

11.9.3.2.2. Add one to three drops of mercury to the extract vial and seal.

11.9.3.2.3. Shake well for 15-30 seconds. If prolonged shaking is required, use a mechanical shaker.

11.9.3.2.4. Remove the extract from the mercury using a disposable pipette and transfer to a clean vial.

11.9.3.2.5. If black precipitate forms, sulfur was present. Shake again, then centrifuge. After centrifugation, transfer the supernate to a clean test tube and repeat. Do this until relatively little precipitate remains, or the screens indicate that cleanup is complete.

11.9.3.2.6. Properly dispose of the mercury waste.

11.9.3.3. Sulfur Removal with Copper

11.9.3.3.1. Transfer 1.0 mL of sample extract into a centrifuge or concentrator tube.

11.9.3.3.2. Add approximately 2 g of cleaned copper powder (see 8.2 for copper cleaning procedure) to the sample extract tube.

11.9.3.3.3. Mix for one minute on a mechanical shaker.

11.9.3.3.4. If the copper changes color, sulfur was present. Repeat the sulfur removal procedure until the copper remains shiny.

11.9.3.3.5. Transfer the supernate to a clean vial.

11.9.3.4. Sulfur Removal with Tetrabutylammonium (TBA) Sulfite Reagent

11.9.3.4.1. Transfer 1.0 mL of sample extract into a culture tube.

11.9.3.4.2. Add 1.0 mL TBA sulfite reagent and 2 mL 2-propanol to the sample extract. Cap and shake for 1 minute. If clear crystals (precipitated sodium sulfite) form, sufficient sodium sulfite is present.

11.9.3.4.3. If a precipitate does not form, add sodium sulfite in approximately 0.1 g portions until a solid residue remains after repeated shaking.

11.9.3.4.4. Add 5 mL organic free reagent water and shake for 1 minute. Allow sample to stand for 5-10 minutes. (Centrifuge if necessary to separate the layers). Transfer the sample extract (top layer) to a vial. The final volume is defined as 1.0 mL in section 11.9.3.4.1.

11.9.4. Sulfuric Acid Cleanup

11.9.4.1. Add approximately 2-5 mL of concentrated sulfuric acid to 2 mL of sample extract in a Teflon capped vial.

**Caution:** There must be no water present in the extract or the reaction may shatter the sample container.

11.9.4.2. Shake or vortex for about thirty seconds and allow to settle. (Centrifuge if necessary)

11.9.4.3. Remove the sample extract (top layer) from the acid using a Pasteur pipette and transfer to a clean vial. ***CAUTION:*** It is not necessary to remove all the extract since the final volume is already determined. Transfer of small amounts

of sulfuric acid along with the extract will result in extremely rapid degradation of the chromatographic column.

11.9.4.4. If the sulfuric acid layer becomes highly colored after shaking with the sample extract, transfer the hexane extract to a clean vial and repeat the cleanup procedure until color is no longer being removed by the acid, or a maximum of 5 acid cleanups.

11.9.4.5. Properly dispose of the acid waste.

11.9.5. Acid/Base Partition Cleanup

11.9.5.1. Place 10 mL of the solvent extract from a prior extraction procedure into a 125 mL separatory funnel.

11.9.5.2. Add 20 mL of methylene chloride to the separatory funnel.

11.9.5.3. Slowly add 20 mL of DI water which has been previously adjusted to a pH of 12 to 13 with 10 N sodium hydroxide.

11.9.5.4. Seal and shake the separatory funnel for at least two minutes with periodic venting to release excess pressure.

**CAUTION:** Methylene chloride creates excessive pressure very rapidly. Initial venting should be done immediately after the separatory funnel has been sealed.

11.9.5.5. Allow the organic layer to separate from the aqueous phase for a minimum of ten minutes.

11.9.5.6. If an emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods.

11.9.5.7. Separate the aqueous phase and transfer it to a 125 mL Erlenmeyer flask. Repeat the extraction two more times using fresh 20 mL aliquots of dilute sodium hydroxide (pH 12-13). Combine the aqueous extracts.

11.9.5.8. Water-soluble organic acids and phenols will be primarily in the aqueous phase. Base/neutral analytes will be in the methylene chloride. If the analytes of interest are only in the aqueous phase discard the methylene chloride and proceed to Section 11.9.5.9. If the analytes of interest are only in the methylene chloride, discard the aqueous phase and proceed to Section 11.9.5.11.

11.9.5.9. Externally cool the flask with ice while adjusting the aqueous phase to a pH of 1-2 with sulfuric acid (1:1). Transfer the cool aqueous phase to a clean 125 mL separatory funnel.

11.9.5.10. Add 20 mL of methylene chloride to the separatory funnel and shake for at least two minutes. Allow the methylene chloride to separate from the aqueous phase and collect the methylene chloride in an Erlenmeyer flask. Repeat the extraction two more times using fresh methylene chloride and extracting at pH 1-2. Combine the three extracts.

11.9.5.11. Dry the extract by passing through a funnel containing 10-20 g anhydrous sodium sulfate. Rinse the funnel with an additional 20-30 mL of clean methylene chloride

11.9.5.12. Cover with aluminum foil if the extract is not concentrated immediately. Refer to section 11.9 for concentration.

11.9.5.13. Dispose of solvent and water remaining in the separatory funnel into the appropriate waste container.

11.9.6. Fluorocarbon Cleanup

*This procedure is appropriate for the removal hydrocarbons from water samples prior to analysis for water soluble alcohols*

11.9.6.1. Transfer 1-2 mL of water sample to a 10 mL culture tube.

11.9.6.2. Add 1-2 mL of fluorocarbon solvent (PF-5080) to the culture and cap.

11.9.6.3. Shake for 30-60 seconds.

11.9.6.4. After the two phases have separated, pipette about 1 mL of water sample (top layer) into an autosampler vial for analysis. If necessary, centrifuge to enhance the phase separation.

## 12. DATA ANALYSIS AND CALCULATIONS

Not applicable

## 13. METHOD PERFORMANCE

13.1. Method detection limit

Each laboratory must generate a valid method detection limit for each analyte of interest. The procedure for the determination of the method detection limit is given in STL North Canton QA Policy #: QA-005

13.2. Initial demonstration

Each laboratory must make an initial demonstration of capability for each individual method. This requires analysis of four QC Check samples. The QC check sample is a well-characterized laboratory generated sample used to monitor method performance, which should contain all the analytes of interest. The spiking level should be equivalent to a mid-level calibration. (For certain tests more than one set of QC check samples may be necessary in order to demonstrate capability for the full analyte list.)

13.2.1. Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation.

13.2.2. Calculations and acceptance criteria for the QC check samples are given in the determinative SOPs. (CORP-GC-0001, CORP-MS-0001, 0002)

13.3. Training Qualification

The group/team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience.

## 14. POLLUTION PREVENTION

Within the constraints of following the methodology in this SOP, use of organic solvents should be minimized.

## 15. WASTE MANAGEMENT

Waste generated in this procedure will be segregated, and disposed according to the facility hazardous waste procedures. The Laboratory Environmental, Health and Safety Coordinator should be contacted if additional information is required.

15.1. Solvent waste must be disposed of in the clearly labeled waste cans.

15.2. Acid waste must be collected in the clearly labeled acid waste containers.

15.3. Solid materials (soil, gloves, soiled paper products) are placed in the solid debris container. Do not put liquids in the solid waste container.

15.4. Methylene chloride saturated water and remaining sample after the extraction is dumped into Methylene chloride waste cans.

## 16. REFERENCES

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update III (December 1996). Sections 3500B, 3510C, 3520C, 3540C, 3550B, 3600C, 3610B, 3620B, 3640A, 3650B, 3660B, AND 3665A.

## 17. MISCELLANEOUS

17.1. Modifications from Reference method

17.1.1. Some surrogate spiking concentrations are modified from those recommended in SW-846, in order to make the concentrations more consistent with the calibration levels in the determinative methods.

17.1.2. Aqueous sample volumes may be determined by weight.

17.1.3. Spiking levels for method 608 have been reduced by a factor of ten to bring the levels within the normal calibration range of the instrument.

17.1.4. 10 g of soil is used for pH determination, rather than the 50 g suggested in the reference method. The volume of water is also adjusted to maintain the sample / water ratio specified in the method.

17.2. Modifications from previous revision

17.2.1. SOP change forms are on record in the Quality Assurance Department.

17.3. Facility Specific SOPs

Each facility shall attach a list of facility specific SOPs or approved attachments (if applicable) which are required to implement this SOP or which are used in conjunction with this SOP. If no facility specific SOPs or amendments are to be attached, a statement must be attached specifying that there are none.

17.4. Tables

**Table 1**
**Liquid /Liquid Extraction Conditions**

| Determinative Method | Initial Ext. pH | Secondary Ext. pH |
|---|---|---|
| BNA: 8270C[1] | 1-2 | 11-12 |
| 625 | 11-12 | 1-2 |
| Pest/PCB: 8081A, 8082 & 608 | 5-9 | None |
| Wisconsin DRO | 2 | |
| OPP: 8141A | as received | None |
| Hydrocarbons: 8015B | as received | None |
| PAH: 8310, & 610 | as received | None |

[1] If the laboratory has validated acid only 8270 extraction for the target compound list required then the base extraction step may be omitted. The required validation consists of a 4 replicate initial demonstration of capability and a method detection limit study. (See section 13). Additionally, either of the base or acid fractions of Method 8270 can be run first.

**Table 2**
**Exchange Solvents and Final Volumes**

| Final Volumes and Exchange Solvents if no cleanup is used | | |
|---|---|---|
| | | |
| Type | Exchange Solvent for Analysis | Final Volume for Analysis in mL |
| Semivolatiles | N/A | 5.0*- Solids, 2.0 for H2O |
| PCB | Hexane | 10.0 for solids 5.0 for H2O 2.0 for H2O** |
| Pesticides | Hexane | 10.0 for solids 5.0 for H2O |
| Pesticides/TCLP | Hexane | 3.0 mL |
| PAH by HPLC | Acetonitrile | 1.0 mL |
| BNA – SIM | N/A | 2.0 mL - Solids & H2O |
| TPH | N/A | 1.0 |
| OPP | Hexane/Acetone | 2.0 |

*Requires high sensitivity mass spec tune (refer to NC-MS-0015 PAH by SIM)
** Michigan work requires a final volume of 2 mL.

| Final Volumes and exchange solvents if GPC cleanup is used CLP ONLY – SOLIDS ONLY | | | |
|---|---|---|---|
| Type | Exchange Solvent for GPC | Final Volume for GPC | Final Volume and solvent for Analysis |
| Semivolatiles | $CH_2Cl_2$ | 10 mL[1] | 0.5 mL $CH_2Cl_2$ - OLM03.1 |
| Semivolatiles | $CH_2Cl_2$ | 10 mL[1] | 2.5 mL $CH_2Cl_2$ - OLM04.2 |
| Pesticides | $CH_2Cl_2$ | 10 mL[1] | 5 mL, Hexane |

[1] Final volume for GPC may be 4 mL if a 2 mL sample loop is used

| Final volumes and exchange solvents if Florisil cleanup is used CLP ONLY | | | |
|---|---|---|---|
| Type | Exchange Solvent for Florisil | Final Volume for Florisil | Final Volume and solvent for Analysis |
| Pesticides | Hexane | 10 mL (2 mL aliquot used) | 2 mL, hexane |

| Final volumes and exchange solvents if both GPC and Florisil cleanup are used CLP ONLY | | | | | |
|---|---|---|---|---|---|
| Type | Exchange Solvent for GPC | Final Volume for GPC | Exchange Solvent for Florisil | Final Volume for Florisil | Final volume for analysis |
| Pesticides | Methylene Chloride | 10 mL | Hexane | 5 mL (2 mL aliquot used) | 2 mL, hexane |

Note: Different final volumes may be necessary to meet special client reporting limit requirements.

**Table 3**

**Surrogate Spiking Solutions**

| Analyte Group | Surrogate Spike Solution ID | Volume (mL) |
|---|---|---|
| BNA-SOLIDS | 100/150 ppm BNA | 0.5 |
| BNA / SIM | 100/150 ppm BNA | .2 / 0.02 |
| BNA-H2O | 100/150 ppm BNA | 0.2 |
| Pest | 0.2 ppm DCB/TCX | 1.0 |
| TPH | 40ng C9 | 1.0 |
| PCB | 0.2 ppm DCB/TCX | 1.0 |
| PAH | 1.0 ug/mL p-Terphenyl-d14<br>5.0 ug/mL Benzo(e)pyrene | 1.0 |
| OPP | 10 ug/mL Triphenyl Phosphate | 1.0 |

**Table 4**

**Matrix Spike and LCS Solutions**

| Analyte Group | Matrix Spike Solution ID | Volume (mL) |
|---|---|---|
| BNA-H2O, BNA-TCLP | 100 ppm BNA All-Analyte Spike & Restek Spike | 0.2 |
| BNA- SOLIDS | 100 ppm BNA All-Analyte Spike & Restek Spike | 0.5 |
| BNA / SIM | 100 ppm BNA All-Analyte Spike & Restek Spike | 0.2 / 0.02 |
| PEST – SOLIDS & H2O | Pest NPDES Spike | 1.0 |
| PEST TCLP | Pest TCLP Spike | 1.0 |
| PCB | 10 ppm PCB Spike | 1.0 |
| PAH | See Spike List – Table 6 | 1.0 |
| TPH | See Spike List – Table 6 | 1.0 |
| OPP | See Spike List – Table 6 | 1.0 |

**Table 5**
**Surrogate Spike Components**

| Type | Compounds | Solvent | Conc. (µg/mL) |
|---|---|---|---|
| BNA | 2-Fluorobiphenyl | Methanol | 100 |
| | Nitrobenzene-d5 | | 100 |
| | p-Terphenyl-d14 | | 100 |
| | 2-Fluorophenol | | 150 |
| | Phenol-d6 | | 150 |
| | 2,4,6-Tribromophenol | | 150 |
| | 1,2-Dichlorobenzene-d4 | | 100 |
| | 2-Chlorophenol-d4 | | 150 |
| Pest/PCB | Decachlorobiphenyl | Methanol Acetone | 0.2 |
| | Tetrachloro-m-xylene | | 0.2 |
| TPH | Nonane (C9) | Methanol | 40.0 |
| PAH | p-Terphenyl-d-14 | CH3CN | 1.0 |
| | Benzo(e)pyrene | | 5.0 |
| OPP | Triphenylphosphate | Acetone | 10.0 |

**Table 6**

| Matrix Spike Components | | | |
|---|---|---|---|
| Type | Compounds | Solvent | Conc. (µg/mL) |
| TCL BNA | Acenaphthene | Methanol | 100 |
| | 4-Chloro-3-Methylphenol | | 150 |
| | 2-Chlorophenol | | 150 |
| | 1,4-Dichlorobenzene | | 100 |
| | 2,4-Dinitrotoluene | | 100 |
| | 4-Nitrophenol | | 150 |
| | N-Nitroso-Di-n-Propylamine | | 100 |
| | Pentachlorophenol | | 150 |
| | Phenol | | 150 |
| | Pyrene | | 100 |
| | 1,2,4-Trichlorobenzene | | 100 |
| BNA TCLP | 1,4-Dichlorobenzene | Methanol | 100 |
| | 2,4-Dinitrotoluene | | 100 |
| | Hexachlorobenzene | | 100 |
| | Hexachlorobutadiene | | 100 |
| | Hexachloroethane | | 100 |
| | 2-Methylphenol | | 100 |
| | 3-Methylphenol | | 100 |
| | 4-Methylphenol | | 100 |
| | Nitrobenzene | | 100 |
| | Pentachlorophenol | | 100 |
| | Pyridine | | 100 |
| | 2,4,5-Trichlorophenol | | 100 |
| | 2,4,6-Trichlorophenol | | 100 |
| BNA NPDES | | Methanol | |

**Table 6**

**Matrix Spike Components**

| Type | Compounds | Solvent | Conc. (µg/mL) |
|---|---|---|---|
| | Acenaphthene | | 100 |
| | Acenaphthylene | | 100 |
| | Anthracene | | 100 |
| | Benzo(a)anthracene | | 100 |
| | Benzo(b)fluoranthene | Methanol | 100 |
| | Benzo(k)fluoranthene | | 100 |
| | Benzo(a)pyrene | | 100 |
| | Benzo(ghi)perylene | | 100 |
| | Benzyl butyl phthalate | | 100 |
| | Bis(2-chloroethyl)ether | | 100 |
| | Bis(2-chloroethoxy)methane | | 100 |
| | Bis(2-ethylhexyl)phthalate | | 100 |
| | Bis(2-chloroisopropyl)ether | | 100 |
| | 4-Bromophenyl phenyl ether | | 100 |
| | 2-Chloronaphthalene | | 100 |
| | 4-Chlorophenyl phenyl ether | | 100 |
| | Chrysene | | 100 |
| | Dibenzo(a,h)anthracene | | 100 |
| | Di-n-butylphthalate | | 100 |
| | 1,3-Dichlorobenzene | | 100 |
| | 1,2-Dichlorobenzene | | 100 |
| | 1,4-Dichlorobenzene | | 100 |
| | 3,3'-Dichlorobenzidine | | 100 |
| | Diethyl phthalate | | 100 |
| | Dimethyl phthalate | | 100 |

**Table 6**

**Matrix Spike Components**

| Type | Compounds | Solvent | Conc. (µg/mL) |
|---|---|---|---|
| | 2,4-Dinitrotoluene | | 100 |
| | 2,6-Dinitrotoluene | | 100 |
| | Di-n-octylphthalate | | 100 |
| | Fluoranthene | | 100 |
| | Fluorene | | 100 |
| | Hexachlorobenzene | | 100 |
| | Hexachlorobutadiene | | 100 |
| | Hexachloroethane | | 100 |
| | Indeno(1,2,3-cd)pyrene | | 100 |
| | Isophorone | | 100 |
| | Naphthalene | | 100 |
| | Nitrobenzene | | 100 |
| | N-Nitrosodi-n-propylamine | | 100 |
| | Phenanthrene | | 100 |
| | Pyrene | | 100 |
| | 1,2,4-Trichlorobenzene | | 100 |
| | 4-Chloro-3-methylphenol | | 100 |
| | 2-Chlorophenol | | 100 |
| | 2,4-Dichlorophenol | | 100 |
| | 2,4-Dimethylphenol | | 100 |
| | 2,4-Dinitrophenol | | 100 |
| | 2-Methyl-4,6-dinitrophenol | | 100 |
| | 2-Nitrophenol | | 100 |
| | 4-Nitrophenol | | 100 |
| | Pentachlorophenol | | 100 |

**Table 6**

**Matrix Spike Components**

| Type | Compounds | Solvent | Conc. (µg/mL) |
|---|---|---|---|
| | Phenol | | 100 |
| | 2,4,6-Trichlorophenol | | 100 |
| | Acetophenone | | 100 |
| | Atrazine | | 100 |
| | Caprolactum | | 100 |
| | Benzaldehyde | | 100 |
| | 1,1′-Biphenyl | | 100 |
| | Safrole | | 100 |
| | 1,4-Dioxane | | 100 |
| | Pronamide | | 100 |
| | p-Chlorobenzilate | | 100 |
| | Phenacetin | | 100 |
| | Ethyl methanesulfonate | | 100 |
| | 2-Picoline | | 100 |
| | Phorate | | 100 |
| | Quinoline | | 100 |
| Pest TCLP | Heptachlor | Methanol Acetone | 0.5 |
| | Heptachlor epoxide | | 0.5 |
| | Lindane | | 0.5 |
| | Endrin | | 0.5 |
| | Methoxychlor | | 1.0 |
| Pest NPDES /Pest | Aldrin | Methanol Acetone | 1.0 |
| | alpha-BHC | | 1.0 |
| | beta-BHC | | 1.0 |

| Table 6 | | | |
|---|---|---|---|
| Matrix Spike Components | | | |
| Type | Compounds | Solvent | Conc. (µg/mL) |
| | delta-BHC | | 1.0 |
| | gamma-BHC (Lindane) | | 1.0 |
| | 4,4'-DDD | | 1.0 |
| | 4,4'-DDE | | 1.0 |
| | 4,4'-DDT | | 1.0 |
| | Dieldrin | | 1.0 |
| | alpha-Endosulfan | | 1.0 |
| | beta-Endosulfan | | 1.0 |
| | Endosulfan Sulfate | | 1.0 |
| | Endrin | | 1.0 |
| | Heptachlor | | 1.0 |
| | Heptachlor Epoxide | | 1.0 |

| Diesel Range Organics (8015B) Spike | |
|---|---|
| **Compound** | **Final Concentration** |
| n-decane | 50 µg/ml |
| n-dodecane | 50 µg/ml |
| n-tetradecane | 50 µg/ml |
| n-hexadecane | 50 µg/ml |
| n-octadecane | 50 µg/ml |
| n-eicosane | 50 µg/ml |
| n-docosane | 50 µg/ml |
| n-tetracosane | 50 µg/ml |
| n-hexacosane | 50 µg/ml |
| n-octacosane | 50 µg/ml |

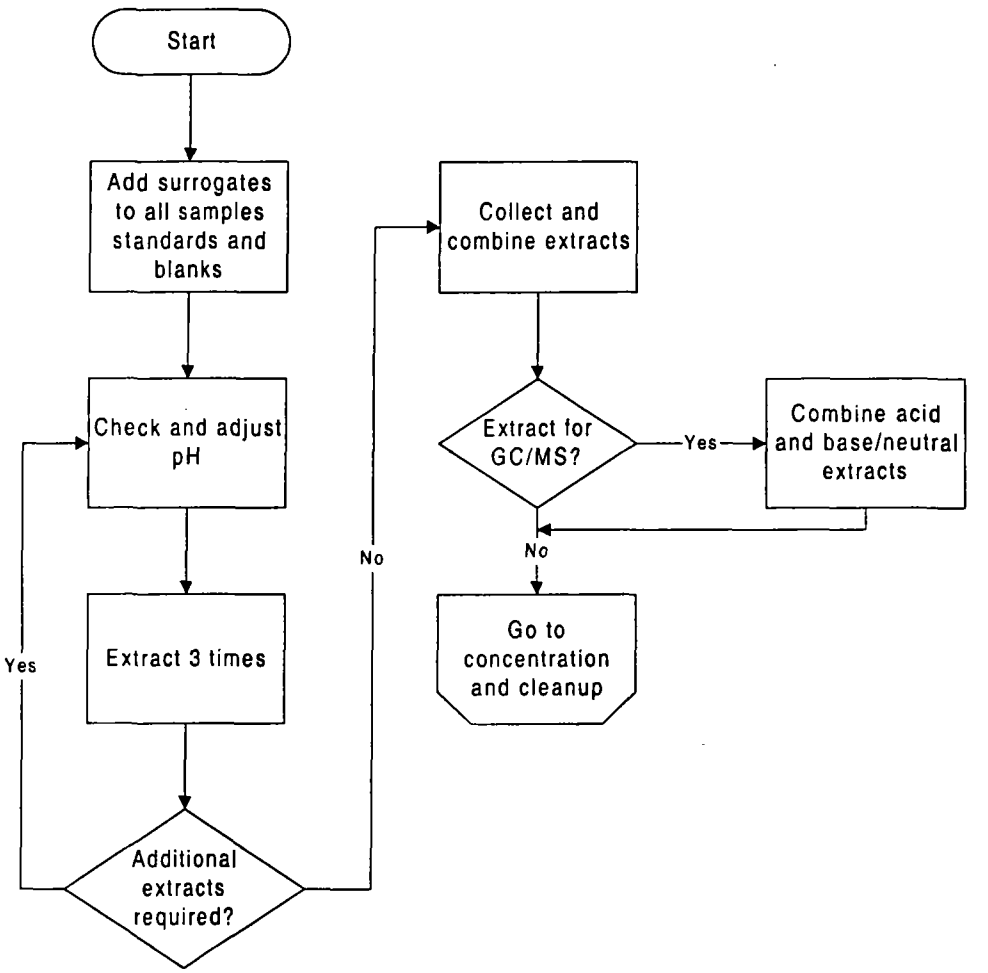
| Organophorphorous Pesticides (8141A) | |
|---|---|
| **Compound** | **Final Concentration** |
| dimethoate | 20 µg/mL |
| disulfoton | 20 µg/mL |

| | |
|---|---|
| famphur | 20 µg/mL |
| methyl parathion | 20 µg/mL |
| parathion (ethyl) | 20 µg/mL |
| phorate | 20 µg/mL |
| sulfotepp | 20 µg/mL |
| thionazin | 20 µg/mL |
| o,o,o-triethyl phosphorothioate | 20 µg/mL |
| triphenylphosphate (surrogate) | 20 µg/mL |

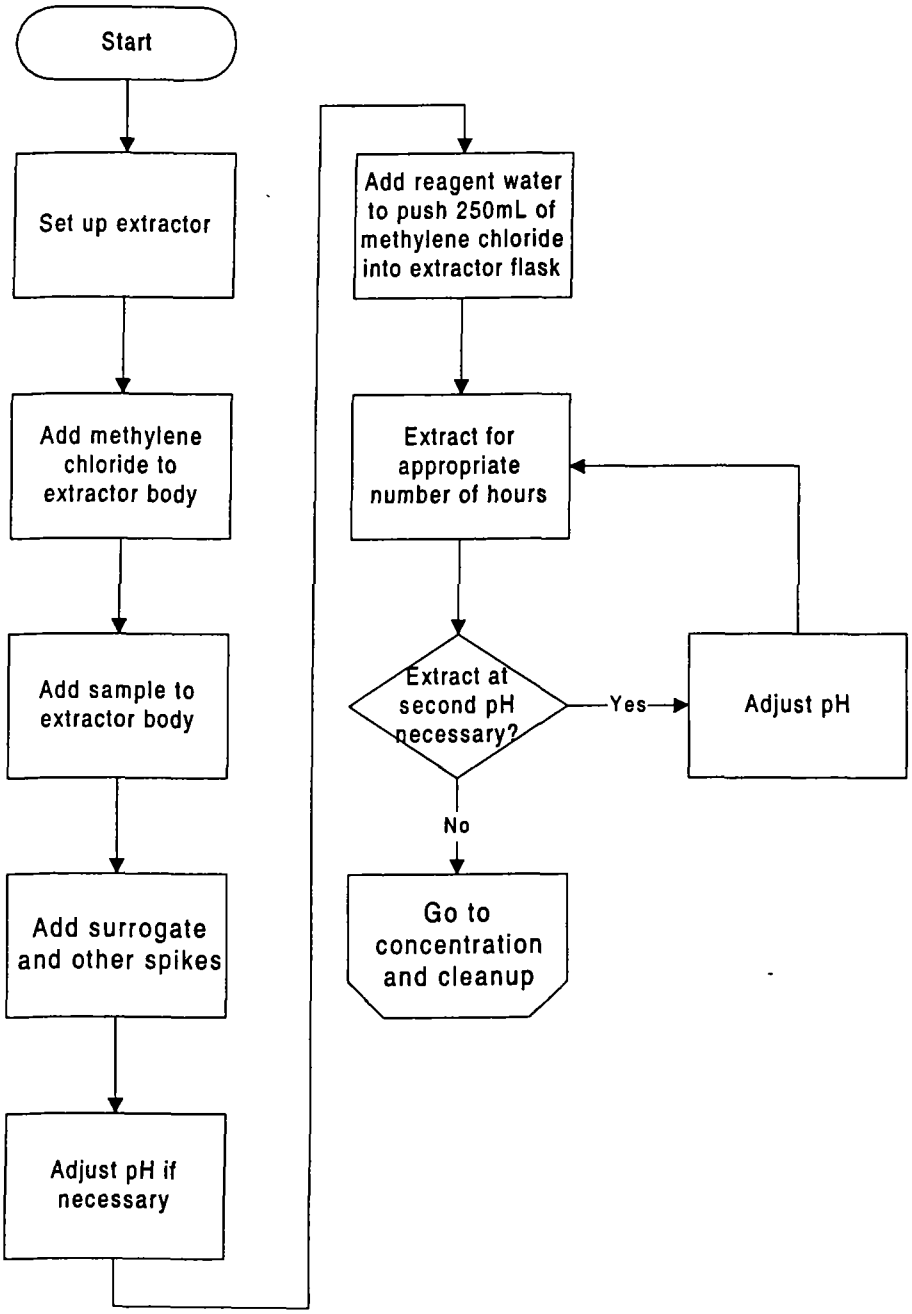
| Polynuclear Aromatic Hydrocarbons (8310) | |
|---|---|
| **Compound** | **Final Concentration** |
| Acenaphthylene | 10 µg/mL |
| Carbazole | 10 µg/mL |
| Naphthalene | 10 µg/mL |
| 1-Methylnaphthalene | 10 µg/mL |
| 2-Methylnaphthalene | 10 µg/mL |
| Acenaphthene | 10 µg/mL |
| Fluorene | 2 µg/mL |
| Phenanthrene | 2 µg/mL |
| Anthracene | 2 µg/mL |
| Fluoranthene | 2 µg/mL |
| Pyrene | 2 µg/mL |
| Benzo(a)anthracene | 2 µg/mL |
| Chrysene | 2 µg/mL |
| Benzo(a)pyrene | 2 µg/mL |
| Benzo(k)fluoranthene | 2 µg/mL |
| Benzo(a)pyrenek)fluoranthene | 2 µg/mL |
| Dibenzo(a,h)anthracene | 2 µg/mL |
| Benzo(g,h,I)perylene | 2 µg/mL |
| Indeno(1,2,3-cd)pyrene | 2 µg/mL |

17.5. Flow diagrams

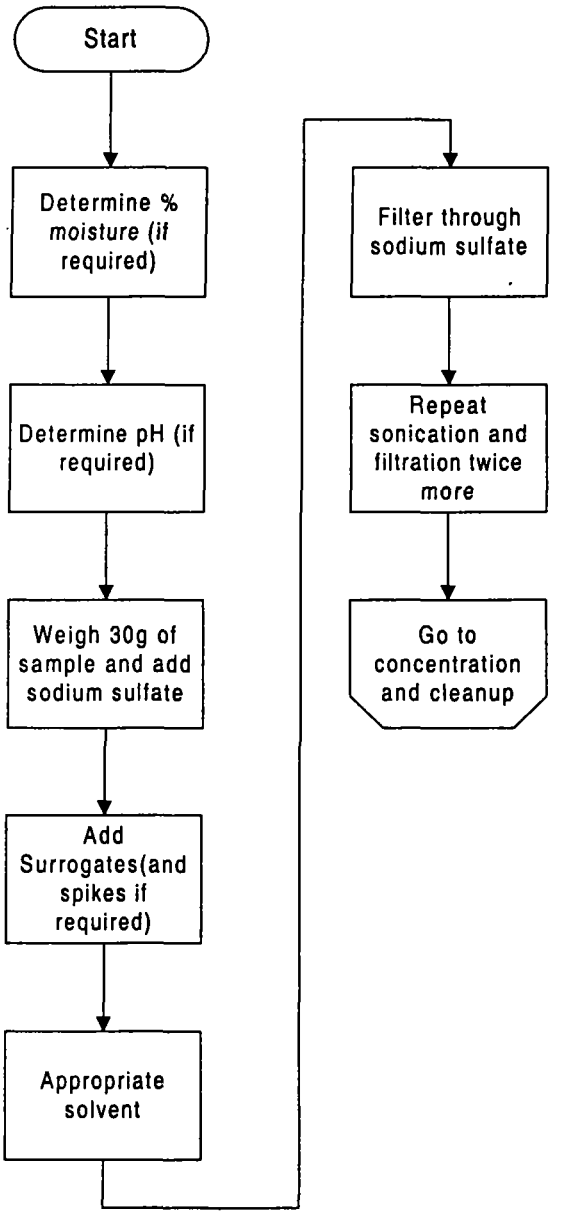
17.5.1. Separatory funnel extraction



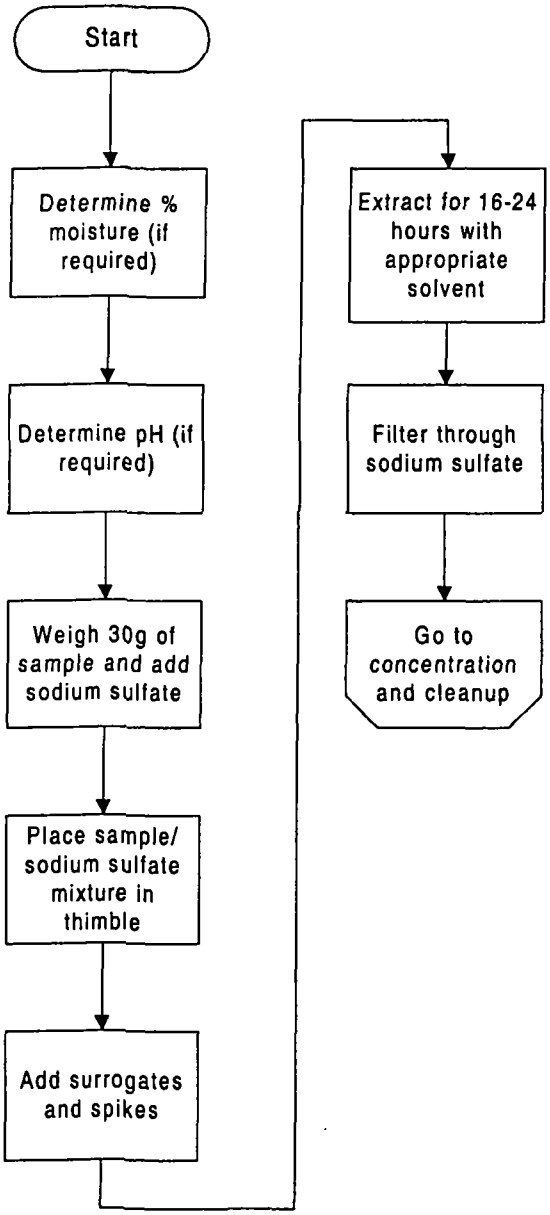

17.5.2. Continuous liquid/liquid extraction


Start
Set up extractor
Add methylene chloride to extractor body
Add sample to extractor body
Add surrogate and other spikes
Adjust pH if necessary
Add reagent water to push 250mL of methylene chloride into extractor flask
Extract for appropriate number of hours
Extract at second pH necessary?
Yes
Adjust pH
No
Go to concentration and cleanup

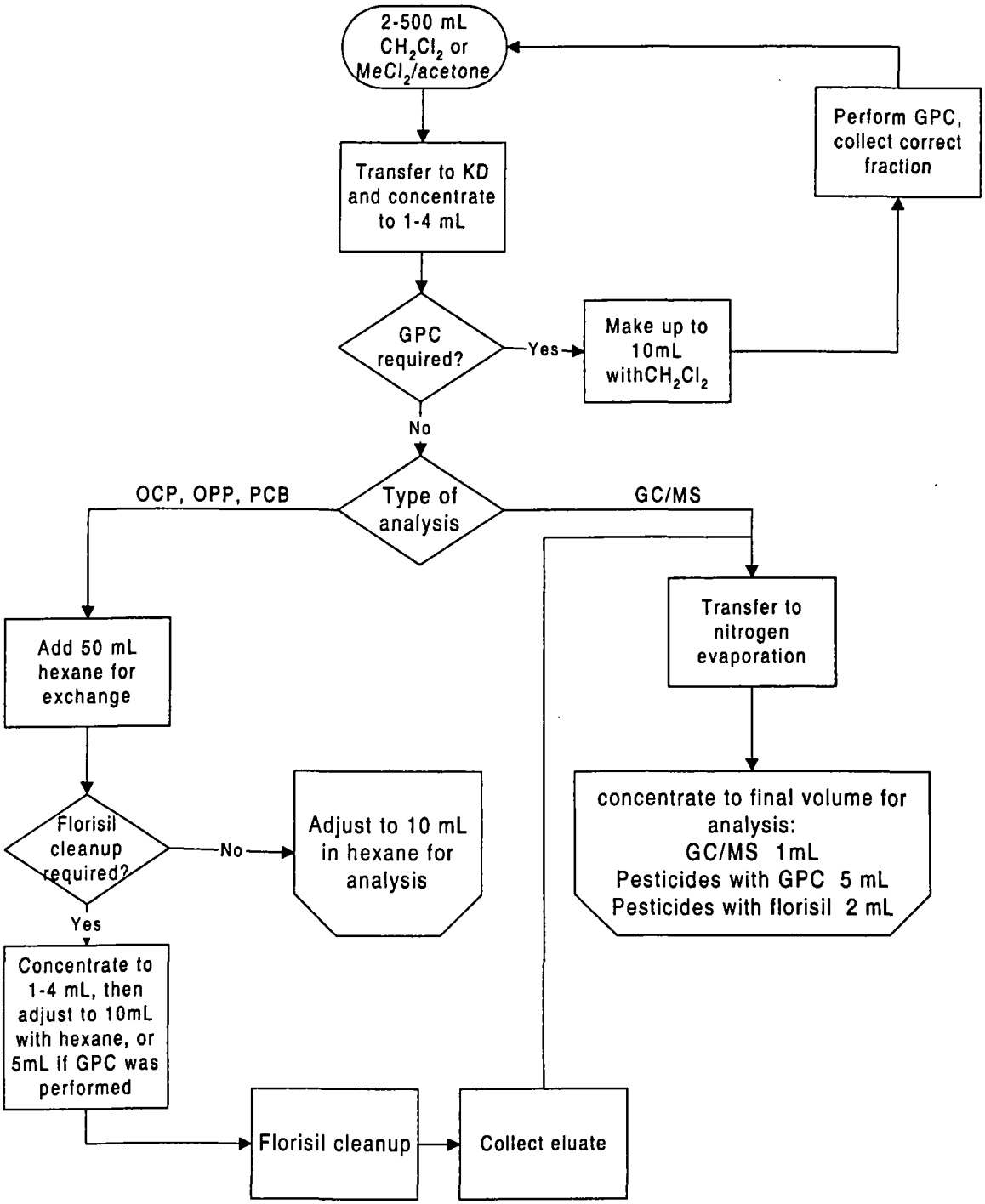
17.5.3. Sonication Extraction



17.5.4. Soxhlet extraction



17.5.5. Concentration and cleanup



## 18. SCOPE AND APPLICATION

This method is applicable to the extraction of chlorinated herbicides in waters, solids, oils, and TCLP extracts. Appropriate compounds for extraction by this method are listed in CORP-GC-0001, Appendix D, Gas Chromatography of Phenoxy Acid Herbicides based on Method 8151A.

## 19. SUMMARY OF METHOD

This method is based on SW846 method 8151A. Aqueous samples are hydrolyzed if esters and acids are to be determined, then washed with methylene chloride by a separatory funnel extraction. After acidifying the sample the free acids are extracted into diethyl ether. Solids are extracted into methylene chloride/ acetone by sonication. If esters and acids are to be determined, the extract is hydrolyzed and extracted into diethyl ether. For both soils and aqueous samples, the free acid herbicides in the ether extract are esterified. The final volume is adjusted to prepare the extract for gas chromatography.

## 20. DEFINITIONS

Refer to section 3 of the main body of this SOP.

## 21. INTERFERENCES

Refer to section 4 of the main body of this SOP.

## 22. SAFETY

22.1. Refer to section 5 of the main body this SOP for basic safety information.

22.2. DIAZOMETHANE is an extremely toxic gas with an explosion potential. Since the explosion potential is catalyzed by imperfections in glass, generation of diazomethane must be carried out in glassware free of scratches, cracks, chips and which does not have ground glass joints. Solutions of diazomethane will be kept at temperatures below 90°C. Diazomethane must be generated and handled in a fume hood.

22.3. Diethyl ether is extremely flammable. It also tends to form peroxides when exposed to air. The peroxides can present an explosion hazard, especially when the ether is concentrated.

22.4. Diethyl ether must be free of peroxides as demonstrated by EM (or equivalent) Quant test strips. This test can be done every time the ether is used or once per week if the bottle is marked with the test date(s).

22.5. Concentrated potassium hydroxide solution is highly caustic.

## 23. EQUIPMENT AND SUPPLIES

23.1. Refer to Section 6 of the main body of this SOP for basic extraction equipment and supplies. Additional equipment and supplies needed for this procedure are listed below.

23.2. Diazomethane generation apparatus

## 24. REAGENTS AND STANDARDS

24.1. Reagents are listed in Section 7 of the main body of this SOP. Additional reagents and standards needed for this procedure are listed below.

24.2. Reagents

24.2.1. Potassium hydroxide solution, 37% aqueous solution, (w/v): Dissolve 37 g of potassium hydroxide pellets in reagent water and dilute to 100 mL. **Caution:** Considerable heat will be generated. Other volumes of solution may be made up as convenient.

24.2.2. Toluene, reagent grade

24.2.3. 2-(2-Ethoxyethoxy)ethanol, trade name Carbitol, 98%+purity

24.2.4. Diazald, 99% purity

24.2.5. Sodium sulfate, $Na_2SO_4$, Anhydrous, granular, acidified: Heat sodium sulfate in a shallow tray at 400°C for a minimum of 4 hours to remove phthalates and other interfering organic substances. In a large beaker, acidify by slurrying 500 g sodium sulfate with just enough diethyl ether to cover. Add 20 mL of concentrated sulfuric acid and mix thoroughly. Place the mixture on a steam bath in a hood to evaporate the ether, or allow the ether to evaporate overnight. Larger or smaller batches of acidified sodium sulfate may be prepared using the reagents in the same proportions.

24.2.6. Sodium Chloride, NaCl

24.2.7. BF3-Methanol, Boron trifluoride-MeOH, lab use only

24.2.8. Diethyl ether, reagent grade.

24.2.9. Methanol, reagent grade.

24.2.10.Silica gel

24.2.11.2% methanolic KOH, semi-conductor grade

24.3. Standards

24.3.1. Surrogate Standard
See Table A3.

24.3.2. Matrix Spike and LCS standard
See Table A4.

## 25. SAMPLE COLLECTION PRESERVATION AND STORAGE

25.1. Sample collection and storage is described in Section 8 of the main body of this SOP.

## 26. QUALITY CONTROL

26.1. Refer to Section 9 of the main body of this SOP for Quality control procedures.

## 27. CALIBRATION AND STANDARDIZATION

Not applicable

## 28. PROCEDURE

28.1. Preparation of Aqueous Samples

28.1.1. Weigh the sample bottle and pour approximately 500 ml (100 mL for TCLP leachates) into a 1 liter wide-mouth amber jar. Reweigh the bottle and record the sample volume on the benchsheet, assuming a density of 1.0. Alternatively, measure 500 ml in a graduated cylinder. If less than 500 mL was used, reagent water may be added to make the volume up to 500 mL.

Note: Aqueous samples must be determined volumetrically for Ohio VAP samples.

28.1.2. Spike each sample blank, LCS and MS with 1.0 mL of DCAA surrogate solution. Spike matrix spikes and LCS with 1 mL of herbicide matrix spiking solution. (Refer to tables A1 and A2 )

28.1.3. Add 60-80 g of NaCl to the sample and shake to dissolve the salt.

28.1.4. Hydrolysis

**Use this step only if herbicide esters in addition to herbicide acids are to be determined. This is normally the case. If the herbicide esters are not to be determined, omit this step and go to 28.1.10.**

Add 3 mL of 10N NaOH to the sample, seal and shake. Check the pH of the sample with pH paper. If the pH of the sample is not ≥12 adjust to ≥12 by adding more NaOH. Let the sample sit at room temperature for 2 hours to complete the hydrolysis.

28.1.6. Add 300 mL of methylene chloride to the amber jar.

28.1.7. Prior to placing samples in tumbler, the samples should be shaken or rotated vigorously for 2 minutes, venting as necessary. Place the samples in tumbler and allow them to tumble for one (1) hour. Allow the organic layer to separate from the aqueous layer. If an emulsion layer greater than one third of the solvent layer forms, use mechanical techniques to complete the phase separation. Suggested techniques are stirring, filtration through glass wool and centrifugation.

28.1.8. Pour contents of amber jar into a pre-rinsed teflon sep funnel.

28.1.9. Discard the **methylene chloride** phase.

28.1.10. Add 6 mL of cold (4°C) 1:1 sulfuric acid to the sample. Seal, and shake to mix. Check the pH of the sample with pH paper. If the pH is not ≤ 2, and more acid to adjust the pH to ≤ 2.

***Caution: Addition of acid may cause heat and / or pressure build up.***

28.1.11. Add 100 mL diethyl ether to the sample and extract by shaking or rotating vigorously for 10 minutes, venting as necessary. Allow the organic layer to separate from the aqueous layer. If an emulsion layer greater than one third of the solvent layer forms, use mechanical techniques to complete the phase separation. Suggested techniques are stirring, filtration through glass wool and centrifugation.

28.1.12. Drain the aqueous layer into a clean flask or beaker. Collect the ether phase in a clean flask or bottle containing approximately 10g of acidified anhydrous sodium sulfate.

28.1.13. Return the aqueous phase to the separatory funnel, add 100 mL diethyl ether and repeat the extraction procedure a second time, combining the ether extracts. Repeat the extraction a third time with

100 mL diethyl ether. Discard the aqueous phase after the third extraction.

28.1.14. Allow the extract to remain in contact with the sodium sulfate for at least 2 hours, shaking periodically. (May be left overnight). The drying step is critical: if the sodium sulfate solidifies in a cake, add a few additional grams of acidified sodium sulfate. The amount of sodium sulfate is sufficient if some free flowing crystals are visible when the flask or bottle is swirled or shaken.

28.1.15. Proceed to section 28.5, concentration.

28.2. Extraction of soil and sediment samples

28.2.1. Decant and discard any water layer on a sediment/soil sample. Record and document if a water layer was discarded on the benchsheet. Homogenize the sample by mixing it thoroughly in the container. If this is not possible place the sample in clean beaker and homogenize. Upon completion of homogenization in beaker return sample to original container. Discard foreign objects such as sticks, leaves and rocks, unless extraction of this material is required by client. If the sample consists primarily of foreign materials consult with the client (via the Project Manager or Administrator).

28.2.2. Weigh 50.0 g of moist solid sample into a clean glass jar. Use 50 g of sodium sulfate for the Method Blank and the LCS. Acidify the sample with 5 mL of concentrated HCl.

28.2.3. There should be a small amount of liquid phase. If not, add reagent water until there is. Stir well with a spatula. (Note: This is not necessary for the method blank or LCS)

28.2.4. After 15 minutes, stir with a spatula and check the pH of the liquid phase. Add more acid if necessary to bring the pH to <2, repeating the stirring and standing time after each acid addition. (Note: The pH of the method blank and LCS are not determined.)

28.2.5. Add 60 g of acidified sodium sulfate and mix well. The sample should be free flowing. If not, add more sodium sulfate.

28.2.6. Spike each sample blank, LCS and MS with 1.0 mL of DCAA surrogate solution. Spike matrix spikes and LCS with 1 mL of herbicide matrix spiking solution. (Refer to tables A1 and A2)

28.2.7. Add a minimum of 100 mL of 1:1 methylene chloride:acetone to the beaker or 100 mL of methylene chloride for long list (dinoseb).

28.2.8. Place the bottom surface of the appropriate disrupter horn tip approximately ½ inch below the surface of the solvent, but above the sediment layer.

28.2.9. Sonicate for 3 minutes, making sure the entire sample is agitated.

28.2.10. Loosely plug the stem of a 75 mm x 75 mm glass funnel with glass wool and/or line the funnel with filter paper. Add 10-20 g of anhydrous sodium sulfate to the funnel cup.

28.2.11. Place the prepared funnel on a collection apparatus. If the herbicide esters are *not* to be determined, the collection apparatus is a bottle or flask containing approximately 10g of anhydrous acidified sodium sulfate. If the herbicide esters *are* to be determined, (normally the case) the collection apparatus is glassware suitable for the hydrolysis step, typically a KD flask or Turbovap tube.

28.2.12. Decant and filter extracts through the prepared funnel into the collection apparatus.

28.2.13. Repeat the extraction two more times with additional 100 mL minimum portions of the appropriate solvent each time. Decant off extraction solvent after each sonication. On the final sonication pour the entire sample (sediment and solvent) into the funnel and rinse with an additional 10 mL-20 mL of the methylene chloride/acetone.

**Note:** Alternatively, the three extracts may be collected together and then filtered through the sodium sulfate.

28.2.14. If the herbicide esters are not to be determined, dry the extract as described in 28.4 or go to cleanup, section 28.3. If the herbicide esters are to be determined (normally the case) proceed to section 28.2.15

28.2.15. Add 5 mL of 37% aqueous potassium hydroxide and 30 mL of water to the extract. Check the pH with pH paper. If the pH is not $\geq$12, adjust with additional KOH.

28.2.16. Heat on a water bath at 60-65°C for 2 hours. Allow to cool. Higher temperatures, up to 90°C, may be used if needed to remove the ether layer within 2 hours.

28.2.17. Transfer the solution to a separatory funnel and extract three times with 100 mL portions of methylene chloride. **Discard the methylene chloride phase.** The aqueous solution contains the herbicides.

28.2.18. Adjust the pH of the solution to $\leq 2$ with 1:1 sulfuric acid.

28.2.19. Extract three times with 60 mL diethyl ether.

28.2.20. Proceed to section 28.3, Cleanup, if required, or Section 28.4, Extract drying.

28.3. Cleanup

This cleanup step may be necessary if the procedure for determining the herbicide acids only is being followed. (See section 28.2.14) It is not normally required if the acids and esters are being determined. (The usual case.) If cleanup is not required, proceed to section 28.4, Extract drying.

28.3.1. Prepare 45 mL of basic extraction fluid by mixing 30 mL of reagent water with 15 mL of 37% KOH. Use three 15 mL portions of this fluid to partition the extract from section 28.2.12 or 28.2.20, using a small separatory funnel. **Discard the organic phase.**

28.3.2. Adjust the pH of the solution to $\leq 2$ with cold (4°C) sulfuric acid. (1:1). Extract once with 40 mL diethyl ether and twice with 20 mL diethyl ether.

***Caution: Addition of acid may cause heat and / or pressure build up.***

28.4. Extract drying

28.4.1. Pour the extracts through a funnel containing acidified sodium sulfate into a flask or bottle containing approximately 10 g acidified sodium sulfate. Rinse the funnel with a little extra diethyl ether.

28.4.2. Allow the extract to remain in contact with the sodium sulfate for at least 2 hours, shaking periodically. (May be left overnight). The drying step is critical: if the sodium sulfate solidifies in a cake, add a few additional grams of acidified sodium sulfate. The amount of sodium sulfate is sufficient if some free flowing crystals are visible when the flask or bottle is swirled or shaken. Proceed to section 28.5, concentration.

28.5. Concentration

28.5.1. Transfer the ether extract into a Turbovap concentrator tube or a 500 mL K-D flask equipped with a 10 mL concentrator tube. Use a stirring rod to crush the caked sodium sulfate during transfer. Rinse the flask or bottle with 20-30 mL ether to complete transfer.

28.5.2. Attach a three ball Snyder column to the K-D apparatus, prewet the column with a few mL of ether from the top, and place the apparatus on a water bath at approximately 60°C. At the proper rate of distillation, the balls of the column will chatter, but the chambers will not flood. When the apparent volume reaches 2 mL, remove from the water bath and allow to completely cool.

28.5.3. For TCLP extracts only, add 4 mL of toluene to the K-D (buffer reacts with diazald solution used in esterification).

28.5.4. Remove TCLP extracts at approximately 2 mL when boiling slows and only toluene is remaining. Cool and cap in CT.

28.5.5. Carefully disassemble the concentrator tube and rinse the lower glass joint with a small amount of diethyl ether.

28.5.6. The extract is now ready for esterification by the Diazomethane Bubbler Method (28.7) or the TCLP esterification by Boron Triflouride Method (28.8).

28.6. Esterification (Bubbler Method)

28.6.1. Assemble the diazomethane apparatus (see figure below) in a hood. Add 25-30 mL of diethyl ether to tube 1. Add 1.5 mL 37% KOH, 1 mL Carbitol, and 1 mL of ether and 3-4 g of diazald to tube 2.

28.6.2. Place the tip of the disposable pipette into the vial containing the first sample extract. Apply nitrogen flow (approx. 10 mL/min) to bubble diazomethane through the sample extract for about 4-5 minutes. Replace the disposable pipette and place the tip into the vial containing the second extract. Replace Tube 2 solution after second extract.

28.6.3. Allow the extracts to stand for 20 minutes, then add approximately 0.2 g of silica gel to each extract. Allow to stand for an additional 20 minutes.

28.6.4. Adjust the volume to 10 mL with hexane. The sample is now ready for gas chromatography.

28.6.5. A routine 10X dilution occurs on final extracts for all samples. Due to a QuantIMS limitation, the dilution factor field in QuantIMS cannot be used when a dilution is routine, because the dilution factor is automatically applied to all reference values creating reporting problems. For the herbicide analysis, the extract volume will be 10mL and an aliquot at 10X dilution will be analyzed. The final extract volume recorded on the laboratory bench sheet will be recorded as 100mL to avoid using the dilution factor field in QuantIMS.

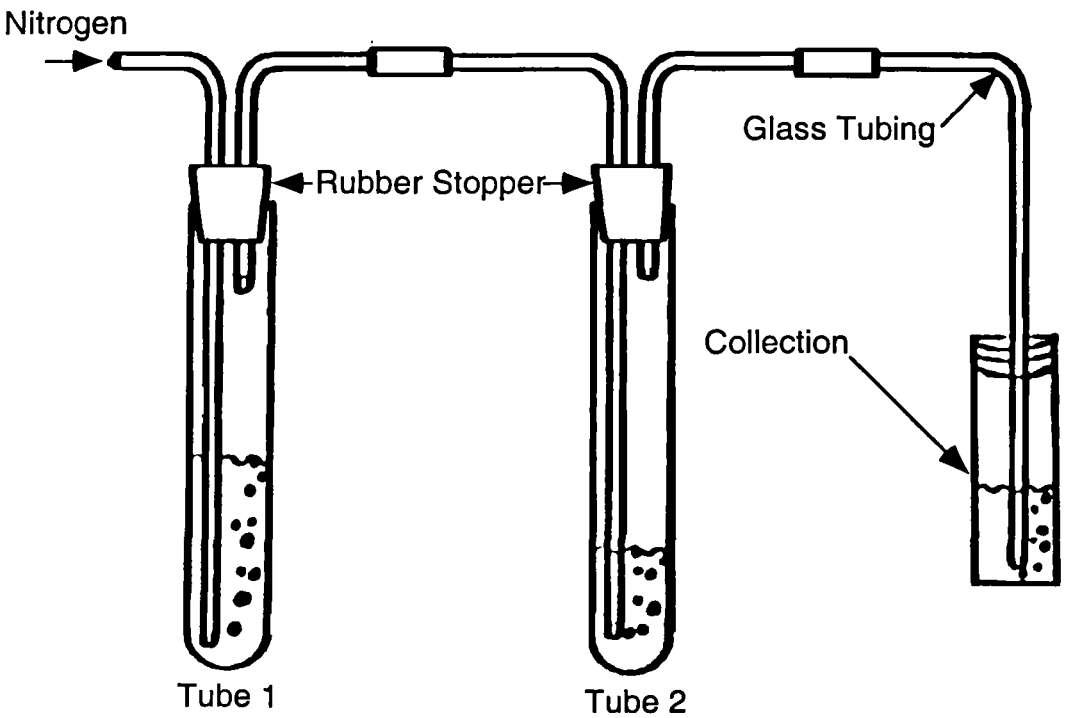
28.7. Exterification by Boron trifluoride (TCLP extracts only).

28.7.1. To the concentrator tube with the extract, add 2 mL of Boron trifluoride. Place a two-ball micro-Snyder column on the concentrator tube and place in the Hot-Blok water bath adjusted to 35-40°C for 60 minutes. Remove and let cool for approximately ten minutes.

28.7.2 With a 10 mL graduated disposable 5-3/4" pipette 4.5 mL of 5% neutral sodium sulfate and place it in the concentrator tube. Seal with a tight fitting ground glass stopper. Vortex the mixture for one minute. Let stand for ten minutes to settle. With a 5-3/4" disposable pipette, withdraw the bottom aqueous layer into a 16 x 100 culture tube for proper disposal.

28.7.3 Prepare a clean up column in a 5-3/4" disposable pipette by placing a small amount of glass wool in the narrow end of the pipette and add about ½ inch – 1 inch of florisil and sodium sulfate each. Leave about a 1 inch gap at the top. Place the extract in the clean-up column and gently force it through by using a pipette bulb into a small test tube. **Care should be taken to avoid channeling.** Rinse the concentrator tube with 1-2 mL of toluene. Transfer the column rinsate into the test tube. Rinse the column with additional toluene. There should be approximately 4 mL collected in the test tube. Bring the final volume to 10 mL with toluene by visually comparing it to a calibrated collection tube.

**Note:** It is critical that all toluene is retained and no water should enter the column.




## 29. DATA ANALYSIS AND CALCULATIONS

Not applicable

## 30. METHOD PERFORMANCE

Refer to CORP-GC-0001 for details of method performance.

## 31. POLLUTION PREVENTION

Refer to section 14 of the main body of this SOP.

## 32. WASTE MANAGEMENT

Refer to section 15 of the main body of this SOP.

## 33. REFERENCES

33.1. SW846, Test Methods for Evaluating Solid Waste, Third Edition, Update III, December 1996, Chlorinated Herbicides, Method 8151A.

## 34. MISCELLANEOUS

34.1. Modifications from Reference Method

34.1.1. Directions to add sufficient reagent water to the soil sample so that the pH can be measured have been added (Section 11.1.2)

34.1.2. The bubbler esterification method uses methanolic KOH in place of the aqueous KOH / carbitol mixture recommended in method 8150B. This has been found to provide a more effective and reliable esterification.

34.2. Modifications from previous revisions
References have been updated

34.3. Tables

**Table A1**
**Herbicide Surrogate Spiking Solutions**

| Analyte Group | Surrogate Spike Solution ID | Volume (mL) |
|---|---|---|
| Herbicides | Herbicides Water | 1.0 |
| Herbicides | Herbicides Soil | 1.0 |

**Table A2**
**Herbicide Matrix Spike and LCS Solutions**

| Analyte Group | Matrix Spike Solution ID | Volume (mL) |
|---|---|---|
| Herbicides | Herbicides MS-Soil | 1.0 |
| Herbicides | Herbicides MS-Water | 1.0 |

**Table A3**

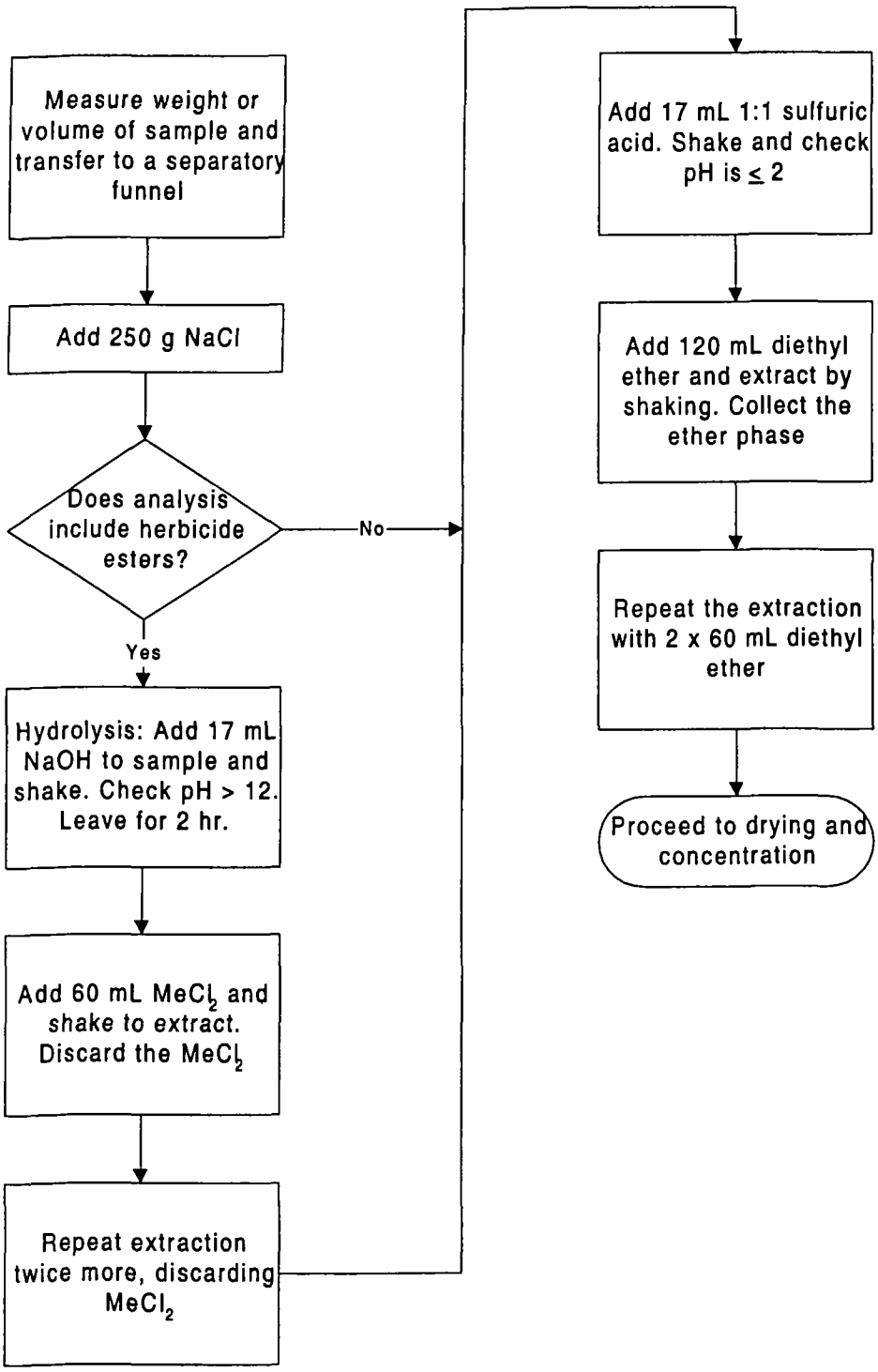
| Herbicide Surrogate Spike Components | | | |
|---|---|---|---|
| Type | Compounds[1] | Solvent | Conc. (ug/mL) |
| Herbicides WS | 2,4-DCAA | Acetone | 2 |
| Herbicides SS | 2,4-DCAA | Acetone Methanol | 20 |

[1]The surrogate is spiked as the free acid

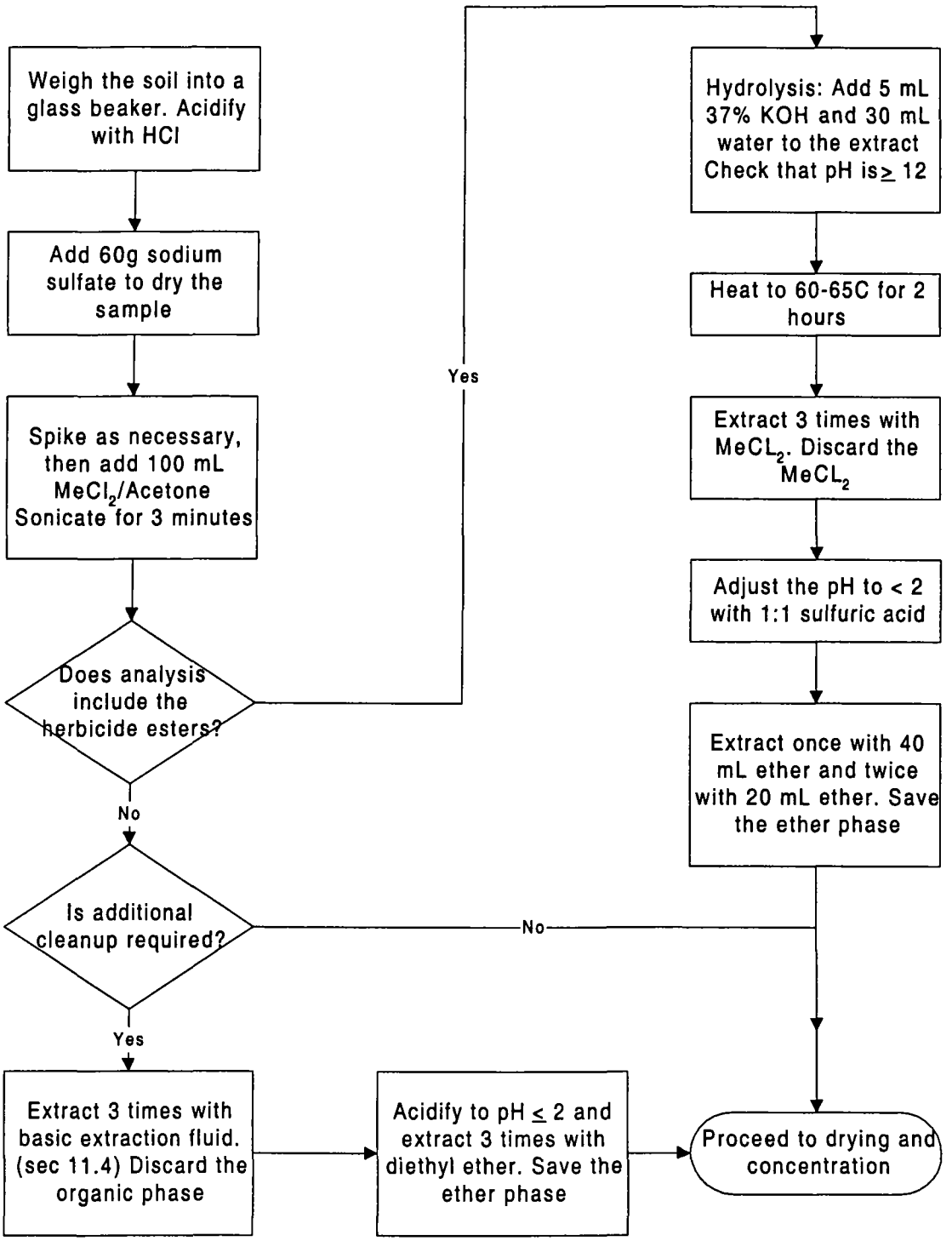
| Table A4 | | | | |
|---|---|---|---|---|
| Herbicide Matrix Spike Components | | | | |
| Type | Compounds[1] | Compounds[1] Solvent | Soil Conc. (ug/mL) Solvent | Water Conc. (ug/mL) |
| Herbicides MS | 2,4-D | Acetone | 20 Methanol | 2 |
| | 2,4-DB | | 20 | 2 |
| | 2,4,5-TP (Silvex) | | 5 | 0.5 |
| | Dalapon | | 10 | 1 |
| | Dicamba | | 10 | 1 |
| | Dichloroprop | | 10 | 1 |
| | Dinoseb | | 3 | .3 |
| | 2,4,5-T | | 5 | 0.5 |

[1]The herbicide spiking solution contains the herbicides as the free acids.

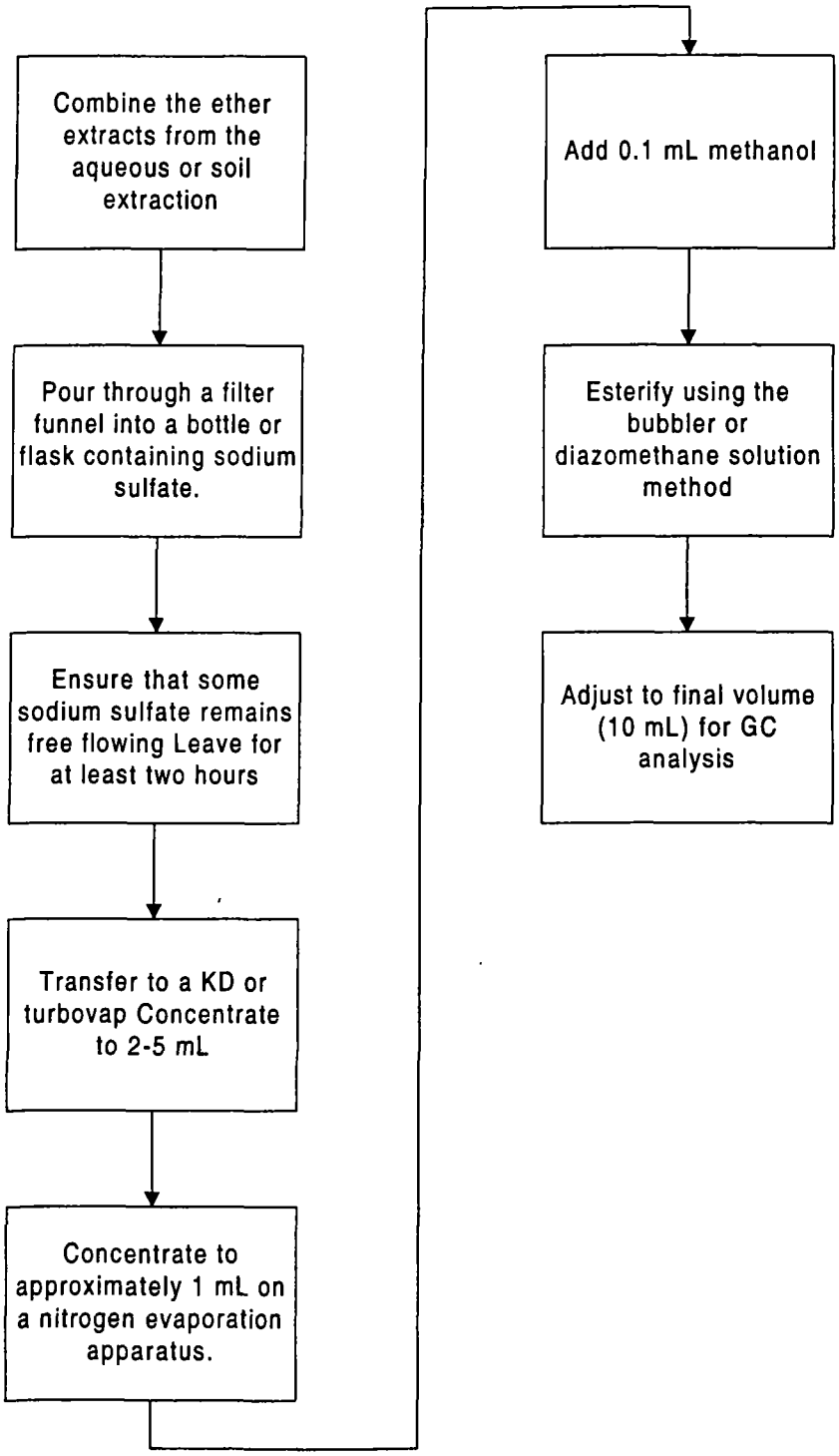
## Extraction of Aqueous Samples



## Extraction of Soils and Sediments



## Drying, Concentration and Esterification



# STL NORTH CANTON STANDARD OPERATING PROCEDURE

## TITLE: GC/MS ANALYSIS BASED ON METHODS 8270C AND 625

## (SUPERSEDES: Revision 2.3, 02/15/01)

Prepared by: _____ Date

Reviewed by: _____
Technology Specialist Date

Approved by: _____
Quality Assurance Manager Date

Approved by: _____
Environmental Health and Safety Date

Approved by: _____
Laboratory Director Date

Approved by: _____ 6/4/01
Coroporate Technology Date

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# 1. SCOPE AND APPLICATION

1.1 This method is based upon SW846 8270C, and is applicable to the determination of the concentration of semivolatile organic compounds in extracts prepared from solid and aqueous matrices. The modifications presented in Attachment A may be followed for analysis of wastewater following method 625. Direct injection of a sample may be used in limited applications. Refer to Tables 1, 2, 3 and 4 for the list of compounds applicable for this method. Note that the compounds are listed in approximate retention time order. Additional compounds may be amenable to this method. If non-standard analytes are required, they must be validated by the procedures described in section 13 before sample analysis.

1.2 The following compounds may require special treatment when being determined by this method:

- Benzidine can be subject to oxidative losses during solvent concentration and exhibits poor chromatography. Neutral extraction should be performed if this compound is expected.
- Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition.
- N-Nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be distinguished from diphenylamine.
- Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, benzoic acid, 2-nitroaniline, 3-nitroaniline, 4-chloroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.
- Hexachlorophene is not amenable to analysis by this method.
- 3-Methylphenol cannot be separated from 4-methylphenol by the conditions specified in this method.

1.3 The standard reporting limit (SRL) of this method for determining an individual compound is approximately 0.33 mg/kg (wet weight) for soil/sediment samples, 1 - 200 mg/kg for wastes (dependent on matrix and method of preparation), and 10 µg/L for groundwater samples. Some compounds have higher reporting limits. Refer to Tables 1 and 2 for specific SRLs. Reporting limits will be proportionately higher for sample extracts that require dilution.

1.4 The associated LIMS codes are QL (8270C) and DP (625).

## 2 SUMMARY OF METHOD

2.1 Aqueous samples are extracted with methylene chloride using a separatory funnel, a continuous extractor or Accelerated One-Step™. Solid samples are extracted with methylene chloride / acetone using sonication, soxhlet, accelerated soxhlet or pressurized fluid extraction. Waste dilution is used for samples that are miscible with the solvent. The extract is dried, concentrated to a volume of 1 mL, and analyzed by GC/MS. Extraction procedures are detailed in SOP# CORP-OP-0001. Qualitative identification of the parameters in the extract is performed using the retention time and the relative abundance of characteristic ions. Quantitative analysis is performed using the internal standard technique with a single characteristic ion.

## 3 DEFINITIONS

3.1 CCC (Calibration Check Compounds) - A subset of target compounds used to evaluate the calibration stability of the GC/MS system. A maximum percent deviation of the CCC's is specified for calibration acceptance.

3.2 SPCC (System Performance Check Compounds) - Target compounds designated to monitor chromatographic performance, sensitivity, and compound instability or degradation on active sites. Minimum response factors are specified for acceptable performance.

3.3 Batch - The batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same time period. The Quality Control batch must contain a matrix spike / spike duplicate (MS/MSD), a Laboratory Control Sample (LCS), and a method blank. In some cases, at client request, the MS/MSD may be replaced with a matrix spike and sample duplicate. Batches are defined at the sample preparation stage. Batches should be kept together through the whole analytical process to the extent possible, but it is not mandatory to analyze prepared extracts on the same instrument or in the same sequence. Refer to the STL North Canton QC Program document (QA-003) for further details of the batch definition.

3.4 Method Blank - An analytical control consisting of all reagents, internal standards and surrogate standards, that is carried through the entire analytical procedure. The

method blank is used to define the level of laboratory background and reagent contamination.

3.5 LCS (Laboratory Control Sample) - A blank spiked with the parameters of interest that is carried through the entire analytical procedure. Analysis of this sample with acceptable recoveries of the spiked materials demonstrates that the laboratory techniques for this method are acceptable.

3.6 MS (Matrix Spike)- aliquot of a matrix (water or soil) fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

3.7 MSD (Matrix Spike Duplicate)- a second aliquot of the same sample as the matrix spike (above) that is spiked in order to determine the precision of the method.

## 4 INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. If an interference is detected it is necessary to determine if the source of interference is in the preparation and/or cleanup of the samples; then take corrective action to eliminate the problem.

4.2 The use of high purity reagents, solvents, and gases helps to minimize interference problems.

4.3 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature of the sample.

4.4 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed with solvent between samples. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross contamination.

4.5 Phthalate contamination is commonly observed in this analysis and its occurrence should be carefully evaluated as an indicator of a contamination problem in the sample preparation step of the analysis.

## 5 SAFETY PRECAUTIONS

5.1 Procedures shall be carried out in a manner that protects the health and safety of all STL North Canton associates. The following requirements must be met:

5.1.1 Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents and reagents are being handled. Disposable gloves that have become contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.1.2 The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the MSDS files maintained in the laboratory. The following specific hazards are known:

5.1.3 Chemicals that have been classified as carcinogens, or potential carcinogens, under OSHA include: Benzo(a)anthracene, benzidine, 3,3'-dichlorobenzidine, benzo(a)pyrene, dibenzo(a,h)anthracene, and n-nitrosodimethylamine. Primary standards should be purchased in solution. If neat materials must be obtained, they shall be handled in a hood.

5.1.4 Exposure to chemicals must be maintained as low as reasonably achievable; therefore, unless they are known to be non-hazardous, all samples should be opened, transferred, and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers should be kept closed unless transfers are being made.

5.1.5 All work must be stopped in the event of a known or potential compromise to the health and safety of a STL North Canton associate. The situation must be reported immediately to a laboratory supervisor.

## 6 EQUIPMENT AND SUPPLIES

6.1 Gas Chromatograph/Mass Spectrometer System: An analytical system complete with a temperature-programmable gas chromatograph suitable for split/splitless injection and all required accessories, including syringes, analytical columns, and gases. The capillary column should be directly coupled to the source.

6.2 Column: 30 m x 0.32 mm I.D. (or 0.25 mm I.D.) 0.5-µm film thickness silicon-coated fused-silica capillary column (J & W Scientific DB-5.625 or equivalent). Alternate columns are acceptable if they provide acceptable performance.

6.3 Mass Spectrometer: Capable of scanning from 35 to 500 AMU every one second or less, using 70 volts (nominal) electron energy in the electron impact ionization mode.

The mass spectrometer must be capable of producing a mass spectrum for decafluorotriphenylphosphine (DFTPP) which meets all of the criteria in Table 6 when 50 ng of the GC/MS tuning standard is injected through the GC.

6.4 GC/MS Interface: Any GC-to-MS interface that gives acceptable calibration points and achieves acceptable tuning performance criteria may be used.

6.5 Data System: A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as the Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIH Mass Spectral Library is recommended.

6.6 Syringe: 10 µL Hamilton Laboratory grade syringes or equivalent.

6.7 Carrier gas: Ultra high purity helium.

## 7 REAGENTS AND STANDARDS

7.1 A minimum five point calibration curve is prepared. The low point should be at or below the reporting limit. Refer to Tables 12 and 13 for typical calibration levels for all analytes. Other calibration levels may be used, depending on instrument capability, but the low standard must support the reporting limit and the high standard defines the range of the calibration.

7.2 An Internal Standard solution is prepared. Compounds in the I.S. Mix are: acenaphthene-d10, chrysene-d12, 1,4-dichlorobenzene-d4, naphthalene-d8, perylene-d12, and phenanthrene-d10.

7.2.1 Internal Standards are added to all standards and extracts to result in 8 ng or 40ng injected onto the column. For example, if the volume of an extract used was 200 µL, 20 µL of a 400 µg/mL internal standard solution would be added for a 1 µL injection.

7.3 Surrogate Standard Spiking Solution: Prepare as indicated in the preparative methods. See appropriate preparation SOP. Surrogate compounds and levels are listed in Table 11.

7.4 GC/MS Tuning Standard: A methylene chloride solution containing 10 µg/mL or 50 µg/mL of decafluorotriphenylphosphine (DFTPP) is prepared. Pentachlorophenol,

benzidine, and DDT, should also be included in the Tuning Standard at 10 µg/mL or 50 µg/mL.

7.5 Laboratory Control Spiking Solution: Prepare as indicated in the preparative methods. See appropriate preparation SOP. LCS compounds and levels are listed in Tables 9 and 10.

7.6 Matrix Spike Solution: Prepare as indicated in the preparative methods. See preparation SOP. The matrix spike compounds and levels are the same as the LCS compounds.

7.7 The standards listed in 7.1 to 7.6 should be refrigerated at $\leq 6^{\circ}C$ when not in use. Refrigeration at -10°C to -20°C may be used if it can be demonstrated that analytes do not fall out of solution at this temperature. The standards must be replaced at least once a year. The continuing calibration standard must be replaced every week and is stored at $\leq 6^{\circ}C$.

## 8 SAMPLE PRESERVATION AND STORAGE

8.1 Reference appropriate facility SOP for sample bottle preservation and storage.

8.2 Samples are stored at $4 \pm 2^{\circ}C$. Samples and extracts should be stored in suitable glass containers with Teflon lined caps. (Extracts will normally be stored for 30 days after invoicing.)

8.3 Water samples are extracted within seven days of sampling and the extracts are analyzed within forty days of extraction. Solids, sludges, and organic liquids are extracted within fourteen days of sampling and the extracts are analyzed within forty days of extraction.

## 9 QUALITY CONTROL

9.1 Initial Demonstration of Capability

9.1.1 For the standard analyte list, the initial demonstration and method detection limit (MDL) studies described in section 13 must be acceptable before analysis of samples may begin. Refer to the flow chart in section 17.4.1.

9.1.2 For non-standard analytes an MDL study should be performed and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed to with the client. In any event, the minimum initial demonstration required is analysis of an extracted standard at the reporting limit and a single point calibration.

9.2 Control Limits

In-house historical control limits must be determined for surrogates, matrix spikes, and laboratory control samples (LCS). These limits must be determined at least annually. The recovery limits are mean recovery +/- 3 standard deviations for surrogates, MS and LCS Precision limits for matrix spikes / matrix spike duplicates are mean relative percent difference +/- 3 standard deviations.

9.2.1 These limits do not apply to dilutions (except for tests without a separate extraction), but surrogate and matrix spike recoveries will be reported unless the dilution is more than 5X.

9.2.2 All surrogate, LCS, and MS recoveries (except for dilutions) must be entered into QuantIMS (when available) or other database so that accurate historical control limits can be generated. For tests without a separate extraction, surrogates and matrix spikes will be reported for all dilutions.

9.2.3 Refer to the QC program document (QA-003) for further details of control limits.

9.3 Method Blank

A method blank is prepared and analyzed with each batch of samples. The method blank consists of reagent water for aqueous samples, and sodium sulfate for soil samples (Refer to SOP No. CORP-OP-0001 for details). Surrogates are added and the method blank is carried through the entire analytical procedure. The method blank must not contain any analyte of interest at or above the reporting limit (except common laboratory contaminants, see below) or at or above 5% of the measured concentration of that analyte in the associated samples, whichever is higher.

- If the analyte is a common laboratory contaminant (phthalate esters), the data may be reported with qualifiers if the concentration of the analyte is less than five times the RL. Such action must be taken in consultation with the client.

- Reanalysis of any samples with reportable concentrations of analytes found in the method blank is required unless other actions are agreed with the client.

- If there is no target analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. Such action should be taken in consultation with the client.

9.3.1 The method blank must have acceptable surrogate recoveries. If surrogate recoveries are not acceptable, the data must be evaluated to determine if the method blank has served the purpose of demonstrating that the analysis is free of contamination. If surrogate recoveries are low and there are reportable analytes in

the associated samples, re-extraction of the blank and affected samples will normally be required. Consultation with the client should take place.

9.3.2 If reanalysis of the batch is not possible due to limited sample volume or other constraints, the method blank is reported, all associated samples are flagged with a "B", and appropriate comments may be made in a narrative to provide further documentation.

9.3.3 Refer to the STL North Canton QC Program document (QA-003) for further details of the corrective actions.

9.3.4 Sample results are NOT blank subtracted unless specific requests and arrangements have been made with a client or agency.

9.4 Instrument Blank

9.4.1 Instruments must be evaluated for contamination during each 12 hour analytical run. This may be accomplished by analysis of a method blank. If a method blank is not available, an instrument blank must be analyzed. An instrument blank consists of methylene chloride with the internal standards added. It is evaluated in the same way as the method blank.

9.5 Laboratory Control Sample (LCS)

9.5.1 A laboratory control sample (LCS) is prepared and analyzed with every batch of samples. All analytes must be within established control limits. The LCS is spiked with the compounds listed in Tables 9 and 10 unless specified by a client or agency.

9.5.2 If any analyte in the LCS is outside the laboratory established historical control limits, corrective action must occur. Corrective action may include re-extraction and reanalysis of the batch.

- If the batch is not re-extracted and reanalyzed, the reasons for accepting the batch must be clearly presented in the project records and the report. (An example of acceptable reasons for not reanalyzing might be that the matrix spike and matrix spike duplicate are acceptable, and sample surrogate recoveries are good, demonstrating that the problem was confined to the LCS).

- If re-extraction and reanalysis of the batch is not possible due to limited sample volume or other constraints, the LCS is reported, all associated samples are flagged, and appropriate comments are made in a narrative to provide further documentation.

9.5.3 Ongoing monitoring of the LCS provides evidence that the laboratory is performing the method within accepted QC guidelines for accuracy and precision.

9.6 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

A matrix spike/matrix spike duplicate (MS/MSD) is prepared and analyzed with every batch of samples. The MS/MSD is spiked with the same subset of analytes as the LCS (See Tables 9 and 10). Compare the percent recovery and relative percent difference (RPD) to that in the laboratory specific historically generated limits.

- If any individual recovery or RPD falls outside the acceptable range, corrective action must occur. The initial corrective action will be to check the recovery of that analyte in the Laboratory Control Sample (LCS). Generally, if the recovery of the analyte in the LCS is within limits, then the laboratory operation is in control and analysis may proceed. The reasons for accepting the batch must be documented.

- If the recovery for any component is outside QC limits for both the Matrix spike / spike duplicate and the LCS, the laboratory is out of control and corrective action must be taken. Corrective action will normally include repreparation and reanalysis of the batch.

- If a MS/MSD is not possible due to limited sample, then a LCS duplicate should be analyzed. RPD of the LCS and LCSD are compared to the matrix spike limits.

- The matrix spike / duplicate must be analyzed at the same dilution as the unspiked sample, even if the matrix spike compounds will be diluted out.

9.7 Surrogates

9.7.1 Every sample, blank, and QC sample is spiked with surrogate standards. Surrogate spike recoveries must be evaluated by determining whether the concentration (measured as percent recovery) falls within the required recovery limits. The compounds routinely included in the surrogate spiking solution, along with recommended standard concentrations, are listed in Table 11.

9.7.2 If any surrogates are outside limits the following corrective actions must take place (except for dilutions):

- Check all calculations for error.

- Ensure that instrument performance is acceptable.

- Recalculate the data and/or reanalyze the extract if either of the above checks reveal a problem.

- Re-extract and reanalyze the sample or flag the data as "Estimated Concentration" if neither of the above resolves the problem.

The decision to reanalyze or flag the data should be made in consultation with the client. It is only necessary to reprepare / reanalyze a sample once to demonstrate that poor surrogate recovery is due to matrix effect, unless the analyst believes that the repeated out of control results are not due to matrix effect.

**Note:** If all associated QC meets criteria (blank, LCS/LCSD), up to one surrogate per fraction may be outside of acceptance criteria , as long as the recovery is greater than 10%.

9.7.3 If the sample with surrogate recoveries outside the recovery limits was a sample used for an MS/MSD and the surrogate recoveries in the MS/MSD are also outside of the control limits, then the sample, the MS, and the MSD do not require reanalysis as this phenomenon would indicate a possible matrix problem.

9.7.4 If the sample is reanalyzed and the surrogate recoveries in the reanalysis are acceptable, then the problem was within the analyst's control and only the reanalyzed data should be reported. (Unless the reanalysis was outside holding times, in which case reporting both sets of results may be appropriate.)

9.7.5 If the reanalysis does confirm the original results, the original analysis is reported and the data flagged as estimated due to matrix effect.

9.8 Nonconformance and Corrective Action

9.8.1 Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the facility QA Manager.

9.9 Quality Assurance Summaries

Certain clients may require specific project or program QC which may supersede these method requirements. Quality Assurance Summaries should be developed to address these requirements.

9.10 STL North Canton QC Program

Further details of QC and corrective action guidelines are presented in the STL North Canton QC Program document (QA-003). Refer to this document if in doubt regarding corrective actions.

# 10 CALIBRATION AND STANDARDIZATION

## 10.1 Summary

10.1.1 The instrument is tuned for DFTPP, calibrated initially with a five-point calibration curve, and verified each 12-hour shift with one or more continuing calibration standard(s). Recommended instrument conditions are listed in Table 5.

10.2 All standards and extracts are allowed to warm to room temperature before injecting.

## 10.3 Instrument Tuning

At the beginning of every twelve hour shift when analyses are to be performed, the GC/MS system must be checked to see if acceptable performance criteria (Table 6) is achieved for DFTPP (decafluorotriphenylphosphine).

10.3.1 Inject 10 ng or 50 ng of the GC/MS tuning standard (Section 7.4) into the GC/MS system. Obtain a background-corrected mass spectra of DFTPP and confirm that all the key m/z criteria in Table 6 are achieved. If all the criteria are not achieved, the analyst must retune the mass spectrometer and repeat the test until all criteria are achieved. The performance criteria must be achieved before any samples, blanks, or standards are analyzed.

10.3.2 The GC/MS tuning standard should also be used to evaluate the inertness of the chromatographic system. Benzidine and pentachlorophenol should not exhibit excessive tailing. If DDT is an analyte of interest, it must be included in the tuning standard, and its breakdown must be < 20%. Refer to section 12 for the appropriate calculations.

## 10.4 Initial Calibration

10.4.1 Internal Standard Calibration Procedure: Internal standards are listed in Table 7. Use the base peak m/z as the primary m/z for quantitation of the standards. If interferences are noted, use one of the next two most intense masses for quantitation.

10.4.2 Compounds should be assigned to the IS with the closest retention time.

10.4.3 Prepare calibration standards at a minimum of five concentration levels for each parameter of interest. Six standards must be used for a quadratic least squares calibration. Quadratic fit may NOT be used for samples analyzed under South Carolina Certification. It may also be useful to analyze six calibration levels and use the lower five for most analytes and the upper five for analytes that have poor

response. Add the internal standard mixture to result in 8 ng or 40 ng on column. The concentrations of all analytes are listed in tables 12 and 13.

10.4.4 Analyze each calibration standard and tabulate the area of the primary characteristic m/z against concentration for each compound and internal standard. Calculate response factors (RF), average response factors, and the percent RSD of the response factors for each compound using the equations in section 12 and verify that the CCC and SPCC criteria in section 10.4.5 and 10.4.6 are met. **No sample analysis may be performed unless these criteria are met.**

10.4.5 System Performance Check Compounds (SPCCs): The minimum average RF for semivolatile SPCCs is 0.050. If the minimum response factors are not met, the system must be evaluated and corrective action must be taken before sample analysis begins. Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. This check must be met before analysis begins.

SPCC Compounds:

N-nitroso-di-n-propylamine
Hexachlorocyclopentadiene
2,4-Dinitrophenol
4-Nitrophenol

10.4.6 Calibration Check Compounds (CCCs): The %RSD of the response factors for each CCC in the initial calibration must be less than 30% for the initial calibration to be considered valid. This criterion must be met before sample analysis begins. Problems similar to those listed under SPCCs could affect this criterion.

10.4.6.1 If none of the CCCs are required analytes, project specific calibration specifications must be agreed with the client.

10.4.6.2 CCC Compounds:

Phenol
Acenaphthene
1,4-Dichlorobenzene
N-nitrosodiphenylamine
2-Nitrophenol
Pentachlorophenol
2,4-Dichlorophenol
Fluoranthene
Hexachlorobutadiene

Di-n-octylphthalate
4-Chloro-3-methylphenol
Benzo(a)pyrene
2,4,6-Trichlorophenol

10.4.7 If the average of all %RSDs in the initial calibration is ≤ 15%, then all analytes may use average response factor for calibration.

10.4.7.1 If the software in use is capable of routinely reporting curve coefficients for data validation purposes, and the necessary calibration reports can be generated, then the analyst should evaluate analytes with %RSD > 15% for calibration on a curve. If it appears that substantially better accuracy would be obtained using quantitation from a curve then the appropriate curve should be used for quantitation.

10.4.7.2 If the average of all the %RSDs in the initial calibration is > 15%, then calibration on a curve must be used for those analytes with %RSD > 15%. Linear or quadratic curve fits may be used. Linear curve fits only may be used for South Carolina Certification. The analyst should consider instrument maintenance to improve the linearity of response. Use of 1/Concentration$^2$ weighting is recommended to improve the accuracy of quantitation at the low end of the curve. If Relative Standard Error (RSE) is used to evaluate the curve it must be better than 15%. If the % RSD is >15%, the analyst may drop the low or high points in the ICAL, as long as a minimum of 5 points are maintained and the quantitation range is adjusted accordingly. If the % RSD is still >15%, a quadratic or linear curve may be used. The correlation coefficient (r) must be ≥ 0.990. If the correlation coefficient is < 0.990, then any hits for these compounds must be flagged as estimated.

10.4.8 Weighting of data points

In a linear or quadratic calibration fit, the points at the lower end of the calibration curve have less weight in determining the curve generated than points at the high concentration end of the curve. For South Carolina Certification, only a linear calibration fit, the points at the lower end of the calibration curve have less weight in determining the curve generated than points at the high concentration end of the curve. However, in environmental analysis, accuracy at the low end of the curve is very important. For this reason it is preferable to increase the weighting of the lower concentration points. 1/Concentration$^2$ weighting (often called $1/X^2$ weighting) will improve accuracy at the low end of the curve and should be used if the data system has this capability.

10.4.9 If time remains in the 12 hour period initiated by the DFTPP injection before the

initial calibration, samples may be analyzed. Otherwise, proceed to continuing calibration.

**10.4.10 Quantitation is performed using the calibration curve or average response factor form the initial curve, not the continuing calibration.**

10.5 Continuing Calibration

10.5.1 At the start of each 12-hour period, the GC/MS tuning standard must be analyzed. A 10 ng or 50 ng injection of DFTPP must result in a mass spectrum for DFTPP which meets the criteria given in Table 6.

10.5.2 Following a successful DFTPP analysis the continuing calibration standard(s) are analyzed. The standards must contain all semivolatile analytes, including all required surrogates. A mid level calibration standard is used for the continuing calibration.

10.5.3 The following criteria must be met for the continuing calibration to be acceptable:

- The SPCC compounds must have a response factor of $\geq 0.05$.
- The percent difference or drift of the CCC compounds from the initial calibration must be $\leq 20\%$. (see section 12 for calculations) In addition, the percent difference or drift of all analytes must be $\leq 50\%$, with allowance being made for up to six target compounds to have percent drift greater than 50%.
- The internal standard response must be within 50-200% of the response in the mid level of the initial calibration.
- The internal standard retention times must be within 30 seconds of the retention times in the mid-level of the initial calibration.
- NOTE: There is no internal standard criteria for samples. Criteria is only for continuing and initial calibrations.
- NOTE: Ohio VAP rules require that any sample with internal standard outliers be reanalyzed.

10.5.3.1 If none of the CCCs are required analytes, project specific calibration specifications must be agreed with the client.

10.5.4 Once the above criteria have been met, sample analysis may begin. Initial calibration average RFs (or the calibration curve) will be used for sample quantitation, not the continuing calibration RFs. Analysis may proceed until 12

hours from the injection of the DFTPP have passed. (A sample *injected* less than 12 hours after the DFTPP is acceptable.)

NOTE: Additional compound analysis outside the TCL (Target Compound List) have no calibration criteria.

# 11 PROCEDURE

## 11.1 Sample Preparation

Samples are prepared following SOP CORP-OP-0001.

## 11.2 Sample Analysis Procedure

11.2.1 Calibrate the instrument as described in section 10. Depending on the target compounds required by the client, it may be necessary to use more than one calibration standard.

11.2.2 All samples must be analyzed using the same instrument conditions as the preceeding continuing calibration standard.

11.2.3 Add internal standard to the extract to result in 40 ng injected on column (for example, 8 µL or 50 µL internal standard solution in 0.5 mL of extract for a 1 µL injection). Mix thoroughly before injection into the instrument.

11.2.4 Inject the sample extract into the GC/MS system using the same injection technique as used for the standards.

11.2.5 The data system will determine the concentration of each analyte in the extract using calculations equivalent to those in section 12. Quantitation is based on the initial calibration, not the continuing calibration.

11.2.6 Identified compounds are reviewed for proper integration. Manual integrations are performed if necessary and are documented by the analyst or automatically by the data system.

11.2.7 Target compounds identified by the data system are evaluated using the criteria listed in section 12.1.

11.2.8 Library searches of peaks present in the chromatogram that are not target compounds (Tentatively Identified Compounds, TIC) may be performed if required by the client. They are evaluated using the criteria in section 12.3.

11.3 Dilutions

If the response for any compound exceeds the working range of the GC/MS system, a dilution of the extract is prepared and analyzed. An appropriate dilution should be in the upper half of the calibration range. Samples may be screened to determine the appropriate dilution for the initial run. If the initial diluted run has no hits or hits below 20% of the calibration range and the matrix allows for analysis at a lesser dilution, the sample must be reanalyzed at a dilution targeted to bring the largest hit above 50% of the calibration range.

11.3.1 Guidance for Dilutions Due to Matrix

If the sample is initially run at a dilution and the baseline rise is less than the height of the internal standards, or if individual non-target peaks are less than two times the height of the internal standards, the sample should be reanalyzed at a more concentrated dilution. This requirement is approximate and subject to analyst judgement. For example, samples containing organic acids may need to be analyzed at a higher dilution to avoid destroying the column.

11.3.2 Reporting Dilutions

The most concentrated dilution with no target compounds above the calibration range will be reported. Other dilutions will only be reported at client request.

11.4 Perform all qualitative and quantitative measurements. When the extracts are not being used for analyses, refrigerate them at $4 \pm 2^{\circ}C$, protected from light in screw cap vials equipped with unpierced Teflon lined septa.

11.5 Retention time criteria for samples

If the retention time for any internal standard changes by more than 0.5 minutes from the last continuing calibration standard, the chromatographic system must be inspected for malfunctions and corrected. Reanalysis of samples analyzed while the system was malfunctioning is required.

11.5.1 If the retention time of any internal standard in any sample varies by more than 0.1 minute from the preceding continuing calibration standard, the data must be carefully evaluated to ensure that no analytes have shifted outside their retention time windows.

11.6 Percent Moisture

Analytical results may be reported as dry or wet weight, as required by the client. Percent moisture must be determined if results will be reported as dry weight. Refer to the facility specific SOP for determination of percent moisture.

11.7 Procedural Variations

11.7.1 One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file. Any unauthorized deviations from this procedure must also be documented as a non-conformance, with a cause and corrective action described.

11.8 Troubleshooting Guide

11.8.1 Daily Instrument Maintenance

In addition to the checks listed in the instrument maintenance schedule in the STL North Canton Quality Assurance Manual (LQM), current version, the following daily maintenance should be performed.

- Clip Column as necessary.
- Install new or cleaned injection port liner as necessary.
- Install new septum as necessary.
- Perform mass calibration as necessary.

11.8.2 Major Maintenance

A new initial calibration is necessary following major maintenance. Major maintenance includes changing the column, cleaning the ion volume or repeller, cleaning the source, and replacing the multiplier. Refer to the manufacturer's manual for specific guidance.

## 12 DATA ANALYSIS AND CALCULATIONS

12.1 Qualitative identification

An analyte is identified by retention time and by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for standard reference may be obtained on the user's GC/MS by analysis of the calibration standards or from the NBS library. Two criteria must be satisfied to verify identification: (1) elution of sample component at

the same GC retention time as the standard component; and (2) correspondence of the sample component and the standard component characteristic ions. (Note: Care must be taken to ensure that spectral distortion due to co-elution is evaluated.)

- The sample component retention time must compare to within ± 0.2 min. of the retention time of the standard component. For reference, the standard must be run within the same twelve hours as the sample.
- All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) should be present in the sample spectrum.
- The characteristic ions of a compound must maximize in the same scan or within one scan of each other.
- The relative intensities of ions should agree to within ±30% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 20% and 80%.)

12.1.1 If a compound cannot be verified by all the above criteria, but in the technical judgment of the analyst the identification is correct, the analyst shall report that identification and proceed with quantitation.

12.2 Mass chromatogram searches.

Certain compounds are unstable in the calibration standard and cannot be calibrated in the normal way. In particular, the compound hexachlorophene (CAS 70-30-4) falls into this category, and is required for Appendix IX analysis. For this analyte a mass chromatogram search is made.

12.2.1 Hexachlorophene

Display the mass chromatograms for mass 196 and mass 198 for the region of the chromatogram from at least 2 minutes before chrysene-d12 to at least 4 minutes after chrysene-d12. If peaks for both ions coincide then the analyst evaluates the spectrum for the presence of hexachlorophene. No quantitation is possible.

12.3 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the type of analyses being conducted. Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample spectra with the nearest library

searches shall the mass spectral interpretation specialist assign a tentative identification. Guidelines for making tentative identification are:

- Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) should be present in the sample spectrum.
- The relative intensities of the major ions should agree within ±20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance should be between 30%and 70%.)
- Molecular ions present in the reference spectrum should be present in the sample spectrum.
- Ions present in the sample spectrum, but not in the reference spectrum, should be reviewed for possible background contamination or presence of coeluting compounds.
- Ions present in the reference spectrum, but not in the sample spectrum, should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.
- Automatic background subtraction can severely distort spectra from samples with unresolved hydrocarbons.

12.4 Anyone evaluating data is trained to know how to handle isomers with identical mass spectra and close elution times. These include:

Dichlorobenzenes
Methylphenols
Trichlorophenols
Phenanthrene, anthracene
Fluoranthene, pyrene
Benzo(b) and (k)fluoranthene
Chrysene, benzo(a)anthracene

Extra precautions concerning these compounds are to more closely scrutinize retention time vs. the calibration standard and also to check that all isomers have distinct retention times.

A second category of problem compounds would be the poor responders or compounds that chromatograph poorly. Included in this category would be:

Benzoic acid
Chloroanilines

Nitroanilines
2,4-Dinitrophenol
4-Nitrophenol
Pentachlorophenol
3,3'-Dichlorobenzidine
Benzyl alcohol
4,6-Dinitro-2-methylphenol

Manually checking the integrations would be appropriate for these compounds.

12.5 Calculations

12.5.1 Percent Relative Standard Deviation for Initial Calibration

$$\%RSD = \frac{SD}{\overline{RF}} \times 100$$

$RF =$ Mean of RFs from intial caibration for a compound

$SD =$ Standard deviation of RFs from initial calibration for a compound,

$$= \sqrt{\sum_{i=1}^{N} \frac{\left(RFi - \overline{RF}\right)^2}{N-1}}$$

$RFi =$ RF for each of the calibration levels

$N =$ Number of RF values

12.5.2 Continuing calibration percent drift

$$\%Drift = \frac{C_{actual} - C_{found}}{C_{actual}} \times 100\%$$

$C_{actual} =$ Known concentration in standard

$C_{found} =$ Measured concentration using selected quantitation method

12.5.3 Concentration in the extract

The concentration of each identified analyte and surrogate in the extract is calculated from the linear or quadratic curve fitted to the initial calibration points, or from the average RF of the initial calibration. For South Carolina Certification the concentration of each identified analyte and surrogate in the extract is calculated from the linear curve only fitted to the initial calibration points, or from the average RF of the initial calibration.

12.5.3.1 Average response factor

If the average of all the %RSDs of the response factors in the initial calibration is ≤ 15%, the average response factor from the initial calibration may be used for quantitation.

$$C_{ex} = \frac{R_x C_{is}}{R_{is} \overline{RF}}$$

12.5.3.2 Linear fit (Use only Linear fit for South Carolina Certification)

$$C_{ex} = A + B\frac{(R_x C_{is})}{R_{is}}$$

$C_{ex}$= Concentration in extract, µg/mL

$R_x$= Response for analyte

$R_{is}$= Response for internal standard

$C_{is}$= Concentration of internal standard

$A$= Intercept

$B$= Slope

12.5.3.3 Quadratic fit

$$C_{ex} = A + B\left(\frac{R_x C_{is}}{R_{is}}\right) + C\left(\frac{R_x C_{is}}{R_{is}}\right)$$

$C$= Curvature

12.5.4 The concentration in the sample is then calculated.

12.5.4.1 Aqueous Calculation

$$\text{Concentration, } \mu g / L = \frac{C_{ex} V_t}{V_o}$$

Where:

$V_t$ = Volume of total extract, µL, taking into account dilutions (i.e., a 1-to-10 dilution of a 1 mL extract will mean $V_t$ = 10,000 µL. If half of the base/neutral extract and half of the acid extract are combined, $V_t$ = 2,000.)

$V_o$ = Volume of water extracted (mL)

12.5.5 Sediment/Soil, Sludge (on a dry-weight basis) and Waste (normally on a wet-weight basis:

$$\text{Concentration, } \mu g / kg = \frac{C_{ex} V_t}{W_s D}$$

$W_s$ = Weight of sample extracted or diluted in grams

$D$ = (100 - % moisture in sample)/100, for a dry weight basis or 1 for a wet weight basis

12.6 MS/MSD percent recovery calculation.

$$\text{Matrix Spike Recovery} = \frac{S_{SR} - S_R}{S_A} \times 100\%$$

$S_{SR}$ = Spike sample result

$S_R$=Sample result

$S_A$ = Spike added

12.7 Relative % Difference calculation for the MS/MSD

$$RPD = \frac{MS_R - MSD_R}{1/2(MS_R + MSD_R)} \times 100$$

$RPD$ = Relative percent difference

$MS_R$ = Matrix spike result

$MSD_R$ = Matrix spike duplicate result

12.8 Relative response factor calculation.

$$RF = \frac{A_x C_{is}}{A_{is} C_x}$$

$A_x$=Area of the characteristic ion for the compound being measured

$A_{is}$=Area of the characteristic ion for the specific internal standard

$C_x$=Concentration of the compound being measured (µg/L)

$C_{is}$ =Concentration of the specific internal standard (µg/L)

12.9 Calculation of TICs: The calculation of TICs (tentatively identified compounds) is identical to the above calculations with the following exceptions:

$A_x$=Area of the total ion chromatogram for the compound being measured

$A_{is}$=Area of the total ion chromatogram for the nearest internal standard without interference

RF=1

12.10 Percent DDT breakdown

$$\%\ \text{DDT breakdown} = \frac{\text{DDEarea} + \text{DDDarea}}{\text{DDTarea} + \text{DDEarea} + \text{DDarea}}$$

The total ion current areas are used for this calculation

# 13 METHOD PERFORMANCE

## 13.1 Method Detection Limit

Each laboratory must generate a valid method detection limit for each analyte of interest. The MDL must be below the reporting limit for each analyte. The procedure for determination of the method detection limit is given in 40 CFR Part 136, Appendix B, and further defined in QA Policy #: QA-005.

## 13.2 Initial Demonstration

Each laboratory must make an initial demonstration of capability for each individual method. Demonstration of capability for both soil and water matrices is required. This requires analysis of QC check samples containing all of the standard analytes for the method. For some tests it may be necessary to use more than one QC check mix to cover all analytes of interest.

13.2.1 Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be equivalent to the level 4 calibration standard.

13.2.2 Calculate the average recovery and standard deviation of the recovery for each analyte of interest. Compare these results with the acceptance criteria given in table 14.

13.2.3 If any analyte does not meet the acceptance criteria the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

## 13.3 Non-standard analytes

For non-standard analytes, an MDL study must be performed and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed to with the client. In any event, the minimum initial demonstration required is analysis of an extracted standard at the reporting limit and a single point calibration.

## 13.4 Training Qualification

The group/team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience.

13.5 Data Quality Objectives (DQO). Refer to project-specific Quality Assurance plans for DQO information.

## 14 POLLUTION PREVENTION

14.1 This section is not applicable to this procedure.

## 15 WASTE MANAGEMENT

15.1 Waste generated during aliquotting and from used vials must be disposed of in accordance with the facility hazardous waste procedures. The Health and Safety Director should be contacted if additional information is required.

## 16 REFERENCES

16.1 SW846, Test Methods for Evaluating Solid Waste, Third Edition, Update II, October 1994, Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS): Capillary Column Technique, Method 8270C.

16.2 J. W. Eichelberger, L. E. Harris, and W. L. Budde, "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography/Mass Spectrometry," Analytical Chemistry, 47, 995 (1975)

## 17 MISCELLANEOUS

17.1 Modifications from Reference Method

17.1.1 A retention time window of 0.2 minutes is used for all components, since some data systems do not have the capability of using the relative retention time units specified in the reference method.

17.1.2 The quantitation and qualifier ions for some compounds have been changed from those recommended in SW-846 in order to improve the reliability of qualitative identification.

17.2 Modifications from Previous Revision

17.2.1 This SOP has been substantially revised to meet the requirements of method 8270C.

17.2.2 Directions for analysis be method 625 have been added as an attachment.

17.2.3 SOP has been revised to include a 5 mL final volume.

17.3 Facility Specific SOPs

Each facility shall attach a list of facility specific SOPs or approved attachments (if applicable) which are required to implement this SOP or which are used in conjunction with this SOP. If no facility specific SOPs or amendments are to be attached, a statement must be attached specifying that there are none.

17.4 Tables

**Table 1**

**STL North Canton Primary Standard[1] and Standard Reporting Limits**

| Analytes | CAS Number | Standard Reporting Limits | |
|---|---|---|---|
| | | Aqueous µg/L | Low Soil/Sediment µg/kg |
| Pyridine | 110-86-1 | 20 | 660 |
| N-nitrosodimethylamine | 62-75-9 | 10 | 330 |
| Aniline | 62-53-3 | 10 | 330 |
| Phenol | 108-95-2 | 10 | 330 |
| Bis(2-chloroethyl)ether | 111-44-4 | 10 | 330 |
| 2-Chlorophenol | 95-57-8 | 10 | 330 |
| 1,3-Dichlorobenzene | 541-73-1 | 10 | 330 |
| 1,4-Dichlorobenzene | 106-46-7 | 10 | 330 |
| Benzyl alcohol | 100-51-6 | 10 | 330 |
| 1,2-Dichlorobenzene | 95-50-1 | 10 | 330 |
| 2-Methylphenol | 95-48-7 | 10 | 330 |
| 2,2'-oxybis(1-chloropropane)[2] | 108-60-1 | 10 | 330 |
| 4-Methylphenol | 106-44-5 | 10 | 330 |
| N-Nitroso-di-n-propylamine | 621-64-7 | 10 | 330 |
| Hexachloroethane | 67-72-1 | 10 | 330 |
| Nitrobenzene | 98-95-3 | 10 | 330 |
| Isophorone | 78-59-1 | 10 | 330 |
| 2-Nitrophenol | 88-75-5 | 10 | 330 |
| 2,4-Dimethylphenol | 105-67-9 | 10 | 330 |
| Benzoic acid | 65-85-0 | 50 | 1600 |
| Bis(2-chloroethoxy)methane | 111-91-1 | 10 | 330 |
| 2,4-Dichlorophenol | 120-83-2 | 10 | 330 |
| 1,2,4-Trichlorobenzene | 120-82-1 | 10 | 330 |
| Naphthalene | 91-20-3 | 10 | 330 |
| 4-Chloroaniline | 106-47-8 | 10 | 330 |
| Hexachlorobutadiene | 87-68-3 | 10 | 330 |
| 4-Chloro-3-methylphenol | 59-50-7 | 10 | 330 |
| 2-Methylnaphthalene | 91-57-6 | 10 | 330 |
| Hexachlorocyclopentadiene | 77-47-4 | 50 | 1600 |
| 2,4,6-Trichlorophenol | 88-06-2 | 10 | 330 |
| 2,4,5-Trichlorophenol | 95-95-4 | 10 | 330 |
| 2-Chloronaphthalene | 91-58-7 | 10 | 330 |
| 2-Nitroaniline | 88-74-4 | 50 | 1600 |
| Dimethyl phthalate | 131-11-3 | 10 | 330 |
| Acenaphthylene | 208-96-8 | 10 | 330 |
| 3-Nitroaniline | 99-09-2 | 50 | 1600 |
| Acenaphthene | 83-32-9 | 10 | 330 |
| 2,4-Dinitrophenol | 51-28-5 | 50 | 1600 |
| 4-Nitrophenol | 100-02-7 | 50 | 1600 |
| Dibenzofuran | 132-64-9 | 10 | 330 |
| 2,4-Dinitrotoluene | 121-14-2 | 10 | 330 |
| 2,6-Dinitrotoluene | 606-20-2 | 10 | 330 |

**Table 1**

**STL North Canton Primary Standard[1] and Standard Reporting Limits**

| Analytes | CAS Number | Standard Reporting Limits | |
|---|---|---|---|
| | | Aqueous µg/L | Low Soil/Sediment µg/kg |
| Diethylphthalate | 84-66-2 | 10 | 330 |
| 4-Chlorophenyl phenyl ether | 7005-72-3 | 10 | 330 |
| Fluorene | 86-73-7 | 10 | 330 |
| 4-Nitroaniline | 100-01-6 | 50 | 1600 |
| 4,6-Dinitro-2-methylphenol | 534-52-1 | 50 | 1600 |
| N-Nitrosodiphenylamine | 86-30-6 | 10 | 330 |
| Azobenzene | 103-33-3 | 10 | 330 |
| 4-Bromophenyl phenyl ether | 101-55-3 | 10 | 330 |
| Hexachlorobenzene | 118-74-1 | 10 | 330 |
| Pentachlorophenol | 87-86-5 | 50 | 1600 |
| Phenanthrene | 85-01-8 | 10 | 330 |
| Anthracene | 120-12-7 | 10 | 330 |
| Carbazole | 86-74-8 | 10 | 330 |
| Di-n-butyl phthalate | 84-74-2 | 10 | 330 |
| Fluoranthene | 206-44-0 | 10 | 330 |
| Benzidine | 92-87-5 | 100 | 3300 |
| Pyrene | 129-00-0 | 10 | 330 |
| Butyl benzyl phthalate | 85-68-7 | 10 | 330 |
| 3,3'-Dichlorobenzidine | 91-94-1 | 50 | 1600 |
| Benzo(a)anthracene | 56-55-3 | 10 | 330 |
| Bis(2-ethylhexyl)phthalate | 117-81-7 | 10 | 330 |
| Chrysene | 218-01-9 | 10 | 330 |
| Di-n-octylphthalate | 117-84-0 | 10 | 330 |
| Benzo(b)fluoranthene | 205-99-2 | 10 | 330 |
| Benzo(k)fluoranthene | 207-08-9 | 10 | 330 |
| Benzo(a)pyrene | 50-32-8 | 10 | 330 |
| Indeno(1,2,3-cd)pyrene | 193-39-5 | 10 | 330 |
| Dibenz(a,h)anthracene | 53-70-3 | 10 | 330 |
| Benzo(g,h,i)perylene | 191-24-2 | 10 | 330 |
| Benzaldehyde | 100-52-7 | 10 | 330 |
| Caprolactam | 105-60-2 | 10 | 330 |
| 1,1-Biphenyl | 92-52-4 | 10 | 330 |
| Atrazine | 1912-24-9 | 10 | 330 |

[1] The STL North Canton primary standard is the standard normally used at F. Additional standards, such as the Appendix IX standard may be necessary to include all target analytes required for some clients.

[2] 2,2'oxybis(1-chloropropane) was formally known as bis(2-chloroisopropyl)ether

**Table 2**

**STL North Canton Appendix IX[1] Standard Reporting Limits**

| Semivolatiles | CAS Number | Standard Reporting Limits | |
|---|---|---|---|
| | | Aqueous µg/L | Low Soil/Sediment µg/kg |
| 2-Picoline | 109-06-8 | 20 | 660 |
| N-Nitrosomethylethylamine | 10595-95-6 | 10 | 330 |
| Methyl methanesulfonate | 66-27-3 | 10 | 330 |
| N-Nitrosodiethylamine | 55-18-5 | 10 | 330 |
| Ethyl methanesulfonate | 62-50-0 | 10 | 330 |
| Pentachloroethane | 76-01-7 | 50 | 1600 |
| Acetophenone | 98-86-2 | 10 | 330 |
| N-Nitrosopyrrolidine | 930-55-2 | 10 | 330 |
| N-Nitrosomorpholine | 59-89-2 | 10 | 330 |
| o-Toluidine | 95-53-4 | 20 | 660 |
| 3-Methylphenol | 108-39-4 | 10 | 330 |
| N-Nitrosopiperidine | 100-75-4 | 10 | 330 |
| o,o,o-Triethyl-Phosphorothioate[2] | 126-68-1 | 50 | 1600 |
| a,a-Dimethyl-phenethylamine | 122-09-8 | 50 | 1600 |
| 2,6-Dichlorophenol | 87-65-0 | 10 | 330 |
| Hexachloropropene | 1888-71-7 | 100 | 3300 |
| p-Phenylenediamine | 106-50-3 | 100 | 3300 |
| n-Nitrosodi-n-butylamine | 924-16-3 | 10 | 330 |
| Safrole | 94-59-7 | 20 | 660 |
| 1,2,4,5-Tetrachlorobenzene | 95-94-3 | 10 | 330 |
| Isosafrole | 120-58-1 | 20 | 660 |
| 1,4-Dinitrobenzene | 100-25-4 | 10 | 330 |
| 1,4-Naphthoquinone | 130-15-4 | 50 | 1600 |
| 1,3-Dinitrobenzene | 99-65-0 | 10 | 330 |
| Pentachlorobenzene | 608-93-5 | 10 | 330 |
| 1-Naphthylamine | 134-32-7 | 10 | 330 |
| 2-Naphthylamine | 91-59-8 | 10 | 330 |
| 2,3,4,6-Tetrachlorophenol | 58-90-2 | 50 | 1600 |
| 5-Nitro-o-toluidine | 99-55-8 | 20 | 660 |
| Thionazin[2] | 297-97-2 | 50 | 1600 |
| 1,3,5-Trinitrobenzene | 99-35-4 | 50 | 1600 |
| Sulfotepp[2] | 3689-24-5 | 50 | 1600 |
| Phorate[2] | 298-02-2 | 50 | 1600 |
| Phenacetin | 62-44-2 | 20 | 660 |
| Diallate[3] | 2303-16-4 | 20 | 660 |
| Dimethoate[2] | 60-51-5 | 20 | 660 |
| 4-Aminobiphenyl | 92-67-1 | 50 | 1600 |
| Pentachloronitrobenzene | 82-68-8 | 50 | 1600 |
| Pronamide | 23950-58-5 | 20 | 660 |
| Disulfoton[2] | 298-04-4 | 50 | 1600 |
| 2-secbutyl-4,6-dinitrophenol (Dinoseb) | 88-85-7 | 20 | 660 |
| *Methyl Parathion[2] | 298-00-0 | 50 | 1600 |
| 4-Nitroquinoline-1-oxide | 56-57-5 | 100 | 3300 |

**Table 2**

**STL North Canton Appendix IX[1] Standard Reporting Limits**

| Semivolatiles | CAS Number | Standard Reporting Limits | |
|---|---|---|---|
| | | Aqueous µg/L | Low Soil/Sediment µg/kg |
| *Parathion[2] | 56-38-2 | 50 | 1600 |
| Methapyrilene | 91-80-5 | 50 | 1600 |
| Aramite | 140-57-8 | 20 | 660 |
| *Isodrin[3] | 465-73-6 | 10 | 330 |
| *Kepone[2] | 143-50-0 | 100 | 3300 |
| Famphur[3] | 52-85-7 | 100 | 3300 |
| p-(Dimethylamino)azobenzene | 60-11-7 | 20 | 660 |
| p-Chlorobenzilate[3] | 510-15-6 | 10 | 330 |
| 3,3'-Dimethylbenzidine | 119-93-7 | 50 | 1600 |
| 2-Acetylaminofluorene | 53-96-3 | 100 | 3300 |
| Dibenz(a,j)acridine | 224-42-0 | 20 | 660 |
| 7,12-Dimethylbenz(a)anthracene | 57-97-6 | 20 | 660 |
| 3-Methylcholanthrene | 56-49-5 | 20 | 660 |

[1] The Appendix IX standard contains additional analytes required for the Appendix IX list. The STL North Canton primary standard must also be analyzed to include all of the Appendix IX list

[2] May also be analyzed by method 8140 or 8141, which can achieve lower reporting limits.

[3] It is highly recommended that Famphur is analyzed by method 8081. It is a poor responder by 8270C.

* These compounds are analyzed by GC methods at STL North Canton.

**Table 2A**
**STL North Canton Michigan Program[1]**

| Semivolatile | CAS Number | Michigan Reporting Limits | |
|---|---|---|---|
| | | Aqueous µg/L | Low Soil/Sediment µg/kg |
| Acenaphthene | 83-32-9 | 5 | 330 |
| Acenaphthylene | 208-96-8 | 5 | 330 |
| Acetophenone | 98-86-2 | 5 | 330 |
| Anthracene | 120-12-7 | 5 | 330 |
| Atrzine | 1912-24-9 | 5 | 330 |
| Benzaldehyde | 100-52-7 | 10 | 330 |
| Benzo(a)anthracene | 56-55-3 | 4 | 330 |
| Benzo(a)pyrene | 50-32-8 | 4 | 330 |
| Benzo(b)fluoranthene | 205-99-2 | 4 | 330 |
| Benzo(g,h,i)perylene | 191-24-2 | 5 | 330 |
| Benzo(k)fluoranthene | 207-08-9 | 5 | 330 |
| 1,1'-Biphenyl | 92-52-4 | 10 | 330 |
| 4-Bromophenylphenyl ehter | 101-55-3 | 5 | 330 |
| Butylbenzylphthalate | 85-68-7 | 5 | 330 |
| di-n-Butylphthalate | 84-74-2 | 5 | 330 |
| Caprolactam | 105-60-2 | 10 | 330 |
| Carbazole | 86-74-8 | 10 | 330 |
| 4-Chloroaniline | 106-47-8 | 20 | 1700 |
| bis(2-Chloroethoxy)methane | 111-91-1 | 5 | 330 |
| bis(2-Chloroethyl)ether | 111-44-4 | 4 | 330 |
| bis(2-Chloroisopropyl)ether | 108-60-1 | 5 | 330 |
| 4-Chloro-3-Methylphenol | 59-50-7 | 5 | 330 |
| 2-Chloronaphthalene | 91-58-7 | 5 | 330 |
| 2-Chlorophenol | 95-57-8 | 5 | 330 |
| 4-Chlorophenyl phenyl ether | 7005-72-3 | 5 | 330 |
| Chrysene | 218-01-9 | 5 | 330 |
| Dibenz(a,h)anthracene | 53-70-3 | 4 | 330 |
| Dibenzofuran | 132-64-9 | 5 | 330 |
| 3,3'-Dichlorobenzidine | 91-94-1 | 4 | 2000 |
| 2,4-Dichlorophenol | 120-83-2 | 10 | 330 |
| Diethylphthalate | 84-66-2 | 5 | 330 |
| 2-4-Dimethylphenol | 105-67-9 | 5 | 330 |
| Dimethylphthalate | 131-11-3 | 5 | 330 |
| 4,6-Dinitro-2-methylphenol | 534-52-1 | 20 | 1700 |
| 2,4-Dinitrophenol | 51-28-5 | 20 | 1700 |
| 2,4-Dinitrotoluene | 121-14-2 | 5 | 330 |
| 2,6-Dinitrotoluene | 606-20-2 | 5 | 330 |
| bis(2-Ethylhexyl)phthalate | 117-81-7 | 5 | 330 |
| Fluoranthene | 206-44-0 | 5 | 330 |
| Fluorene | 86-73-7 | 5 | 330 |
| Hexachlorobenzene | 118-74-1 | 5 | 330 |
| Hexachlorobutadiene | 87-68-3 | 5 | 330 |
| Hexachlorocyclopentadiene | 77-47-4 | 5 | 330 |
| Hexachloroethane | 67-72-1 | 5 | 330 |

**Table 2A**
**STL North Canton Michigan Program[1]**

| Semivolatile | CAS Number | Michigan Reporting Limits | |
|---|---|---|---|
| | | Aqueous µg/L | Low Soil/Sediment µg/kg |
| Indeno(1,2,3-cd)pyrene | 193-39-5 | 4 | 330 |
| Isophorone | 78-59-1 | 5 | 330 |
| 2-Methylnapthalene | 91-57-6 | 5 | 330 |
| 2-Methylphenol | 95-48-7 | 5 | 330 |
| 4-Methylphenol | 106-44-5 | 5 | 330 |
| Naphthalene | 91-20-3 | 5 | 330 |
| 2-Nitroaniline | 88-74-4 | 20 | 1700 |
| 3-Nitroaniline | 99-09-2 | 20 | 1700 |
| 4-Nitroaniline | 100-01-6 | 20 | 1700 |
| Nitrobenzene | 95-95-3 | 4 | 330 |
| 2-Nitrophenol | 88-75-5 | 5 | 330 |
| 4-Nitrophenol | 100-02-7 | 20 | 1700 |
| N-Nitroso-di-n-propylamine | 621-64-7 | 5 | 330 |
| N-Nitrosodiphenylamine (diphenylamine) | 62-75-9 | 5 | 330 |
| di-n-Octylphthalate | 117-84-0 | 5 | 330 |
| Pentachlorophenol | 87-86-5 | 20 | 800 |
| Phenanthrene | 85-01-8 | 5 | 330 |
| Phenol | 108-95-2 | 5 | 330 |
| Pyrene | 129-00-0 | 5 | 330 |
| 2,4,5-Trichlorophenol | 95-95-4 | 5 | 330 |
| 2,4,6-Trichlorophenol | 88-06-2 | 4 | 330 |

[1] Reporting Limits are only for samples performed under the Michigan program.

**Table 3**

**Reportable Analytes for STL North Canton Standard Tests, Primary Standard**

| Analyte | CAS Number | STL North Canton Standard List | TCLP | TCL | Appendix IX |
|---|---|---|---|---|---|
| Pyridine | 110-86-1 | | X | | X |
| N-nitrosodimethylamine | 62-75-9 | | | | X |
| Aniline | 62-53-3 | | | | X |
| Phenol | 108-95-2 | X | | X | X |
| Bis(2-chloroethyl)ether | 111-44-4 | X | | X | X |
| 2-Chlorophenol | 95-57-8 | X | | X | X |
| 1,3-Dichlorobenzene | 541-73-1 | X | | X | X |
| 1,4-Dichlorobenzene | 106-46-7 | X | X | X | X |
| Benzyl alcohol | 100-51-6 | | | | X |
| 1,2-Dichlorobenzene | 95-50-1 | X | | X | X |
| 2-Methylphenol | 95-48-7 | X | X | X | X |
| 2,2'-oxybis(1-chloropropane)[1] | 180-60-1 | X | | X | X |
| 4-Methylphenol | 106-44-5 | X | X | X | X |
| N-Nitroso-di-n-propylamine | 621-64-7 | X | | X | X |

**Table 3**

**Reportable Analytes for STL North Canton Standard Tests, Primary Standard**

| Analyte | CAS Number | STL North Canton Standard List | TCLP | TCL | Appendix IX |
|---|---|---|---|---|---|
| Hexachloroethane | 67-72-1 | X | X | X | X |
| Nitrobenzene | 98-95-3 | X | X | X | X |
| Isophorone | 78-59-1 | X | | X | X |
| 2-Nitrophenol | 88-75-5 | X | | X | X |
| 2,4-Dimethylphenol | 105-67-9 | X | | X | X |
| Benzoic acid | 65-85-0 | | | | |
| Bis(2-chloroethoxy)methane | 111-91-1 | X | | X | X |
| 2,4-Dichlorophenol | 120-83-2 | X | | X | X |
| 1,2,4-Trichlorobenzene | 120-82-1 | X | | X | X |
| Naphthalene | 91-20-3 | X | | X | X |
| 4-Chloroaniline | 106-47-8 | X | | X | X |
| Hexachlorobutadiene | 87-68-3 | X | X | X | X |
| 4-Chloro-3-methylphenol | 59-50-7 | X | | X | X |
| 2-Methylnaphthalene | 91-57-6 | X | | X | X |
| Hexachlorocyclopentadiene | 77-47-4 | X | | X | X |
| 2,4,6-Trichlorophenol | 88-06-2 | X | X | X | X |
| 2,4,5-Trichlorophenol | 95-95-4 | X | X | X | X |
| 2-Chloronaphthalene | 91-58-7 | X | | X | X |
| 2-Nitroaniline | 88-74-4 | X | | X | X |
| Dimethyl phthalate | 131-11-3 | X | | X | X |
| Acenaphthylene | 208-96-8 | X | | X | X |
| 3-Nitroaniline | 99-09-2 | X | | X | X |
| Acenaphthene | 83-32-9 | X | | X | X |
| 2,4-Dinitrophenol | 51-28-5 | X | | X | X |
| 4-Nitrophenol | 100-02-7 | X | | X | X |
| Dibenzofuran | 132-64-9 | X | | X | X |
| 2,4-Dinitrotoluene | 121-14-2 | X | X | X | X |
| 2,6-Dinitrotoluene | 606-20-2 | X | | X | X |
| Diethylphthalate | 84-66-2 | X | | X | X |
| 4-Chlorophenyl phenyl ether | 7005-72-3 | X | | X | X |
| Fluorene | 86-73-7 | X | | X | X |
| 4-Nitroaniline | 100-01-6 | X | | X | X |
| 4,6-Dinitro-2-methylphenol | 534-52-1 | X | | X | X |
| N-Nitrosodiphenylamine | 86-30-6 | X | | X | X |
| Azobenzene[4] | 103-33-3 | | | | |
| 4-Bromophenyl phenyl ether | 101-55-3 | X | | X | X |
| Hexachlorobenzene | 118-74-1 | X | X | X | X |
| Pentachlorophenol | 87-86-5 | X | X | X | X |
| Phenanthrene | 85-01-8 | X | | X | X |
| Anthracene | 120-12-7 | X | | X | X |
| Carbazole | 86-74-8 | X | | X | |
| Di-n-butyl phthalate | 84-74-2 | X | | X | X |
| Fluoranthene | 206-44-0 | X | | X | X |
| Benzidine | 92-87-5 | | | | |
| Pyrene | 129-00-0 | X | | X | X |

**Table 3**

**Reportable Analytes for STL North Canton Standard Tests, Primary Standard**

| Analyte | CAS Number | STL North Canton Standard List | TCLP | TCL | Appendix IX |
|---|---|---|---|---|---|
| Butyl benzyl phthalate | 85-68-7 | X | | X | X |
| 3,3'-Dichlorobenzidine | 91-94-1 | X | | X | X |
| Benzo(a)anthracene | 56-55-3 | X | | X | X |
| Bis(2-ethylhexyl)phthalate | 117-81-7 | X | | X | X |
| Chrysene | 218-01-9 | X | | X | X |
| Di-n-octylphthalate | 117-84-0 | X | | X | X |
| Benzo(b)fluoranthene | 205-99-2 | X | | X | X |
| Benzo(k)fluoranthene | 207-08-9 | X | | X | X |
| Benzo(a)pyrene | 50-32-8 | X | | X | X |
| Indeno(1,2,3-cd)pyrene | 193-39-5 | X | | X | X |
| Dibenz(a,h)anthracene | 53-70-3 | X | | X | X |
| Benzo(g,h,i)perylene | 191-24-2 | X | | X | X |
| Benzaldehyde | 100-52-7 | | | X | |
| Caprolactam | 105-60-2 | | | X | |
| 1,1-Biphenyl | 92-52-4 | | | X | |
| Atrazine | 1912-24-9 | | | X | |

[1] 2,2'oxybis(1-chloropropane) was formally known as bis(2-chloroisopropyl)ether

[2] Azobenzene is formed by decomposition of 1,2-diphenlyhydrazine. If 1,2-diphenylhydrazine is requested, it will be analyzed as azobenzene.

**Table 4**

**Reportable analytes for STL North Canton Standard Tests, Appendix IX Standard**

| Semivolatiles | CAS Number | STL North Canton Standard List | TCLP | TCL | Appendix IX |
|---|---|---|---|---|---|
| 2-Picoline | 109-06-8 | | | | X |
| N-Nitrosomethylethylamine | 10595-95-6 | | | | X |
| Methyl methanesulfonate | 66-27-3 | | | | X |
| N-Nitrosodiethylamine | 55-18-5 | | | | X |
| Ethyl methanesulfonate | 62-50-0 | | | | X |
| Pentachloroethane | 76-01-7 | | | | X |
| Acetophenone | 98-86-2 | | | X | X |
| N-Nitrosopyrrolidine | 930-55-2 | | | | X |
| N-Nitrosomorpholine | 59-89-2 | | | | X |
| o-Toluidine | 95-53-4 | | | | X |
| 3-Methylphenol | 108-39-4 | | | | X |
| N-Nitrosopiperidine | 100-75-4 | | | | X |
| o,o,o-Triethyl-Phosphorothioate[2] | 126-68-1 | | | | X |
| a,a-Dimethyl-phenethylamine | 122-09-8 | | | | X |
| 2,6-Dichlorophenol | 87-65-0 | | | | X |
| Hexachloropropene | 1888-71-7 | | | | X |
| p-Phenylenediamine | 106-50-3 | | | | X |
| n-Nitrosodi-n-butylamine | 924-16-3 | | | | X |
| Safrole | 94-59-7 | | | | X |
| 1,2,4,5-Tetrachlorobenzene | 95-94-3 | | | | X |
| Isosafrole | 120-58-1 | | | | X |
| 1,4-Dinitrobenzene | 100-25-4 | | | | |
| 1,4-Naphthoquinone | 130-15-4 | | | | X |
| 1,3-Dinitrobenzene | 99-65-0 | | | | X |
| Pentachlorobenzene | 608-93-5 | | | | X |
| 1-Naphthylamine | 134-32-7 | | | | X |
| 2-Naphthylamine | 91-59-8 | | | | X |
| 2,3,4,6-Tetrachlorophenol | 58-90-2 | | | | X |
| 5-Nitro-o-toluidine | 99-55-8 | | | | X |
| Thionazin[2] | 297-97-2 | | | | X |
| 1,3,5-Trinitrobenzene | 99-35-4 | | | | X |
| Sulfotepp[2] | 3689-24-5 | | | | X |
| Phorate[2] | 298-02-2 | | | | X |
| Phenacetin | 62-44-2 | | | | X |
| Diallate | 2303-16-4 | | | | X |
| Dimethoate[2] | 60-51-5 | | | | X |
| 4-Aminobiphenyl | 92-67-1 | | | | X |
| Pentachloronitrobenzene | 82-68-8 | | | | X |
| Pronamide | 23950-58-5 | | | | X |
| Disulfoton[2] | 298-04-4 | | | | X |
| 2-secbutyl-4,6-dinitrophenol (Dinoseb)[2] | 88-85-7 | | | | X |
| *Methyl parathion[2] | 298-00-0 | | | | X |
| 4-Nitroquinoline-1-oxide | 56-57-5 | | | | X |

**Table 4**

**Reportable analytes for STL North Canton Standard Tests, Appendix IX Standard**

| Semivolatiles | CAS Number | STL North Canton Standard List | TCLP | TCL | Appendix IX |
|---|---|---|---|---|---|
| *Parathion[2] | 56-38-2 | | | | X |
| *Isodrin[3] | 465-73-6 | | | | X |
| *Kepone [2] | 143-50-0 | | | | X |
| Famphur[2] | 52-85-7 | | | | X |
| Methapyrilene | 91-80-5 | | | | X |
| Aramite | 140-57-8 | | | | X |
| p-(Dimethylamino)azobenzene | 60-11-7 | | | | X |
| p-Chlorobenzilate[3] | 510-15-6 | | | | X |
| 3,3'-Dimethylbenzidine | 119-93-7 | | | | X |
| 2-Acetylaminofluorene | 53-96-3 | | | | X |
| Dibenz(a,j)acridine | 224-42-0 | | | | |
| 7,12-Dimethylbenz(a)anthracene | 57-97-6 | | | | X |
| 3-Methylcholanthrene | 56-49-5 | | | | X |
| Hexachlorophene[4] | 70-30-4 | | | | X |
| Diphenylamine[5] | 122-39-4 | | | | X |

[2] May also be analyzed by method 8140 or 8141, which can achieve lower reporting limits.

[3] May also be analyzed by method 8080 or 8081, which can achieve lower reporting limits

[4] Hexachlorophene is a required analyte for Appendix IX. This compound is not stable, and therefore not included in the calibration standard. The characteristic ions for hexachlorophene are searched for in the chromatogram. (See section 12.2.1)

[5] Diphenylamine is a required compound for Appendix IX. N-nitrosodiphenylamine decomposes in the injection port to form diphenylamine. Therefore these two compounds cannot be distinguished. Diphenylamine is not included in the calibration standard.

* These compounds are analyzed by GC methods at STL North Canton.

**Table 5**

**Suggested Instrumental Conditions**

| | |
|---|---|
| Mass Range | 35-500 amu |
| Scan Time | ≤1 second/scan |
| Initial Column Temperature/Hold Time | 40°C for 2 minutes |
| Column Temperature Program | 40 - 320°C at 11.5°C/min |
| Final Column Temperature/Hold Time | 320°C (until at least one minute after benzo(g,h,i)perylene has eluted) |
| Injector Temperature | 250 - 300°C |
| Transfer Line Temperature | 250 - 300°C |
| Source Temperature | According to manufacturer's specifications |
| Injector | Grob-type, split / splitless |
| Sample Volume | 1 or 2 µl |
| Carrier Gas | Helium at 30 cm/sec |

**Table 6**

**DFTPP Key Ions and Ion Abundance Criteria**

| Mass | Ion Abundance Criteria |
|---|---|
| 51 | 30 - 60% of mass 198 |
| 68 | <2% of mass 69 |
| 70 | <2% of mass 69 |
| 127 | 40 - 60% of mass 198 |
| 197 | <1% of mass 198 |
| 198 | Base peak, 100% relative abundance |
| 199 | 5 - 9% of mass 198 |
| 275 | 10 - 30% of mass 198 |
| 365 | >1% of mass 198 |
| 441 | Present, but less than mass 443 |
| 442 | >40% of mass 198 |
| 443 | 17 - 23% of mass 442 |

**Table 7**

**Analytes in Approximate Retention Time Order and Characteristic Ions, Primary Standard**

| Analyte | Primary | Secondary | Tertiary |
|---|---|---|---|
| N-nitrosodimethylamine | 74 | 42 | |
| Pyridine | 79 | 52 | |
| **2-Fluorophenol (Surrogate Standard)** | 112 | 64 | 63 |
| **Phenol-d5 (Surrogate Standard)** | 99 | 42 | 71 |
| Benzaldehyde | 77 | 105 | 106 |
| Aniline | 93 | 66 | |
| Phenol | 94 | 65 | 66 |
| Bis(2-chloroethyl)ether | 93 | 63 | 95 |
| 2-Chlorophenol | 128 | 64 | 130 |
| 1,3-Dichlorobenzene | 146 | 148 | 113 |
| **1,4-Dichlorobenzene-d4 (Internal Standard)** | 152 | 150 | 115 |
| 1,4-Dichlorobenzene | 146 | 148 | 113 |
| Benzyl Alcohol | 108 | 79 | 77 |
| 1,2-Dichlorobenzene | 146 | 148 | 113 |
| 2-Methylphenol | 108 | 107 | 79 |
| 2,2'-oxybis(1-chloropropane)[1] | 45 | 77 | 79 |
| 4-Methylphenol | 108 | 107 | 79 |
| N-Nitroso-di-n-propylamine | 70 | 42 | 101,130 |
| Hexachloroethane | 117 | 201 | 199 |
| **Nitrobenzene-d5 (Surrogate Standard)** | 82 | 128 | 54 |
| Nitrobenzene | 77 | 123 | 65 |
| Isophorone | 82 | 95 | 138 |
| 2-Nitrophenol | 139 | 65 | 109 |
| 2,4-Dimethylphenol | 107 | 121 | 122 |
| Benzoic Acid | 122 | 105 | 77 |
| Bis(2-chloroethoxy)methane | 93 | 95 | 123 |
| 2,4-Dichlorophenol | 162 | 164 | 98 |
| 1,2,4-Trichlorobenzene | 180 | 182 | 145 |
| **Naphthalene-d8 (Internal Standard)** | 136 | 68 | 54 |
| Naphthalene | 128 | 129 | 127 |
| 4-Chloroaniline | 127 | 129 | 65 |
| Hexachlorobutadiene | 225 | 223 | 227 |
| Caprolactam | 113 | 55 | 56 |
| 4-Chloro-3-methylphenol | 107 | 144 | 142 |
| 2-Methylnaphthalene | 142 | 141 | 115 |
| Hexachlorocyclopentadiene | 237 | 235 | 272 |
| 2,4,6-Trichlorophenol | 196 | 198 | 200 |
| 2,4,5-Trichlorophenol | 196 | 198 | 200 |
| 1,1'-Biphenyl | 154 | 153 | 76 |
| **2-Fluorobiphenyl (Surrogate Standard)** | 172 | 171 | 170 |
| 2-Chloronaphthalene | 162 | 164 | 127 |
| 2-Nitroaniline | 65 | 92 | 138 |

**Table 7**

**Analytes in Approximate Retention Time Order and Characteristic Ions, Primary Standard**

| Analyte | Primary | Secondary | Tertiary |
|---|---|---|---|
| Dimethylphthalate | 163 | 194 | 164 |
| Acenaphthylene | 152 | 151 | 153 |
| 2,6-Dinitrotoluene | 165 | 63 | 89 |
| **Acenaphthene-d10 (Internal Standard)** | 164 | 162 | 160 |
| 3-Nitroaniline | 138 | 108 | 92 |
| Acenaphthene | 153 | 152 | 154 |
| 2,4-Dinitrophenol | 184 | 63 | 154 |
| Dibenzofuran | 168 | 139 | 84 |
| 4-Nitrophenol | 109 | 139 | 65 |
| 2,4-Dinitrotoluene | 165 | 63 | 89 |
| Diethylphthalate | 149 | 177 | 150 |
| Fluorene | 166 | 165 | 167 |
| 4-Chlorophenylphenylether | 204 | 206 | 141 |
| 4-Nitroaniline | 138 | 92 | 108 |
| 4,6-Dinitro-2-methylphenol | 198 | 182 | 77 |
| N-Nitrosodiphenylamine | 169 | 168 | 167 |
| **2,4,6-Tribromophenol (Surrogate Standard)** | 330 | 332 | 141 |
| Azobenzene | 77 | 182 | 105 |
| 4-Bromophenylphenylether | 248 | 250 | 141 |
| Hexachlorobenzene | 284 | 142 | 249 |
| Atrazine | 200 | 173 | 215 |
| Pentachlorophenol | 266 | 264 | 268 |
| **Phenanthrene-d10 (Internal Standard)** | 188 | 94 | 80 |
| Phenanthrene | 178 | 179 | 176 |
| Anthracene | 178 | 179 | 176 |
| Carbazole | 167 | 166 | 139 |
| Di-n-butylphthalate | 149 | 150 | 104 |
| Fluoranthene | 202 | 101 | 100 |
| Benzidine | 184 | 92 | 185 |
| Pyrene | 202 | 101 | 100 |
| **Terphenyl-d14 (Surrogate Standard)** | 244 | 122 | 212 |
| Butylbenzylphthalate | 149 | 91 | 206 |
| Benzo(a)Anthracene | 228 | 229 | 226 |
| **Chrysene-d12 (Internal Standard)** | 240 | 120 | 236 |
| 3,3'-Dichlorobenzidine | 252 | 254 | 126 |
| Chrysene | 228 | 226 | 229 |
| Bis(2-ethylhexyl)phthalate | 149 | 167 | 279 |
| Di-n-octylphthalate | 149 | 167 | 43 |
| Benzo(b)fluoranthene | 252 | 253 | 125 |
| Benzo(k)fluoranthene | 252 | 253 | 125 |
| Benzo(a)pyrene | 252 | 253 | 125 |
| **Perylene-d12 (Internal Standard)** | 264 | 260 | 265 |
| Indeno(1,2,3-cd)pyrene | 276 | 138 | 277 |
| Dibenz(a,h)anthracene | 278 | 139 | 279 |

**Table 7**

**Analytes in Approximate Retention Time Order and Characteristic Ions, Primary Standard**

| Analyte | Primary | Secondary | Tertiary |
|---|---|---|---|
| Benzo(g,h,i)perylene | 276 | 138 | 277 |

**Table 8**

**Analytes in Approximate Retention Time Order and Characteristic Ions, Appendix IX Standard**

| Analyte | Primary | Secondary | Tertiary |
|---|---|---|---|
| 2-Picoline | 93 | 66 | 92 |
| N-Nitrosomethylethylamine | 88 | 42 | 43 |
| Methyl methanesulfonate | 80 | 79 | 65 |
| N-Nitrosodiethylamine | 102 | 44 | 57 |
| Ethyl methanesulfonate | 79 | 109 | 97 |
| Pentachloroethane | 117 | 119 | 167 |
| Acetophenone | 105 | 77 | 120 |
| N-Nitrosopyrrolidine | 100 | 41 | 42 |
| N-Nitrosomorpholine | 116 | 56 | 86 |
| o-Toluidine | 106 | 107 | |
| 3-Methylphenol | 108 | 107 | 77 |
| N-Nitrosopiperidine | 114 | 42 | 55 |
| o,o,o-Triethyl-Phosphorothioate | 198 | 121 | 93 |
| a,a-Dimethyl-phenethylamine | 58 | 91 | |
| 2,6-Dichlorophenol | 162 | 164 | 63 |
| Hexachloropropene | 213 | 215 | 211 |
| p-Phenylenediamine | 108 | 80 | |
| n-Nitrosodi-n-butylamine | 84 | 57 | 41 |
| Safrole | 162 | 104 | 77 |
| 1,2,4,5-Tetrachlorobenzene | 216 | 214 | 218 |
| Isosafrole 1 | 162 | 104 | 131 |
| Isosafrole 2 | 162 | 104 | 131 |
| 1,4-Dinitrobenzene | 168 | 75 | 122 |
| 1,4-Naphthoquinone | 158 | 104 | 102 |
| 1,3-Dinitrobenzene | 168 | 75 | 76 |
| Pentachlorobenzene | 250 | 248 | 252 |
| 1-Naphthylamine | 143 | 115 | |
| 2-Naphthylamine | 143 | 115 | |
| 2,3,4,6-Tetrachlorophenol | 232 | 230 | 131 |
| 5-Nitro-o-toluidine | 152 | 77 | 106 |
| Thionazin | 97 | 96 | 143 |
| 1,3,5-Trinitrobenzene | 213 | 75 | 120 |
| Sulfotepp | 97 | 322 | 202 |
| Phorate | 75 | 97 | 121 |
| Phenacetin | 108 | 179 | 109 |
| Diallate | 86 | 234 | |
| Dimethoate | 87 | 93 | 125 |
| 4-Aminobiphenyl | 169 | | |
| Pentachloronitrobenzene | 237 | 142 | 214 |
| Pronamide | 173 | 175 | 255 |
| Disulfoton | 88 | 97 | 89 |
| 2-secbutyl-4,6-dinitrophenol (Dinoseb) | 211 | 163 | 147 |
| Methyl parathion | 109 | 125 | 263 |
| 4-Nitroquinoline-1-oxide | 190 | 128 | 160 |
| Parathion | 109 | 97 | 291 |

**Table 8**

**Analytes in Approximate Retention Time Order and Characteristic Ions, Appendix IX Standard**

| Analyte | Primary | Secondary | Tertiary |
|---|---|---|---|
| Isodrin | 193 | 66 | 195 |
| Kepone | 272 | 274 | 237 |
| Famphur | 218 | 125 | 93 |
| Methapyrilene | 97 | 58 | |
| Aramite 1 | 185 | 319 | |
| Aramite 2 | 185 | 319 | |
| p-(Dimethylamino)azobenzene | 120 | 225 | 77 |
| p-Chlorobenzilate | 251 | 139 | 253 |
| 3,3'-Dimethylbenzidine | 212 | 106 | |
| 2-Acetylaminofluorene | 181 | 180 | 223 |
| Dibenz(a,j)acridine | 279 | 280 | |
| 7,12-Dimethylbenz(a)anthracene | 256 | 241 | 120 |
| 3-Methylcholanthrene | 268 | 252 | 253 |

**Table 9**

**8270C LCS Compounds**

| LCS Compounds | Spiking Level, ng/µL in extract[1] |
|---|---|
| 1,2,4-Trichlorobenzene | 100 |
| Acenaphthene | 100 |
| 2,4-Dinitrotoluene | 100 |
| Pyrene | 100 |
| N-Nitroso-di-n-propylamine | 100 |
| 1,4-Dichlorobenzene | 100 |
| Pentachlorophenol | 150 |
| Phenol | 150 |
| 2-Chlorophenol | 150 |
| 4-Chloro-3-methylphenol | 150 |
| 4-Nitrophenol | 150 |

[1] Levels are 50 and 75 ng/µL if 2 µL injection is used

**Table 10**

**TCLP LCS Compounds**

| LCS Compounds | Spiking Level, ng/µL in extract[1] |
|---|---|
| 1,4-Dichlorobenzene | 100 |
| 2,4-Dinitrotoluene | 100 |
| Hexachlorobenzene | 100 |
| Hexachlorobutadiene | 100 |
| Hexachloroethane | 100 |
| 2-Methylphenol | 100 |
| 3-Methylphenol | 100 |
| 4-Methylphenol | 100 |
| Nitrobenzene | 100 |
| Pentachlorophenol | 100 |
| Pyridine | 100 |
| 2,4,5-Trichlorophenol | 100 |
| 2,4,6-Trichlorophenol | 100 |

[1] Levels are 50 ng/µL if 2 µL injection is used

Recovery limits for the LCS and for matrix spikes are generated from historical data and are maintained by the QA department.

**Table 11**

**8270C Surrogate Compounds**

| Surrogate Compounds | Spiking Level, ng/µL in extract[2] |
|---|---|
| Nitrobenzene-d5 | 100 |
| 2-Fluorobiphenyl | 100 |
| Terphenyl-d14 | 100 |
| 1,2-Dichlorobenzene-d4[1] | 100 |
| Phenol-d5 | 150 |
| 2-Fluorophenol | 150 |
| 2,4,6-Tribromophenol | 150 |
| 2-Chlorophenol-d4[1] | 150 |

[1] Included in standard mix, but not routinely evaluated for method 8270B

[2] Levels are 50 and 75 ng/µL if 2 µL injection is used

Recovery limits for surrogates are generated from historical data and are maintained by the QA department.

**Table 12[3]**
**Calibration Levels, Primary Standard, µg/mL**

| Analyte | Level 1 | Level 2 | Level 3 | Level 4 | Level 5 |
|---|---|---|---|---|---|
| Pyridine | 10 | 25 | 40 | 60 | 80 |
| N-nitrosodimethylamine | 10 | 25 | 40 | 60 | 80 |
| Aniline | 10 | 25 | 40 | 60 | 80 |
| Phenol | 10 | 25 | 40 | 60 | 80 |
| Bis(2-chloroethyl)ether | 10 | 25 | 40 | 60 | 80 |
| 2-Chlorophenol | 10 | 25 | 40 | 60 | 80 |
| 1,3-Dichlorobenzene | 10 | 25 | 40 | 60 | 80 |
| 1,4-Dichlorobenzene | 10 | 25 | 40 | 60 | 80 |
| Benzyl alcohol | 10 | 25 | 40 | 60 | 80 |
| 1,2-Dichlorobenzene | 10 | 25 | 40 | 60 | 80 |
| 2-Methylphenol | 10 | 25 | 40 | 60 | 80 |
| 2,2'-oxybis(1-chloropropane)[1] | 10 | 25 | 40 | 60 | 80 |
| 4-Methylphenol | 10 | 25 | 40 | 60 | 80 |
| N-Nitroso-di-n-propylamine | 10 | 25 | 40 | 60 | 80 |
| Hexachloroethane | 10 | 25 | 40 | 60 | 80 |
| Nitrobenzene | 10 | 25 | 40 | 60 | 80 |
| Isophorone | 10 | 25 | 40 | 60 | 80 |
| 2-Nitrophenol | 10 | 25 | 40 | 60 | 80 |
| 2,4-Dimethylphenol | 10 | 25 | 40 | 60 | 80 |
| Benzoic acid | 10 | 25 | 40 | 60 | 80 |
| Bis(2-chloroethoxy)methane | 10 | 25 | 40 | 60 | 80 |
| 2,4-Dichlorophenol | 10 | 25 | 40 | 60 | 80 |
| 1,2,4-Trichlorobenzene | 10 | 25 | 40 | 60 | 80 |
| Naphthalene | 10 | 25 | 40 | 60 | 80 |
| 4-Chloroaniline | 10 | 25 | 40 | 60 | 80 |
| Hexachlorobutadiene | 10 | 25 | 40 | 60 | 80 |
| 4-Chloro-3-methylphenol | 10 | 25 | 40 | 60 | 80 |
| 2-Methylnaphthalene | 10 | 25 | 40 | 60 | 80 |
| Hexachlorocyclopentadiene | 10 | 25 | 40 | 60 | 80 |
| 2,4,6-Trichlorophenol | 10 | 25 | 40 | 60 | 80 |
| 2,4,5-Trichlorophenol | 10 | 25 | 40 | 60 | 80 |
| 2-Chloronaphthalene | 10 | 25 | 40 | 60 | 80 |
| 2-Nitroaniline | 10 | 25 | 40 | 60 | 80 |
| Dimethyl phthalate | 10 | 25 | 40 | 60 | 80 |
| Acenaphthylene | 10 | 25 | 40 | 60 | 80 |
| 3-Nitroaniline | 10 | 25 | 40 | 60 | 80 |
| Acenaphthene | 10 | 25 | 40 | 60 | 80 |
| 2,4-Dinitrophenol | 10 | 25 | 40 | 60 | 80 |
| 4-Nitrophenol | 10 | 25 | 40 | 60 | 80 |
| Dibenzofuran | 10 | 25 | 40 | 60 | 80 |
| 2,4-Dinitrotoluene | 10 | 25 | 40 | 60 | 80 |
| 2,6-Dinitrotoluene | 10 | 25 | 40 | 60 | 80 |
| Diethylphthalate | 10 | 25 | 40 | 60 | 80 |
| 4-Chlorophenyl phenyl ether | 10 | 25 | 40 | 60 | 80 |
| Fluorene | 10 | 25 | 40 | 60 | 80 |
| 4-Nitroaniline | 10 | 25 | 40 | 60 | 80 |
| 4,6-Dinitro-2-methylphenol | 10 | 25 | 40 | 60 | 80 |

**Table 12[3]**
**Calibration Levels, Primary Standard, µg/mL**

| Analyte | Level 1 | Level 2 | Level 3 | Level 4 | Level 5 |
|---|---|---|---|---|---|
| N-Nitrosodiphenylamine | 10 | 25 | 40 | 60 | 80 |
| Azobenzene[2] | 10 | 25 | 40 | 60 | 80 |
| 4-Bromophenyl phenyl ether | 10 | 25 | 40 | 60 | 80 |
| Hexachlorobenzene | 10 | 25 | 40 | 60 | 80 |
| Pentachlorophenol | 10 | 25 | 40 | 60 | 80 |
| Phenanthrene | 10 | 25 | 40 | 60 | 80 |
| Anthracene | 10 | 25 | 40 | 60 | 80 |
| Carbazole | 10 | 25 | 40 | 60 | 80 |
| Di-n-butyl phthalate | 10 | 25 | 40 | 60 | 80 |
| Fluoranthene | 10 | 25 | 40 | 60 | 80 |
| Benzidine | 10 | 25 | 40 | 60 | 80 |
| Pyrene | 10 | 25 | 40 | 60 | 80 |
| Butyl benzyl phthalate | 10 | 25 | 40 | 60 | 80 |
| 3,3'-Dichlorobenzidine | 10 | 25 | 40 | 60 | 80 |
| Benzo(a)anthracene | 10 | 25 | 40 | 60 | 80 |
| Bis(2-ethylhexyl)phthalate | 10 | 25 | 40 | 60 | 80 |
| Chrysene | 10 | 25 | 40 | 60 | 80 |
| Di-n-octylphthalate | 10 | 25 | 40 | 60 | 80 |
| Benzo(b)fluoranthene | 10 | 25 | 40 | 60 | 80 |
| Benzo(k)fluoranthene | 10 | 25 | 40 | 60 | 80 |
| Benzo(a)pyrene | 10 | 25 | 40 | 60 | 80 |
| Indeno(1,2,3-cd)pyrene | 10 | 25 | 40 | 60 | 80 |
| Dibenz(a,h)anthracene | 10 | 25 | 40 | 60 | 80 |
| Benzo(g,h,i)perylene | 10 | 25 | 40 | 60 | 80 |
| Benzaldehyde | 10 | 25 | 40 | 60 | 80 |
| Caprolactam | 10 | 25 | 40 | 60 | 80 |
| 1,1'-Biphenyl | 10 | 25 | 40 | 60 | 80 |
| Atrazine | 10 | 25 | 40 | 60 | 80 |

[1] 2,2'oxybis(1-chloropropane) was formally known as bis(2-chloroisopropyl)ether

[2]Azobenzene is formed by decomposition of 1,2-diphenlyhydrazine. If 1,2-diphenylhydrazine is requested, it will be analyzed as azobenzene.

[3]Optional concentration levels = 1/5 of the listed concentrations for samples with a final volume of 5 mL.

**Table 13[1]**

**Calibration Levels, Appendix IX Standard, µg/mL**

| Semivolatiles | Level 1 | Level 2 | Level 3 | Level 4 | Level 5 |
|---|---|---|---|---|---|
| 2-Picoline | 10 | 25 | 40 | 60 | 80 |
| N-Nitrosomethylethylamine | 10 | 25 | 40 | 60 | 80 |
| Methyl methanesulfonate | 10 | 25 | 40 | 60 | 80 |
| N-Nitrosodiethylamine | 10 | 25 | 40 | 60 | 80 |
| Ethyl methanesulfonate | 10 | 25 | 40 | 60 | 80 |
| Pentachloroethane | 10 | 25 | 40 | 60 | 80 |
| Acetophenone | 10 | 25 | 40 | 60 | 80 |
| N-Nitrosopyrrolidine | 10 | 25 | 40 | 60 | 80 |
| N-Nitrosomorpholine | 10 | 25 | 40 | 60 | 80 |
| o-Toluidine | 10 | 25 | 40 | 60 | 80 |
| 3-Methylphenol | 10 | 25 | 40 | 60 | 80 |
| N-Nitrosopiperidine | 10 | 25 | 40 | 60 | 80 |
| o,o,o-Triethyl-Phosphorothioate | 10 | 25 | 40 | 60 | 80 |
| a,a-Dimethyl-phenethylamine | 10 | 25 | 40 | 60 | 80 |
| 2,6-Dichlorophenol | 10 | 25 | 40 | 60 | 80 |
| Hexachloropropene | 10 | 25 | 40 | 60 | 80 |
| p-Phenylenediamine | 10 | 25 | 40 | 60 | 80 |
| n-Nitrosodi-n-butylamine | 10 | 25 | 40 | 60 | 80 |
| Safrole | 10 | 25 | 40 | 60 | 80 |
| 1,2,4,5-Tetrachlorobenzene | 10 | 25 | 40 | 60 | 80 |
| Isosafrole 1 + 2 | 10 | 25 | 40 | 60 | 80 |
| 1,4-Dinitrobenzene | 10 | 25 | 40 | 60 | 80 |
| 1,4-Naphthoquinone | 10 | 25 | 40 | 60 | 80 |
| 1,3-Dinitrobenzene | 10 | 25 | 40 | 60 | 80 |
| Pentachlorobenzene | 10 | 25 | 40 | 60 | 80 |
| 1-Naphthylamine | 10 | 25 | 40 | 60 | 80 |
| 2-Naphthylamine | 10 | 25 | 40 | 60 | 80 |
| 2,3,4,6-Tetrachlorophenol | 10 | 25 | 40 | 60 | 80 |
| 5-Nitro-o-toluidine | 10 | 25 | 40 | 60 | 80 |
| Thionazin | 10 | 25 | 40 | 60 | 80 |
| 1,3,5-Trinitrobenzene | 10 | 25 | 40 | 60 | 80 |
| Sulfotepp | 10 | 25 | 40 | 60 | 80 |
| Phorate | 10 | 25 | 40 | 60 | 80 |
| Phenacetin | 10 | 25 | 40 | 60 | 80 |
| Diallate 1 + 2 | 10 | 25 | 40 | 60 | 80 |
| Dimethoate | 10 | 25 | 40 | 60 | 80 |
| 4-Aminobiphenyl | 10 | 25 | 40 | 60 | 80 |
| Pentachloronitrobenzene | 10 | 25 | 40 | 60 | 80 |
| Pronamide | 10 | 25 | 40 | 60 | 80 |
| Disulfoton | 10 | 25 | 40 | 60 | 80 |
| 2-secbutyl-4,6-dinitrophenol (Dinoseb) | 10 | 25 | 40 | 60 | 80 |
| *Methyl parathion | 10 | 25 | 40 | 60 | 80 |
| 4-Nitroquinoline-1-oxide | 10 | 25 | 40 | 60 | 80 |
| *Parathion | 10 | 25 | 40 | 60 | 80 |
| *Isodrin | 10 | 25 | 40 | 60 | 80 |

**Table 13[1]**

**Calibration Levels, Appendix IX Standard, µg/mL**

| Semivolatiles | Level 1 | Level 2 | Level 3 | Level 4 | Level 5 |
|---|---|---|---|---|---|
| *Kepone | 10 | 25 | 40 | 60 | 80 |
| Famphur | 10 | 25 | 40 | 60 | 80 |
| Methapyrilene | 10 | 25 | 40 | 60 | 80 |
| Aramite 1 and 2 | 10 | 25 | 40 | 60 | 80 |
| p-(Dimethylamino)azobenzene | 10 | 25 | 40 | 60 | 80 |
| p-Chlorobenzilate | 10 | 25 | 40 | 60 | 80 |
| 3,3'-Dimethylbenzidine | 10 | 25 | 40 | 60 | 80 |
| 2-Acetylaminofluorene | 10 | 25 | 40 | 60 | 80 |
| Dibenz (a,j)acridine | 10 | 25 | 40 | 60 | 80 |
| 7,12-Dimethylbenz(a)anthracene | 10 | 25 | 40 | 60 | 80 |
| 3-Methylcholanthrene | 10 | 25 | 40 | 60 | 80 |

* These compounds are not in the STL North Canton Standard Mix,

[2]Optional concentration levels = 1/5 of the listed concentrations for samples with a final volume of 5 mL.

**Table 14**
**Initial demonstration recovery and precision limits**

| Compound | Spiking concentration µg/L | Limit for Relative Standard Deviation | Limit for average recovery, % |
|---|---|---|---|
| Acenaphthene | 60 | 27.6 | 60.1-132.3 |
| Acenaphthylene | 60 | 40.2 | 53.5-126.0 |
| Aldrin[1] | 60 | 39.0 | 7.2-152.2 |
| Anthracene | 60 | 32.0 | 43.4-118.0 |
| Benz(a)anthracene | 60 | 27.6 | 41.8-133.0 |
| Benzo(b)fluoranthene | 60 | 38.8 | 42.0-140.4 |
| Benzo(k)fluoranthene | 60 | 32.3 | 25.2-145.7 |
| Benzo(a)pyrene | 60 | 39.0 | 31.7-148.0 |
| Benzo(ghi)perylene | 60 | 58.9 | D-195.0 |
| Benzylbutyl phthalate | 60 | 23.4 | D-139.9 |
| B-BHC[1] | 60 | 31.5 | 41.5-130.6 |
| d-BHC[1] | 60 | 21.6 | D-100.0 |
| Bis(2-chloroethyl) ether | 60 | 55.0 | 42.9-126.0 |
| Bis(2-chloroethoxy)methane | 60 | 34.5 | 49.2-164.7 |
| Bis(2-chloroisopropyl) ether | 60 | 46.3 | 62.8-138.6 |
| Bis(2-ethylhexyl) phthalate | 60 | 41.1 | 28.9-136.8 |
| 4-Bromophenyl phenyl ether | 60 | 23.0 | 64.9-114.4 |
| 2-Chloronaphthalene | 60 | 13.0 | 64.5-113.5 |
| 4-Chlorophenyl phenyl ether | 60 | 33.4 | 38.4-144.7 |
| Chrysene | 60 | 48.3 | 44.1-139.9 |
| 4,4'-DDD[1] | 60 | 31.0 | D-134.5 |
| 4,4'-DDE[1] | 60 | 32.0 | 19.2-119.7 |
| 4,4'-DDT[1] | 60 | 61.6 | D-170.6 |

**Table 14**
**Initial demonstration recovery and precision limits**

| Compound | Spiking concentration µg/L | Limit for Relative Standard Deviation | Limit for average recovery, % |
|---|---|---|---|
| Dibenzo(a,h)anthracene | 60 | 70.0 | D-199.7 |
| Di-n-butyl phthalate | 60 | 16.7 | 8.4-111.0 |
| 1,2-Dichlorobenzene | 60 | 30.9 | 48.6-112.0 |
| 1,3-Dichlorobenzene | 60 | 41.7 | 16.7-153.9 |
| 1,4-Dichlorobenzene | 60 | 32.1 | 37.3-105.7 |
| 3,3'-Dichlorobenzidine | 60 | 71.4 | 8.2-212.5 |
| Dieldrin[1] | 60 | 30.7 | 44.3-119.3 |
| Diethyl phthalate | 60 | 26.5 | D-100.0 |
| Dimethyl phthalate | 60 | 23.2 | D-100.0 |
| 2,4-Dinitrotoluene | 60 | 21.8 | 47.5-126.9 |
| 2,6-Dinitrotoluene | 60 | 29.6 | 68.1-136.7 |
| Di-n-octylphthalate | 60 | 31.4 | 18.6-131.8 |
| Endosulfan sulfate[1] | 60 | 16.7 | D-103.5 |
| Endrin aldehyde | 60 | 32.5 | D-188.8 |
| Fluoranthene | 60 | 32.8 | 42.9-121.3 |
| Fluorene | 60 | 20.7 | 71.6-108.4 |
| Heptachlor[1] | 60 | 37.2 | D-172.2 |
| Heptachlor epoxide[1] | 60 | 54.7 | 70.9-109.4 |
| Hexachlorobenzene | 60 | 24.9 | 7.8-141.5 |
| Hexachlorobutadiene | 60 | 26.3 | 37.8-102.2 |
| Hexachloroethane | 60 | 24.5 | 55.2-100.0 |
| Indeno(1,2,3-cd)pyrene | 60 | 44.6 | D-150.9 |
| Isophorone | 60 | 63.3 | 46.6-180.2 |
| Naphthalene | 60 | 30.1 | 35.6-119.6 |
| Nitrobenzene | 60 | 39.3 | 54.3-157.6 |
| N-Nitrosodi-n-propylamine | 60 | 55.4 | 13.6-197.9 |
| PCB-1260[1] | 60 | 54.2 | 19.3-121.0 |
| Phenanthrene | 60 | 20.6 | 65.2-108.7 |
| Pyrene | 60 | 25.2 | 69.6-100.0 |
| 1,2,4-Trichlorobenzene | 60 | 28.1 | 57.3-129.2 |
| 4-Chloro-3-methylphenol | 60 | 37.2 | 40.8-127.9 |
| 2-Chlorophenol | 60 | 28.7 | 36.2-120.4 |
| 2,4-Chlorophenol | 60 | 26.4 | 52.5-121.7 |
| 2,4-Dimethylphenol | 60 | 26.1 | 41.8-109.0 |
| 2,4-Dinitrophenol | 60 | 49.8 | D-172.9 |
| 2-Methyl-4,6-dinitrophenol | 60 | 93.2 | 53.0-100.0 |
| 2-Nitrophenol | 60 | 35.2 | 45.0-166.7 |
| 4-Nitrophenol | 60 | 47.2 | 13.0-106.5 |
| Pentachlorophenol | 60 | 48.9 | 38.1-151.8 |
| Phenol | 60 | 22.6 | 16.6-100.0 |
| 2,4,6-Trichlorophenol | 60 | 31.7 | 52.4-129.2 |

[1]Since the organochlorine pesticides and PCBs are normally determined by method 8080 at STL North Canton, they will not be included in the initial demonstration of capability for method 8270B.

# ATTACHMENT A

## MODIFICATIONS REQUIRED FOR ANALYSIS OF WASTEWATER FOLLOWING METHOD 625

## 18. REQUIREMENTS FOR METHOD 625

18.1 Method 625 is required for demonstration of compliance with NPDES wastewater discharge permits. The standard analyte list and reporting limits are listed in Table A-1.

18.2 This method can be applied only to aqueous matrices.

18.3 The tune period for this method is defined as 24 hours.

18.4 Initial calibration curve requirements:

18.4.1 The initial calibration curve for this method requires at least three points.

18.4.2 Target compounds must have RSD ≤ 35%.

18.4.3 If this requirement can not be met, a regression curve must be constructed for the non-compliant compounds.

18.5 Continuing calibration verification requirements: All target compounds must have %D ≤ 20%.

18.6 Matrix Spike and LCS requirements:

18.6.1 A full analyte spike is required for method 625. The spiking levels are given in Table A-2.

*Table A-1. STL North Canton Method 625 standard reporting list and reporting limits.*

| Analytes | CAS Number | Aqueous µg/L |
|---|---|---|
| Phenol | 108-95-2 | 10 |
| Bis(2-chloroethyl)ether | 111-44-4 | 10 |
| 2-Chlorophenol | 95-57-8 | 10 |
| 1,3-Dichlorobenzene | 541-73-1 | 10 |
| 1,4-Dichlorobenzene | 106-46-7 | 10 |
| 1,2-Dichlorobenzene | 95-50-1 | 10 |
| 2,2'-oxybis(1-chloropropane) | 108-60-1 | 10 |
| N-Nitroso-di-n-propylamine | 621-64-7 | 10 |
| Hexachloroethane | 67-72-1 | 10 |
| Nitrobenzene | 98-95-3 | 10 |
| Isophorone | 78-59-1 | 10 |
| 2-Nitrophenol | 88-75-5 | 10 |
| 2,4-Dimethylphenol | 105-67-9 | 10 |
| Bis(2-chloroethoxy)methane | 111-91-1 | 10 |
| 2,4-Dichlorophenol | 120-83-2 | 10 |
| 1,2,4-Trichlorobenzene | 120-82-1 | 10 |
| Naphthalene | 91-20-3 | 10 |
| Hexachlorobutadiene | 87-68-3 | 10 |
| 4-Chloro-3-methylphenol | 59-50-7 | 10 |
| Hexachlorocyclopentadiene | 77-47-4 | 50 |
| 2,4,6-Trichlorophenol | 88-06-2 | 10 |
| 2-Chloronaphthalene | 91-58-7 | 10 |
| Dimethyl phthalate | 131-11-3 | 10 |
| Acenaphthylene | 208-96-8 | 10 |
| Acenaphthene | 83-32-9 | 10 |
| 2,4-Dinitrophenol | 51-28-5 | 50 |
| 4-Nitrophenol | 100-02-7 | 50 |
| 2,4-Dinitrotoluene | 121-14-2 | 10 |
| 2,6-Dinitrotoluene | 606-20-2 | 10 |
| Diethylphthalate | 84-66-2 | 10 |
| 4-Chlorophenyl phenyl ether | 7005-72-3 | 10 |
| Fluorene | 86-73-7 | 10 |
| 4,6-Dinitro-2-methylphenol | 534-52-1 | 50 |
| N-Nitrosodiphenylamine | 86-30-6 | 10 |
| 4-Bromophenyl phenyl ether | 101-55-3 | 10 |
| Hexachlorobenzene | 118-74-1 | 10 |
| Pentachlorophenol | 87-86-5 | 50 |
| Phenanthrene | 85-01-8 | 10 |
| Anthracene | 120-12-7 | 10 |
| Di-n-butyl phthalate | 84-74-2 | 10 |
| Fluoranthene | 206-44-0 | 10 |
| Benzidine | 92-87-5 | 100 |
| Pyrene | 129-00-0 | 10 |
| Butyl benzyl phthalate | 85-68-7 | 10 |

| Analytes | CAS Number | Aqueous µg/L |
|---|---|---|
| 3,3'-Dichlorobenzidine | 91-94-1 | 50 |
| Benzo(a)anthracene | 56-55-3 | 10 |
| Bis(2-ethylhexyl)phthalate | 117-81-7 | 10 |
| Chrysene | 218-01-9 | 10 |
| Di-n-octylphthalate | 117-84-0 | 10 |
| Benzo(b)fluoranthene | 205-99-2 | 10 |
| Benzo(k)fluoranthene | 207-08-9 | 10 |
| Benzo(a)pyrene | 50-32-8 | 10 |
| Indeno(1,2,3-cd)pyrene | 193-39-5 | 10 |
| Dibenz(a,h)anthracene | 53-70-3 | 10 |
| Benzo(g,h,i)perylene | 191-24-2 | 10 |

*Table A-2. Method 625 LCS and MS compounds and spike concentrations.*

| LCS Compounds | Spiking Level, ng/µL in extract[1] |
|---|---|
| Phenol | 100 |
| Bis(2-chloroethyl)ether | 100 |
| 2-Chlorophenol | 100 |
| 1,3-Dichlorobenzene | 100 |
| 1,4-Dichlorobenzene | 100 |
| 1,2-Dichlorobenzene | 100 |
| 2,2'-oxybis(1-chloropropane) | 100 |
| N-Nitroso-di-n-propylamine | 100 |
| Hexachloroethane | 100 |
| Nitrobenzene | 100 |
| Isophorone | 100 |
| 2-Nitrophenol | 100 |
| 2,4-Dimethylphenol | 100 |
| Bis(2-chloroethoxy)methane | 100 |
| 2,4-Dichlorophenol | 100 |
| 1,2,4-Trichlorobenzene | 100 |
| Naphthalene | 100 |
| Hexachlorobutadiene | 100 |
| 4-Chloro-3-methylphenol | 100 |
| Hexachlorocyclopentadiene | 100 |
| 2,4,6-Trichlorophenol | 100 |
| 2-Chloronaphthalene | 100 |
| Dimethyl phthalate | 100 |
| Acenaphthylene | 100 |
| Acenaphthene | 100 |
| 2,4-Dinitrophenol | 100 |
| 4-Nitrophenol | 100 |
| 2,4-Dinitrotoluene | 100 |
| 2,6-Dinitrotoluene | 100 |
| Diethylphthalate | 100 |
| 4-Chlorophenyl phenyl ether | 100 |
| Fluorene | 100 |
| 4,6-Dinitro-2-methylphenol | 100 |
| N-Nitrosodiphenylamine | 100 |
| 4-Bromophenyl phenyl ether | 100 |
| Hexachlorobenzene | 100 |
| Pentachlorophenol | 100 |
| Phenanthrene | 100 |
| Anthracene | 100 |
| Di-n-butyl phthalate | 100 |
| Fluoranthene | 100 |
| Benzidine | 100 |
| Pyrene | 100 |
| Butyl benzyl phthalate | 100 |
| 3,3'-Dichlorobenzidine | 100 |
| Benzo(a)anthracene | 100 |

| LCS Compounds | Spiking Level, ng/µL in extract[1] |
|---|---|
| Bis(2-ethylhexyl)phthalate | 100 |
| Chrysene | 100 |
| Di-n-octylphthalate | 100 |
| Benzo(b)fluoranthene | 100 |
| Benzo(k)fluoranthene | 100 |
| Benzo(a)pyrene | 100 |
| Indeno(1,2,3-cd)pyrene | 100 |
| Dibenz(a,h)anthracene | 100 |
| Benzo(g,h,i)perylene | 100 |

[1]. Levels are 50 and 75 ng/µL if 2 µL injection is used

# STL NORTH CANTON STANDARD OPERATING PROCEDURE

## TITLE: ANALYSIS OF POLYNUCLEAR AROMATIC HYDROCARBONS BY SELECTIVE ION MONITORING (SUPERSEDES: 0.0)

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Date

Reviewed by: Tom Hus 5/14/02
Technical Specialist, Date

Approved by: Beth Lambert 5/14/02
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Approved by: 5-16-02
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# STL NORTH CANTON STANDARD OPERATING PROCEDURE

## TITLE: ANALYSIS OF POLYNUCLEAR AROMATIC HYDROCARBONS BY SELECTIVE ION MONITORING (SUPERSEDES: 0.0)

Prepared by: _____
Date

Reviewed by: _____
Technical Specialist, Date

Approved by: _____
Quality Assurance Manager, Date

Approved by: _____
Environmental Health and Safety Coordinator, Date

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## 1. SCOPE AND APPLICATION

1.1. This procedure is a Gas Chromatography/Mass Spectrometry (GC/MS) technique developed for the purposes of measuring polynuclear aromatic hydrocarbons (PAH) at a reporting level of 0.2 µg/L.(about 50 times lower than normal 8270C levels. Samples containing greater than 10 µg/L semivolatile organics should be analyzed by normal 8270C methodology.

1.2. The LIMs method code is FX.

## 2. SUMMARY OF METHOD

2.1. This analysis is performed by the isolation of the target analytes by liquid-liquid extraction of a water sample with an organic solvent. One liter of sample volume is extracted with methylene chloride. A solid sample (30 g) is extracted with 1:1 methylene chloride/acetone. The extract is concentrated to a volume of 5.0 mL. Identification and quantitation of the target analytes is performed by GC/MS instrument that is set up in the selected ion monitoring mode (SIM). The analyte's retention time (RT) and primary to secondary ion area ratio from analytical standards are used for identification of target analytes in samples. Quantitation is performed using the primary ion area.

## 3. DEFINITIONS

3.1. Selected Ion Monitoring - A mass spectrometry technique that provides lower detection level capability.

3.2. Primary Ion Area - The signal chosen for quantitation purposes.

3.3. Secondary Ion Area - The signal chosen for identification purposes.

## 4. INTERFERENCES

4.1. Method interferences may be caused by contaminants on solvents, reagents, glassware and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the ion current profiles. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analyses by analyzing laboratory reagent blanks.

4.2. Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of the matrix interferences will vary considerably from source to source, depending upon the nature of the environment being sampled.

4.3. An interference that is unique to selected ion monitoring techniques can arise from the presence of an interfering compound that contains the quantitation mass ion. This event results in a positive interference to the reported value for the compound of interest. This interference is controlled to some degree by acquiring data for a confirmation ion. If the ion ratios between the quantitation ion and the confirmation ion are not within the specified limits, then interferences may be detected.

## 5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all STL associates.

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately. VITON gloves may be worn when halogenated solvents are used for extraction or sample preparation, nitrile gloves may be used when other solvents are handled.

**Note**: VITON is readily degraded by acetone; all solvents will readily pass through disposable latex rubber gloves.

5.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory. The following specific hazards are known:

5.3.1. Chemicals that have been classified as **carcinogens**, or **potential carcinogens**, under OSHA include:

Methylene chloride.

5.3.2. Chemicals known to be **flammable** are:

Acetone, methanol.

5.3.3. The following materials are known to be **corrosive**:

Sodium hydroxide, sulfuric acid

5.4. Exposure to chemicals must be maintained **as low as reasonably achievable**, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.5. The preparation of standards and reagents and glassware cleaning procedures that involve solvents such as methylene chloride will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.6. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL associate. The situation must be reported **immediately** to a laboratory supervisor.

## 6. EQUIPMENT AND SUPPLIES

6.1. Refer to SOP CORP-OP-0001NC for sample preparation equipment and supplies.

6.2. Gas Chromatograph/Mass Spectrometer - Hewlett Packard model no. 5973A equipped with a Hewlett Packard 6890 Gas Chromatograph, or equivalent.

## 7. REAGENTS AND STANDARDS

7.1. Refer to SOP CORP-OP-0001NC for sample preparation reagents and standards.

7.2. Surrogate Spiking Solution - The compounds in the surrogate solution are Nitrobenzene–d5, 2-Fluorobiphenyl, Terphenyl–d14, Phenol–d5, 2-Fluorphenol, 2,4,6-Tribromophenol . The surrogate mix is prepared in methanol at a concentration of 100/150 µg /mL. 20 µL is added to a 1 L sample.

7.3. Internal Standard Solution - The compounds in the internal standard solution are 1,4-Dichlorobenzene–d4, Naphthalene–d8, Acenaphthene-d10, Phenanthene-d10, Chrysene–d12, and Perylene–d12. The internal standard mix is prepared in methylene chloride at a concentration of 80 µg/mL. The internal standard solution is added to an aliquot of the sample extract prior to analysis to provide an internal standard concentration of 0.8 µg/mL in the final extract.

7.4. Matrix Spike - A 100ug/mL solution of the TCL–PAH list. 20 µL is added to a 1 L sample. Laboratory Control Spike – a 100 µg/mL solution of the TCL–PAH list. If PAH-SIM method is run by itself, then one LCS is prepared with 20 µL to 1L. If PAH-SIM is run in conjunction with 8270C, then 2 LCS's are prepared – one spiked with 500 µL to 1 L, the second with 20 µL to 1L.

7.5. Calibration Standards - The target analytes for this method are listed Table I. Standard reference materials are obtained from commercial sources and independently verified at the laboratory. The standard mixture is prepared in methylene chloride for the initial calibration curve at a minimum of 5 concentration levels from the following: 0.1 , 0.2, 0.5, 1, 2, 5, 10 , 20 µg/mL.. Injection volume is 2 µL.

## 8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. The samples are collected into 1 L amber glass container chilled to 4°C ± 2°C and shipped via over-night carrier to the laboratory. The samples are stored at 4°C ± 2°C at the laboratory until extraction. The extracts must be protected from light and stored refrigerated until the time of analysis.

8.2. Holding times - The water samples must be extracted within 7 days from the date of sample collection. The solid samples must be extracted with 14 days from the date of sample collection. The extracts must be analyzed within 40 days from the date of sample extraction.

## 9. QUALITY CONTROL

9.1. SIM – PAH QC Approach (3 options)

9.1.1. Option #1 – Use when performing 8270C and PAH- SIM on same sample

9.1.1.1. Single extract, 2 analyses

9.1.1.2. Normal 8270C surrogate levels in samples, blanks, 8270C LCS, MS/MSD

9.1.1.3. One low level LCS at 1/10 the normal 8270C analysis

9.1.1.4. Only low level LCS reported for SIM analysis (no blank surrogates, no sample MS/MSD)

9.1.2. Option #2 – Separate extractions for 8270C and PAH-SIM

9.1.2.1. One standard BNA 8270 extraction batch with normal QC

9.1.2.2. One low level PAH-SIM extraction batch. All surrogates, LCS and normal spike level

9.1.2.3. All SIM QC reported (blank surrogates, sample surrogates, LCS and MS/MSD)

9.1.3. Option #3

9.1.3.1. One low level SIM extraction batch. All surrogates, LCS, MS/MSD and 1/10 level

9.1.3.2. All SIM QC reported (blank surrogates, sample surrogates, LCS and MS/MSD)

The Quality Control measures defined for this method are summarized in Table I

TABLE I

| QC Type | Frequency |
|---|---|
| Internal Standards | each sample |
| Surrogate | each sample |

| | |
|---|---|
| Matrix spike/spike duplicate | 1 set per analytical batch or every 20 samples - which ever is most frequent |
| Laboratory Control Sample | 1 or 2 per analytical batch or every 20 samples - which ever is most frequent* |
| Method Blank | 1 per analytical batch |

*See Section 9.3.

9.2. Method Blank

9.2.1. The method reagent water is analyzed with each analytical batch not exceeding 20 samples.

9.2.2. Due to the low level nature of this analysis, low level contamination of target analytes is routinely encountered. All target compounds should be below the reporting limits presented in Table II. Target analytes that are detected above the reporting limit in the blank must be flagged on any associated sample's report with a "B" qualifier.

9.3. Matrix Spike and Spike Duplicate Analyses

9.3.1. Samples designated for matrix spike analysis are spiked as described in section 7.4.

9.3.2. The laboratory will perform a matrix spike/ spike duplicate pair of QC samples for each analytical batch not exceeding 20 samples.

9.4. Laboratory Control Samples

9.4.1. A Laboratory Control Sample (LCS) is spiked as described in section 7.4. and analyzed with each analytical batch not exceeding 20 samples. Note: If PAH-SIM and 8270C are prepared together, then 2 LCS's are prepared – one spiked with 50 µL l to 1L , the other with 500 µL to 1L.

9.4.2. The LCS results are compared to interum limits of 30 to 130% until sufficient data is available to established spike recovery limits.

9.5. Internal Standards

9.5.1. The internal standards are monitored in all field samples and QC samples. The internals standards areas should be between 50% and 200% of the standard area.

9.6. QC Acceptance Criteria

9.6.1. Control limits are established by the laboratory as described in NC-QA-0018.

## 10. CALIBRATION AND STANDARDIZATION

10.1. Initial Calibration – A minimum of five point calibration sequence in analyzed demonstrating the calibration range of the analysis. The standard concentrations used to construct the curve are a minimum of 5 points selected from 0.1, 0.2, 0.5, 1.0, 2.0, 5.0, 10.0 ug/mL. The percent RSD for all TCL-PAHs must be less than 35%. Any additional compounds requested are excepted from this criteria due to possible poor response by this method (e.g.. phenols, or other TCL compounds.) A minimum response factor criteria for these analytes has been set at 0.010. The minimum response factor TCL- PAH analytes is set at 0.100.

10.2. Continuing Calibration - A continuing calibration check is analyzed at any mid-level std. every 12 hours of instrument operation. The percent difference between the response factor from the continuing calibration and the average response factor from the curve must be within 35% for each analyte. As in the initial calibration, any additional compounds are excepted from this criteria. The criteria for these compounds is a minimum response factor of 0.010. The minimum response factor for TCL- PAH analytes is set at 0.100.

## 11. PROCEDURE

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.3. Sample Extraction

11.3.1. Refer to SOP CORP-OP-0001NC for sample preparation.

11.4. Sample Analysis

11.4.1. All samples are analyzed within 12 hours of the calibration standard injection time.

11.4.2. An aliquot on the internal standard solution is transferred to the sample vial to produce a final internal standard concentration of 0.8 µg/mL in the sample extract. 2 µL aliquots are injected into the gas chromatograph using the following, or equivalent, conditions.

| | |
|---|---|
| Injector Temperature | 275 °C |
| Column Head Pressure Program | 20 psi for 0.5 min. |
| Source Temperature | 300°C |
| Initial Oven Temperature | 40 °C |
| Initial Hold Time | 2 minute |
| Ramp Rate | 12 °C /minute |
| Final Temperature | 325 °C |

11.4.3. The mass spectrometer is operated in the selected ion monitoring (SIM) mode using appropriate mass windows to include the quantitation and confirmation masses for each PAH as shown in table I.

## 12. DATA ANALYSIS AND CALCULATIONS

12.1. Qualitative Analysis

12.1.1. Specific mass chromatographic plots are printed for each target analyte, internal standard compound and surrogate compound that meet the established retention time and chromatographic criteria.

12.1.2. The characteristic masses of each analyte of interest must maximize within 0.075 minutes of each other.

12.1.3. The retention time of each analyte of interest must be detected within ± 10 seconds from the analytes retention time in the standard.

12.1.4. The relative peak areas of the primary ion compared to the secondary ion must be within ± 30% of the expected ion ratio from the standard.

12.1.5. In some instances a compound that does not meet the above criteria may be determined to be a positive result based upon the interpretation of the mass spectroscopist. In these instances, the analysts reasoning will be documented in the data package and peer reviewed prior to reporting.

12.1.6. Structural isomers that produce similar mass spectra and have less than 30 seconds difference in retention time, may be separately identified only if the resolution between authentic isomers in a standard mix is acceptable. Acceptable resolution is achieved if the baseline to valley height between the isomers is less than 25% of the sum of the two peaks heights. Structural isomers not meeting this criteria are identified and reported as isomeric totals.

12.2. Quantitative Analysis

12.2.1. The following formula is used to calculate the response factors of the internal standard to each of the calibrated standards:

$$RF = \left(\frac{\mathbf{As \times Cis}}{\mathbf{Ais \times Cs}}\right)$$

where:
As = Area of the primary ion for the analyte being measured
Ais = Area of the primary ion for the internal standard
Cis = Concentration of the internal standard, (µg/mL)
Cs = Concentration of the analyte being measured, (µg/mL).

12.2.2. Sample extract concentrations for each analyte being measured is calculated using the following formula:

$$Ce = \left(\frac{\mathbf{As \times Is}}{\mathbf{Ais \times RF}}\right)$$

where:
Ce = Sample extract concentration, (µg/mL)
As = Area of the primary ion of the analyte being measured
Ais = Area of the primary ion of the internal standard
Is = Amount of internal standard added to the sample extract, (µg/mL)
RF = Average RF from the initial calibration.

12.3. The sample concentration is calculated using the following formula:

$$C = \mathbf{Ce \times \frac{VE}{Vs}}$$

where:
C = Concentration in the sample (µg/L)
VE = The final extract volume (mL)
Vs = The original volume of the sample extracted (L)
Ce = The sample extract concentration (µg/mL).

## 13. METHOD PERFORMANCE

### 13.1. Target Analyte Lists

The routine PAH analytes that are listed have been validated for this method are listed in Table II.

### 13.2. Training Requirements

13.2.1. This method is to be performed only by analysts that have been trained in the specialized technique and have demonstrated the ability to produce Laboratory Control Sample results within the established QC limits.

13.2.2. The analytical area group leaders have the responsibility to ensure that this procedure is performed by associates who have been properly trained in the use of these procedures and has the proper experience.

## 14. POLLUTION PREVENTION

Minimize the amount of solvent used for the solvent rinse steps for glassware preparation (section 11.3.1). The solvent rinse volume may be sequentially transferred from one extractor to the next during the rinse procedure.

## 15. WASTE MANAGEMENT

The sample and extract waste generated by this procedure must be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be notified if accidents or injuries occur during the use of this procedure.

## 16. REFERENCES

16.1. STL Inc. SOP CORP-OP-0001NC

16.2. Test Methods For Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Methods 3510C, 3520C, 3540C, 3550B, 8270C and 8280A.

16.3. Associated SOP

16.3.1. Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018.

## 17. MISCELLANEOUS (TABLES, APPENDICES, ETC...)

17.1. Table I: Target Compounds - Primary and Secondary Mass Ions

17.2. Table II: Reporting Limits and CAS Numbers

17.3. Appendix I: Sample Preparation Flow Chart

17.4. Appendix II: Sample Analysis Flow Chart

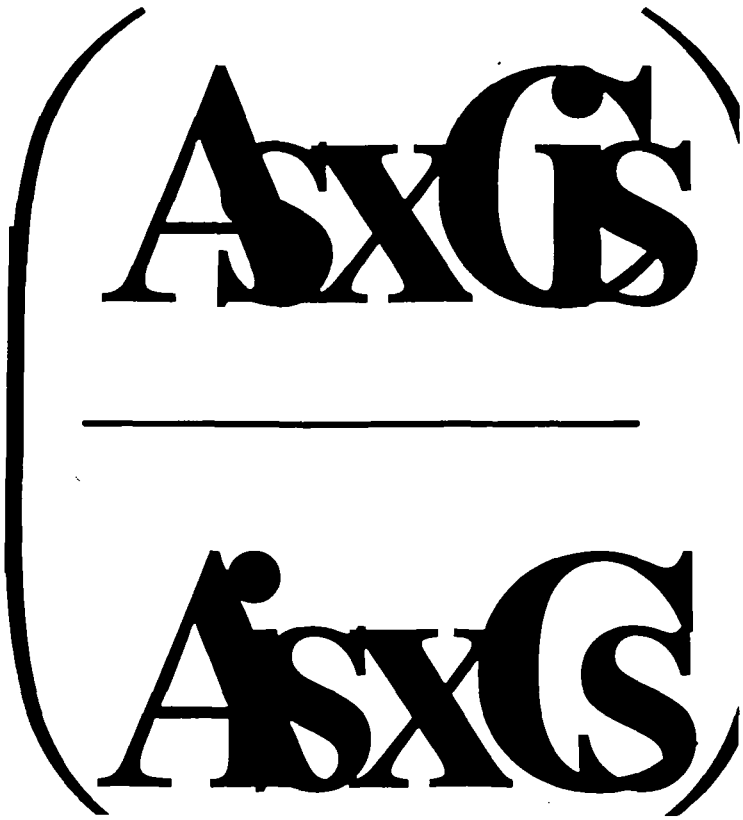
**Table I: Target Compounds - Primary (1') and Secondary (2') Mass Ions**

| Compound | 1' | 2' |
|---|---|---|
| Naphthalene | 128 | 102 |
| Acenaphthylene | 152 | 151 |
| Acenapthene | 154 | 153 |
| Fluorene | 166 | 165 |
| Phenanthrene | 178 | 176 |
| Anthracene | 178 | 176 |
| Fluoranthene | 202 | 200 |
| Pyrene | 202 | 200 |
| Benzo(a)anthracene | 228 | 226 |
| Chrysene | 228 | 226 |
| Benzo(b)fluoranthene | 252 | 250 |
| Benzo(k)fluoranthene | 252 | 250 |
| Benzo(a)pyrene | 252 | 250 |
| Indeno(1,2,3-cd)pyrene | 276 | 274 |
| Dibenz(a,h)anthracene | 278 | 279 |
| Benzo(g,h,i)perylene | 276 | 274 |
| Pentachlorophenol | 266 | 264 |
| 2-methylnaphthalene | 141 | 115 |
| 1-methylnaphthalene | 141 | 115 |
| 2- Chloronaphthalene | 162 | 127 |
| Carbazole | 167 | 166 |
| Dibenzofuran | 168 | 139 |

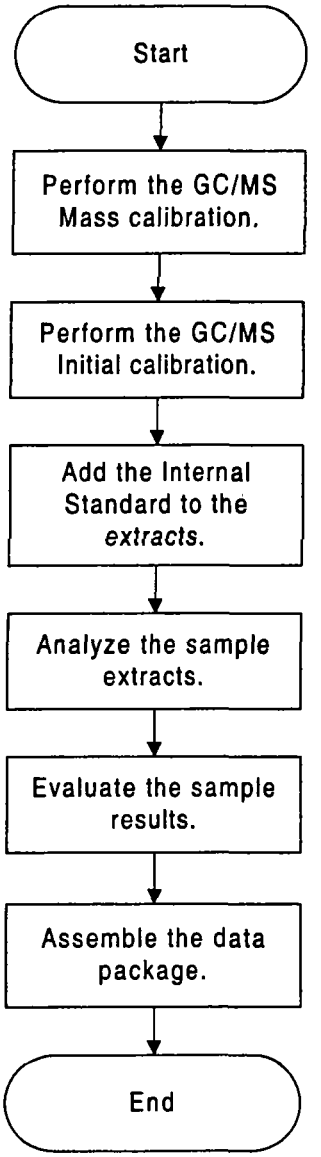
## Table II: Reporting Limits and CAS Numbers

| Compound | CAS # | Soil RL in ug/L | Water RL in ug/L |
|---|---|---|---|
| Naphthalene | 91-20-3 | 7 | 0.2 |
| Acenaphthene | 208-96-8 | 7 | 0.2 |
| Acenapthene | 83-32-9 | 7 | 0.2 |
| Fluorene | 86-73-7 | 7 | 0.2 |
| Phenanthrene | 85-01-8 | 7 | 0.2 |
| Anthracene | 120-12-7 | 7 | 0.2 |
| Fluoranthene | 206-44-0 | 7 | 0.2 |
| Pyrene | 129-00-0 | 7 | 0.2 |
| Benzo(a)anthracene | 56-55-3 | 7 | 0.2 |
| Chrysene | 218-01-9 | 7 | 0.2 |
| Benzo(b)fluoranthene | 205-99-2 | 7 | 0.2 |
| Benzo(k)fluoranthene | 207-08-9 | 7 | 0.2 |
| Benzo(a)pyrene | 50-32-8 | 7 | 0.2 |
| Indeno(1,2,3-cd)pyrene | 193-39-5 | 7 | 0.2 |
| Dibenz(a,h)anthracene | 53-70-3 | 7 | 0.2 |
| Benzo(g,h,i)perylene | 191-24-2 | 7 | 0.2 |
| Pentachlorophenol | 87-86-5 | 10 | 1.0 |
| 2-methylnaphthalene | 91-57-6 | 7 | 0.2 |
| 1-methylnaphthalene | 90-12-0 | 7 | 0.2 |
| 2- Chloronaphthalene | 91-58-7 | 7 | 0.2 |
| Carbazole | 86-74-8 | 7 | 0.2 |
| Dibenzofuran | 132-64-9 | 7 | 0.2 |

## Appendix I: Sample Preparation Flow Chart



## Appendix II: Sample Analysis Flow Chart



# STL STANDARD OPERATING PROCEDURE

## TITLE: TOXICITY CHARACTERISTIC LEACHING PROCEDURE AND SYNTHETIC PRECIPITATION LEACHING PROCEDURE

(SUPERSEDES: REVISION 1, REVISION DATE 02/01/00)

| | | |
|---|---|---|
| Prepared by: | | 10/17/00 Date |
| Reviewed by: | Technology Specialist | 10/17/00 Date |
| Approved by: | Quality Assurance Manager | 10/17/00 Date |
| Approved by: | Environmental Health and Safety Coordinator | 10-17-00 Date |
| Approved by: | Laboratory Director | 10-17-00 Date |

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## 1. SCOPE AND APPLICATION

1.1. This SOP describes the application of the Toxicity Characteristic Leaching Procedure (TCLP), SW846 Method 1311. The Toxicity Characteristic (TC) of a waste material is established by determining the levels of 8 metals and 31 organic chemicals in the aqueous leachate of a waste. The TC is one of four criteria in 40 CFR Part 261 to determine whether a solid waste is classified as a hazardous waste. The other three are corrosivity, reactivity and ignitability. The TC Rule utilizes the TCLP method to generate the leachate under controlled conditions that were designed to simulate leaching through a landfill. EPA's "worst case" waste disposal model assumes mismanaged wastes will be exposed to leaching by the acidic fluids generated in municipal landfills. The EPA's model also assumes the acid/base characteristics of the waste will be dominated by the landfill fluids. The TCLP procedure directs the testing laboratory to use a more acidic leaching fluid if the sample is an alkaline waste, again in keeping with the model's assumption that the acid fluids will dominate leaching chemistry over time.

1.2. The specific list of TC analytes and regulatory limits may be found in Appendix A.

**Note:** The list in Appendix A does not include the December 1994 EPA rule for Universal Treatment Standards for Land Disposal Restrictions. Those requirements include 216 specific metallic and organic compounds and, in some cases, lower detection limit requirements (see 40 CFR 268.40). TCLP leachates are part of the new Universal Treatment Standards, but the conventional analytical methods will not necessarily meet the new regulatory limits. Consult with the client and with STL Technical Specialists before establishing the instrumental methods for these regulations.

1.3. This SOP also describes the application of the Synthetic Precipitation Leaching Procedure (SPLP) which was designed to simulate the leaching that would occur if a waste was disposed in a landfill and exposed only to percolating rain water. The procedure is based on SW846 Method 1312. The list of analytes for SPLP may extend beyond the toxicity characteristic compounds shown in Appendix A. With the exception of the use of a modified extraction fluid, the SPLP and TCLP protocols are essentially equivalent. Where slight differences may exist between the SPLP and TCLP they are distinguished within this SOP.

1.4. The procedure is applicable to liquid, solid, and multiphase wastes.

1.5. The results obtained are highly dependent on the pH of the extracting solution, the length of time that the sample is exposed to the extracting solution, the temperature

during extraction, and the particle size/surface area of the sample. These parameters must be carefully controlled.

1.6. The reporting limits are based on the individual samples as well as the individual analysis techniques. However, the sample is determined to be hazardous if it contains any analyte at levels greater than or equal to the regulatory limits.

1.7. If a total analysis of the waste demonstrates that individual analytes are not present in the waste, or that they are present but at such low concentrations that the appropriate regulatory levels could not possibly be exceeded, the procedure need not be run. If the total analysis results indicate that TCLP is not required, the decision to cease TCLP analysis should be remanded to the client.

1.8. If an analysis of any one of the liquid fractions of the procedure leachate indicates that a regulated compound is present at such a high concentration that, even after accounting for dilution from the other fractions of the leachate, the concentration would be equal to or above the regulatory level for that compound, then the waste is hazardous and it may not be necessary to analyze the remaining fractions of the leachate. However, the remaining analyses should not be terminated without the approval of the client.

1.9. Volatile organic analysis of the leachate obtained using a bottle extraction, normally used for extractable organics and metals, can be used to demonstrate that a waste is hazardous, but only the ZHE option can be used to demonstrate that the concentration of volatile organic compounds is below regulatory limits due to potential analyte loss into the headspace during the bottle extraction.

## 2. SUMMARY OF METHOD

2.1. For liquid wastes that contain less than 0.5% dry solid material, the waste, after filtration through 0.6 to 0.8 μm glass fiber filter, is defined as the TCLP leachate.

2.2. For wastes containing greater than or equal to 0.5% solids, the liquid, if any, is separated from the solids and stored for later analysis or recombination with the leachate. The particle size of the remaining solid phase is reduced, if necessary. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. For TCLP, the extraction fluid employed for extraction of non-volatile analytes is a function of the alkalinity of the solid phase of the waste. For SPLP, the extraction fluid employed is a function of the region of the country where the sample site is located if the sample is a soil. If the sample is a waste or wastewater the extraction fluid employed is a pH 4.2 solution. Two leachates may be generated: a) one for analysis of non-volatile constituents (semi-volatile organics, pesticides, herbicides and metals and/or b) one from a Zero Headspace Extractor (ZHE) for

analysis of volatile organic constituents. Following extraction, the liquid leachate is separated from the solid phase by filtration through a 0.6 to 0.8 μm fiber filter.

2.3. If compatible (i.e., multiple phases will not form on combination), the initial liquid filtrate of the waste is added to the liquid leachate and these are prepared and analyzed together. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume-weighted average concentration.

## 3. DEFINITIONS

3.1. "Leachate" is used to refer to the solutions generated from these procedures (TCLP, SPLP, deionized water leach).

3.2. "Wet Solids" is that fraction of a waste sample from which no liquid may be forced out by pressure filtration.

## 4. INTERFERENCES

4.1. Oily wastes may present unusual filtration and drying problems. If requested by the client and as recommended by EPA (see Figure 3), oily wastes can be assumed to be 100% liquid and analysis for total concentrations of contaminants will be performed. This applies specifically to samples containing viscous non-aqueous liquids that would be difficult to filter. Alternately, the oil may be subjected to pressure filtration. The portion that passes through the filter will be prepared and analyzed separately as an organic waste. The "wet solid" portion that remains behind on the filter will be subjected to leaching, prepared and analyzed. The results will then be mathematically combined.

4.2. Wastes containing free organic liquids (e.g., oil, paint thinner, fuel) usually require dilution prior to analysis to address the matrix interferences. In most instances this results in reporting limits elevated above the TCLP regulatory limits.

4.3. Solvents, reagents, glassware and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks as described in Section 9 and the individual determinative SOPs.

4.4. Glassware and equipment contamination may result in analyte degradation. Soap residue on glassware and equipment may contribute to this. All glassware and equipment should be rinsed very carefully to avoid this problem.

4.5. Phthalates may be eliminated by proper glassware cleanup and by avoiding plastics. Only glass, Teflon or Type 316 stainless steel tumblers may be used for leachates to be

analyzed for organics. Plastic tumblers may be used for leachates to be analyzed for the metals.

4.6. Overexposure of the sample to the environment will result in the loss of volatile components.

4.7. Potential interferences that may be encountered during analysis are discussed in the individual analytical methods.

## 5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all STL associates.

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory. The following specific hazards are known:

5.3.1. Chemicals that have been classified as carcinogens, or potential carcinogens, under OSHA include:
Methylene chloride

5.3.2. Chemicals known to be flammable are:
Methanol

5.3.3. The following materials are known to be corrosive:
Hydrochloric acid, nitric acid, sulfuric acid, acetic acid, sodium hydroxide

5.3.4. The following materials are known to be oxidizing agents:
Nitric Acid.

5.4. Gas pressurized equipment is employed in this procedure. Be sure all valves and gauges are operating properly and that none of the equipment, especially tubing, is over-pressurized. CAUTION: Do not open equipment that has been pressurized until it has returned to ambient pressure.

5.5. A rotary agitation apparatus is used in this procedure. Certain samples may break the glass jars used in the procedure. For these samples, extra caution, including plastic or polyethylene overwraps of the glass jar, may be necessary. Turning the jar or bottle sideways rather than tumbling end over end may also reduce the chance of breakage. If sideways tumbling is used, note this change in the logbook comment section.

5.6. Secure tumbler and extraction apparatus before starting rotary agitation apparatus.

5.7. During sample rotation, pressure may build up inside the bottle. Periodic venting of the bottle will relieve pressure.

5.8. Exposure to hazardous chemicals must be maintained as low as reasonably achievable, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.9. The preparation of standards and reagents and glassware cleaning procedures that involve solvents such as methylene chloride will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.10. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL associate. The situation must be reported immediately to a laboratory supervisor.

5.11. Due to the potential for ignition, flammability or production of noxious fumes, do not attempt to dry non-aqueous liquid samples in an oven. Use extended drying in a ventilation hood.

## 6. EQUIPMENT AND SUPPLIES

6.1. Extraction vessels

6.1.1. For volatile analytes - zero-headspace extraction (ZHE) vessel, gas-pressure actuated, Millipore YT3009OHW or equivalent (see Figure 2).

6.1.2. For metals - either borosilicate glass jars (2.5 L, with Teflon lid inserts) or 2.5 L HDPE (Nalgene or equivalent) bottles may be used.

6.1.3. For non-volatile organics - only borosilicate glass may be used.

6.2. Vacuum filtration apparatus and stainless steel pressure filtration apparatus (142 mm diameter), capable of 0 - 50 psi.

6.3. Borosilicate glass fiber filters, 0.6 - 0.8 µm (Whatman GF/F 14.2 cm, 9.0 cm, 4.7 cm, 0.7 µm or equivalent). When analyzing for metals, wash the filters with 1 N nitric acid and de-ionized water prior to use, or purchase pre-washed filters. Glass fiber filters are fragile and should be handled with care.

6.4. Rotary agitation apparatus, multiple-vessel, Associated Design and Manufacturing Company 3740-6 or equivalent (see Figure 1). The apparatus must be capable of rotating the extraction vessel in an end-over-end fashion at 30 ± 2 rpm.

6.5. ZHE Extract Collection Device: Gas-tight syringes, 50 or 100 mL capacity, Hamilton 0158330 or equivalent.

6.6. Top loading balance, capable of 0 - 4000 ± 0.01g (all measurements are to be within ± 0.1 grams).

6.7. pH meter and probe capable of reading to the nearest 0.01 unit, and with automatic temperature compensation.

6.8. pH probes.

6.9. Magnetic stirrer/hotplate and stirring bars.

6.10. VOA vials, 40 mL, with caps and septa.

6.11. Glass bottles, 1 liter, with Teflon lid-inserts.

6.12. Nalgene plastic bottles or equivalent, 1 liter.

6.13. Miscellaneous laboratory glassware and equipment.

## 7. REAGENTS AND STANDARDS

7.1. Reagent water for non-volatile constituents must be produced by a Millipore DI system or equivalent. For volatile constituents, water must be passed through an activated carbon filter bed (Milli-Q or tap water passed through activated carbon). Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

7.2. Hydrochloric acid, 1 N: Carefully add 83 mL concentrated reagent grade HCl to 800 mL reagent water, cool and dilute to 1 liter with reagent water. Cap and shake to mix well.

7.3. Sodium hydroxide, 1 N: Carefully add 40 g reagent grade NaOH pellets to 800 mL reagent water, stir until the pellets are completely dissolved, cool and dilute to 1 liter with reagent water.

CAUTION: Heat is generated during this process.

7.4. Acetic acid, glacial: concentrated, reagent grade liquid (HOAc).

7.6. pH calibration solutions: buffered to a pH of 4, 7, and 10. Commercially available.

7.5. TCLP Leaching Fluids

7.5.1. General Comments

7.5.1.1. The pH of both solutions listed below should be monitored daily and the pH probes are to be calibrated prior to use.

7.5.1.2. The leaching fluids MUST be prepared correctly. If the desired pH range is not achieved and maintained, the TCLP may yield erroneous results due to improper leaching. If the pH is not within the specifications, the fluid must be discarded and fresh extraction fluid prepared.

7.5.1.3. Additional volumes of extraction fluids listed below may be prepared by multiplying the amounts of acetic acid and NaOH by the number of liters of extraction fluid required.

7.5.2. TCLP Fluid #1: Carefully add 5.7 mL glacial acetic acid and 64.3 mL of 1 N NaOH to 500 mL reagent water in a 1 liter volumetric flask. Dilute to a final volume of 1 L with reagent water, cap and shake to mix well. For 8 L of fluid use 45.6 mL glacial acetic acid and 514 mL 1N NaOH, dilute to 8 L with reagent water. When correctly prepared, the pH of this solution is 4.93 ± 0.05. The density of TCLP fluid #1 is 0.997 g/mL.

7.5.3. TCLP Fluid #2: Carefully add 5.7 mL glacial acetic acid to 500 mL reagent water in a 1 liter volumetric flask. Dilute to a final volume of 1 L with reagent water, cap and shake to mix well. For 8 L of fluid use 45.6 mL glacial acetic acid, dilute to 8 L with reagent water. When correctly prepared, the pH of this solution is 2.88 ± 0.05. The density of TCLP fluid #2 is 0.997 g/mL.

7.6. Nitric acid, 50% solution: Slowly and carefully add 500 mL concentrated $HNO_3$ to 500 mL reagent water. Cap and shake to mix well.

7.7. Sulfuric acid / nitric acid (60/40 weight percent mixture) $H_2SO_4/HNO_3$. Cautiously mix 60 g of concentrated sulfuric acid with 40 g of concentrated nitric acid.

7.8. SPLP Leaching fluids

7.8.1. SPLP solutions are unbuffered and exact pH may not be attained. The pH of TCLP and SPLP fluids should be checked prior to use. If not within specifications, the fluid should be discarded and fresh fluid prepared.

7.8.2. SPLP fluid #1: Add 60/40 weight percent mixture of sulfuric and nitric acids to reagent water until the pH is 4.20 ± 0.05 This fluid is used for soils from a site that is east of the Mississippi River and for wastes and wastewaters.

7.8.3. SPLP fluid #2: Add 60/40 weight percent mixture of sulfuric and nitric acids to reagent water until the pH is 5.00 ± 0.05. This fluid is used for soils from a site that is west of the Mississippi River.

7.8.4. SPLP fluid #3: This fluid is reagent water and is used for leaching of volatiles. Additionally, any cyanide-containing waste or soil is leached with fluid #3 because leaching of cyanide containing samples under acidic conditions may result in the formation of hydrogen cyanide gas.

7.9. Methanol and methylene chloride - used to aid in cleaning oil contaminated equipment.

## 8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Samples being analyzed for non-volatile organic compounds should be collected and stored in glass containers with Teflon lid liners. Chemical preservatives shall NOT be added UNTIL AFTER leachate generation.

8.2. Samples being analyzed for metals only can be collected in either glass or polyethylene containers.

8.3. When the waste is to be evaluated for volatile analytes, care should be taken to minimize the loss of volatiles. Samples shall be collected and stored in a manner intended to prevent the loss of volatile analytes (e.g., samples should be collected in Teflon lined septum capped vials with minimal headspace and stored at 4 ± 2°C). Samples should be opened only immediately prior to extraction.

8.4. Samples should be refrigerated to 4 ± 2°C unless refrigeration results in irreversible physical changes to the waste. If precipitation occurs, the entire sample (including precipitate) should be extracted.

8.5. The minimum TCLP sample collection size is determined by the physical state or states of the waste and the analytes of concern. The amount of waste required varies with the percent solids. The lower the percent solids, the more waste will be required for preliminary and final testing. For aqueous samples containing between 0.5 and 10% solids, several kilograms of sample are required to complete the analyses. The general minimal requirements when the samples are 100% solids include: 1 - 32 oz jar for semi-volatile organic analysis and metals, and 1 - 4 oz jar for volatile organic analysis. Low density sample materials, such as rags or vegetation, will require larger volumes of sample. For liquid samples (less than 50% solids), minimum requirements are 2 - 32 oz jars for semi-volatile organic analysis and metals, and 2 - 8 oz jars for volatile organic analysis. If volatile organic analysis is the only requested parameter, 2 separate jars are required. If matrix spike or duplicate control samples are requested, additional sample volume is required. If sufficient sample volumes were not received, analyses cannot be started and the client should be notified as soon as possible.

8.6. TCLP leachates should be prepared for analysis and analyzed as soon as possible following extraction. Leachates or portions of leachates for metallic analyte determinations must be acidified with nitric acid to a pH less than 2, unless precipitation occurs. If precipitation occurs upon addition of nitric acid to a small aliquot of the leachate, then the remaining portion of the leachate shall not be acidified and the leachate shall be analyzed as soon as possible. All other leachates should be stored under refrigeration (4 ± 2°C) until analyzed. ZHE leachates must be stored in VOA vials filled to eliminate all headspace.

8.7. Samples are subject to appropriate treatment within the following time periods:

**Table 1 – Holding Times (days)**

| Parameter | Collection to Start of TCLP Leach | End of TCLP Tumble to Preparation | Start of TCLP Leach or Semi- volatile Prep Extraction to Analysis | Total Elapsed Time |
|---|---|---|---|---|
| Volatiles: | 14 | N/A | 14 | 28 |
| Semi-volatiles: | 14 | 7 | 40 | 61 |
| Mercury: | 28 | N/A | 28 | 56 |
| Other Metals: | 180 | N/A | 180 | 360 |

NOTE: The initial holding time is measured from date of collection to date TCLP extraction started. (This should be the TCLP extraction date in QuanTims.) Semi-volatile method prep holding time is measured from the day tumbling is complete to the start of method extraction. Subsequent analysis holding times are measured from the date extraction (TCLP or method prep) starts. If sample holding times are exceeded, the values obtained will be considered minimal concentrations. Exceeding holding times is not acceptable in establishing that a waste does not exceed the regulatory level. Exceeding the holding time will not invalidate characterization if the waste exceeds the regulatory limit. The Total Elapsed Time is to be used as guidance. If preps are initiated at the last possible moment of a holding time, the elapsed times may be exceeded.

## 9. QUALITY CONTROL

9.1. Quality Control Batch (QC Batch) - QA-003 defines a QC Batch as a set of up to 20 field samples of similar matrix that behave similarly and are processed using the same procedures, reagents and standards within the same time period. The same lot of reagents must be used within a batch. A minimum of one TCLP extraction blank (Method Blank), one Laboratory Control Sample (LCS), one Matrix Spike (MS), and one Matrix Spike Duplicate (MSD) will be prepared with each TCLP leachate batch.

9.2. TCLP Extraction Blanks - A minimum of one blank (using the same extraction fluid as used for the samples) must be prepared and analyzed for every batch of samples extracted in a particular vessel type. The blanks are generated in the same way as the samples (i.e., blanks will be tumbled and filtered with the samples). ZHE Extraction vessels will be uniquely numbered. Consult the STL QC Program and the individual analysis SOPs for blank acceptance criteria.

9.3. Laboratory Control Sample (LCS) - A LCS is required with each batch of 20 or fewer samples. The LCS shall be generated after a batch of TCLP leachates have been generated (i.e., at the time of the preparative digestion or extraction) by spiking an aliquot of the appropriate extraction fluid used for that batch or reagent water. Consult the individual analysis SOPs for additional LCS guidance (i.e., spike amounts, spike levels, recovery criteria, etc.).

9.4. Matrix Spike (MS/MSD) - Matrix spikes are used to monitor the performance of the analytical methods on the matrix and to assess the presence of interferences. A MS/MSD pair are required with each batch of 20 or fewer samples.

9.4.1. Matrix spikes are to be added after filtration of the TCLP leachate. Spikes are not to be added prior to the TCLP leaching. For metals, matrix spikes are to be added before preservation with nitric acid.

9.4.2. Consult the individual analysis SOPs for additional guidance on spike compounds and levels.

9.5. Corrective Actions

9.5.1. Consult the STL QC Program and individual analysis SOPs for corrective action for blanks and LCS

9.5.2. Method of Standard Additions (MSA) shall be used for metals if all of the following conditions are met:

- Recovery of the analyte in matrix spike is not at least 50%,
- the concentration of the analyte does not exceed the regulatory level, and
- the concentration of the analyte measured in the sample is within 20% of the appropriate regulatory level.

If the matrix spike recovery is 5% or less due to dilution or matrix interference, contact the project manager and client for guidance. The client should also be contacted prior to initiation of any MSA steps. Refer to the individual analysis SOPs for details on how to perform MSA analysis.

## 10. CALIBRATION AND STANDARDIZATION

10.1. Refer to appropriate analysis SOPs.

## 11. PROCEDURE

### 11.1. GENERAL COMMENTS

11.1.1. One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented on a Nonconformance Memo kept in the project file and described in the final report. The variation must be approved by a project manager, Technical Specialist and QA Manager. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.1.2. All masses should be recorded to the nearest 0.1 g.

### 11.2. PRELIMINARY SAMPLE EVALUATIONS (Refer to Flow Chart #1, Appendix D)

11.2.1. Determine the total volume of TCLP leachate (solid phase leachate + liquid filtrate) that needs to be generated for analysis according to the following:

**Table 2. Recommended TCLP Leachate Volume**

| Analysis | TCLP Required Volume (mL) | SPLP Required Volume (mL) |
|---|---|---|
| Volatiles | 3 x 40 | 3 x 40 |
| Semi-volatiles | 500 | 1000 |

| | | |
|---|---|---|
| Pesticides | 500 | 1000 |
| Herbicides | 500 | 1000 |
| Metals | 300 | 300 |

11.2.1.1. For TCLP and SPLP samples used for matrix spike and matrix spike duplicate analysis, two to three times the listed volumes are required.

11.2.2. Sample Description (determine sample matrix)

11.2.2.1.Solid - If the waste will obviously yield no free liquid when subjected to pressure filtration , then proceed to Section 11.2.5 or 11.4 (Bottle Extraction Procedure or ZHE Procedure).

11.2.2.2.Liquid - If the sample is a monophasic liquid, proceed to Section 11.2.3 (Percent Solid Determination).

11.2.2.3. Multiphasic – The sample has discernible layers (liquid/liquid or liquid/solid). If more than one container of multi-phasic materials is received from the field, each container might show different amounts of each phase. Consult client to determine sample selection alternatives (composite all sample containers, select one, resample, etc.) if this occurs.

11.2.3. Solids Determination

11.2.3.1.Determine Type of Filtration Apparatus and Process

11.2.3.1.1.Percent Solids and ZHE Extractions - The ZHE filtration apparatus cannot accurately determine percent solids less than 5%. If an extraction is to be performed solely for volatile organic compounds and the percent solids concentration is apparently greater than 5%, proceed to Section 11.4 (ZHE Extraction Procedure, Volatile Constituents). Otherwise, continue with Section 11.2.3.2. The aliquot of sample used here cannot be used again for the ZHE extraction.

11.2.3.1.2.If the sample is mostly a non-viscous liquid (water or non-viscous organic liquid) of low solids content (expected to be < 0.5%) , vacuum filtration should be used initially. Proceed to determination of percent dry solids (Section 11.2.3.2)

11.2.3.1.3.If the sample is viscous (sludge, oil, or is expected to have solids content > 0.5%), use pressure filtration. Proceed to determination of wet solids (Section 11.2.3.3).

11.2.3.2.Determination of percent dry solids

11.2.3.2.1.Measure and record the weight of the filter. Load the filter into the filter holder and assemble vacuum filter apparatus.

11.2.3.2.2.Homogenize the waste, then transfer 100 g subsample to a glass beaker. Record the sample weight in the percent dry solids section of the logbook.

11.2.3.2.3.Turn on vacuum source. Transfer the sample to the vacuum filtration device attempting to spread the waste sample evenly over the surface of the filter. Be sure to transfer all particulates from the beaker to the filter. Use a reagent water rinse if necessary.

11.2.3.2.4.Once all liquid has been pulled though the filter, remove the filter with the wet solids from the vacuum filtration apparatus.

11.2.3.2.5.Dry the filter and solid phase at 100 ± 20 ° C for approximately 15 minutes.

11.2.3.2.6.Remove the filter from the oven and allow to cool in a desiccator.

11.2.3.2.7.Weigh and record the dry weight of filter + particulates.

11.2.3.2.8.Calculate and record the percent dry solids.

11.2.3.2.9.If the percent dry solids is ≥ 0.5%, repeat the drying step. Weigh and record the second filter + particulates dry weight. If the two weighings do not agree within 1%, perform additional drying and weighing until successive weighings agree within 1%.

11.2.3.2.10.If the dry solids result is ≥ 0.5%, proceed to Section 11.2.3.3 using a fresh wet portion of the multiphase waste.

11.2.3.2.11.If the percent solids result is less than 0.5%, discard the solid phase. No leaching will be necessary. Filter sufficient

sample with either the pressure filtration system or ZHE system as described in Sections 11.3 and 11.4. The filtrate is the TCLP leachate.

11.2.3.3.Determination of wet solids

11.2.3.3.1.Assemble the pressure filtration apparatus (use blunt forceps to handle the 0.6 to 0.8 μm filter membrane).

11.2.3.3.2.Homogenize the waste, transfer a minimum of a 100 mL subsample to the glass beaker. Measure and record the gross weight (logbook column A).

11.2.3.3.3.Measure and record the tare weight of the filtrate collection bottle (logbook column D).

11.2.3.3.4.Transfer the sample to the filtration device attempting to spread the waste sample evenly over the surface of the filter. Measure and record the tare weight of the empty glass beaker and any residual sample (logbook column B).

11.2.3.3.5.Calculate and record the net weight of sample used for testing (logbook column C).

11.2.3.3.6.Slowly apply gentle pressure of 10 psi to the filtration apparatus. Allow the sample to filter until no SIGNIFICANT additional liquid has passed through the filter during a 2 minute period.

11.2.3.3.7.If necessary, repeat previous step by increasing the pressure in 10 psi increments until a maximum of 50 psi is reached. Stop the filtration when no additional filtrate is generated within a 2 minute period.

Note: Some samples will contain liquid material that does not filter (e.g., oil). Do not attempt to filter the sample again by exchanging filters. Viscous oils or any wastes which do not pass through the filter are classified by the method as a solid.

11.2.3.3.8.Remove the filtrate collection bottle, weigh and record the gross weight (logbook column E).

11.2.3.3.9.Calculate and record the net weight of filtrate (logbook column F). This result will be used in the percent solids calculation.

11.2.3.3.10.Pour the filtrate into an appropriately sized graduated cylinder. Measure and record the volume of the filtrate in the logbook.

11.2.3.3.11.Retain the filtrate for possible recombination with the leachate in Section 11.3.6. Retain the filter and wet solids for the leaching in Section 11.3.

11.2.3.3.12.For multiphase sample preparations, calculate the total weight of wet solids and record the result in logbook column G.

11.2.4. Particle-size Reduction for Fluid Selection

11.2.4.1.The subsample used for fluid selection must consist of particles less than approximately 1 mm in diameter (versus the less than 1 cm requirement for the material used for the actual extraction). The method requires a smaller particle size to partially compensate for the shorter duration of contact time with the leachate solution as compared to the full extraction. Inappropriate use of coarser materials could result in the selection of the wrong fluid type.

11.2.4.2.Surface area exclusion - size reduction is not required if the sample surface area is greater than or equal to 3.1 $cm^2$ per gram.

11.2.4.3.If the sample contains particles greater than approximately 1 mm in diameter, crush, cut, or grind the solids to the required size.

11.2.4.4.Consult a supervisor or manager when dealing with unusual sample matrices (e.g., wood, cloth, metal, brick).

11.2.5. Determination of Appropriate Extraction Fluid

11.2.5.1.If the solid content is greater than or equal to 0.5%, and if the sample is being analyzed for metals or nonvolatile organic compounds, the type of leaching solution must be determined.

11.2.5.2.Follow times, temperature, and particle size specified in this section as closely as possible. If reaction time between the acid solution and solid

waste is too short or too long, the procedure may produce false pH readings.

11.2.5.3.For SPLP, refer to Section 7.8 for fluid selection. Record the fluid type in the logbook.

11.2.5.4.The TCLP leaching fluid for all volatiles is TCLP Fluid #1.

11.2.5.5.TCLP leach fluid determination for non-volatile analytes

11.2.5.5.1.Calibrate the pH meter with fresh buffer solution in accordance with the pH SOP.

11.2.5.5.2.Weigh out a 5.0 ± 0.1 g subsample (less than 1 mm particle size) of the solid phase into a glass container, and record in the logbook. Note: If sample quantity is limited, consult supervisor or manager.

Note: Many multiphase samples have limited solids quantity . In these instances use a 5 g aliquot of the whole sample. Document this difference in the logbook comment section.

11.2.5.5.3.Add 96.5 ± 1.0 mL of reagent water, cover with a watchglass, and stir for 5 minutes.

11.2.5.5.4.Measure and record the pre-test sample pH in the logbook.

**Note:** To avoid damaging a glass pH probe when organic liquid is present, use narrow range pH indicator paper or an ISFET pH meter.

11.2.5.5.5.If the pH is less than or equal to 5.0, use TCLP Fluid #1.

1.1.1.1.6.If the fluid pH is greater than 5.0, add 3.5 mL 1 N HCl. Slurry the sample briefly. Clip thermometer to the inside edge of one sample in each pre-test sample group to monitor the temperature. All samples in the group must go on the hot plate at the same time in order for the temperature of the one monitored sample to represent the others. Heat to 50°C and maintain for 10 minutes.

**Note:** The heating cycle is a critical step. If the solid waste does not remain in contact with the acidic solution under specified

time and temperature conditions, an erroneous pH may be measured.

11.2.5.5.7.Cool to room temperature.

11.2.5.5.8.Measure and record the pH immediately after the sample has reached room temperature.

11.2.5.5.8.1.If the pH is less than or equal to 5.0, use TCLP Fluid #1. Record the buffer in the logbook.

11.2.5.5.8.2.If the pH is greater than 5.0, use TCLP Fluid #2. Record the buffer in the logbook.

11.2.6. For samples requiring analysis for semi-volatile organics, pesticides, herbicides or metals proceed to Section 11.3.

11.2.7. For samples requiring analysis for volatile organics (ZHE), proceed to Section 11.4.

11.3. BOTTLE EXTRACTION PROCEDURE: NON-VOLATILE CONSTITUENTS: SEMI-VOLATILES, PESTICIDES, HERBICIDES, METALS (Refer to Flow Chart #2, Appendix D)

11.3.1. Evaluate the solid portion of the waste for particle size. If it contains particles greater than 1 cm in size, prepare the solid portion of the waste for leaching by crushing, cutting, or grinding such that all particles are less than 1 cm in size (i.e., capable of passing through a 9.5 mm, 0.375 inch, standard sieve). Size reduction is not required if the sample surface area is greater than or equal to 3.1 $cm^2$ per gram. If particle size reduction was required, record this in comments column in logbook.

11.3.1.1.Consult your supervisor or manager when dealing with unusual sample matrices (e.g., wood, cloth, metal, brick). Scissors or shears may be used to cut cloth, plastic or sheet metal. Saws may be used for wood or solid metal. Determination of particle size reduction tools should take into account the requested analytes (e.g. avoid chromium steel tools when TCLP metals have been requested). Bricks, rocks, or other solids amenable to grinding may be subcontracted out for particle size reduction. (Contact PA or PM.) Note that size reduction to fine powder is not appropriate, and could invalidate results. If necessary, consult client for guidance.

11.3.2. Determine the minimum total volume of solid phase leachate that needs to be generated. Refer to Section 11.2.1.

11.3.3. Use 100 g of solid unless sample quantity is limited. If limited sample, divide the total volume of solid phase leachate required by 20 to determine the minimum mass of solid phase required for leaching. Round this mass UP to the nearest 5g. Client must be notified if less than 100 g of solid material is used.

**Note**: Solid phase material is often in limited quantity from multiphase samples. Generally all the *solid* phase material and the filter from Section 11.2.3.3.11 are transferred to the leaching bottle

11.3.4. Weigh the required mass of solid phase into an appropriate bottle (plastic for metals only, glass for all others) and **slowly** add 20 times its mass of appropriate leaching fluid (e.g., 100 g of sample would require 2000 mL of leaching fluid). Record the weight of the sample aliquoted for the extraction. Record the volume of extraction fluid added in the logbook if other than 2000 mL.

11.3.5. Ensure any effervescence has stopped before capping the bottle tightly. Secure in a rotary agitator and rotate end-over-end at 28-32 rpm for 16-20 hours. The temperature of the room should be 23 ± 2°C. Record the rotary agitator I.D. and the date and time extraction is started and completed in the logbook.

**NOTE:** As agitation continues, pressure may build up within the bottle for some types of wastes. To relieve excessive pressure, the bottle may be removed and opened periodically in a properly vented hood to relieve any built-up pressure

11.3.6. After tumbling in the rotary agitator is completed, remove the bottle and allow the solids to settle. Record the date and time the extraction is completed in the logbook. If sample was multiphase with an initial filtrate, drop a few drops of the filtrate (with a disposable glass pipette) into the extraction bottle and observe whether the filtrate is insoluble or forms a precipitate with the leachate. If so then the filtrate is not compatible with the leachate and must be bottled and analyzed separately. The results are normally mathematically recombined (Section 12.1.2). If the filtrate is compatible with the leachate (ie completely soluble) then pour the entire filtrate into the leachate bottle, recap and mix. Proceed with the leachate filtration step in the next section.

11.3.7. Filter the sample using pressure filtration by filtering through a new glass fiber filter. For final filtration of the TCLP leachate, the glass fiber filter may be

changed, if necessary, to facilitate filtration. Filters must be acid washed if metals are to be determined (see Section 6.3). The entire sample need not be filtered; however, sufficient volume should be generated to support the required analyses.

11.3.8. Measure the pH of the TCLP leachate and record in the logbook. (Use narrow range pH paper or ISFET pH meter to measure the pH of oily samples as a glass pH probe may be damaged .)

11.3.9. Prepare subsamples for metals for MS/MSD quality control testing using the appropriate TCLP spiking solution (do not spike for organics). Refer to the appropriate determinative SOPs for further guidance on the spike components, levels and action criteria.

11.3.10. Immediately preserve the leachate as follows:

| | |
|---|---|
| Metals | pH < 2 w/ $HNO_3$ for aqueous filtrates and leachates (do not acidify oils and other non-aqueous liquids) |
| All others | Refrigerate to 4 ± 2 °C |

**Note**: Refer to Section 8.6 if precipitation occurs upon preservation.

11.3.11. Label each sample with the appropriate information and submit to the appropriate analytical groups for prep and analysis. For multiphase samples requiring mathematical recombination provide copies of the TCLP preparation logbook sheets to the sample preparation and analysis groups. Most mathematically recombined samples will require data entry for the filtrate and leachate portions as well as for the mathematically recombined results. Contact the project manager to ensure the proper sample login is completed.

11.4. **ZHE EXTRACTION PROCEDURE: VOLATILE CONSTITUENTS** (Refer to Flow Chart #3, Appendix D)

11.4.1. Use the ZHE device to obtain a TCLP leachate for analysis of volatile compounds only. Leachate resulting from the use of the ZHE shall NOT be used to evaluate the mobility of non-volatile analytes (e.g., metals, pesticides, herbicides and semi-volatile organics).

11.4.2. Due to some shortcomings of the method, losses of volatile compounds may occur. Extra care should be observed during the ZHE procedure to ensure that such losses are minimized. Charge the ZHE with sample only once and do not open the device until the final extract has been collected. Do not allow the

waste, the initial liquid phase, or the extract to be exposed to the atmosphere any longer than necessary.

11.4.3. Install new O-rings and adjust the ZHE piston in the ZHE body to the appropriate height (slightly moisten the O-rings with leaching fluid if necessary).

11.4.4. If the preliminary evaluations indicated the need for particle size reduction, homogenize the waste, weigh out a sufficient size subsample and prepare for leaching by crushing, cutting, or grinding such that all particles are less than 1 cm in size as measured with a ruler (Do NOT sieve the sample). Size reduction is not required if the sample surface area is greater than or equal to 3.1 $cm^2$ per gram If particle size reduction was required record this in the comments column of the logbook.

**Note:** To minimize loss of volatiles, samples for volatiles that require particle size reduction should be kept in sample storage (at 4°C) until immediately before size reduction. Aggressive reduction which would generate heat should be avoided and exposure of the waste to the atmosphere should be avoided to the extent possible. Size reduction to a fine powder is not appropriate. Also see Section 11.3.1.

11.4.4.1. Consult your supervisor or manager when dealing with unusual sample matrices (e.g., wood, cloth, metal, brick). Scissors or shears may be used to cut cloth, plastic or sheet metal. Saws may be used for wood or solid metal. Bricks, rocks, or other solids amenable to grinding may be subcontracted out for particle size reduction (Contact PM).

11.4.5. Homogenize and transfer an appropriate size subsample of the waste into the ZHE and record the mass in the logbook.

11.4.5.1. For wastes that are solid, a 15 g sample is used.

11.4.5.2. For wastes containing < 0.5% solids, the liquid portion of the waste, after filtration, is defined as the TCLP leachate. Filter enough of the sample to support all of the volatile analyses required.

11.4.5.3. If the sample has ≥ 0.5% solids and has non-volatile TCLP/SPLP requested, the appropriate sample size should be estimated based on the wet solids content determined in Section 11.2.3.3. If ZHE only, use visual wet solids estimate to sample subaliquot.

**Note:** For wastes containing greater than 0.5% wet or dry solids, the "solids" value from the ZHE filtration process may be used to determine the volume of fluid to load into the ZHE. This approach is recommended since the solids value from Section 11.2.3.3 may differ from the ZHE filtration solids due to sample variability or differences in the filtration apparatus.

11.4.6. Carefully place the glass fiber filter between the support screens and secure to the ZHE. Tighten all the fittings.

11.4.7. Place the ZHE in a vertical position; open both the gas AND liquid inlet/outlet valves. Attach a gas line to the gas inlet/outlet valve.

11.4.8. If the waste is solid, slowly increase the pressure to a maximum of 50 psi to force out as much headspace as possible and proceed to Section 11.4.13.

11.4.9. If this is a mutliphase sample, carefully apply gentle pressure of 10 psi (or more, if necessary) to force all headspace slowly out of the ZHE. At the FIRST appearance of liquid from the liquid inlet/outlet valve, quickly close the valve and discontinue gas pressure.

11.4.10. Assemble a syringe and place the plunger in all the way. Attach the pre-weighed syringe to the liquid inlet/outlet valve and open the valve. Record the tare weight of the collection syringe in column D of the logbook. .

11.4.11. Carefully apply gas pressure of no more than 10 psi to force out the liquid phase. Allow the sample to filter until no SIGNIFICANT additional filtrate has passed in a 2 minute period.

**Note:** If the capacity of the syringe is reached, close the liquid inlet/outlet valve, discontinue gas pressure, remove the syringe, weigh, record weight in column E and filtrate volume in the logbook. Return to Section 11.4.10.

11.4.12. Repeat previous step increasing the pressure in 10 PSI increments until 50 psi is reached and no significant liquid has passed in a 2 minute period. Close the valve and discontinue gas pressure. Remove the collection device and record the total weight of the collection device with filtrate in column E and filtrate volume in the logbook. Transfer the filtrate to VOA vials and label appropriately. Calculate the weight of filtrate collected and record in column F in the logbook.

**Notes:** If the original waste contained less than 0.5% solids (Section 11.2.3.2), this filtrate is defined as the TCLP leachate and you may proceed to Section

11.4.22. Otherwise, save the vials by storing at 4°C under minimal headspace conditions, for recombination as in Section 11.4.21.

The material remaining in the ZHE is defined to be the "solid" phase. Calculate the weight of the solid phase and record in column G of the logbook by subtracting the weight of the filtrate from the weight of the sample.

11.4.13. Determine the amount of buffer to use. Solid samples use 300 mL of leach fluid (20 X 15 g). For multiphase samples use the wet solids (column G) amount and multiply by 20. Record the leach fluid volume in column H of the logbook.

**Note:** The TCLP ZHE prep uses only TCLP fluid #1; the SPLP ZHE prep uses only SPLP fluid #3.

11.4.14. Load the fluid transfer reservoir with an excess of Fluid #1 and preflush the transfer line to eliminate air pockets. Be sure the required volume remains.

11.4.15. Attach the transfer line to the liquid inlet/outlet valve and open the valve. Carefully pump the required volume into the ZHE and close the valve. Disconnect the transfer line.

11.4.16. Check the ZHE to make sure all the valves are closed and manually rotate the ZHE (end-over-end) 2 or 3 times. Reposition the ZHE in the vertical position.

11.4.17. Pressurize the ZHE to 5-10 psi. If the ZHE appears to be leaking, follow the corrective action protocols recommended by the manufacturer and repeat the analysis.

11.4.18. Slowly open the liquid inlet/outlet valve to bleed out any headspace that may have been introduced during the introduction of the Fluid. Upon the first sign of liquid from the valve, close the valve.

11.4.19. Repressurize the ZHE to 5-10 psi and place in the rotary agitator. Rotate at 28-32 rpm for 16-20 hours. Room temperature should be 23 ± 2 °C. The room temperature is recorded using a continuous temperature monitor.

11.4.20. Confirm that the pressure of 5-10 psi was maintained throughout the leaching. If it was NOT maintained, return to Section 11.4 and repeat the leachate with a new aliquot of sample.

11.4.21. If there is an initial liquid filtrate (Sec 11.4.12) determine if it is compatible with the leachate if the filtrate has not been previously tested (Sec. 11.3.6).

11.4.21.1.Remove the plunger from the syringe and attach the barrel to the ZHE vessel. Open the outlet valve and pressurize as necessary to transfer about 1 mL of leachate into the syringe. Close the outlet valve.

11.4.21.2.With a glass pipette transfer a few drops of initial filtrate into the open syringe barrel. Formation of separate layers or a precipitate indicates the filtrate and leachate are not compatible. Bottle the filtrate for separate preparation and analysis. The results are normally mathematically recombined.

11.4.21.3.If the filtrate is compatible gently pour the remainder of the filtrate into the syringe barrel. Install the plunger. Bleed any pressure in the ZHE piston. Open the inlet/outlet valve and depress the syringe plunger to inject the filtrate into the ZHE vessel. Do not inject the air bubble (if present) from the syringe.

11.4.21.4.Close the valve and rotate a few times to mix. Proceed with leachate filtration as described in the next section.

11.4.22.Attach an empty syringe to the outlet valve. Open the valve and pressurize the piston to expel the leachate from the ZHE vessel. Following collection, store the TCLP leachate in 2 or 3 40-mL VOA vials with minimal headspace at 4 ± 2 °C and prepare for analysis as soon as possible using the appropriate organic analysis procedure (see Section 16.3).

11.4.23.If the individual phases are analyzed separately, combine the results mathematically by using the recombination calculation in Section 12.1.2. . Provide copies of the TCLP preparation logbook sheets to the sample preparation and analysis groups. Most mathematically recombined samples will require data entry for the filtrate and leachate portions as well as for the mathematically recombined results. Contact the project manager to ensure the proper sample login is completed.

## 12. DATA ANALYSIS AND CALCULATIONS

### 12.1. Calculations

12.1.1. Calculation of weight of extraction fluid to use:

Volume of extraction fluid = 20 X weight of wet solids to be extracted

12.1.2. Mathematical recombination of analytical results:

$$Final\ Analyte\ Concentration = \frac{(V_1 \times C_1) + (V_2 \times C_2)}{V_1 + V_2}$$

$V_1$ = total volume of the initial filtrate phase (L).
$C_1$ = analyte concentration in initial filtrate phase (mg/L).
$V_2$ = volume of the theoretical solid phase leachate (L).
$C_2$ = analyte concentration in solid phase leachate (mg/L).,

12.2. REPORTING REQUIREMENTS

12.2.1. Follow these reporting conventions for multi-phase samples:

12.2.1.1. If both phases have positive results, use the values from each phase to calculate the recombined result. Use the reporting limit for each phase to calculate the recombined reporting limit.

12.2.1.2. If both phases are "ND" (not detected) the recombined result is "ND," and the reporting limit is calculated from the reporting limit for each phase.

12.2.1.3. If one phase is "ND" and the other phase has a positive result, use the zero for the "ND" phase and the positive value for the other phase to calculate the combined result. This will produce a minimum known concentration. Alternatively, at client request, the maximum possible concentration can be calculated by using the reporting limit for the "ND" phase rather than zero. The combined reporting limit is based on the reporting limit for both phases

12.2.2. Units - regardless of the nature of the sample, all TCLP and SPLP results are reported in units of mg/L.

12.2.3. For limits and significant figures, consult the appropriate analytical methods (Section 16.3).

12.2.4. Anomalies - all anomalies observed during the leach procedure must be noted on the worksheet or an NCM form. Some examples of such anomalies are:

12.2.4.1. Sample was monolithic - particle size reduction not possible due to nature of matrix.

12.2.4.2.Insufficient sample - less than the required 100 g minimum was available.

12.3. REVIEW REQUIREMENTS

12.3.1. Review all applicable holding times. If a holding time was exceeded, confirm that a holding time violation was properly documented in an NCM.

12.3.2. If Total analysis results are available, those results may be compared with the TCLP analysis results according to the following:

$$Total \geq 20 \times TCLP$$

**NOTE:** Assumes the sample is 100% Solids.

12.3.3. Total constituent analysis results can be used to demonstrate the TCLP protocol is unnecessary. In performing a TCLP analysis, there is a 20:1 dilution of the original sample with the leaching solution. Thus, if the "total constituent" result is less than 20 times the TC level, it is impossible for the leachate to "fail" and the TCLP does not need to be performed. For example, the TC level for lead is 5.0 mg/L (ppm). Therefore, if a sample of lead-contaminated soil contains less than 100 ppm total lead, a TCLP test need not be run to demonstrate that lead is less than the TCLP limit.

## 13. METHOD PERFORMANCE

13.1. Refer to individual analysis SOPs.

13.2. Training Qualification:

The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

## 14. POLLUTION PREVENTION

14.1. This method does not contain any specific modifications that serve to minimize or prevent pollution.

## 15. WASTE MANAGEMENT

15.1. Waste generated in this procedure must be segregated and disposed according to the facility's hazardous wastes procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

## 16. REFERENCES

16.1. Method 1311, Toxicity Characteristic Leaching Procedure, Revision 0, July 1992, SW-846 Final Update I.

16.2. Method 1312, Synthetic Precipitation Leaching Procedure, Revision 0, November 1994, SW-846 Update II.

16.3. Related Documents

16.3.1. Toxicity Characteristic: Corrections to Final Rule. Method 1311, Federal Register, Vol. 55, No. 126, Friday, June 29, 1990.

16.3.2. Toxicity Characteristic: Final Rule. Method 1311, Federal Register, Vol. 55, No. 61, Thursday, March 29, 1990.

16.3.3. Technical Background Document and Response To Comments, Method 1311, Toxicity Characteristic Leaching Procedure, USEPA/OSW, April, 1989.

16.3.4. QA-003, Quality Control Program

16.3.5. CORP-IP-0003NC: Acid Digestion of Aqueous Samples by SW846 and MCAWW 200 Series Methods.

16.3.6. CORP-MT-0001NC: Inductively Coupled Plasma-Atomic Emission Spectroscopy, Spectrometric Method for Trace Element Analysis, Method 6010B and Method 200.7.

16.3.7. CORP-MT-0003NC: Graphite Furnace Atomic Absorption Spectroscopy, (Thallium only)

16.3.8. CORP-MT-0005NC: Preparation and Analysis of Mercury in Aqueous Samples by Cold Vapor Atomic Absorption, SW-846 7470A and MCAWW 245.1.

16.3.9. CORP-MS-0002NC: Determination of Volatile Organics by GC/MS based on Methods 8260B, 624, and 524.2.

16.3.10. CORP-MS-0001NC : GC/MS Analysis Based on Method 8270C and 625.

16.3.11. CORP-GC-0001NC: Gas Chromatographic Analysis Based on Methods 8000B, 8021B, 8081A, 8082, 8151A, 8310, 610, and 8141A.

16.3.12.CORP-OP-0001NC: Extraction and Cleanup of Organic Compounds from Waters and Soils, Based on SW846 3500 Series, 3600 Series, 8151A and 600 Series Methods.

## 17. MISCELLANEOUS

17.1. Modifications/Interpretations from Reference Methods

17.1.1. Section 11.2: Preliminary Evaluations. Section 7.1 of the source method 1311 states that the sample aliquot used for the preliminary evaluation "...may not actually undergo TCLP extraction." Section 7.1.5 of the source method indicates that the portion used for the preliminary evaluation may be used for either the ZHE or non-volatile extraction if the sample was 100% solid. Section 7.1.5 further indicates that if the sample was subjected to filtration (i.e., < 100% solid) that this aliquot may be used for the non-volatile extraction procedure only as long as sufficient sample is available (minimum 100 g). Samples which have been subjected to the oven drying step may not be used for TCLP extraction because solid phase degradation may result upon heating.

17.1.2. Sections 11.3.6 and 11.4.21: Determination of Filtrate/Extraction Fluid Compatibility. Section 7.2.13 of the source method provides no guidance as to how to make this determination. As a result, the procedure herein was developed.

17.1.3. Section 9.2: TCLP Extraction Blanks. Section 8.1 of the source method states that a minimum of one blank for every 20 extractions "...that have been conducted in an extraction vessel." STL has interpreted this to mean one blank per twenty samples leached per TYPE of leaching vessel (i.e., Bottle or ZHE) per leach fluid used.

17.1.4. Section 11.2.5.5.8.1: Determination of Appropriate Extraction Fluid. Method 1311 does not address the appropriate approach to take if the pH equals 5.0. This SOP requires that Fluid #1 must be used if the pH is less than or equal to 5.0.

17.1.5. Section 9.4: QA/QC - Matrix Spikes. Section 8.2 of the source method states "A matrix spike shall be performed for each waste type..." and "A minimum of one matrix spike must be analyzed for each analytical batch." Further, Section 8.2.3 of the source method also states "The purpose of the matrix spike is to monitor the performance of the analytical methods used, and to

determine whether matrix interferences exist." The standard STL LQM is designed to address the performance monitoring of analytical methodology through the LCS program. A minimum of one MS and MSD will be prepared for each TCLP leachate batch. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, the MS/MSD results have immediate bearing only on the specific sample spiked and not all samples in the batch.

17.1.6. Section 8.2.2 of the source method states that "In most cases, matrix spikes should be added at a concentration equivalent to the corresponding regulatory level." The method also states "If the analyte concentration is less than one half the regulatory level, the spike concentration may be as low as one half of the analyte concentration but may not be less than five times the method detection limit". For several analytes, spiking at the regulatory level is inappropriate to the range of analysis afforded by the determinative methods. Due to the wide range in these levels, STL spikes at the levels specified in the determinative SOPs.

17.2. Modifications from Previous SOP

17.3. Facility Specific SOPs

Each facility shall attach a list of facility specific SOPs or approved attachments (if applicable) which are required to implement this SOP or which are used in conjunction with this SOP. If no facility specific SOPs or amendments are to be attached, a statement must be attached specifying that there are none. Refer to the Appendices for any facility specific information required to support this SOP.

# APPENDIX A

# TABLES

## Table 3 - Toxicity Characteristic Analytes and Regulatory Levels (Final Rule)

| Contaminant | mg/L |
|---|---|
| Arsenic | 5.0 |
| Barium | 100.0 |
| Benzene | 0.5 |
| Cadmium | 1.0 |
| Carbon tetrachloride | 0.5 |
| Chlordane | 0.03 |
| Chlorobenzene | 100.0 |
| Chloroform | 6.0 |
| Chromium | 5.0 |
| o-Cresols | 200.0 |
| m-Cresols | 200.0 |
| p-Cresols | 200.0 |
| Total Cresols (used if isomers not resolved) | 200.0 |
| 2,4-D | 10.0 |
| 1,4-Dichlorobenzene | 7.5 |
| 1,2-Dichloroethane | 0.5 |
| 2,4-Dinitrotoluene | 0.13 |
| 1,1-Dichloroethylene | 0.7 |
| Endrin | 0.02 |
| Heptachlor (& epoxide) | 0.008 |
| Hexachlorobenzene | 0.13 |
| Hexachlorobutadiene | 0.5 |
| Hexachloroethane | 3.0 |
| Lead | 5.0 |
| Lindane | 0.4 |
| Mercury | 0.2 |
| Methoxychlor | 10.0 |
| Methyl ethyl ketone | 200.0 |
| Nitrobenzene | 2.0 |
| Pentachlorophenol | 100.0 |
| Pyridine | 5.0 |
| Selenium | 1.0 |
| Silver | 5.0 |
| Tetrachloroethylene | 0.7 |
| Toxaphene | 0.5 |
| Trichloroethylene | 0.5 |
| 2,4,5-Trichlorophenol | 400.0 |
| 2,4,6-Trichlorophenol | 2.0 |
| 2,4,5-TP (Silvex) | 1.0 |
| Vinyl chloride | 0.2 |

# APPENDIX B

# FIGURES

Figure 1 & 2 - Rotary Agitation Apparatus and Zero Headspace Extraction Vessel (ZHE)

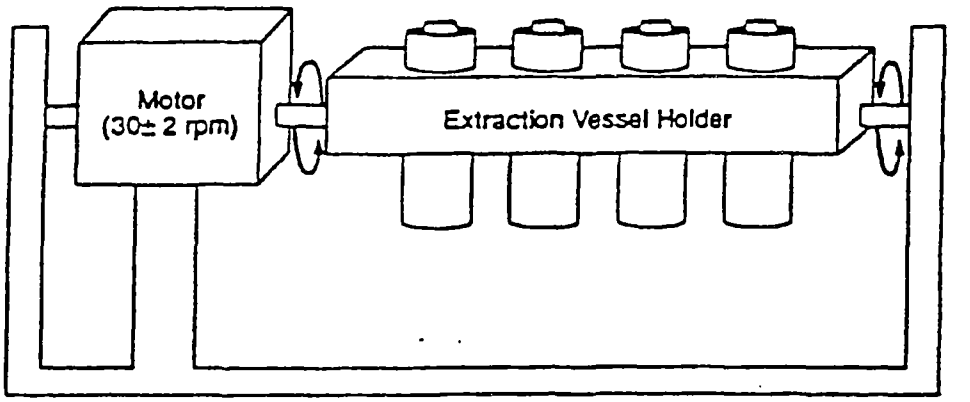


Figure 1. Rotary Agitation Apparatus

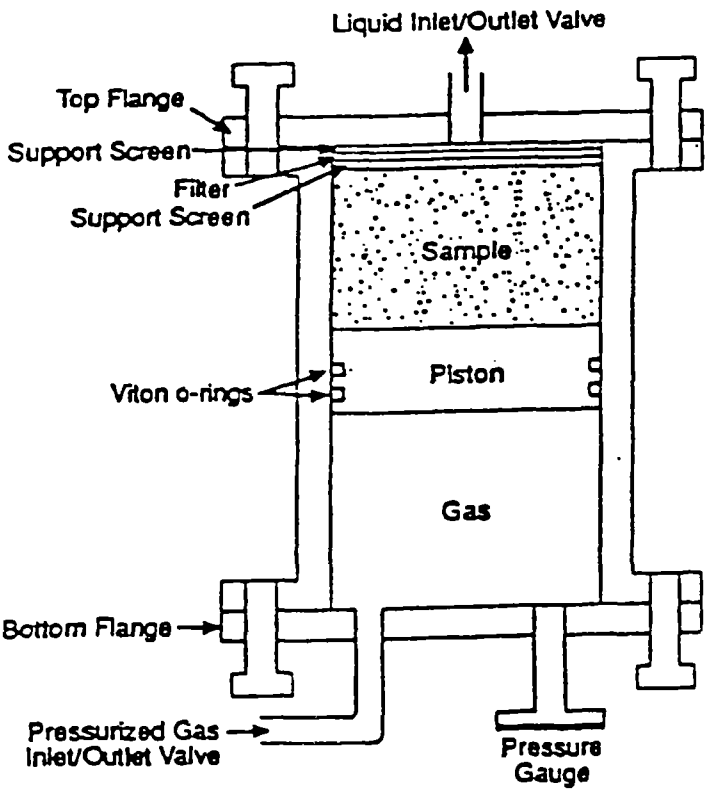

Figure 3 - US Environmental Protection Agency Memorandum #35, Page 1

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF
SOLID WASTE AND EMERGENCY RESPONSE

MEMORANDUM # 35

DATE: June 12, 1992

SUBJECT: Notes on RCRA Methods and QA Activities

From: Gail Hansen, Chief
Methods Section (OS-331)

This memo addresses the following topics:

- 1992 Symposium on Waste Testing and Quality Assurance
- SW-846 Update
  - Final Rule for January 23, 1989 Proposed Rule
  - Notice, Proposed Rulemaking for the Second Update to the Third Edition
- Chlorofluorocarbon 113 (CFC-113) Solvent Replacement Update
- Environmental Monitoring Methods Index (EMMI)
- Sampling Work Group Formation
- MICE Update
- Oily Waste Analysis
- Electronic SW-846 Availability.



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Figure 3 - US Environmental Protection Agency Memorandum #35, Page 10

Oily Waste Analysis

One of the most frequently asked questions on the MICE Service concerns the application of the TCLP, Method 1311, to oily wastes. Many callers request technical guidance on the extraction of oily wastes due to the difficulty in the filtration on these types of waste. In many cases, an oily waste does not filter completely due to premature clogging of the glass fiber filter. This can result in the retention of standing liquid on the glass fiber filter. Material that do not pass through the glass fiber filter at the conclusion of the filtration step is defined by the method as the solid phase of the waste. The solid phase is then subjected to the leaching procedure of the TCLP. For oily wastes, clogging of the glass fiber filter can result in an overestimation of the amount of solid material available for leaching.

To solve this problem, the Agency recommends a conservative approach, one that probably will overestimate the amount of leaching. Rather than performing the TCLP extraction on the unfiltered portion of the oily waste, assume the waste is 100% liquid (e.g., will pass through the glass fiber filter) and perform a totals analysis on the oily waste to determine if the oil exceeds the appropriate regulatory level.

Filterable waste oil generated during the TCLP must be analyzed for a variety of organic and inorganic analytes. The OSW recognizes the difficulty in achieving acceptable performance for the analysis of waste oil using methods currently provided in SW-846. As a result, the Agency will provide several new methods for the preparation and analysis of oil samples to the Organic Methods Workgroup in July. In addition, a microwave assisted digestion procedure should improve the analysis of metals and will be proposed as part of the Second Update of the Third Edition of SW-846. Brief descriptions of these techniques are provided below, for additional information on the organic procedures contact Barry Lesnik at (202) 260-7459. For additional information on microwave digestion contact Ollie Fordham (202) 260-4778.

The use of purge-and-trap (Method 5030) for volatiles in oil generally results in severe contamination of analytical instrumentation. Traps, transfer lines and chromatography columns may become contaminated with oil. This leads to elevated baselines, hydrocarbon background in subsequent analyses, and cross-contamination. Headspace (Method 3810) is currently allowed only as a screening procedure in SW-846. The Agency is evaluating the use of headspace in conjunction with isotope dilution mass spectrometry for the quantitative analysis of volatiles in oil. Headspace reduces interference problems encountered with purge-and-trap. However, headspace quantitation can be questionable because the distribution of analytes is not

# APPENDIX C

## Logbook Pages

## TCLP/SPLP ZHE Logbook

STL NORTH CANTON ZHE LOGBOOK

| Sample Number | Extraction Vessel ID | Matrix | Sample Wt (g) | Extraction Buffer ID | Date On | Time On | Date Off | Time Off | Tumbler ID | Tumbler Speed 30±2 rpm | Extraction Fluid ID | Initial ZHE Pressure | Final ZHE Pressure | Comments |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
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STL NORTH CANTON ZHE LOGBOOK

| | A | B | C | D | E | F | | G | H | |
|---|---|---|---|---|---|---|---|---|---|---|
| Sample Number | Weight of Container + Sample (g) | Weight of Container + Residue (g) | Difference (A – B) Sample Weight (g) | Weight of the Syringe (or vials) (g) | Weight of the Syringe (or vials) + Filtrate (g) | Difference (E – D) Filtrate Weight (g) | Volume of Filtrate* (mL) | Difference (C – F) Wet Solids Weight (g) | G x 20 Buffer Amount (mL) | Initials |
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* Filtrate volume only needed when filtrate is incompatible with leachate

## TCLP/SPLP Bottle Extraction Logbook

SOP No.: NC-IP-0005 STL NORTH CANTON TCLP LOGBOOK

| | | | | Pre-Test | | | % Dry Solids | | | | Leach Start | | | | | Leach Finish | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Pre-Prep Batch | Sample Number | Parameters | Matrix | Sample Wt (g) | pH after water | pH after heating | Sample Wt (g) | Filter Wt (g) | Filter + Particulates Wt (g) | % Dry Solids | Sample Wt (g) | Buffer # / ID | Date On | Time On | pH On | Date Off | Time Off | pH Off | Tumbler ID | Initials | Comments |
| | | M B<br>P H | | | | | | | | | | | | | | | | | | | |
| | | M B<br>P H | | | | | | | | | | | | | | | | | | | |
| | | M B<br>P H | | | | | | | | | | | | | | | | | | | |
| | | M B<br>P H | | | | | | | | | | | | | | | | | | | |
| | | M B<br>P H | | | | | | | | | | | | | | | | | | | |
| | | M B<br>P H | | | | | | | | | | | | | | | | | | | |
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| | | M B<br>P H | | | | | | | | | | | | | | | | | | | |
| | | M B<br>P H | | | | | | | | | | | | | | | | | | | |
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| | | M B<br>P H | | | | | | | | | | | | | | | | | | | |
| | | M B<br>P H | | | | | | | | | | | | | | | | | | | |
| | | M B<br>P H | | | | | | | | | | | | | | | | | | | |
| | | M B<br>P H | | | | | | | | | | | | | | | | | | | |

SOP No.: NC-IP-0005

STL NORTH CANTON TCLP LOGBOOK

| | A | B | C | D | E | F | | G | H | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample Number | Weight of Container + Sample (g) | Weight of Container + Residue (g) | Difference (A – B) Sample Weight (g) | Weight of the Filtrate Bottle (g) | Weight of the Filtrate bottle + Filtrate(g) | Difference (E – D) Filtrate Weight (g) | Volume of Filtrate* (mL) | Difference (C – F) Wet Solids Weight (g) | G x 20 Buffer Amount (mL) | Initials | Comments |
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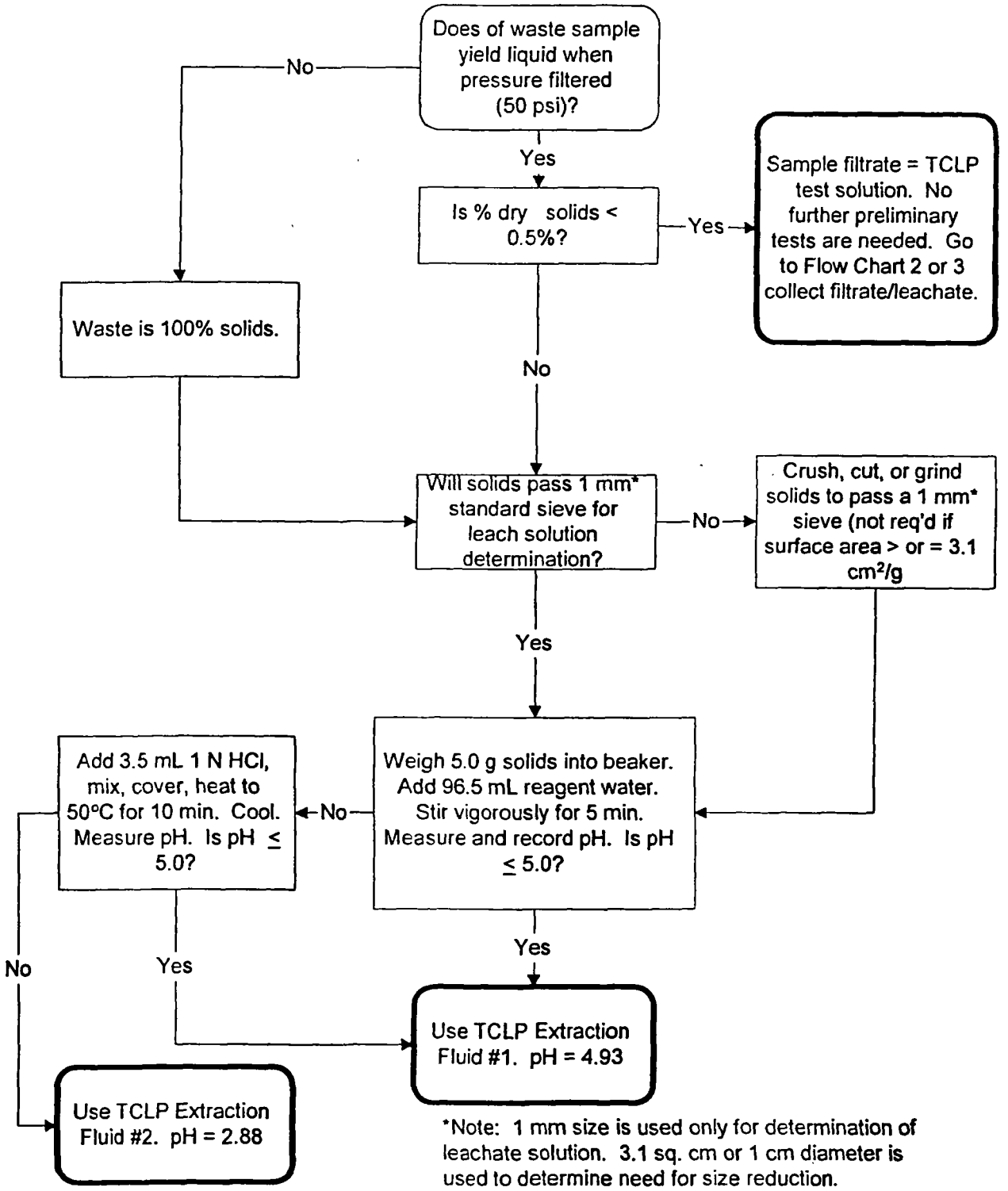
* Filtrate volume only needed when filtrate is incompatible with leachate

# APPENDIX D

# FLOW CHARTS

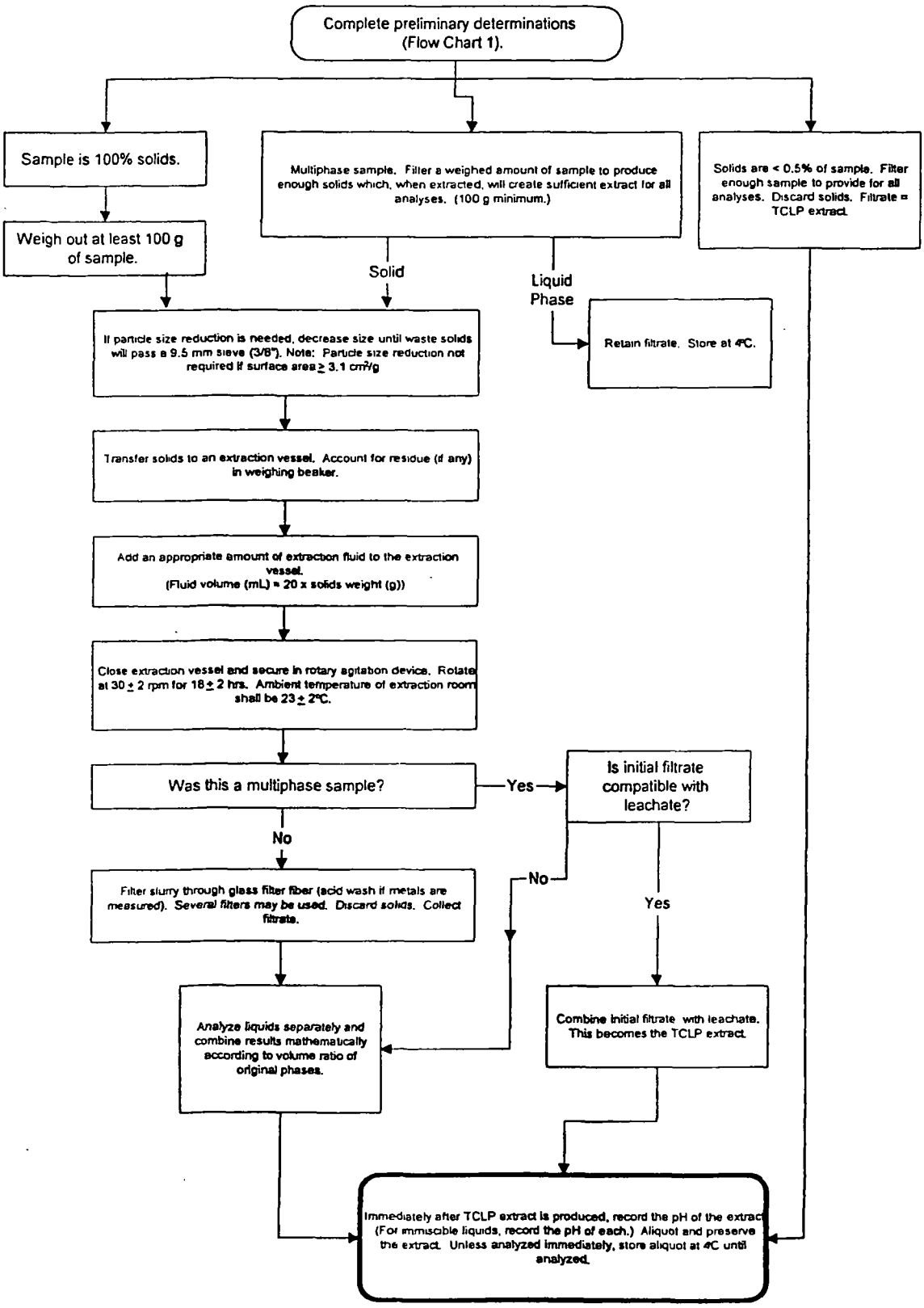
**Flow Chart 1. Preliminary Sample Evaluation (Section 11.2)**



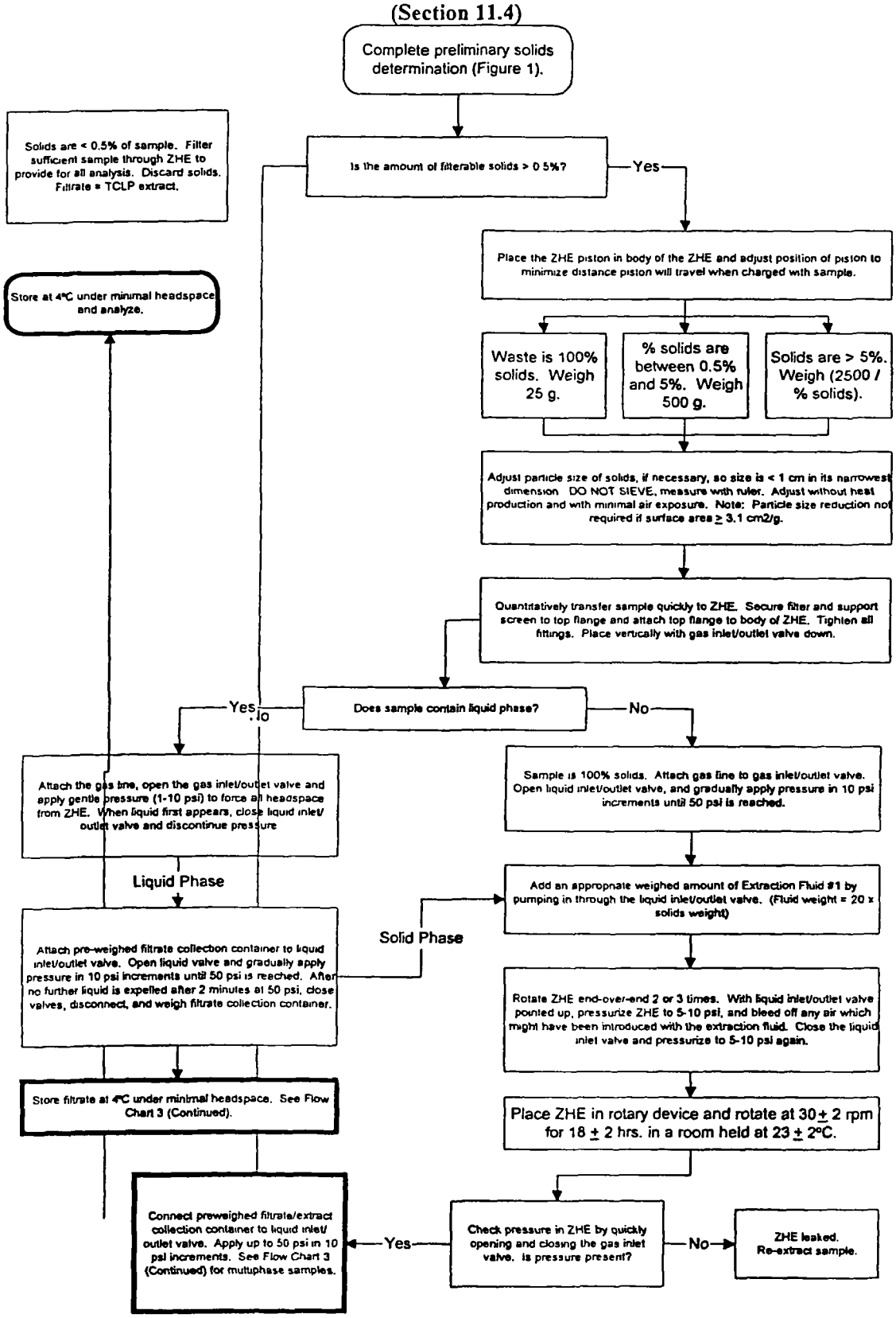

*Note: 1 mm size is used only for determination of leachate solution. 3.1 sq. cm or 1 cm diameter is used to determine need for size reduction.

x

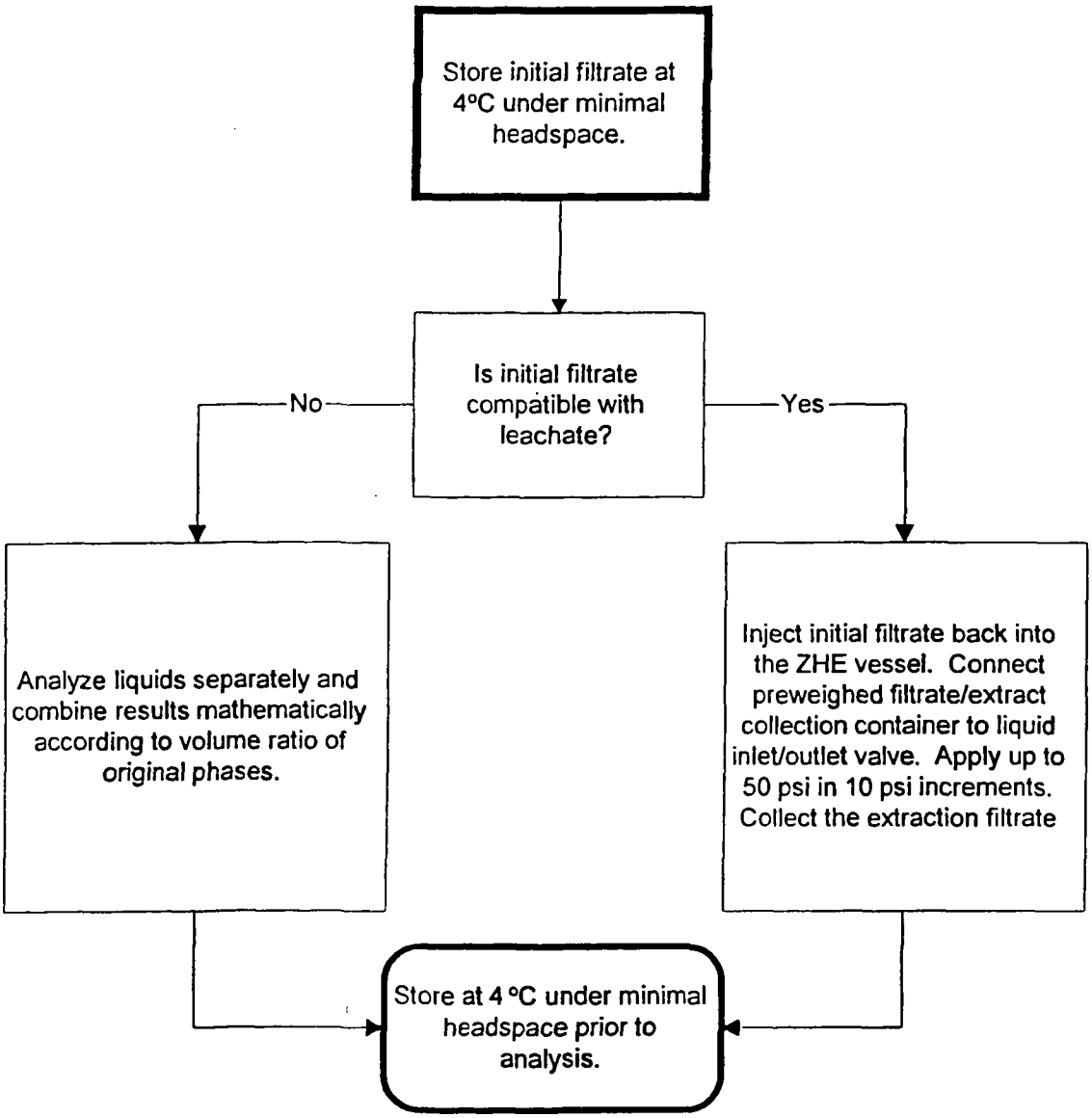
## Flow Chart 2. Bottle Extraction, Non-Volatile Constituents (Section 11.3)



## Flow Chart 3. ZHE Extraction, Volatile Constituents (Section 11.4)



**Flow Chart 3. ZHE Extraction (Continued)**



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SOP No. CORP-MS-0002NC
Revision No. 2.3
Revision Date: 05/23/01


# STL STANDARD OPERATING PROCEDURE

## TITLE: DETERMINATION OF VOLATILE ORGANICS BY GC/MS BASED ON METHOD 8260B, 8260A, AND 624

(SUPERSEDES: REVISION 2.2, DATED 11/28/00)

| | | |
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## 1.0 SCOPE AND APPLICATION

1.1. This method is applicable to the determination of Volatile Organic Compounds in waters, wastewater, soils, sludges and other solid matrices. Standard analytes are listed in Tables 5 and 6.

1.2. This SOP is applicable to method 8260B. It may also be used for analysis following method 8260A. Appendix A presents modifications to the procedures in the main SOP that are necessary for analysis of wastewater by method 624. The associated LIMS method codes are QK (8260B), DN (624), and MZ (8260A). Ohio VAP projects are distinguished by Program Code 2J. The following Prep Codes are used: 15 (5 mL purge), 25 (25 mL purge), 4B (Methanol preservation, EnCore™ ), 4D (Sodium Bisulfate preservation, EnCore™ ), 4P (Frozen, EnCore™ ), and 73 (5030A Methanol Prep).

1.3. This method can be used to quantify most volatile organic compounds that have boiling points below 200°C and are insoluble or slightly soluble in water. Volatile water soluble compounds can be included in this analytical technique; however, for more soluble compounds, quantitation limits are approximately ten times higher because of poor purging efficiency.

1.4. The method is based upon a purge and trap, gas chromatograph/mass spectrometric (GC/MS) procedure. The approximate working range is 5 to 200 µg/L for 5 mL waters, 1 to 40 µg/L for 25 mL purge waters, 5 to 200 µg/kg for low-level soils, and 250 to 25,000 µg/kg for medium-level soils. Reporting limits are listed in Tables 1 and 3.

1.5. Method performance is monitored through the use of surrogate compounds, matrix spike/matrix spike duplicates, and laboratory control spike samples.

## 2. SUMMARY OF METHOD

2.1. Volatile compounds are introduced into the gas chromatograph by the purge and trap method. The components are separated via the chromatograph and detected using a mass spectrometer, which is used to provide both qualitative and quantitative information.

2.2. Aqueous samples are purged directly. Generally, soils are preserved by extracting the volatile analytes into methanol. If especially low detection limits are required, soil samples may be preserved with sodium bisulfate and purged directly.

2.3. In the purge and trap process, an inert gas is bubbled through the solution at ambient temperature or at 40°C (40°C required for low level soils) and the volatile components are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept

through a sorbant column where the volatile components are trapped. After purging is completed, the sorbant column (trap) is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column. The gas chromatographic column is then heated to elute the components which are detected with a mass spectrometer.

2.4. Qualitative identifications are confirmed by analyzing standards under the same conditions used for samples and comparing the resultant mass spectra and GC retention times. Each identified component is quantified by relating the MS response for an appropriate selected ion produced by that compound to the MS response for another ion produced by an internal standard.

## 3. DEFINITIONS

### 3.1. Batch

The batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same time period. Using this method, each BFB analysis will normally start a new batch. Batches for medium level soils are defined at the sample preparation stage and may be analyzed on multiple instruments over multiple days, although reasonable effort should be made to keep the samples together.

3.1.1. The Quality Control batch must contain a matrix spike/spike duplicate (MS/MSD), a Laboratory Control Sample (LCS), and a method blank. In some cases, at client request, the MS/MSD may be replaced with a matrix spike and sample duplicate. Refer to the STL QC Program document (QA-003) for further details of the batch definition.

3.2. Method Blank

3.2.1. A method blank consisting of all reagents added to the samples must be analyzed with each batch of samples. The method blank is used to identify any background interference or contamination of the analytical system which may lead to the reporting of elevated concentration levels or false positive data.

3.3. Laboratory Control Sample (LCS)

3.3.1. Laboratory Control Samples are well characterized, laboratory generated samples used to monitor the laboratory's day-to-day performance of routine analytical methods. The LCS, spiked with a group of target compounds representative of the method analytes, is used to monitor the accuracy of the analytical process, independent of matrix effects. Ongoing monitoring of the LCS results provides evidence that the laboratory is performing the method within accepted QC guidelines for accuracy and precision.

3.4. Surrogates

3.4.1. Surrogates are organic compounds which are similar to the target analyte(s) in chemical composition and behavior in the analytical process, but which are not normally found in environmental samples. Each sample, blank, LCS, and MS/MSD is spiked with surrogate standards. Surrogate spike recoveries must be evaluated by determining whether the concentration (measured as percent recovery) falls within the required recovery limits.

3.5. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

3.5.1. A matrix spike is an environmental sample to which known concentrations of target analytes have been added. A matrix spike duplicate is a second aliquot of the same sample which is prepared and analyzed along with the sample and matrix spike. Matrix spikes and duplicates are used to evaluate accuracy and precision in the actual sample matrix.

3.6. Calibration Check Compound (CCC)

3.6.1. CCCs are a representative group of compounds which are used to evaluate initial calibrations and continuing calibrations. Relative percent difference for the initial calibration and % drift for the continuing calibration response factors are calculated and compared to the specified method criteria.

3.7. System Performance Check Compounds (SPCC)

SPCCs are compounds which are sensitive to system performance problems and are used to evaluate system performance and sensitivity. A response factor from the continuing calibration is calculated for the SPCC compounds and compared to the specified method criteria.

## 4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. The use of ultra high purity gases, pre-purged purified reagent water, and approved lots of purge and trap grade methanol will greatly reduce introduction of contaminants. In extreme cases the purging vessels may be pre-purged to isolate the instrument from laboratory air contaminated by solvents used in other parts of the laboratory.

4.2. Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) into the sample through the septum seal during shipment and storage. A field blank prepared from reagent water and carried through the sampling and handling protocol can serve as a check on such contamination.

4.3. Matrix interferences may be caused by non-target contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source depending upon the nature and diversity of the site being sampled.

4.4. Cross-contamination can occur whenever high-level and low-level samples are analyzed sequentially or in the same purge position on an autosampler. Whenever an unusually concentrated sample is analyzed, it should be followed by one or more blanks to check for cross-contamination. The purge and trap system may require extensive bake-out and cleaning after a high-level sample.

4.5. Some samples may foam when purged due to surfactants present in the sample. When this kind of sample is encountered an antifoaming agent (e.g., J.T. Baker's Antifoam B silicone emulsion) can be used. A blank spiked with this agent must be analyzed with the sample because of the non-target interferences associated with the agent.

## 5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all STL associates.

5.2. The Chemical Hygiene Plan (CHP) gives details about the specific health and safety practices which are to be followed in the laboratory area. Personnel must receive training in

the CHP, including the written Hazard Communication plan, prior to working in the laboratory. Consult the CHP, the STL Health and Safety Policies and Procedures Manual, and available Material Safety Data Sheets (MSDS) prior to using the chemicals in the method.

5.3. Consult the STL Health and Safety Policies and Procedures Manual for information on Personal Protective Equipment. Eye protection that protects against splash and a laboratory coat must be worn in the lab. Appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately. Disposable gloves shall not be reused.

5.4. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined, therefore each chemical compound should be treated as a potential health hazard. Additional health and safety information can be obtained from the MSDS files maintained in the laboratory. The following specific hazards are known:

5.4.1. Chemicals that have been classified as carcinogens, or potential carcinogens, under OSHA include: Acrylonitrile, benzene, carbon tetrachloride, chloroform, 1,2-dibromo-3-chloropropane, 1,4-dichlorobenzene, and vinyl chloride.

5.4.2. Chemicals known to be flammable are: **Methanol.**

5.5. Exposure to chemicals must be maintained **as low as reasonably achievable**, therefore, unless they are known to be non-hazardous, all samples should be opened, transferred, and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.6. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operations will permit.

5.7. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL associate. The situation must be reported **immediately** to a laboratory supervisor.

5.8. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices outlined in the STL Health and Safety Manual. These employees must have training on the hazardous waste disposal practices initially upon assignment of these tasks, followed by an annual refresher training.

## 6. EQUIPMENT AND SUPPLIES

6.1. Microsyringes: 10 µL and larger, 0.006 inch ID needle.

6.2. Syringe: 5 or 25 mL glass with luerlok tip, if applicable to the purging device.

6.3. Balance: Analytical, capable of accurately weighing 0.0001 g, and a top-loading balance capable of weighing 0.1 g

6.4. Glassware:

6.4.1. Vials: 20 mL with screw caps and Teflon liners.

6.4.2. Volumetric flasks: 10 mL and 100 mL, class A with ground-glass stoppers.

6.5. Spatula: Stainless steel.

6.6. Disposable pipets: Pasteur.

6.7. pH paper: Wide range.

6.8. Gases:

6.8.1. Helium: Ultra high purity, gr. 5, 99.999%.

6.8.2. Nitrogen: Ultra high purity, from cylinders of gas generators, may be used as an alternative to helium for purge gas.

6.8.3. Compressed air: Used for instrument pneumatics.

6.8.4. Liquid nitrogen: Used for cryogenic cooling if necessary.

6.9. Purge and Trap Device: The purge and trap device consists of the sample purger, the trap, and the desorber.

6.9.1. Sample Purger: The recommended purging chamber is designed to accept 5 mL samples with a water column at least 3 cm deep. The purge gas must pass through the water column as finely divided bubbles, each with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. Alternative sample purge devices may be used provided equivalent performance is demonstrated. Low level soils are purged directly from a VOA vial.

6.9.2. Trap: A variety of traps may be used, depending on the target analytes required. For most purposes the Vocarb 3000 trap is suitable. Other traps, such as Vocarb 4000, or Tenax / Silica gel / Charcoal may be used if the Quality Control criteria are met.

6.9.3. Desorber: The desorber should be capable of rapidly heating the trap to 180°C. Many such devices are commercially available.

6.9.4. Sample Heater: A heater capable of maintaining the purge device at 40°C is necessary for low level soil analysis.

6.10. Gas Chromatograph/Mass Spectrometer System:

6.10.1. Gas Chromatograph: The gas chromatograph (GC) system must be capable of temperature programming.

6.10.2. Gas Chromatographic Columns: Capillary columns are used. Some typical columns are listed below:

6.10.2.1. Column 1: 105m x 0.53 ID Rtx-624 with 3 µm film thickness.

6.10.2.2. Column 2: 75 m x 0.53 ID DB-624 widebore with 3 µm film thickness.

6.10.2.3. Mass Spectrometer: The mass spectrometer must be capable of scanning 35-300 AMU every two seconds or less, using 70 volts electron energy in the electron impact mode and capable of producing a mass spectrum that meets the required criteria when 50 ng of 4-Bromofluorobenzene (BFB) are injected onto the gas chromatograph column inlet.

6.10.3. GC/MS interface: In general glass jet separators are used but any interface (including direct introduction to the mass spectrometer) that achieves all acceptance criteria may be used.

6.10.4. Data System: A computer system that allows the continuous acquisition and storage on machine readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between the specified time or scan-number limits. Also, for the non-target compounds, software must be available that allows for the comparison of sample spectra against reference library spectra. The most recent release of the NIST/EPA mass spectral library should be used as the reference library. The computer system must also be capable of backing up data for long-term off-line storage.

6.10.5. Cryogenic Cooling: Some columns require the use of liquid nitrogen to achieve the subambient temperature required for the proper separation of the gases.

# 7. REAGENTS AND STANDARDS

## 7.1. Reagents

7.1.1. Methanol: Purge and Trap Grade, High Purity

7.1.2. Reagent Water: High purity water that meets the requirements for a method blank when analyzed. (See section 9.4) Reagent water may be purchased as commercial distilled water and prepared by purging with an inert gas overnight. Other methods of preparing reagent water are acceptable.

## 7.2. Standards

7.2.1. Calibration Standard

7.2.1.1. Stock Solutions: Stock solutions may be purchased as certified solutions from commercial sources or prepared from pure standard materials as appropriate. These standards are prepared in methanol and stored in Teflon-sealed screw-cap bottles with minimal headspace at -10° to -20°C.

7.2.1.2. Working standards: A working solution containing the compounds of interest prepared from the stock solution(s) in methanol. These standards are stored in the freezer or as recommended by the manufacturer. Working standards are monitored by comparison to the initial calibration curve. If any of the calibration check compounds drift in response from the initial calibration by more than 20% then corrective action is necessary. This may include steps such as instrument maintenance, preparing a new calibration verification standard or tuning the instrument. If the corrective actions do not correct the problem then a new initial calibration must be performed.

7.2.1.3. Aqueous Calibration Standards are prepared in reagent water using the secondary dilution standards. These aqueous standards must be prepared daily.

7.2.1.4. If stock or secondary dilution standards are purchased in sealed ampoules they may be used up to the manufacturers expiration date.

7.2.2. Internal Standards: Internal standards are added to all samples, standards, and blank analyses. Refer to Table 7 for internal standard components.

7.2.3. Surrogate Standards: Refer to Table 8 for surrogate standard components and spiking levels.

7.2.4. Laboratory Control Sample Spiking Solutions: Refer to Table 9 for LCS components and spiking levels.

7.2.5. Matrix Spiking Solutions: The matrix spike contains the same components as the LCS. Refer to Table 9.

7.2.6. Tuning Standard: A standard is made up that will deliver 50 ng on column upon injection. A recommended concentration of 25 ng/µL of 4-Bromofluorobenzene in methanol is prepared as described in Sections 7.2.1.1 and 7.2.1.2.

## 8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Holding times for all volatile analysis are 14 days from sample collection.

8.2. Water samples are normally preserved at pH $\leq$ 2 with 1:1 hydrochloric acid. If residual chlorine is present, 2 drops of 10% sodium thiosulfate are added.

8.3. Solid samples are field preserved with sodium bisulfate solution for low level analysis, or with methanol for medium level analysis. Soil samples can also be taken using the EnCore™ sampler and preserved in the lab within 48 hours of sampling. At specific client request, unpreserved soil samples may be accepted.

8.4. There are several methods of sampling soil. The recommended method, which provides the minimum of field difficulties, is to take an EnCore™ sample. (The 5 g or 25 g sampler can be used, depending on client preference). Following shipment back to the lab the soil is preserved in methanol. This is the medium level procedure. If very low detection limits are needed (< 50 µg/kg for most analytes) then it will be necessary to use two additional 5 g EnCore™ samplers or to use field preservation.

8.5. Sample collection for medium level analysis using EnCore™ samplers.

8.5.1. Ship one 5 g (or 25 g) EnCore™ sampler per field sample position.

8.5.2. An additional bottle must be shipped for percent moisture determination.

8.5.3. When the samples are returned to the lab, extrude the (nominal) 5g (or 25 g) sample into a tared VOA vial containing 5 mL methanol (25 mL methanol for the 25 g sampler). Obtain the weight of the soil added to the vial and note on the label.

8.5.4. Add the correct amount of surrogate spiking mixture. (Add 25 µL of 2500 µg/mL solution for a nominal 25 g sample, 5 µL for a nominal 5 g sample.) Refer to Section 17.8 for Michigan project criteria.

8.5.5. Add the correct amount of matrix spiking solution to the matrix spike and matrix spike duplicate samples. (Add 500 µL of 50 µg/mL solution for a nominal 25 g sample, 100 µL for a nominal 5 g sample.) Reduce the volume of methanol added to ensure the final volume is 25 mL for nominal 25 g sample or 5 mL methanol for a nominal 5 g sample. Refer to Section 17.8 for Michigan project criteria.

8.5.6. Prepare an LCS for each batch by adding the correct amount of matrix spiking solution to clean methanol. (50 µL of spike to 25 mL methanol or 10 µL spike to 5 mL methanol). Refer to Section 17.8 for Michigan project criteria.

8.5.7. Shake the samples for two minutes to distribute the methanol throughout the soil.

8.5.8. Allow to settle, then remove a portion of methanol and store in a clean Teflon capped vial at 4 ±2°C until analysis.

8.6. Sample collection for medium level analysis using field methanol preservation

8.6.1. Prepare a 2 oz sample container by adding 25 mL purge and trap grade methanol. (If a 5 g sample is to be used, add 5 mL methanol to a 2 oz container or VOA vial).

8.6.2. Seal the bottle and attach a label.

8.6.3. Weigh the bottle to the nearest 0.01g and note the weight on the label.

8.6.4. Ship with appropriate sampling instructions.

8.6.5. Each sample will require an additional bottle with no preservative for percent moisture determination.

8.6.6. At client request, the methanol addition and weighing may also be performed in the field.

8.6.7. When the samples are returned to the lab, obtain the weight of the soil added to the vial and note on the label.

8.6.8. Add the correct amount of surrogate spiking mixture. (Add 25 µL of 2500 µg/mL solution for a nominal 25 g sample, 5 µL for a nominal 5 g sample.) Refer to Section 17.8 for Michigan project criteria.

8.6.9. Add the correct amount of matrix spiking solution to the matrix spike and matrix spike duplicate samples. (Add 25 µL of 50 µg/mL solution for a nominal 25 g sample, 100 µL for a nominal 5 g sample.) Reduce the volume of methanol added to ensure

the final volume is 25 mL for nominal 25 g sample or 5 mL methanol for a nominal 5 g sample. Refer to Section 17.8 for Michigan project criteria.

8.6.10. Prepare an LCS for each batch by adding the correct amount of matrix spiking solution to clean methanol. (500 µL of spike to 25 mL methanol or 100 µL spike to 5 mL methanol). Refer to Section 17.8 for Michigan project criteria.

8.6.11. Shake the samples for two minutes to distribute the methanol throughout the soil.

8.6.12. Allow to settle, then remove a portion of methanol and store in a clean Teflon capped vial at 4+2°C until analysis.

8.7. Low level procedure

8.7.1. If low detection limits are required (typically < 50 µg/kg) sodium bisulfate preservation must be used. However, it is also necessary to take a sample for the medium level (field methanol preserved or using the EnCore™ sampler) procedure, in case the concentration of analytes in the soil is above the calibration range of the low level procedure.

8.7.2. A purge and trap autosampler capable of sampling from a sealed vial is required for analysis of samples collected using this method. (Varian Archon or O.I. 4552).

8.7.3. The soil sample is taken using a 5g EnCore™ sampling device and returned to the lab. It is recommended that two EnCore™ samplers be used for each field sample position, to allow for any reruns than may be necessary. A separate sample for % moisture determination is also necessary.

8.7.4. Prepare VOA vials by adding a magnetic stir bar, approximately 1 g of sodium bisulfate and 5 mL of reagent water.

8.7.5. Seal and label the vial. It is strongly recommended that the vial is labeled with an indelible marker rather than a paper label, since paper labels may cause the autosampler to bind and malfunction. The label absolutely must not cover the neck of the vial or the autosampler will malfunction.

8.7.6. Weigh the vial to the nearest 0.1g and note the weight on the label.

8.7.7. Extrude the soil sample from the EnCore™ sampler into the prepared VOA vial. Reweigh the vial to obtain the weight of soil and note on the label.

**Note:** Soils containing carbonates may effervesce when added to the sodium bisulfate solution. If this is the case at a specific site, add 5 mL of water instead, and freeze at

<-10°C within 48 hours, analyzed within 12 days after preserving with water, and stored at a 45 degree angle in the freezer.

**Note:** Freezing is not allowed for Ohio VAP soil samples.

8.7.9. Alternatively the sodium bisulfate preservation may be performed in the field. This is not recommended because of the many problems that can occur in the field setting. Ship at least two vials per sample. The field samplers must determine the weight of soil sampled. Each sample will require an additional bottle with no preservative for percent moisture determination, and an additional bottle preserved with methanol for the medium level procedure. Depending on the type of soil it may also be necessary to ship vials with no or extra preservative.

*8.8. Unpreserved soils*

*8.8.1. At specific client request unpreserved soils packed into glass jars or brass tubes may be accepted and subsampled in the lab. This is the old procedure based on method 5030A and method 8260A. It is no longer included in SW846 and is likely to generate results that are biased low, possibly be more than an order of magnitude.*

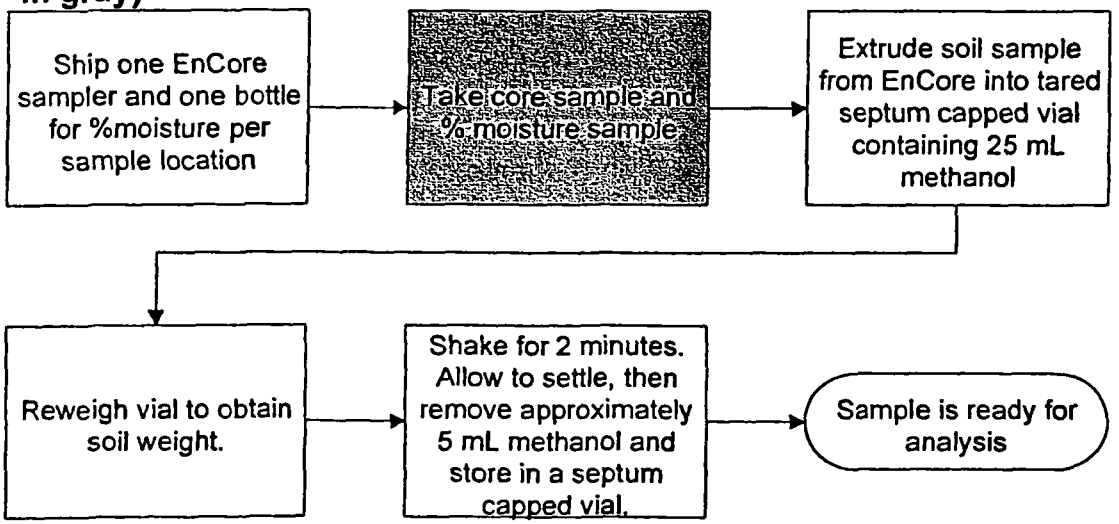
8.9. Aqueous samples are stored in glass containers with Teflon lined septa at 4°C +/- 2°C, with minimum headspace.

8.10. Medium level solid extracts are aliquoted into 2 - 5 mL glass vials with Teflon lined caps and stored at 4°C +/- 2°C. The extracts are stored with minimum headspace.

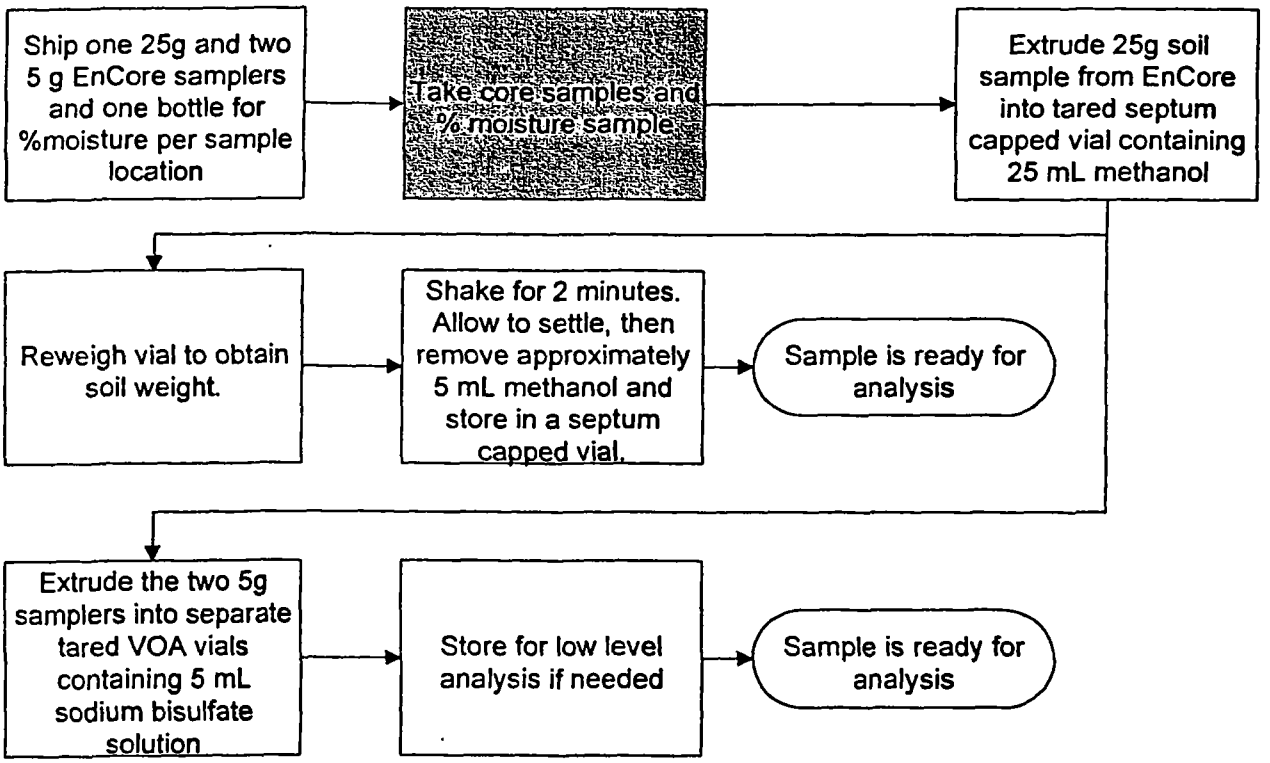
8.11. The maximum holding time is 14 days from sampling until the sample is analyzed. (Samples that are found to be unpreserved still have a 14 day holding time. However they should be analyzed as soon as possible. The lack of preservation should be addressed in the case narrative). Maximum holding time for the EnCore™ sampler (before the sample is added to methanol or sodium bisulfate) is 48 hours.

8.12. A holding blank is stored with the samples. This is analyzed and replaced if any of the trip blanks show any contamination. Otherwise it is replaced every 14 days.

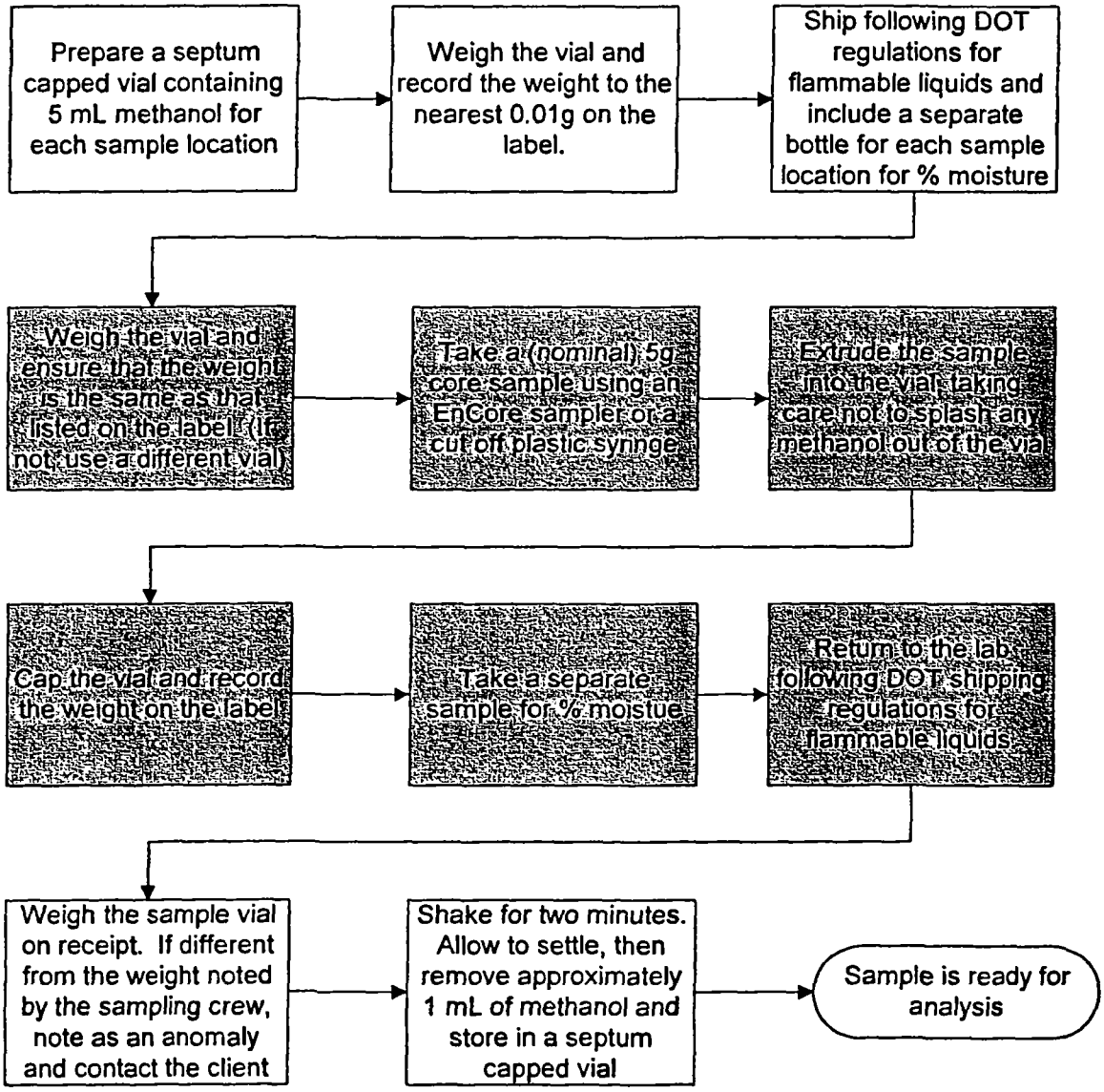
## EnCore procedure when low level is not required (field steps in gray)



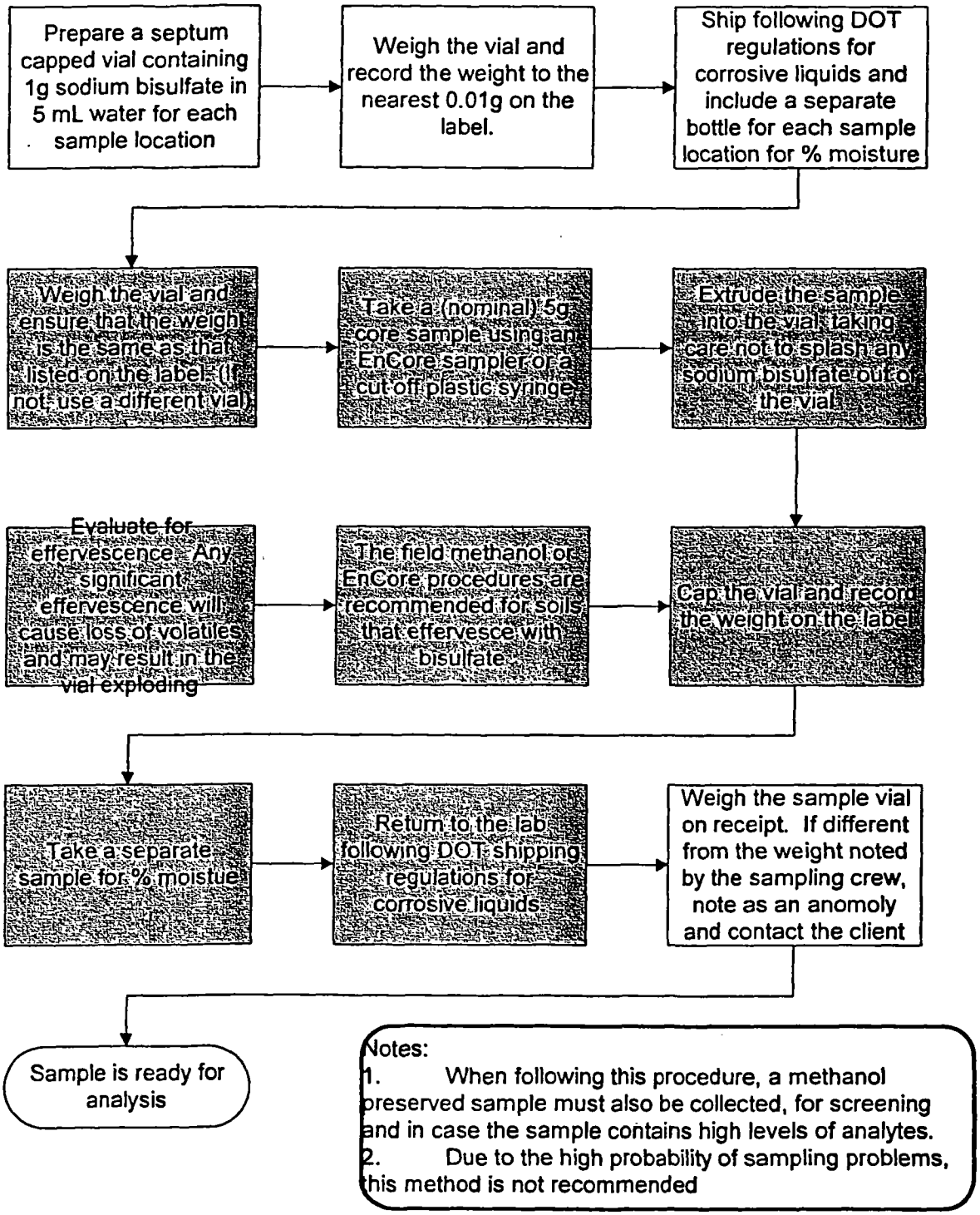

## EnCore procedure when low level is required



## Field methanol extraction procedure (field steps in gray)



## Field bisulfate preservation procedure (field steps in gray)




Notes:
1. When following this procedure, a methanol preserved sample must also be collected, for screening and in case the sample contains high levels of analytes.
2. Due to the high probability of sampling problems, this method is not recommended

# 9. QUALITY CONTROL

## 9.1. Initial Demonstration of Capability

9.1.1. For the standard analyte list, the initial demonstration described in Section 13 and method detection limit (MDL) studies must be acceptable before analysis of samples may begin. MDLs should be analyzed for low and medium soils and aqueous samples.

9.1.2. For non-standard analytes, a MDL study must be performed and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed to with the client. In any event, the minimum initial demonstration required is analysis of a standard at the reporting limit and a single point calibration.

## 9.2. Control Limits

In-house historical control limits must be determined for surrogates, matrix spikes, and laboratory control samples (LCS). These limits must be determined at least annually. The recovery limits are mean recovery +/- 3 standard deviations for surrogates, matrix spikes and LCS. Precision limits for matrix spikes / matrix spike duplicates are 0 to mean relative percent difference + 3 standard deviations.

9.2.1. All surrogate, LCS, and MS recoveries (except for dilutions) must be entered into QuantIMS (when available) or other database so that accurate historical control limits can be generated. For tests without a separate extraction, surrogates and matrix spikes will be reported for all dilutions.

9.2.2. Refer to the QC Program document (QA-003) for further details of control limits.

## 9.3. Surrogates

Every sample, blank, and QC sample is spiked with surrogates. Surrogate recoveries in samples, blanks, and QC samples must be assessed to ensure that recoveries are within established limits. The compounds included in the surrogate spiking solutions are listed in Table 8. If any surrogates are outside limits, the following corrective actions must take place (except for dilutions):

- Check all calculations for error.
- Ensure that instrument performance is acceptable.
- Recalculate the data and/or reanalyze if either of the above checks reveal a problem.

- Reprepare and reanalyze the sample or flag the data as "Estimated Concentration" if neither of the above resolves the problem.

The decision to reanalyze or flag the data should be made in consultation with the client. It is only necessary to reprepare/reanalyze a sample once to demonstrate that poor surrogate recovery is due to matrix effect, unless the analyst believes that the repeated out of control results are not due to matrix effect.

9.3.1. If the surrogates are out of control for the sample, matrix spike, and matrix spike duplicate, then matrix effect has been demonstrated for that sample and repreparation is not necessary. If the sample is out of control and the MS and/or MSD is in control, then reanalysis or flagging of the data is required.

9.3.2. Refer to the STL QC Program document (QA-003) for further details of the corrective actions.

9.4. Method Blanks

9.4.1. For each batch of samples, analyze a method blank. The method blank is analyzed after the calibration standards, normally before any samples. For low-level volatiles, the method blank consists of reagent water. For medium-level volatiles, the method blank consists of 25.0 mL of methanol. Surrogates are added and the method blank is carried through the entire analytical procedure. The method blank must not contain any analyte of interest at or above the reporting limit (except common laboratory contaminants, see below) or at or above 5% of the measured concentration of that analyte in the associated samples, whichever is higher.

- If the analyte is a common laboratory contaminant (methylene chloride, acetone, 2-butanone) the data may be reported with qualifiers if the concentration of the analyte is less than five times the reporting limit. Such action must be taken in consultation with the client.

- Reanalysis of samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples.

- If there is no target analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. Such action should be done in consultation with the client.

9.4.2. The method blank must have acceptable surrogate recoveries. If surrogate recoveries are not acceptable, the data must be evaluated to determine if the method blank has served the purpose of demonstrating that the analysis is free of contamination. If surrogate recoveries are low and there are reportable analytes in the associated samples

re-extraction of the blank and affected samples will normally be required. Consultation with the client should take place.

9.4.3. If reanalysis of the batch is not possible due to limited sample volume or other constraints, the method blank is reported, all associated samples are flagged with a "B," and appropriate comments may be made in a narrative to provide further documentation.

9.4.4. Refer to the STL QC Program document (QA-003) for further details of the corrective actions.

9.5. Laboratory Control Samples (LCS)

9.5.1. For each batch of samples, analyze a LCS. The LCS is analyzed after the calibration standard, and normally before any samples. The LCS contains a representative subset of the analytes of interest (See Table 9), and must contain the same analytes as the matrix spike. If any analyte or surrogate is outside established control limits, the system is out of control and corrective action must occur. Corrective action will normally be repreparation and reanalysis of the batch.

- If the batch is not re-extracted and reanalyzed, the reasons for accepting the batch must be clearly presented in the project records and the report. (Examples of acceptable reasons for not reanalyzing might be that the matrix spike and matrix spike duplicate are acceptable, and sample surrogate recoveries are good, demonstrating that the problem was confined to the LCS.)

- If re-extraction and reanalysis of the batch is not possible due to limited sample volume or other constraints, the LCS is reported, all associated samples are flagged, and appropriate comments are made in a narrative to provide further documentation.

9.5.2. Refer to the STL QC Program document (QA-003) for further details of the corrective action.

9.5.3. If full analyte spike lists are used at client request, it will be necessary to allow a percentage of the components to be outside control limits as this would be expected statistically. These requirements should be negotiated with the client. Refer to Section 17.5 for Ohio VAP specific analytes.

9.6. Matrix Spikes

9.6.1. For each QC batch, analyze a matrix spike and matrix spike duplicate. Spiking compounds and levels are given in Table 9. Compare the percent recovery and relative percent difference (RPD) to that in the laboratory specific historically generated limits. See Section 17.5 for Ohio VAP specific analytes.

- If any individual recovery or RPD falls outside the acceptable range, corrective action must occur. The initial corrective action will be to check the recovery of that analyte in the Laboratory Control Sample (LCS). Generally, if the recovery of the analyte in the LCS is within limits, then the laboratory operation is in control and analysis may proceed. The reasons for accepting the batch must be documented.

- If the recovery for any component is outside QC limits for both the matrix spike/ spike duplicate and the LCS, the laboratory is out of control and corrective action must be taken. Corrective action will normally include reanalysis of the batch.

- If a MS/MSD is not possible due to limited sample, then a LCS duplicate should be analyzed. RPD of the LCS and LCSD are compared to the matrix spike limits.

- The matrix spike/duplicate must be analyzed at the same dilution as the unspiked sample, even if the matrix spike compounds will be diluted out.

9.7. Nonconformance and Corrective Action

9.7.1. Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the facility QA Manager.

9.8. Quality Assurance Summaries

Certain clients may require specific project or program QC which may supersede these method requirements. Quality Assurance Summaries should be developed to address these requirements.

9.9. STL QC Program

Further details of QC and corrective action guidelines are presented in the STL QC Program document (QA-003). Refer to this document if in doubt regarding corrective actions.

# 10. CALIBRATION AND STANDARDIZATION

## 10.1. Summary

10.1.1. Prior to the analysis of samples and blanks, each GC/MS system must be tuned and calibrated. Hardware tuning is checked through the analysis of the 4-Bromofluorobenzene (BFB) to establish that a given GC/MS system meets the standard mass spectral abundance criteria. The GC/MS system must be calibrated initially at a minimum of five concentrations (analyzed under the same BFB tune), to determine the linearity of the response utilizing target calibration standards. Once the system has been calibrated, the calibration must be verified each twelve hour time period for each GC/MS system.

10.2.1. General

| | |
|---|---|
| Electron Energy: | 70 volts (nominal) |
| Mass Range: | 35–300 AMU |
| Scan Time: | to give at least 5 scans/peak, but not to exceed 2 second/scan |
| Injector Temperature: | 200–250°C |
| Source Temperature: | According to manufacturer's specifications |
| Transfer Line | Temperature: 250–300°C |
| Purge Flow: | 40 mL/minute |
| Carrier Gas | Flow: 15 mL/minute |
| Make-up Gas Flow: | 25–30 mL/minute |

10.2.2. Gas chromatograph suggested temperature program

10.2.2.1. BFB Analysis

| | |
|---|---|
| Isothermal: | 170°C |

10.2.2.2. Sample Analysis

| | |
|---|---|
| Initial Temperature: | 40°C |
| Initial Hold Time: | 4 minutes |
| Temperature Program: | 8°C/minute |
| Final Temperature: | 184°C |
| Second Temperature | Program: 40°C/minute |
| Final Temperature: | 240°C |
| Final Hold Time: | 2.6 minutes |

## 10.3. Instrument Tuning

10.3.1. Each GC/MS system must be hardware-tuned to meet the abundance criteria listed in Table 10 for a maximum of a 50 ng injection or purging of BFB. Analysis must not begin until these criteria are met. These criteria must be met for each twelve-hour time period. The twelve-hour time period begins at the moment of injection of BFB.

10.4. Initial Calibration

10.4.1. A series of five initial calibration standards is prepared and analyzed for the target compounds and each surrogate compound. Six standards must be used for a quadratic least squares calibration. Suggested calibration levels for a 5 mL purge are: 5, 20, 50, 100, and 200 µg/L. Certain analytes are prepared at higher concentrations due to poor purge performance. Suggested calibration levels for a 25 mL purge are 1, 5, 10, 20, and 40 µg/L. Again, some analytes are prepared at higher levels. Tables 2 and 4 list the calibration levels for each analyte. Other calibration levels and purge volumes may be used depending on the capabilities of the specific instrument. (For example, adequate sensitivity can be obtained on the Agilent 5973 instruments to use a 5 mL purge volume to reach the same reporting limits that once required a 25 mL purge. The calibration levels will still be the same 1, 5, 10, 20, 40µg/L.) However, the same purge volume must be used for calibration and sample analysis, and the low level standard must be at or below the reporting limit.

10.4.2. It may be necessary to analyze more than one set of calibration standards to encompass all of the analytes required for same tests. For example, the Appendix IX list requires the Primary standard (Table 5) and the Appendix IX standard (Table 6). If acceptable analytical performance can be obtained the primary and appendix IX standards may be analyzed together.

10.4.3. Internal standard calibration is used. The internal standards are listed in Table 7. Target compounds should reference the nearest internal standard. Each calibration standard is analyzed and the response factor (RF) for each compound is calculated using the area response of the characteristic ions against the concentration for each compound and internal standard. See equation 1, Section 12, for calculation of response factor.

10.4.4. The % RSD of the calibration check compounds (CCC) must be less than 30%. Refer to Table 12 for the CCCs.

10.4.4.1. If none of the CCCs are required analytes, project specific calibration specifications must be agreed with the client.

10.4.5. The average RF must be calculated for each compound. A system performance check is made prior to using the calibration curve. The five system performance check compounds (SPCC) are checked for a minimum average response factor. Refer to Table 11 for the SPCC compounds and required minimum response factors.

10.4.6. If the average of all the %RSDs in the calibration is ≤ 15%, then all analytes may use average response factor for calibration.

10.4.6.1. If the software in use is capable of routinely reporting curve coefficients for data validation purposes, and the necessary calibration reports can be generated, then the analyst should evaluate analytes with %RSD > 15% for calibration on a curve. If it appears that substantially better accuracy would be obtained using quantitation from a curve then the appropriate curve should be used for quantitation. If Relative Standard Error (RSE) is used to evaluate the curve it must be better than 15%. Otherwise the correlation coefficient (coefficient of determination for non-linear curves) must be ≥ 0.990.

10.4.6.2. If the average of all the %RSDs in the calibration is > 15% then calibration on a curve must be used for all analytes with %RSD > 15%. Linear or quadratic curve fits may be used. The analyst should consider instrument maintenance to improve the linearity of response. If Relative Standard Error (RSE) is used to evaluate the curve it must be better than 15%. If the % RSD is > 15%, the analyst may drop the low or high in the ICAL , as long as a minimum of 5 points are maintained and the quantitation range is adjusted accordingly. Otherwise the correlation coefficient, (coefficient of determination, $r^2$ for non-linear curves) must be ≥ 0.990. If the correlation coefficient is < 0.990, then any hit for these compounds must be flagged as estimated.

10.4.6.3. Refer to Section 17.5 for specific Ohio VAP criteria.

10.4.7. Weighting of data points

In a linear or quadratic calibration fit, the points at the lower end of the calibration curve have less weight in determining the curve generated than points at the high concentration end of the curve. However, in environmental analysis, accuracy at the low end of the curve is very important. For this reason it is preferable to increase the weighting of the lower concentration points. $1/\text{Concentration}^2$ weighting (often called $1/X^2$ weighting) will improve accuracy at the low end of the curve and should be used if the data system has this capability.

10.4.8. If time remains in the 12-hour period initiated by the BFB injection before the initial calibration, samples may be analyzed. Otherwise, proceed to continuing calibration.

10.4.9. The calibration standards for the initial 5-point calibration for low level soils that are not preserved in sodium bisulfate (i.e. are preserved by freezing, or not preserved) must be heated to 40°C for purging. Using this calibration curve for water samples is acceptable as long as all calibration, QC, and samples are also heated to 40°C. A separate five point calibration must be prepared for analysis of low level soils that are preserved with sodium bisulfate. Low level soils analysis requires the use of a closed vial autosampler

such as the Varian Archon, O.I. 4552 or Tekmar Precept. Each standard for analysis of sodium bisulfate preserved samples is prepared by spiking the methanolic standard solution through the septum of a VOA vial containing 5 mL of water and 1 g sodium bisulfate. The standards are heated to 40°C for purging. All low-level soil samples, standards, and blanks must also be heated to 40°C for purging. Medium soil extracts should be analyzed using the water (unheated or optionally heated) calibration curve as long as all calibration standards, samples, and QC samples are purged at the same temperature.

10.4.10. Non-standard analytes are sometimes requested. For these analytes, it is acceptable to analyze a single standard at the reporting limit with each continuing calibration rather than a five point initial calibration. If the analyte is detected in any of the samples, a five point initial calibration must be generated and the sample(s) reanalyzed for quantitation. However, if the analyte is not detected, the non-detect may be reported and no further action is necessary.

**Note:** This procedure is may not be used for Ohio VAP samples.

10.5. Continuing Calibration: The initial calibration must be verified every twelve hours.

10.5.1. Continuing calibration begins with analysis of BFB as described in Section 10.3. If the system tune is acceptable, the continuing calibration standard(s) are analyzed. The level 3 calibration standard is used as the continuing calibration.

10.5.2. The RF data from the standards are compared with the average RF from the initial five-point calibration to determine the percent drift of the CCC compounds. The calculation is given in equation 4, Section 12.3.4.

10.5.3. The % drift of the CCCs must be $\leq$ 20% for the continuing calibration to be valid. The SPCCs are also monitored. The SPCCs must meet the criteria described in Table 11. In addition, the % drift of all analytes must be $\leq$ 50% with allowance for up to six target analytes to have % drift > 50%.

10.5.3.1. If none of the CCCs are required analytes, project specific calibration specifications must be agreed with the client.

10.5.3.2. Cyclohexanone, one of the components of the Appendix IX standard, is unstable in the calibration solution, forming 1,1-dimethoxycyclohexane. No calibration criteria are applied to cyclohexanone and quantitation is tentative. Cyclohexanone is included on the Universal Treatment Standard and FO-39 regulatory lists (but not on Appendix IX).

10.5.3.3. Refer to Table 12 for specific Ohio VAP analytes.

10.5.4. If the CCCs and or the SPCCs do not meet the criteria in Sections 10.5.3 and 10.5.4, the system must be evaluated and corrective action must be taken. The BFB tune and continuing calibration must be acceptable before analysis begins. Extensive corrective action such as a different type of column will require a new initial calibration.

10.5.5. Once the above criteria have been met, sample analysis may begin. **Initial calibration average RFs (or the calibration curve) will be used for sample quantitation, not the continuing calibration RFs.** Analysis may proceed until 12 hours from the injection of the BFB have passed. (A sample *desorbed* less than or equal to 12 hours after the BFB is acceptable.)

## 11. PROCEDURE

### 11.1. Procedural Variations

11.1.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation shall be completely documented using a Nonconformance Memo and approved by a Supervisor or group leader and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.1.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

### 11.2. Preliminary Evaluation

11.2.1. Where possible, samples are screened by headspace or GC/MS off-tune analysis to determine the correct aliquot for analysis. Alternatively, an appropriate aliquot can be determined from sample histories.

11.2.2. Dilutions should be done just prior to the GC/MS analysis of the sample. Dilutions are made in volumetric flasks or in a Luerlok syringe. Calculate the volume of reagent water required for the dilution. Fill the syringe with reagent water, compress the water to vent any residual air and adjust the water volume to the desired amount. Adjust the plunger to the mark and inject the proper aliquot of sample into the syringe. If the dilution required would use less than 1 µL of sample then serial dilutions must be made in volumetric flasks.

11.2.2.1. The diluted concentration is to be estimated to be in the upper half of the calibration range.

11.3. Sample Analysis Procedure

11.3.1. All analysis conditions for samples must be the same as for the continuing calibration standards (including purge time and flow, desorb time and temperature, column temperatures, multiplier setting etc.).

11.3.2. All samples must be analyzed as part of a batch. The batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same time period. The batch also must contain a MS/MSD, a LCS, and a method blank.

11.3.2.1. If there is insufficient time in the 12-hour tune period to analyze 20 samples, the batch may be continued into the next tune period. However, if any re-tuning of the instrument is necessary, or if a period of greater than 24 hours from the preceding BFB tune has passed, a new batch must be started. For medium level soils the batch is defined at the sample preparation stage.

11.3.2.2. Laboratory generated QC samples (Blank, LCS, MS/MSD) do not count towards the maximum 20 samples in a batch. Field QC samples are included in the batch count.

11.3.2.3. It is not necessary to reanalyze batch QC with reanalyses of samples. However, any reruns must be as part of a valid batch.

11.4. Water Samples

11.4.1. All samples and standard solutions must be at ambient temperature before analysis.

11.4.2. Fill a syringe with the sample. If a dilution is necessary it may be made in the syringe if the sample aliquot is $\geq$ 5 µL. Check and document the pH of the remaining sample.

11.4.3. Add 250 ng of each internal and surrogate standard (10 µL of a 25 µg/mL solution, refer to Tables 7, 8 and 16). The internal standards and the surrogate standards may be mixed and added as one spiking solution (this results in a 50 µg/L solution for a 5 mL sample, and a 10 µg/L solution for a 25 mL sample). Inject the sample into the purging chamber.

11.4.3.1. For TCLP samples use 0.5 mL of TCLP leachate with 4.5 mL reagent water and spike with 10 µL of the 25 µg/mL TCLP spiking solution. (Note that TCLP reporting limits will be 10 times higher than the corresponding aqueous limits).

11.4.4. Purge the sample for eleven minutes (the trap must be below 35°C).

11.4.5. After purging is complete, desorb the sample, start the GC temperature program, and begin data acquisition. After desorption, bake the trap for approximately 3-10 minutes

to condition it for the next analysis. When the trap is cool, it is ready for the next sample.

11.4.6. Desorb and bake time and temperature are optimized for the type of trap in use. The same conditions must be used for samples and standards.

11.5. Methanol Extract Soils

11.5.1. Rinse a gas-tight syringe with organic free water. Fill the syringe with the same volume of organic free water as used in the calibrations. Add no more than 2% (v/v) (100 µL for a 5 mL purge) methanolic extract (from Section 8.5 or 8.6) to the syringe. Add internal standard (if used). Load the sample onto the purge and trap device and analyze as for aqueous samples. If less than 5µL of methanolic extract is to be added to the water, dilute the methanolic extract such that a volume greater than 5µL will be added to the water in the syringe. Refer to Section 17.8 for Michigan project requirements.

11.6. Liquid wastes that are soluble in methanol and insoluble in water.

11.6.1. Pipet 2 mL of the sample into a tared vial. Use a top-loading balance. Record the weight to the nearest 0.1 gram.

11.6.2. Quickly add 7 mL of methanol, then add 1 mL of surrogate spiking solution to bring the final volume to 10 mL. Cap the vial and shake for 2 minutes to mix thoroughly. For a MS/MSD or LCS, 6 mL of methanol, 1 mL of surrogate solution, and 1 mL of matrix spike solution is used.

11.6.3. Rinse a gas-tight syringe with organic free water. Fill the syringe with the same volume of organic free water as used in the calibrations. Add no more than 2% (v/v) (100 µL for a 5 mL purge) methanolic extract (from Section 8.5 or 8.6) to the syringe. Add internal standard (if used). Load the sample onto the purge and trap device and analyze as for aqueous samples. If less than 5µL of methanolic extract is to be added to the water, dilute the methanolic extract such that a volume greater than 5µL will be added to the water in the syringe.

11.7. Aqueous and Low level Soil Sample Analysis (Purge and Trap units that sample directly from the VOA vial)

11.7.1. Units which sample from the VOA vial should be equipped with a module which automatically adds surrogate and internal standard solution to the sample prior to purging the sample.

11.7.2. If the autosampler uses automatic IS/SS injection, no further preparation of the VOA vial is needed. Otherwise the internal and surrogate standards must be added to the vial. *Note:* Aqueous samples with high amounts of sediment present in the vial may not be suitable for analysis on this instrumentation, or they may need to analyzed as soils.

11.7.3. Soil samples must be quantitated against a curve prepared with standards containing about the same amount of sodium bisulfate as the samples (1 g in 5 mL).

11.7.4. Sample remaining in the vial after sampling with one of these mechanisms is no longer valid for further analysis. A fresh VOA vial must be used for further sample analysis.

11.7.5. For aqueous samples, check the pH of the sample remaining in the VOA vial after analysis is completed.

*11.8. Low-Level Solids Analysis using discrete autosamplers, Method 8260A, 5030A.*

**Note: This technique may seriously underestimate analyte concentration and must not be used except at specific client request for the purpose of comparability with previous data. It is no longer part of SW-846.**

*This method is based on purging a heated soil/sediment sample mixed with reagent water containing the surrogates and internal standards. Analyze all reagent blanks and standards under the same conditions as the samples (e.g., heated). The calibration curve is also heated during analysis. Purge temperature is 40°C.*

*11.8.1. Do not discard any supernatant liquids. Mix the contents of the container with a narrow metal spatula.*

*11.8.2. Weigh out 5 g (or other appropriate aliquot) of sample into a disposable culture tube or other purge vessel. Record the weight to the nearest 0.1 g. If method sensitivity is demonstrated, a smaller aliquot may be used. Do not use aliquots less than 1.0 g. If the sample is contaminated with analytes such that a purge amount less than 1.0 g is appropriate, use the medium level method. For the medium level method, add 4g soil to 10 mL methanol containing the surrogates, mix for two minutes, allow to settle then remove a portion of the methanol and store in a clean Teflon capped vial at 4°C until analysis. Analyze as described in section 11.5.*

*11.8.3. Connect the purge vessel to the purge and trap device.*

*11.8.4. Rinse a 5 mL gas-tight syringe with organic free water, and fill. Compress to 5 mL. Add surrogate/internal standard (and matrix spike solutions if required.). Add directly to the sample from 11.5.2.*

*11.8.5. The above steps should be performed rapidly and without interruption to avoid loss of volatile organics.*

*11.8.6. Add the heater jacket or other heating device and start the purge and trap unit.*

*11.8.7. Soil samples that have low IS recovery when analyzed (<50%) should be reanalyzed once to confirm matrix effect.*

11.9. Medium-Level Soil/Sediment and Waste Samples

11.9.5. Sediments/soils and waste that are insoluble in methanol.

11.9.5.1. Sediments/soils and waste that are insoluble in methanol.

11.9.5.1.1. Gently mix the contents of the sample container with a narrow metal or wood spatula. Weigh 4 g (wet weight) into a tared vial. Use a top-loading balance. Record the weight to 0.1 gram. Do not discard any supernatant liquids.

11.9.5.1.2. Quickly add 9 mL of methanol, and 1 mL of surrogate spiking solution to bring the final volume of methanol to 10 mL. For an LCS or MS/MSD sample add 8 mL of methanol, 1 mL of surrogate spike solution, and 1 mL of matrix spike solution. Cap the vial and vortex to mix thoroughly.

NOTE: Sections 11.9.5.1.1 and 11.9.5.1.2 must be performed rapidly and without interruption to avoid the loss of volatile organics.

11.10. Initial review and corrective actions

11.10.1. If the retention time for any internal standard in the continuing calibration changes by more than 0.5 minutes from the mid-level initial calibration standard, the chromatographic system must be inspected for malfunctions and corrected. Reanalysis of samples analyzed while the system was malfunctioning is required.

11.10.2. If the internal standard response in the continuing calibration is more than 200% or less than 50% of the response in the mid-level of the initial calibration standard, the chromatographic system must be inspected for malfunctions and corrected. Reanalysis of samples analyzed while the system was malfunctioning is required.

11.10.2.1. Any samples that do not meet the internal standard criteria for the continuing calibration must be evaluated for validity. If the change in sensitivity is a matrix effect confined to an individual sample reanalysis is not necessary. If the change

in sensitivity is due to instrumental problems all affected samples must be reanalyzed after the problem is corrected.

11.10.3. The surrogate standard recoveries are evaluated to ensure that they are within limits. Corrective action for surrogates out of control will normally be to reanalyze the affected samples. However, if the surrogate standard response is out high and there are no target analytes or tentatively identified compounds, reanalysis may not be necessary. Out of control surrogate standard response may be a matrix effect. It is only necessary to reanalyze a sample once to demonstrate matrix effect, but reanalysis at a dilution should be considered.

11.11. Dilutions

If the response for any compound exceeds the working range of the GC/MS system, a dilution of the extract is prepared and analyzed. An appropriate dilution should be in the upper half of the calibration range. Samples may be screened to determine the appropriate dilution for the initial run. If the initial diluted run has no hits or hits below 20% of the calibration range and the matrix allows for analysis at a lesser dilution, then the sample must be reanalyzed at a dilution targeted to bring the largest hit above 50% of the calibration range.

11.10.1. Guidance for Dilutions Due to Matrix

If the sample is initially run at a dilution and the baseline rise is less than half the height of the internal standards, or if individual non target peaks are less than twice the height of the internal standards, then the sample should be reanalyzed at a more concentrated dilution. This requirement is approximate and subject to analyst judgement.

11.10.2. Reporting Dilutions

The most concentrated dilution with no target compounds above the calibration range will be reported. Other dilutions will only be reported at client request.

## 12. DATA ANALYSIS AND CALCULATIONS

12.1. Qualitative identification

An analyte is identified by retention time and by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for standard reference may be obtained on the user's GC/MS by analysis of the calibration standards or from the NIST Library. Two criteria must be satisfied to verify identification: (1) elution of sample component at the same GC retention time as the standard component; and (2) correspondence of the sample

component and the standard component characteristic ions. (Note: Care must be taken to ensure that spectral distortion due to co-elution is evaluated.)

- The sample component retention time must compare to within ± 0.2 min. of the retention time of the standard component. For reference, the standard must be run within the same twelve hours as the sample.

- All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) should be present in the sample spectrum.

- The relative intensities of ions should agree to within ±30% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 20 and 80 percent.)

12.1.1. If a compound cannot be verified by all the above criteria, but in the technical judgment of the analyst, the identification is correct, then the analyst shall report that identification and proceed with quantitation.

12.2. Tentatively Identified Compounds (TICs)

12.2.1. If the client requests components not associated with the calibration standards, a search of the NIST library may be made for the purpose of tentative identification. Guidelines are:

12.2.1.1. Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.

12.2.1.2. The relative intensities of the major ions should agree to within 20%. (Example: If an ion shows an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30% and 70%).

12.2.1.3. Molecular ions present in the reference spectrum should be present in the sample spectrum.

12.2.1.4. Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

12.2.1.5. Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the spectrum because of background contamination or coeluting peaks. (Data system reduction programs can sometimes create these discrepancies.)

12.2.1.6. Computer-generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual inspection of the sample with the nearest library searches should the analyst assign a tentative identification.

12.3. Calculations.

12.3.1. Response factor (RF):

***Equation 1***

$$RF = \frac{A_x C_{is}}{A_{is} C_x}$$

Where:

$A_x$ = Area of the characteristic ion for the compound to be measured

$A_{is}$ = Area of the characteristic ion for the specific internal standard

$C_{is}$ = Concentration of the specific internal standard, ng

$C_x$ = Concentration of the compound being measured, ng

12.3.2. Standard deviation (SD):

***Equation 2***

$$SD = \sqrt{\sum_{i=1}^{N} \frac{(Xi - X)^2}{N-1}}$$

$X_i$ = Value of X at i through N

$N$ = Number of points

$X$ = Average value of $X_i$

12.3.3. Percent relative standard deviation (%RSD):

***Equation 3***

$$\%RSD = \frac{\text{Standard Deviation}}{\overline{RFi}} \times 100$$

$\overline{RFi}$ = **Mean of RF values in the curve**

12.3.4. Percent drift between the initial calibration and the continuing calibration:

***Equation 4***

$$\% \text{ Drift} = \frac{C_{expected} - C_{found}}{C_{expected}} \times 100$$

Where

$C_{expected}$ = Known concentration in standard

$C_{found}$ = Measured concentration using selected quantitation method

12.3.5. Target compound and surrogate concentrations:

Concentrations in the sample may be determined from linear or second order (quadratic) curve fitted to the initial calibration points, or from the average response factor of the initial calibration points. Average response factor may only be used when the % RSD of the response factors in the initial calibration is $\leq$ 15%.

12.3.5.1. Calculation of concentration using Average Response Factors

***Equation 5***

$$\text{Concentration } \mu g / L = \frac{x}{RF}$$

12.3.5.2. Calculation of concentration using Linear fit

***Equation 6***

$$\text{Concentration } \mu g / L = A + Bx$$

12.3.5.3. Calculation of concentration using Quadratic fit

***Equation 7***

$$\text{Concentration } \mu g / L = A + Bx + Cx^2$$

$x$ is defined in equations 8, 9 and 10

$A$ is a constant defined by the intercept

$B$ is the slope of the curve

$C$ is the curvature

12.3.5.4. Calculation of $x$ for Water and water-miscible waste:

***Equation 8***

$$x = \frac{(A_x)(I_s)(D_f)}{(A_{is})(V_o)}$$

Where:

$A_x$ = Area of characteristic ion for the compound being measured (secondary ion quantitation is allowed only when there are sample interferences with the primary ion)

$A_{is}$ = Area of the characteristic ion for the internal standard

$I_s$ = Amount of internal standard added in ng

$$\text{Dilution Factor} = D_f = \frac{\text{Total volume purged (mL)}}{\text{Volume of original sample used (mL)}}$$

$V_o$ = Volume of water purged, mL

12.3.5.5. Calculation of $x$ for Medium level soils:

***Equation 9***

$$x = \frac{(A_x)(I_s)(V_t)(1000)(D_f)}{(A_{is})(V_a)(W_s)(D)}$$

Where:

$A_x$, $I_s$, $D_f$, $A_{is}$, same as for water.

$V_t$ = Volume of total extract, mL (Typically 25 mL)

$V_a$ = Volume of extract added for purging, µL

$W_s$ = Weight of sample extracted, g

$$D = \frac{100 - \%\text{moisture}}{100}$$

12.3.5.6. Calculation of $x$ for Low level soils:

***Equation 10***

$$x = \frac{(A_x)(I_s)}{(A_{is})(W_s)(D)}$$

Where:

$A_x$, $I_s$, $A_{is}$, same as for water.

D is as for medium level soils

$W_s$ = Weight of sample added to the purge vessel, g

12.3.5.7. Calculation of TICs: The calculation of TICs (tentatively identified compounds) is identical to the above calculations with the following exceptions:

$A_x$ = Area in the total ion chromatogram for the compound being measured

$A_{is}$ = Area of the total ion chromatogram for the nearest internal standard without interference

RF = 1

In other words, the concentration is equal to $x$ as defined in equations 8, 9 and 10.

12.3.6. MS/MSD Recovery

***Equation 11***

$$\text{Matrix Spike Recovery, \%} = \frac{SSR - SR}{SA} \times 100$$

$SSR$ = Spike sample result

$SR$ = Sample result

$SA$ = Spike added

12.3.7. Relative % Difference calculation for the MS/MSD

***Equation 12***

$$\mathbf{RPD} = \frac{|\mathbf{MSR} - \mathbf{MSDR}|}{\frac{1}{2}(\mathbf{MSR} + \mathbf{MSDR})} \times 100$$

Where:

**RPD** = Relative percent difference

**MSR** = Matrix spike result

**MSDR** = Matrix spike duplicate result

## 13. METHOD PERFORMANCE

13.1. Method Detection Limit

13.2. Generally, each laboratory must generate a valid method detection limit for each analyte of interest. The MDL must be below the reporting limit for each analyte. The procedure for determination of the method detection limit is given in 40 CFR Part 136, Appendix B, and further defined in QA Policy #: QA-005. When non-standard compounds are analyzed at client request, lesser requirements are possible with client agreement. At a minimum, a standard at the reporting limit must be analyzed to demonstrate the capability of the method.

13.3. Initial Demonstration

13.4. Each laboratory must make a one time initial demonstration of capability for each individual method. Demonstration of capability for both soil and water matrices is required. This requires analysis of QC check samples containing all of the standard analytes for the method. For some tests it may be necessary to use more than one QC check mix to cover all analytes of interest. The QC check sample is made up at 20 µg/L. (Some compounds will be at higher levels, refer to the calibration standard levels for guidance.)

13.4.1. Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation.

13.4.2. Calculate the average recovery and standard deviation of the recovery for each analyte of interest. The %RSD should be $\leq$ 15% for each analyte, and the % recovery should be within 80-120%.

13.4.3. If any analyte does not meet the acceptance criteria, check the acceptance limits in the reference methods (Table 6 of method 8240B, paragraph 8.3.5 of method 8260A). If the recovery or precision is outside the limits in the reference methods, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

13.4.4. Training Qualification

13.4.4.1. The group/team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience.

## 14. POLLUTION PREVENTION

14.1. This method does not contain any specific modifications that serve to minimize or prevent pollution.

## 15. WASTE MANAGEMENT

15.1. Waste generated in the procedure must be segregated and disposed according to the facility hazardous waste procedures. The Health and Safety Director should be contacted if additional information is required.

## 16. REFERENCES

16.1. SW846, *Test Methods for Evaluating Solid Waste,* Third Edition, Gas Chromatography/Mass Spectrometry for Volatile Organics, Method 8260B, Update III, December 1996

16.2. SW846, *Test Methods for Evaluating Solid Waste,* Third Edition, Gas Chromatography/Mass Spectrometry for Volatile Organics, Method 8260A, Update II, September 1994.

## 17. MISCELLANEOUS

17.1. Modifications from the reference method

17.1.1. Ion 119 is used as the quantitation ion for chlorobenzene-d5 for 25 mL purge tests.

17.1.2. A retention time window of 0.2 minutes is used for all components, since some data systems do not have the capability of using the relative retention time units specified in the reference method.

17.1.3. The quantitation and qualifier ions for some compounds have been changed from those recommended in SW-846 in order to improve the reliability of qualitative identification.

17.1.4. Method 8260A recommends that the purge vessel is run through an additional purge cycle after 25 mL sample analysis to remove carryover. Instead, purge vessels are oven baked between analyses or disposable vessels are used one time only.

17.1.5. SW-846 recommends that a curve be used for any analytes with %RSD of the response factors > 15%. However, some industry standard data systems and forms generation software cannot report this data with the necessary information for data validation. In addition most software available does not allow weighting of the curve.

Unweighted curves may exhibit serious errors in quantitation at the low end, resulting in possible false positives or false negatives. Therefore, this SOP allows used of average response factors if the average %RSD for all compounds is ≤ 15%.

17.2. Modifications from previous revision

This SOP has been substantially revised to reflect the changes included in Update III to SW-846. Directions for method 524.2 and method 624 have also been added.

17.3. Facility specific SOPs

Each facility shall attach a list of facility-specific SOPs or approved attachments (if applicable) which are required to implement this SOP or which are used in conjunction with this SOP. If no facility specific SOPs or amendments are to be attached, a statement must be attached specifying that there are none.

17.4. Flow diagrams

17.4.1. Initial Demonstration and MDL

17.5. The following are protocols that must be followed when analyzing OhioVAP samples:

- Sections 9.5 and 9.6: n-Hexane must be spiked and reported for both the LCS and MS/MSD.
- Sections 10.4.6: All analytes must have a %RSDs ≤ 15%. Corrective action must be completed for any compounds failing the <15% requirement.
- Section 11.1 and 17.1.5 (Method deviations) are not to be performed.
- Section 11.9.2: For OhioVAP projects, the laboratory will reanalyze any sample where the internal standard fails and there is no evidence of matrix interference.

17.6. The following are protocols that must be followed when analyzing BP Oil – Lima Refinery RFI work plan.

- Section 8.1 STL will continue to follow the 14 day holding time specified in the Corporate SOP.
- Delete for this project Section 8.3 At specific client request, unpreserved soil samples may be accepted.
- Delete for this project Section 8.8.1 At specific client request unpreserved soils packed into glass jars or brass tubes may be accepted and subsampled in the lab. This is the old

procedure based on method 5030A. It is no longer included and is likely to generate results that are biased low, possibly by more than an order of magnitude.

- Modify Section 8.5.8 For the purpose of this project, the soil/methanol mixture may be stored for two days prior to analysis.

- Modify Section 8.6.12 For the purpose of this project, the soil/methanol mixture may be stored for two days prior to analysis.

- Modify (per discussion with Region V representative) to Section 10.4.6.2 Compounds with %RSD >15% are to be calibrated using an alternate calibration technique (e.g. linear or quadratic calibration curve). For poor responders, the alternate calibration technique requirements may not be met either. This sentence is added for those cases.If the correlation coefficient is < 0.990, then any hit for these compounds must be flagged as estimated.

- Modify Section 10.4.2 It is necessary to analyze the Appendix IX standard separately from the primary standard due to the presence of xylene solvent in the Appendix IX standard. Alternatively, STL will purchase the Appendix IX standard in a solvent other than xylene.

- Modify Section 10.4.9 For this project, this section will be modified to comply with the requirement of adding methanol to the calibration standards so that those standards contain the same amount of methanol as the diluted soil extracts.

- Modify Table 6

- For the project specific SOP, acetonitrile will be removed from table 6, page 49 and appended onto table 5, page 48. Acetonitrile will be calibrated as part of the STL primary standard, using a separate acetonitrile standard. This will ensure that the calibration curve for acetonitrile will be done free from any interference from allyl chloride.

17.7. The following are protocols that must be followed when analyzing South Carolina Projects only.

- **Delete** from Section 10.4.7 In a linear *or quadratic* calibration fit, the points at the lower end of the calibration curve have less weight in determining the curve generated than points at the high concentration end of the curve.

- **Delete** from Section 12.3.5 Concentrations in the sample may be determined from linear *or second order (quadratic)* curve fitted to the initial calibration points, or from the average response factor of the initial calibration points.

- **Delete** from Section 12.3.5.1

- Calculation of concentration using Quadratic fit

***Equation 13***

**Concentration** $\mu g / L = A + Bx + Cx^2$

$x$ is defined in equations 8, 9 and 10

$A$ is a constant defined by the intercept

$B$ is the slope of the curve

$C$ is the curvature

- **Change** Section 9.3 The compounds included in the surrogate spiking solutions are listed in Tables 8 *and 9.*

17.8. The following are protocols that must be followed to achieve the lower reporting limits required when analyzing Michigan projects.

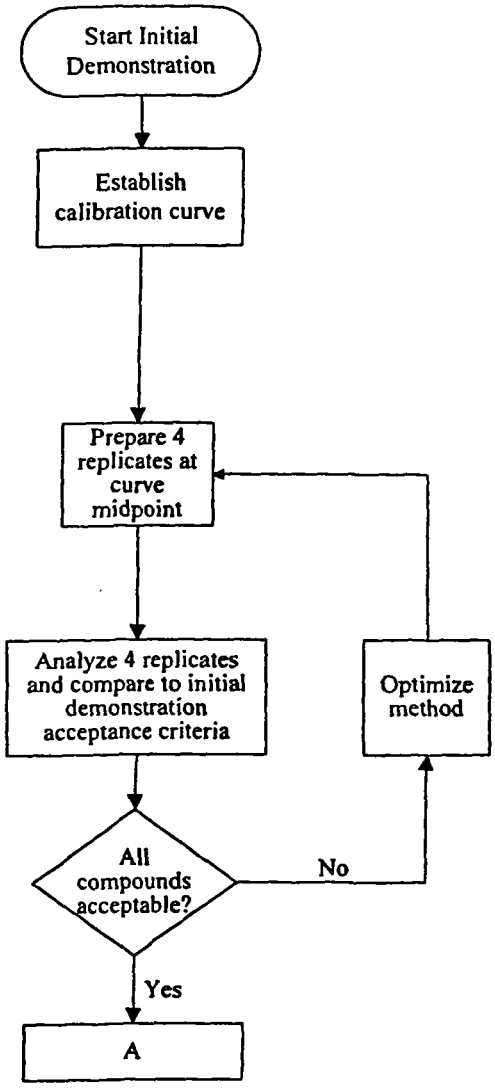
17.8.1. Modify Section 8.5.4 and 8.6.8 (add 5 uL of 2500 ug/mL surrogate solution for a nominal 25 g sample).

17.8.2. Modify Section 8.5.5 and 8.6.9 (add 100 uL of 50 ug/mL spike solution for a nominal 25 g sample).

17.8.3. Modify Section 8.5.6 and 8.6.10 (add 100 uL of 50 ug/mL spike solution for a nominal 25g sample).

17.8.4. Michigan reporting limits for methanol preserved soils are achieved by injecting 100 uL of the methanol extract in a 5 mL purge. The instrument is calibrated using the recommended calibration levels in water of 1 ug/L, 2 ug/L (if a quadratic calibration is to be used), 5 ug/L, 10 ug/L, 20 ug/L and 40 ug/L. Some analytes are prepared at higher concentrations.

17.8.5. Samples for Michigan projects frequently require calibration for 2-Methylnaphthalene. Recommended calibration levels for this compounds are 2 ug/L, 10 ug/L, 20 ug/L, 40 ug/L and 80 ug/L.


Start Initial Demonstration
Establish calibration curve
Prepare 4 replicates at curve midpoint
Analyze 4 replicates and compare to initial demonstration acceptance criteria
Optimize method
All compounds acceptable?
No
Yes
A

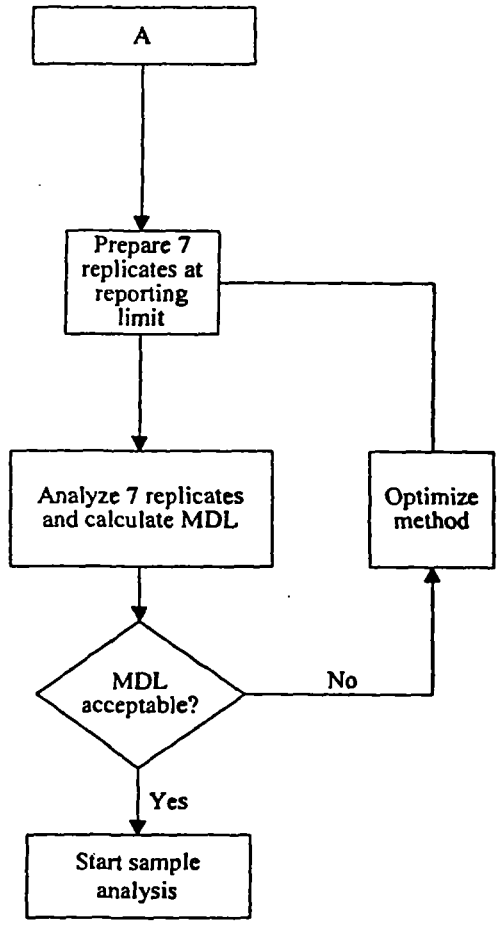

A
Prepare 7 replicates at reporting limit
Analyze 7 replicates and calculate MDL
Optimize method
MDL acceptable?
No
Yes
Start sample analysis

**Table 1**

**STL Primary Standard and Reporting Limits**

| Compound | CAS Number | Reporting Limits[1] | | | | |
|---|---|---|---|---|---|---|
| | | 5 mL Water µg/L | 25 mL[3] water µg/L | Low soil µg/kg | 8260B/ 5035 Soil ug/kg | 8260A 5030A Med Level Soil µg/kg |
| Dichlorodifluoromethane | 75-71-8 | 10 | 2 | 10 | 250 | 1200 |
| Chloromethane | 74-87-3 | 10 | 2 | 10 | 250 | 1200 |
| Bromomethane | 74-83-9 | 10 | 2 | 10 | 250 | 1200 |
| Vinyl chloride | 75-01-4 | 10 | 2 | 10 | 250 | 1200 |
| Chloroethane | 75-00-3 | 10 | 2 | 10 | 250 | 1200 |
| Trichlorofluoromethane | 75-69-4 | 10 | 2 | 10 | 250 | 1200 |
| Acrolein | 107-02-8 | 100 | 20 | 100 | 5000 | 12000 |
| Acetone | 67-64-1 | 20 | 10 | 20 | 1000 | 2500 |
| Trichlorotrifluoroethane | 76-13-1 | 5 | 1 | 5 | 250 | 620 |
| Iodomethane | 74-88-4 | 5 | 1 | 5 | 250 | 620 |
| Carbon disulfide | 75-15-0 | 5 | 1 | 5 | 250 | 620 |
| Methylene chloride | 75-09-2 | 5 | 1 | 5 | 250 | 620 |
| tert-Butyl alcohol | 75-65-0 | 200 | 50 | 200 | 10,000 | 25000 |
| 1,1-Dichloroethene | 75-35-4 | 5 | 1 | 5 | 250 | 620 |
| 1,1-Dichloroethane | 75-34-3 | 5 | 1 | 5 | 250 | 620 |
| trans-1,2-Dichloroethene | 156-60-5 | 5.0 | 1.0 | 5.0 | 250 | 310 |
| Acrylonitrile | 107-13-1 | 100 | 20 | 100 | 5000 | 12000 |
| Methyl *tert*-butyl ether (MTBE) | 1634-04-4 | 20 | 5 | 20 | 1000 | 2500 |
| Hexane | 110-54-3 | 5 | 1 | 5 | 250 | 620 |
| cis-1,2-Dichloroethene | 156-59-2 | 5.0 | 1.0 | 5.0 | 250 | 310 |
| 1,2-Dichloroethene (Total) | 540-59-0 | 5 | 1 | 5 | 250 | 620 |
| Tetrahydrofuran | 109-99-9 | 20 | 5 | 20 | 1000 | 2500 |
| Chloroform | 67-66-3 | 5 | 1 | 5 | 250 | 620 |
| 1,2-Dichloroethane | 107-06-2 | 5 | 1 | 5 | 250 | 620 |
| Dibromomethane | 74-95-3 | 5 | 1 | 5 | 250 | 620 |
| 2-Butanone | 78-93-3 | 20 | 5 | 20 | 1000 | 2500 |
| 1,4-Dioxane | 123-91-1 | 500 | 200 | 500 | 25000 | 62000 |
| 1,1,1-Trichloroethane | 71-55-6 | 5 | 1 | 5 | 250 | 620 |
| Carbon tetrachloride | 56-23-5 | 5 | 1 | 5 | 250 | 620 |
| Bromodichloromethane | 75-27-4 | 5 | 1 | 5 | 250 | 620 |
| 1,2-Dichloropropane | 78-87-5 | 5 | 1 | 5 | 250 | 620 |
| cis-1,3-Dichloropropene | 10061-01-5 | 5 | 1 | 5 | 250 | 620 |

**Table 1**

**STL Primary Standard and Reporting Limits**

| Compound | CAS Number | Reporting Limits[1] | | | | |
|---|---|---|---|---|---|---|
| | | 5 mL Water µg/L | 25 mL[3] water µg/L | Low soil µg/kg | 8260B/ 5035 Soil ug/kg | 8260A 5030A Med Level Soil µg/kg |
| Trichloroethene | 79-01-6 | 5 | 1 | 5 | 250 | 620 |
| Dibromochloromethane | 124-48-1 | 5 | 1 | 5 | 250 | 620 |
| 1,2-Dibromoethane | 106-93-4 | 5 | 1 | 5 | 250 | 620 |
| 1,2,3-Trichloropropane | 96-18-4 | 5 | 1 | 5 | 250 | 620 |
| 1,1,2-Trichloroethane | 79-00-5 | 5 | 1 | 5 | 250 | 620 |
| Benzene | 71-43-2 | 5 | 1 | 5 | 250 | 620 |
| Ethylmethacrylate | 97-63-2 | 5 | 1 | 5 | 250 | 620 |
| trans-1,3-Dichloropropene | 10061-02-6 | 5 | 1 | 5 | 250 | 620 |
| Bromoform | 75-25-2 | 5 | 1 | 5 | 250 | 620 |
| 4-Methyl-2-pentanone | 108-10-1 | 20 | 5 | 20 | 1000 | 2500 |
| 2-Hexanone | 591-78-6 | 20 | 5 | 20 | 1000 | 2500 |
| Tetrachloroethene | 127-18-4 | 5 | 1 | 5 | 250 | 620 |
| Toluene | 108-88-3 | 5 | 1 | 5 | 250 | 620 |
| 1,1,2,2-Tetrachloroethane | 79-34-5 | 5 | 1 | 5 | 250 | 620 |
| 2-Chloroethyl vinyl ether | 110-75-8 | N/A[2] | N/A | 50 | 1000 | 6200 |
| Vinyl acetate | 108-05-4 | 10 | 2 | 10 | 500 | 1200 |
| Chlorobenzene | 108-90-7 | 5 | 1 | 5 | 250 | 620 |
| Ethylbenzene | 100-41-4 | 5 | 1 | 5 | 250 | 620 |
| Styrene | 100-42-5 | 5 | 1 | 5 | 250 | 620 |
| t-1,4-Dichloro-2-butene | 110-57-6 | 5 | 1 | 5 | 250 | 620 |
| m and p Xylenes | | 5.0 | 0.5 | 2.5 | 125 | 310 |
| o-xylene | 95-47-6 | 5.0 | 0.5 | 2.5 | 125 | 310 |
| Total xylenes | 1330-20-7 | 5 | 1 | 5 | 250 | 620 |
| 1,3-Dichlorobenzene | 541-73-1 | 5 | 1 | 5 | 250 | 620 |
| 1,4-Dichlorobenzene | 106-46-7 | 5 | 1 | 5 | 250 | 620 |
| 1,2-Dichlorobenzene | 95-50-1 | 5 | 1 | 5 | 250 | 620 |
| 2,2-Dichloropropane | 590-20-7 | 5 | 1 | 5 | 250 | |
| Bromochloromethane | 74-97-5 | 5 | 1 | 5 | 250 | |
| 1,1-Dichloropropene | 563-58-6 | 5 | 1 | 5 | 250 | |
| Bromodichloromethane | 75-27-4 | 5 | 1 | 5 | 250 | |
| 1,2-Dichloropropane | 78-87-5 | 5 | 1 | 5 | 250 | |
| 1,3-Dichloropropane | 142-28-9 | 5 | 1 | 5 | 250 | |

**Table 1**

**STL Primary Standard and Reporting Limits**

| Compound | CAS Number | Reporting Limits[1] | | | | |
|---|---|---|---|---|---|---|
| | | 5 mL Water µg/L | 25 mL[3] water µg/L | Low soil µg/kg | 8260B/ 5035 Soil ug/kg | 8260A 5030A Med Level Soil µg/kg |
| Isopropylbenzene | 98-82-8 | 5 | 1 | 5 | 250 | |
| Bromobenzene | 108-86-1 | 5 | 1 | 5 | 250 | |
| n-Propylbenzene | 103-65-1 | 5 | 1 | 5 | 250 | |
| 2-Chlorotoluene | 95-49-8 | 5 | 1 | 5 | 250 | |
| 4-Chlorotoluene | 106-43-4 | 5 | 1 | 5 | 250 | |
| 1,3,5-Trimethylbenzene | 108-67-8 | 5 | 1 | 5 | 250 | |
| tert-Butylbenzene | 98-06-6 | 5 | 1 | 5 | 250 | |
| 1,2,4-Trimethylbenzene | 95-63-6 | 5 | 1 | 5 | 250 | |
| sec-butylbenzene | 135-98-8 | 5 | 1 | 5 | 250 | |
| 4-Isopropyltoluene | 99-87-6 | 5 | 1 | 5 | 250 | |
| n-Butylbenzene | 104-51-8 | 5 | 1 | 5 | 250 | |
| 1,2,4-Trichlorobenzene | 120-82-1 | 5 | 1 | 5 | 250 | |
| Napthalene | 91-20-3 | 5 | 1 | 5 | 250 | |
| Hexachlorobutadiene | 87-68-3 | 5 | 1 | 5 | 250 | |
| 1,2,3-Trichlorobenzene | 87-61-6 | 5 | 1 | 5 | 250 | |
| Acetonitrile | 75-05-8 | 100 | 20 | 100 | 5000 | |

1 Reporting limits listed for soil/sediment are based on wet weight. The reporting limits calculated by the laboratory for soil/sediment calculated on dry weight basis, will be higher.

2 2-Chloroethyl vinyl ether cannot be reliably recovered from acid preserved samples

3 Optionally, 5 mL purge volume if adequate sensitivity is obtained.

**Table 2**

**STL Primary Standard Calibration Levels, 5 mL purge[1]**

| Compound | Calibration Level ug/L | | | | |
|---|---|---|---|---|---|
| | Level 1 | Level 2 | Level 3 | Level 4 | Level 5 |
| 1,2-Dichloroethane-d4 (Surrogate) | 5 | 20 | 50 | 100 | 200 |
| Toluene-d8 (Surrogate) | 5 | 20 | 50 | 100 | 200 |
| 4-Bromofluorobenzene (Surrogate) | 5 | 20 | 50 | 100 | 200 |
| Dichlorodifluoromethane | 5 | 20 | 50 | 100 | 200 |
| Chloromethane | 5 | 20 | 50 | 100 | 200 |
| Bromomethane | 5 | 20 | 50 | 100 | 200 |
| Vinyl chloride | 5 | 20 | 50 | 100 | 200 |
| Chloroethane | 5 | 20 | 50 | 100 | 200 |
| Trichlorofluoromethane | 5 | 20 | 50 | 100 | 200 |
| Acrolein | 50 | 200 | 500 | 1000 | 2000 |
| Acetone | 5 | 20 | 50 | 100 | 200 |
| Trichlorotrifluoroethane | 5 | 20 | 50 | 100 | 200 |
| Iodomethane | 5 | 20 | 50 | 100 | 200 |
| Carbon disulfide | 5 | 20 | 50 | 100 | 200 |
| Methylene chloride | 5 | 20 | 50 | 100 | 200 |
| tert-Butyl alcohol | 100 | 400 | 1,000 | 2,000 | 4,000 |
| 1,1-Dichloroethene | 5 | 20 | 50 | 100 | 200 |
| 1,1-Dichloroethane | 5 | 20 | 50 | 100 | 200 |
| trans-1,2-Dichloroethene | 5 | 20 | 50 | 100 | 200 |
| Acrylonitrile | 50 | 200 | 500 | 1,000 | 2,000 |
| Methyl *tert*-butyl ether (MTBE) | 5 | 20 | 50 | 100 | 200 |
| Hexane | 5 | 20 | 50 | 100 | 200 |
| cis-1,2-Dichloroethene | 5 | 20 | 50 | 100 | 200 |
| Tetrahydrofuran | 5 | 20 | 50 | 100 | 200 |
| Chloroform | 5 | 20 | 50 | 100 | 200 |
| 1,2-Dichloroethane | 5 | 20 | 50 | 100 | 200 |
| Dibromomethane | 5 | 20 | 50 | 100 | 200 |
| 2-Butanone | 5 | 20 | 50 | 100 | 200 |
| 1,4-Dioxane | 250 | 1000 | 2,500 | 5,000 | 10,000 |
| 1,1,1-Trichloroethane | 5 | 20 | 50 | 100 | 200 |
| Carbon tetrachloride | 5 | 20 | 50 | 100 | 200 |
| Bromodichloromethane | 5 | 20 | 50 | 100 | 200 |
| 1,2-Dichloropropane | 5 | 20 | 50 | 100 | 200 |
| cis-1,3-Dichloropropene | 5 | 20 | 50 | 100 | 200 |
| Trichloroethene | 5 | 20 | 50 | 100 | 200 |
| Dibromochloromethane | 5 | 20 | 50 | 100 | 200 |

**Table 2**

**STL Primary Standard Calibration Levels, 5 mL purge[1]**

| Compound | Calibration Level ug/L | | | | |
|---|---|---|---|---|---|
| | Level 1 | Level 2 | Level 3 | Level 4 | Level 5 |
| 1,2-Dibromoethane | 5 | 20 | 50 | 100 | 200 |
| 1,2,3-Trichloropropane | 5 | 20 | 50 | 100 | 200 |
| Acetonitrile | 50 | 200 | 500 | 1000 | 2000 |
| 1,1,2-Trichloroethane | 5 | 20 | 50 | 100 | 200 |
| Benzene | 5 | 20 | 50 | 100 | 200 |
| Ethylmethacrylate | 5 | 20 | 50 | 100 | 200 |
| trans-1,3-Dichloropropene | 5 | 20 | 50 | 100 | 200 |
| Bromoform | 5 | 20 | 50 | 100 | 200 |
| 4-Methyl-2-pentanone | 5 | 20 | 50 | 100 | 200 |
| 2-Hexanone | 5 | 20 | 50 | 100 | 200 |
| Tetrachloroethene | 5 | 20 | 50 | 100 | 200 |
| Toluene | 5 | 20 | 50 | 100 | 200 |
| 1,1,2,2-Tetrachloroethane | 5 | 20 | 50 | 100 | 200 |
| 2-Chloroethyl vinyl ether | 10 | 40 | 100 | 200 | 400 |
| Vinyl acetate | 5 | 20 | 50 | 100 | 200 |
| Chlorobenzene | 5 | 20 | 50 | 100 | 200 |
| Ethylbenzene | 5 | 20 | 50 | 100 | 200 |
| Styrene | 5 | 20 | 50 | 100 | 200 |
| t-1,4-Dichloro-2-butene | 5 | 20 | 50 | 100 | 200 |
| m and p Xylenes | 10 | 40 | 100 | 200 | 400 |
| o-xylene | 5 | 20 | 50 | 100 | 200 |
| 1,3-Dichlorobenzene | 5 | 20 | 50 | 100 | 200 |
| 1,4-Dichlorobenzene | 5 | 20 | 50 | 100 | 200 |
| 1,2-Dichlorobenzene | 5 | 20 | 50 | 100 | 200 |
| 2,2-Dichloropropane | 5 | 20 | 50 | 100 | 200 |
| Bromochloromethane | 5 | 20 | 50 | 100 | 200 |
| 1,1-Dichloropropene | 5 | 20 | 50 | 100 | 200 |
| Bromodichloromethane | 5 | 20 | 50 | 100 | 200 |
| 1,2-Dichloropropane | 5 | 20 | 50 | 100 | 200 |
| 1,3-Dichloropropane | 5 | 20 | 50 | 100 | 200 |
| Isopropylbenzene | 5 | 20 | 50 | 100 | 200 |
| Bromobenzene | 5 | 20 | 50 | 100 | 200 |
| n-Propylbenzene | 5 | 20 | 50 | 100 | 200 |
| 2-Chlorotoluene | 5 | 20 | 50 | 100 | 200 |
| 4-Chlorotoluene | 5 | 20 | 50 | 100 | 200 |
| 1,3,5-Trimethylbenzene | 5 | 20 | 50 | 100 | 200 |

**Table 2**

**STL Primary Standard Calibration Levels, 5 mL purge[1]**

| Compound | Calibration Level ug/L | | | | |
|---|---|---|---|---|---|
| | Level 1 | Level 2 | Level 3 | Level 4 | Level 5 |
| tert-Butylbenzene | 5 | 20 | 50 | 100 | 200 |
| 1,2,4-Trimethylbenzene | 5 | 20 | 50 | 100 | 200 |
| sec-butylbenzene | 5 | 20 | 50 | 100 | 200 |
| 4-Isopropyltoluene | 5 | 20 | 50 | 100 | 200 |
| n-Butylbenzene | 5 | 20 | 50 | 100 | 200 |
| 1,2,4-Trichlorobenzene | 5 | 20 | 50 | 100 | 200 |
| Napthalene | 5 | 20 | 50 | 100 | 200 |
| Hexachlorobutadiene | 5 | 20 | 50 | 100 | 200 |
| 1,2,3-Trichlorobenzene | 5 | 20 | 50 | 100 | 200 |
| | | | | | |

[1] **Levels for 25 mL purge are 5 times lower in all cases**

**Table 2A**

**STL Primary Standard Calibration Levels, Low Level [1]**

| Compound | Calibration Level ug/L | | | | |
|---|---|---|---|---|---|
| | Level 1 | Level 2 | Level 3 | Level 4 | Level 5 |
| Dibromofluoromethane (Surrogate) | 1 | 5 | 10 | 20 | 40 |
| 1,2-Dichloroethane-d4 (Surrogate) | 1 | 5 | 10 | 20 | 40 |
| Toluene-d8 (Surrogate) | 1 | 5 | 10 | 20 | 40 |
| Bromofluorobenzene (Surrogate) | 1 | 5 | 10 | 20 | 40 |
| Dichlorodifluoromethane | 1 | 5 | 10 | 20 | 40 |
| Chloromethane | 1 | 5 | 10 | 20 | 40 |
| Vinyl Chloride | 1 | 5 | 10 | 20 | 40 |
| Bromomethane | 1 | 5 | 10 | 20 | 40 |
| Chloroethane | 1 | 5 | 10 | 20 | 40 |
| Trichlorofluoromethane | 1 | 5 | 10 | 20 | 40 |
| Acrolein | 10 | 50 | 100 | 200 | 400 |
| Acetone | 2 | 10 | 20 | 40 | 80 |
| 1,1-Dichloroethene | 1 | 5 | 10 | 20 | 40 |
| Trichlorotrifluoroethane | 1 | 5 | 10 | 20 | 40 |
| Iodomethane | 1 | 5 | 10 | 20 | 40 |
| Carbon Disulfide | 1 | 5 | 10 | 20 | 40 |
| Methylene Chloride | 1 | 5 | 10 | 20 | 40 |
| Acetonitrile | 10 | 50 | 100 | 200 | 400 |
| Acrylonitrile | 10 | 50 | 100 | 200 | 400 |
| Methyl tert-butyl ether | 1 | 5 | 10 | 20 | 40 |
| trans-1,2-Dichloroethene | 1 | 5 | 10 | 20 | 40 |
| Hexane | 1 | 5 | 10 | 20 | 40 |
| Vinyl acetate | 1 | 5 | 10 | 20 | 40 |
| 1,1-Dichloroethane | 1 | 5 | 10 | 20 | 40 |
| tert-Butyl Alcohol | 20 | 100 | 200 | 400 | 800 |
| 2-Butanone | 2 | 10 | 20 | 40 | 80 |
| cis-1,2-dichloroethene | 1 | 5 | 10 | 20 | 40 |
| 2,2-Dichloropropane | 1 | 5 | 10 | 20 | 40 |
| Bromochloromethane | 1 | 5 | 10 | 20 | 40 |
| Chloroform | 1 | 5 | 10 | 20 | 40 |
| Tetrahydrofuran | 1 | 5 | 10 | 20 | 40 |
| 1,1,1-Trichloroethane | 1 | 5 | 10 | 20 | 40 |
| 1,1-Dichloropropene | 1 | 5 | 10 | 20 | 40 |
| Carbon Tetrachloride | 1 | 5 | 10 | 20 | 40 |
| 1,2-Dichloroethane | 1 | 5 | 10 | 20 | 40 |
| Benzene | 1 | 5 | 10 | 20 | 40 |
| Trichloroethene | 1 | 5 | 10 | 20 | 40 |
| 1,2-Dichloropropane | 1 | 5 | 10 | 20 | 40 |

**Table 2A**

**STL Primary Standard Calibration Levels, Low Level [1]**

| Compound | Calibration Level ug/L | | | | |
|---|---|---|---|---|---|
| | Level 1 | Level 2 | Level 3 | Level 4 | Level 5 |
| 1,4-Dioxane | 50 | 250 | 500 | 1000 | 2000 |
| Dibromomethane | 1 | 5 | 10 | 20 | 40 |
| Bromodichloromethane | 1 | 5 | 10 | 20 | 40 |
| 2-Chloroethyl vinyl ether | 2 | 10 | 20 | 40 | 80 |
| cis-1,3-Dichloropropene | 1 | 5 | 10 | 20 | 40 |
| 4-Methyl-2-pentanone | 2 | 10 | 20 | 40 | 80 |
| Toluene | 1 | 5 | 10 | 20 | 40 |
| trans-1,3-Dichloropropene | 1 | 5 | 10 | 20 | 40 |
| Ethyl Methacrylate | 1 | 5 | 10 | 20 | 40 |
| 1,1,2-Trichloroethane | 1 | 5 | 10 | 20 | 40 |
| 1,3-Dichloropropane | 1 | 5 | 10 | 20 | 40 |
| Tetrachloroethene | 1 | 5 | 10 | 20 | 40 |
| 2-Hexanone | 2 | 10 | 20 | 40 | 80 |
| Dibromochloromethane | 1 | 5 | 10 | 20 | 40 |
| 1,2-Dibromoethane | 1 | 5 | 10 | 20 | 40 |
| Chlorobenzene | 1 | 5 | 10 | 20 | 40 |
| 1,1,1,2-Tetrachloroethane | 1 | 5 | 10 | 20 | 40 |
| Ethylbenzene | 1 | 5 | 10 | 20 | 40 |
| m + p-Xylene | 2 | 10 | 20 | 40 | 80 |
| Xylene-o | 1 | 5 | 10 | 20 | 40 |
| Styrene | 1 | 5 | 10 | 20 | 40 |
| Bromoform | 1 | 5 | 10 | 20 | 40 |
| Isopropylbenzene | 1 | 5 | 10 | 20 | 40 |
| 1,1,2,2-Tetrachloroethane | 1 | 5 | 10 | 20 | 40 |
| 1,4-Dichloro-2-butene | 1 | 5 | 10 | 20 | 40 |
| 1,2,3-Trichloropropane | 1 | 5 | 10 | 20 | 40 |
| Bromobenzene | 1 | 5 | 10 | 20 | 40 |
| n-Propylbenzene | 1 | 5 | 10 | 20 | 40 |
| 2-Chlorotoluene | 1 | 5 | 10 | 20 | 40 |
| 1,3,5-Trimethylbenzene | 1 | 5 | 10 | 20 | 40 |
| 4-Chlorotoluene | 1 | 5 | 10 | 20 | 40 |
| tert-Butylbenzene | 1 | 5 | 10 | 20 | 40 |
| 1,2,4-Trimethylbenzene | 1 | 5 | 10 | 20 | 40 |
| sec-Butylbenzene | 1 | 5 | 10 | 20 | 40 |
| 4-Isopropyltoluene | 1 | 5 | 10 | 20 | 40 |
| 1,3-Dichlorobenzene | 1 | 5 | 10 | 20 | 40 |
| 1,4-Dichlorobenzene | 1 | 5 | 10 | 20 | 40 |
| n-Butylbenzene | 1 | 5 | 10 | 20 | 40 |

**Table 2A**

**STL Primary Standard Calibration Levels, Low Level [1]**

| Compound | Calibration Level ug/L | | | | |
|---|---|---|---|---|---|
| | Level 1 | Level 2 | Level 3 | Level 4 | Level 5 |
| 1,2-Dichlorobenzene | 1 | 5 | 10 | 20 | 40 |
| 1,2-Dibromo-3-chloropropane | 1 | 5 | 10 | 20 | 40 |
| 1,2,4-Trichlorobenzene | 1 | 5 | 10 | 20 | 40 |
| Hexachlorobutadiene | 1 | 5 | 10 | 20 | 40 |
| Naphthalene | 1 | 5 | 10 | 20 | 40 |
| 1,2,3-Trichlorobenzene | 1 | 5 | 10 | 20 | 40 |
| Cyclohexane | 1 | 5 | 10 | 20 | 40 |
| Methyl Acetate | 2 | 10 | 20 | 40 | 80 |
| Methylcyclohexane | 1 | 5 | 10 | 20 | 40 |
| 1,3,5-Trichlorobenzene | 1 | 5 | 10 | 20 | 40 |

[1] **25 mL purge samples analyzed at 5 mL purge on more sensitive equipment.**

**Table 3**

**STL Appendix IX Standard and Reporting Limits, 5 mL purge**

| Compound | CAS Number | Reporting Limits | | | |
|---|---|---|---|---|---|
| | | 5 mL Water µg/L | 25mL[2] water µg/L | Low Soil µg/kg | Medium Soil µg/mL |
| Allyl Chloride | 107-05-1 | 10 | 2 | 10 | 500 |
| Acetonitrile | 75-05-8 | 100 | 20 | 100 | 5000 |
| Dichlorofluoromethane | | 10 | 2 | 10 | 500 |
| Isopropyl ether | 108-20-3 | 10 | 2 | 10 | 500 |
| Chloroprene | 126-99-8 | 5 | 2 | 5 | 250 |
| n-Butanol | 71-36-3 | 200 | 50 | 200 | 10,000 |
| Propionitrile | 107-12-0 | 20 | 4 | 20 | 1000 |
| Methacrylonitrile | 126-98-7 | 5 | 2 | 5 | 250 |
| Isobutanol | 78-83-1 | 200 | 50 | 200 | 10,000 |
| Methyl methacrylate | 80-62-6 | 5 | 2 | 5 | 250 |
| 1,1,1,2-Tetrachloroethane | 630-20-6 | 5 | 1 | 5 | 250 |
| 1,2-Dibromo-3-chloropropane | 96-12-8 | 10 | 2 | 10 | 500 |
| Ethyl ether | 60-29-7 | 10 | 2 | 10 | 500 |
| Ethyl Acetate | 141-78-6 | 20 | 4 | 20 | 1,000 |
| 2-Nitropropane | 79-46-9 | 10 | 4 | 10 | 500 |
| Cyclohexanone | 108-94-1 | N/A[1] | N/A[1] | N/A[1] | N/A[1] |
| Isopropylbenzene | 98-82-8 | 5 | 1 | 5 | 250 |
| 2-Methylnaphthalene (Michigan only) | 91-57-6 | NA | 5 | NA | 330 |

[1] Cyclohexanone decomposes to 1,1-dimethoxycyclohexane in methanolic solution. Reporting limits cannot be accurately determined.

[2] Optionally, 5 mL purge volume if adequate sensitivity is obtained.

**Table 4**

**Recommended/STL Appendix IX Standard Calibration Levels, µg/L**

| Compound | Level 1 | Level 2 | Level 3 | Level 4 | Level 5 |
|---|---|---|---|---|---|
| Allyl Chloride | 5 | 20 | 50 | 100 | 200 |
| Acetonitrile | 50 | 200 | 500 | 1,000 | 2,000 |
| Dichlorofluoromethane | 5 | 20 | 50 | 100 | 200 |
| Isopropyl ether | 5 | 20 | 50 | 100 | 200 |
| Chloroprene | 5 | 20 | 50 | 100 | 200 |
| n-Butanol | 100 | 400 | 1,000 | 2,000 | 4,000 |
| Propionitrile | 10 | 40 | 100 | 200 | 400 |
| Methacrylonitrile | 5 | 20 | 50 | 100 | 200 |
| Isobutanol | 100 | 400 | 1,000 | 2,000 | 4,000 |
| Methyl methacrylate | 5 | 20 | 50 | 100 | 200 |
| 1,1,1,2-Tetrachloroethane | 5 | 20 | 50 | 100 | 200 |
| 1,2-Dibromo-3-chloropropane | 10 | 40 | 100 | 200 | 400 |
| Ethyl ether | 5 | 20 | 50 | 100 | 200 |
| Ethyl Acetate | 10 | 40 | 100 | 200 | 400 |
| 2-Nitropropane | 10 | 40 | 100 | 200 | 400 |
| Cyclohexanone | 50 | 200 | 500 | 1,000 | 2,000 |
| 2-Methylnaphthalene (Michigan only) | 2 | 10 | 20 | 40 | 80 |

**Table 5**

**Reportable Analytes for STL Standard Tests, Primary Standard**

| Compound | CAS Number | STL Standard List | TCLP | TCL | Appendix IX | UTS |
|---|---|---|---|---|---|---|
| Dichlorodifluoromethane | 75-71-8 | | | | X | X |
| Chloromethane | 74-87-3 | X | | X | X | X |
| Bromomethane | 74-83-9 | X | | X | X | X |
| Vinyl chloride | 75-01-4 | X | X | X | X | X |
| Chloroethane | 75-00-3 | X | | X | X | X |
| Trichlorofluoromethane | 75-69-4 | | | | X | X |
| Acrolein | 107-02-8 | | | | X | X |
| Acetone | 67-64-1 | X | | X | X | X |
| Trichlorotrifluoroethane | 76-13-1 | | | | | X |
| Ethanol | 64-17-5 | | | | | |
| Iodomethane | 74-88-4 | | | | X | X |
| Carbon disulfide | 75-15-0 | X | | X | X | X |
| Methylene chloride | 75-09-2 | X | | X | X | X |
| tert-Butly alcohol | 75-65-0 | | | | | |
| 1,1-Dichloroethene | 75-35-4 | X | X | X | X | X |
| 1,1-Dichloroethane | 75-34-3 | X | | X | X | X |
| trans-1,2-Dichloroethene | 156-60-5 | X | | X | X | X |
| Total dichloroethene | | X | | X | X | X |
| Acrylonitrile | 107-13-1 | | | | X | X |
| Methyl *tert*-butyl ether (MTBE) | 1634-04-4 | | | | | |
| Hexane | 110-54-3 | | | | | |
| cis-1,2-Dichloroethene | 156-59-2 | X | | X | | |
| Tetrahydrofuran | 109-99-9 | | | | | |
| Chloroform | 67-66-3 | X | X | X | X | X |
| 1,2-Dichloroethane | 107-06-2 | X | X | X | X | X |
| Dibromomethane | 74-95-3 | | | | X | X |
| 2-Butanone | 78-93-3 | X | X | X | X | X |
| 1,4-Dioxane | 123-91-1 | | | | X | X |
| 1,1,1-Trichloroethane | 71-55-6 | X | | X | X | X |
| Carbon tetrachloride | 56-23-5 | X | X | X | X | X |
| Bromodichloromethane | 75-27-4 | X | | X | X | X |
| 1,2-Dichloropropane | 78-87-5 | X | | X | X | X |
| cis-1,3-Dichloropropene | 10061-01- | X | | X | X | X |

**Table 5**

**Reportable Analytes for STL Standard Tests, Primary Standard**

| Compound | CAS Number | STL Standard List | TCLP | TCL | Appendix IX | UTS |
|---|---|---|---|---|---|---|
| | 5 | | | | | |
| Trichloroethene | 79-01-6 | X | X | X | X | X |
| Dibromochloromethane | 124-48-1 | X | | X | X | X |
| 1,2-Dibromoethane | 106-93-4 | | | | X | X |
| 1,2,3-Trichloropropane | 96-18-4 | | | | X | X |
| 1,1,2-Trichloroethane | 79-00-5 | X | | X | X | X |
| Benzene | 71-43-2 | X | X | X | X | X |
| Ethylmethacrylate | 97-63-2 | | | | X | X |
| trans-1,3-Dichloropropene | 10061-02-6 | X | | X | X | X |
| Bromoform | 75-25-2 | X | | X | X | X |
| 4-Methyl-2-pentanone | 108-10-1 | X | | X | X | X |
| 2-Hexanone | 591-78-6 | X | | X | X | |
| Tetrachloroethene | 127-18-4 | X | X | X | X | X |
| Toluene | 108-88-3 | X | | X | X | X |
| 1,1,2,2-Tetrachloroethane | 79-34-5 | X | | X | X | X |
| 2-Chloroethyl vinyl ether | 110-75-8 | | | | | |
| Vinyl acetate | 108-05-4 | | | | X | |
| Chlorobenzene | 108-90-7 | X | X | X | X | X |
| Ethylbenzene | 100-41-4 | X | | X | X | X |
| Styrene | 100-42-5 | X | | X | X | |
| t-1,4-Dichloro-2-butene | 110-57-6 | | | | X | |
| m and p Xylenes | | X | | X | X | X |
| o-xylene | 95-47-6 | X | | X | X | X |
| Total xylenes | 1330-20-7 | X | | X | X | X |
| 1,3-Dichlorobenzene | 541-73-1 | | | | | |
| 1,4-Dichlorobenzene | 106-46-7 | | | | | |
| 1,2-Dichlorobenzene | 95-50-1 | | | | | |

**Table 6**

**Reportable Analytes for STL Standard Tests, Appendix IX standard**

| Compound | Number | STL Standard List | TCLP | TCL | Appendix IX | UTS |
|---|---|---|---|---|---|---|
| Allyl Chloride | 107-05-1 | | | | X | |
| Acetonitrile | 75-05-8 | | | | X | X |
| Dichlorofluoromethane | 75-43-4 | | | | | |
| Isopropyl ether | 108-20-3 | | | | | |
| Chloroprene | 126-99-8 | | | | X | |
| n-Butanol | 71-36-3 | | | | | |
| Propionitrile | 107-12-0 | | | | X | |
| Methacrylonitrile | 126-98-7 | | | | X | X |
| Isobutanol | 78-83-1 | | | | X | X |
| Methyl methacrylate | 80-62-6 | | | | X | X |
| 1,1,1,2-Tetrachloroethane | 630-20-6 | | | | X | X |
| 1,2-Dibromo-3-chloropropane | 96-12-8 | | | | X | X |
| Ethyl ether | 60-29-7 | | | | | X |
| Ethyl Acetate | 141-78-6 | | | | | X |
| 2-Nitropropane | 79-46-9 | | | | | |
| Cyclohexanone | 108-94-1 | | | | | X |

**Table 7**

**Internal Standards**

| | Standard Concentration µg/mL | Quantitation ion (5 mL purge) | Quantitation ion (25 mL purge) |
|---|---|---|---|
| Fluorobenzene | 50 | 96 | 96 |
| Chlorobenzene-d5 | 50 | 117 | 119 |
| 1,4-Dichlorobenzene-d4 | 50 | 152 | 152 |

Notes:

1) 5 µL of the internal standard is added to the sample. This results in a concentration of each internal in the sample of 50µg/L for a 5 mL purge or 10 µg/L for a 25 mL purge.

2) Except for medium level soils, the surrogate and internal standards may be combined in one solution.

**Table 8**

**Surrogate Standards**

| Surrogate Compounds | Standard Concentration µg/mL |
|---|---|
| 1,2-Dichloroethane-$d_4$ | 50 |
| Dibromofluoromethane | 50 |
| Toluene-$d_8$ | 50 |
| 4-Bromofluorobenzene | 50 |

Notes:

1) 5 µL of the surrogate standard is added to the sample. This results in a concentration of each surrogate in the sample of 50µg/L for a 5 mL purge or 10 µg/L for a 25 mL purge.

2) Except for medium level soils, the surrogate and internal standards may be combined in one solution.

3) Recovery limits for surrogates are generated from historical data and are maintained by the QA department.

**Table 9**

**Matrix Spike / LCS Control Compounds**

| Compound | Standard Concentration µg /mL |
|---|---|
| 1,1-Dichloroethene | 50 |
| Trichloroethene | 50 |
| Toluene | 50 |
| Benzene | 50 |
| Chlorobenzene | 50 |
| n-Hexane (Ohio VAP only) | 50 |

Notes:

1) 5 µL of the standard is added to the LCS or matrix spiked sample. This results in a concentration of each spike analyte in the sample of 50µg/L for a 5 mL purge or 10 µg/L for a 25 mL purge.

2) Recovery and precision limits for LCS and MS/MSD are generated from historical data and are maintained by the QA dedartment.

3) Full analyte spikes may also be used at the laboratories option or at client request.

**Table 10**

**BFB Key Ion Abundance Criteria**

| Mass | Ion Abundance Criteria |
|---|---|
| 50 | 15% to 40% of Mass 95 |
| 75 | 30% to 60% of Mass 95 |
| 95 | Base Peak, 100% Relative Abundance |
| 96 | 5% to 9% of Mass 95 |
| 173 | Less Than 2% of Mass 174 |
| 174 | Greater Than 50% of Mass 95 |
| 175 | 5% to 9% of Mass 174 |
| 176 | Greater Than 95%, But Less Than 101% of Mass 174 |
| 177 | 5% to 9% of Mass 176 |

**Table 11**

**SPCC Compounds and Minimum Response Factors**

| Compound | 8260B, 8260A Min. RF |
|---|---|
| Chloromethane | 0.100 |
| 1,1-Dichloroethane | 0.100 |
| Bromoform | >0.100 |
| 1,1,2,2-Tetrachloroethane | 0.300 |
| Chlorobenzene | 0.300 |

**Table 12**

**CCC compounds**

| Compound | Max. %RSD from Initial Calibration | Max. %D for continuing calibration |
|---|---|---|
| Vinyl Chloride | <30.0 | <20.0 |
| 1,1-Dichloroethene | <30.0 | <20.0 |
| Chloroform | <30.0 | <20.0 |
| 1,2-Dichloropropane | <30.0 | <20.0 |
| Toluene | <30.0 | <20.0 |
| Ethylbenzene | <30.0 | <20.0 |
| n-Hexane (Ohio VAP only) | <30.0 | <20.0 |

**Table 13**

**Characteristic ions**

| Compound | Primary* | Secondary | Tertiary |
|---|---|---|---|
| 1,2-Dichloroethane-$d_4$ (Surrogate) | 65 | 102 | |
| Dichlorodifluoromethane | 85 | 87 | 50, 101,103 |
| Chloromethane | 50 | 52 | 49 |
| Vinyl chloride | 62 | 64 | 61 |
| Bromomethane | 94 | 96 | 79 |
| Chloroethane | 64 | 66 | 49 |
| Trichlorofluoromethane | 101 | 103 | 66 |
| 1,1-Dichloroethene | 96 | 61 | 98 |

**Table 13**

**Characteristic ions**

| Compound | Primary* | Secondary | Tertiary |
|---|---|---|---|
| Acrolein | 56 | 55 | 58 |
| Iodomethane | 142 | 127 | 141 |
| Carbon disulfide | 76 | 78 | |
| Trichlorotrifluoroethane | 151 | 101 | 153 |
| Ethanol | 45 | 46 | |
| Acetone | 43 | 58 | |
| Methylene chloride | 84 | 49 | 51, 86 |
| tert-Butyl alcohol | 59 | 74 | |
| trans-1,2-Dichloroethene | 96 | 61 | 98 |
| Acrylonitrile | 53 | 52 | 51 |
| Methyl *tert* butyl ether | 73 | | |
| Hexane | 57 | 43 | |
| 1,1-Dichloroethane | 63 | 65 | 83 |
| cis-1,2-Dichloroethene | 96 | 61 | 98 |
| 2-Butanone | 43 | 72** | |
| Tetrahydrofuran | 42 | 71 | |
| Chloroform | 83 | 85 | 47 |
| 1,2-Dichloroethane | 62 | 64 | 98 |
| Dibromomethane | 93 | 174 | 95, 172, 176 |
| 1,4-Dioxane | 88 | 58 | |
| Vinyl acetate | 43 | 86 | |
| 1,1,1-Trichloroethane | 97 | 99 | 117 |
| Carbon tetrachloride | 117 | 119 | 121 |
| Benzene | 78 | 52 | 77 |
| Trichloroethene | 130 | 95 | 97, 132 |
| 1,2-Dichloropropane | 63 | 65 | 41 |
| Bromodichloromethane | 83 | 85 | 129 |
| 2-Chloroethyl vinyl ether | 63 | 65 | 106 |
| cis-1,3-Dichloropropene | 75 | 77 | 39 |
| trans-1,3-Dichloropropene | 75 | 77 | 39 |
| 1,1,2-Trichloroethane | 97 | 83 | 85, 99 |
| Chlorodibromomethane | 129 | 127 | 131 |
| Bromoform | 173 | 171 | 175, 252 |
| 1,2,3-Trichloropropane | 75 | 110 | 77, 112, 97 |
| Toluene-$d_8$ (Surrogate) | 98 | 70 | 100 |
| 4-Bromofluorobenzene (Surrogate) | 95 | 174 | 176 |
| Toluene | 91 | 92 | 65 |
| 4-Methyl-2-pentanone | 43 | 58 | 57, 100 |
| Tetrachloroethene | 164 | 166 | 131 |

**Table 13**

**Characteristic ions**

| Compound | Primary* | Secondary | Tertiary |
|---|---|---|---|
| Ethyl methacrylate | 69 | 41 | 99, 86, 114 |
| 2-Hexanone | 43 | 58 | 57, 100 |
| Chlorobenzene | 112 | 114 | 77 |
| Ethylbenzene | 106 | 91 | |
| Xylenes | 106 | 91 | |
| Styrene | 104 | 103 | 78, 51, 77 |
| Dichlorobenzene (all isomers) | 146 | 148 | 111 |
| trans 1,4-Dichloro-2-butene | 53 | 75 | 89, 77, 124 |
| 1,1,2,2-Tetrachloroethane | 83 | 85 | 131, 133 |
| Allyl Chloride | 76 | 41 | 78 |
| Acetonitrile | 40 | 41 | |
| Dichlorofluoromethane | 67 | 69 | |
| Isopropyl ether | 87 | 59 | 45 |
| Chloroprene | 53 | 88 | 90 |
| n-Butanol | 56 | 41 | 42 |
| Propionitrile | 54 | 52 | 55 |
| Methacrylonitrile | 41 | 67 | 52 |
| Isobutanol | 41 | 43 | 74 |
| Methyl methacrylate | 41 | 69 | 100 |
| 1,1,1,2-Tetrachloroethane | 131 | 133 | 119 |
| 1,2-Dibromo-3-chloropropane | 157 | 155 | 75 |
| Ethyl ether | 59 | 74 | |
| Ethyl Acetate | 43 | 88 | 61 |
| 2-Nitropropane | 41 | 43 | 46 |
| Cyclohexanone | 55 | 42 | 98 |
| Isopropylbenzene | 105 | 120 | |

* The primary ion should be used for quantitation unless interferences are present, in which case a secondary ion may be used.

** m/z 43 may be used for quantitation of 2-Butanone, but m/z 72 must be present for positive identification.

## 1. REQUIREMENTS FOR EPA 624

1.1. Method 624 is required for demonstration of compliance with NPDES wastewater discharge permits. This method can be applied only to aqueous matrices. The standard analyte list and reporting limits are listed in Table B-1.

1.2. The tune period for this method is defined as 24 hours.

1.3. The initial calibration curve for this method requires at least three points.

1.4. Sample concentrations are calculated using the average RRF from the initial calibration curve.

1.5. Each target analyte is assigned to the closest eluting internal standard.

1.6. Initial demonstration of Proficiency

1.6.1. The spiking level for the four replicate initial demonstration of proficiency is 20 µg/L. The acceptance criteria are listed in Table B-2

1.7. Initial calibration curve requirements:

1.7.1. Target compounds must have RSD ≤ 35%.

1.7.2. If this requirement can not be met, a regression curve must be constructed for the non-compliant compounds. There is no correlation coefficient requirement for the regression curve.

1.8. Continuing calibration verification requirements:

1.8.1. The continuing calibration standard is from a different source than the initial calibration standard. The acceptance criteria are listed in Table B-2.

1.9. Matrix Spike and LCS requirements

1.9.1. The matrix spike and LCS are spiked at 20 µg/L. A matrix spike duplicate is not necessary for this method. The recovery limits for matrix spike and LCS recovery are listed in Table C-2.

1.10. Method clarifications, modifications and additions

1.10.1. Section 5.2.2 of the source method describes the trap packing materials as Tenax GC, Methyl silicone, silica gel and coconut charcoal. STL routinely employs the Supelco VOCARB 3000, which consists of Carbopack B and Carboxen 1000 and 1001.

1.10.2. Section 5.3.2 of the source method describes a packed analytical column. STL routinely employs capillary columns when performing this method.

1.10.3. The source method provides a suggested list of compounds for internal and surrogate standards. STL uses the following two compounds which are not on the table: Chlorobenzene-$d_5$ (internal standard) and 1,2-Difluorobenzene-$d_4$ (surrogate).

## Table A-1.

## Method 624 Analytes and Reporting Limits

| Analytes | µg/L |
|---|---|
| Benzene | 5 |
| Bromodichloromethane | 5 |
| Bromoform | 5 |
| Bromomethane | 5 |
| Carbon tetrachloride | 5 |
| Chlorobenzene | 5 |
| Chloroethane | 5 |
| 2-Chloroethyl vinyl ether | 5 |
| Chloroform | 5 |
| Chloromethane | 5 |
| Dibromochloromethane | 5 |
| 1,2-Dichlorobenzene | 5 |
| 1,3-Dichlorobenzene | 5 |
| 1,4-Dichlorobenzene | 5 |
| 1,1-Dichloroethane | 5 |
| 1,2-Dichloroethane | 5 |
| 1,1-Dichloroethene | 5 |
| trans-1,2-Dichloroethene | 5 |
| 1,2-Dichloropropane | 5 |
| cis-1,3-Dichloropropene | 5 |
| trans-1,3-Dichloropropene | 5 |
| Ethylbenzene | 5 |
| Methylene chloride | 5 |
| 1,1,2,2-Tetrachloroethane | 5 |
| Tetrachloroethene | 5 |
| Toluene | 5 |
| 1,1,1-Trichloroethane | 5 |
| 1,1,2-Trichloroethane | 5 |
| Trichloroethene | 5 |
| Trichlorofluoromethane | 5 |
| Vinyl chloride | 5 |

## Table A-2.

## Method 624 QC Acceptance Criteria

| Analytes | Daily QC check acceptance criteria (20µg/L spike) | Mean recovery, 4 replicate initial demonstration acceptance criteria (20µg/L spike) | Standard deviation, 4 replicate initial demonstration acceptance criteria (20µg/L spike) | Matrix spike and LCS acceptance criteria (% recovery) |
|---|---|---|---|---|
| Benzene | 12.8-27.2 | 15.2-26.0 | 6.9 | 37-151 |
| Bromodichloromethane | 13.1-26.9 | 10.1-28.0 | 6.4 | 35-155 |
| Bromoform | 14.2-25.8 | 11.4-31.1 | 5.4 | 45-169 |
| Bromomethane | 2.8-37.2 | D-41.2 | 17.9 | D-242 |
| Carbon tetrachloride | 14.6-25.4 | 17.2-23.5 | 5.2 | 70-140 |
| Chlorobenzene | 13.2-26.8 | 16.4-27.4 | 6.3 | 37-160 |
| Chloroethane | 7.6-32.4 | 8.4-40.4 | 11.4 | 14-230 |
| 2-Chloroethyl vinyl ether | D-44.8 | D-50.4 | 25.9 | D-305 |
| Chloroform | 13.5-26.5 | 13.7-24.2 | 6.1 | 51-138 |
| Chloromethane | D-40.8 | D-45.9 | 19.8 | D-273 |
| Dibromochloromethane | 13.5-26.5 | 13.8-26.6 | 6.1 | 53-149 |
| 1,2-Dichlorobenzene | 12.6-27.4 | 11.8-34.7 | 7.1 | 18-190 |
| 1,3-Dichlorobenzene | 14.6-25.4 | 17.0-28.8 | 5.5 | 59-156 |
| 1,4-Dichlorobenzene | 12.6-27.4 | 11.8-34.7 | 7.1 | 18-190 |
| 1,1-Dichloroethane | 14.5-25.5 | 14.2-28.5 | 5.1 | 59-155 |
| 1,2-Dichloroethane | 13.6-26.4 | 14.3-27.4 | 6.0 | 49-155 |
| 1,1-Dichloroethene | 10.1-29.9 | 3.7-42.3 | 9.1 | D-234 |
| trans-1,2-Dichloroethene | 13.9-26.1 | 13.6-28.5 | 5.7 | 54-156 |
| 1,2-Dichloropropane | 6.8-33.2 | 3.8-36.2 | 13.8 | D-210 |
| cis-1,3-Dichloropropene | 4.8-35.2 | 1.0-39.0 | 15.8 | D-227 |
| trans-1,3-Dichloropropene | 10.0-30.0 | 7.6-32.4 | 10.4 | 17-183 |
| Ethylbenzene | 11.8-28.2 | 17.4-26.7 | 7.5 | 37-162 |
| Methylene chloride | 12.1-27.9 | D-41.0 | 7.4 | D-221 |
| 1,1,2,2-Tetrachloroethane | 12.1-27.9 | 13.5-27.2 | 7.4 | 46-157 |
| Tetrachloroethene | 14.7-25.3 | 17.0-26.6 | 5.0 | 64-148 |
| Toluene | 14.9-25.1 | 16.6-26.7 | 4.8 | 47-150 |
| 1,1,1-Trichloroethane | 15.0-25.0 | 13.7-30.1 | 4.6 | 52-162 |
| 1,1,2-Trichloroethane | 14.2-25.8 | 14.3-27.1 | 5.5 | 52-150 |
| Trichloroethene | 13.3-26.7 | 18.6-27.6 | 6.6 | 71-157 |
| Trichlorofluoromethane | 9.6-30.4 | 8.9-31.5 | 10.0 | 17-181 |
| Vinyl chloride | 0.8-39.2 | D-43.5 | 20.0 | D-251 |

Implementation Date: 12/3/02

## STL NORTH CANTON STANDARD OPERATING PROCEDURE

## TITLE: PREPARATION AND ANALYSIS OF MERCURY IN AQUEOUS SAMPLES BY COLD VAPOR ATOMIC ABSORPTION, SW846 7470A AND MCAWW 245.1

**(SUPERSEDES: REVISION 2.3, DATED 05/15/01)**

| | | |
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| Prepared by: | Karen L. Counts | 11-25-02 Date |
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## 1. SCOPE AND APPLICATION

1.1. This procedure describes the preparation and analysis of mercury (Hg, CAS # 7439-97-6) by Cold Vapor Atomic Absorption Spectroscopy (CVAA) using SW-846 Method 7470A and MCAWW Method 245.1.

1.2. The associated LIMs method codes are BL (Method 245.1) and O8 (Method 7470A).

1.3. CVAA analysis provides for the determination of total mercury (organic and inorganic). The combination of the oxidants, potassium permanganate and potassium persulfate, has been found to give 100% recovery with both types of compounds. Detection limits, sensitivity and optimum concentration ranges for mercury analysis will vary with the matrices, instrumentation and volume of sample used.

1.4. Method 7470A is applicable to the preparation and analysis of mercury in ground water, aqueous samples, TCLP, and other leachates/extracts. Certain solid and sludge type wastes may also be analyzed, however Method 7471A (see CORP-MT-0007NC) is usually the method of choice. All matrices require sample preparation prior to analysis.

1.5. Method 245.1 is applicable to the determination of mercury in drinking, surface and saline waters and domestic and industrial wastes. All matrices require sample preparation prior to analysis.

1.6. The STL North Canton reporting limit for mercury in aqueous matrices is 0.0002 mg/L except for TCLP or SPLP leachates for which the reporting limit is 0.002 mg/L.

## 2. SUMMARY OF METHOD

2.1. This SOP describes a technique for the determination of mercury in solution. The procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. A representative portion of the sample is digested in sulfuric and nitric acids. Organic mercury compounds are oxidized with potassium permanganate and potassium persulfate and the mercury reduced to its elemental state with stannous chloride and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance is measured as a function of mercury concentration. Concentration of the analyte in the

sample is determined by comparison of the sample absorbance to the calibration curve (absorbance vs. concentration).

## 3. DEFINITIONS

3.1. Dissolved Metals: Those elements which pass through a 0.45 um membrane. (Sample is acidified after filtration).

3.2. Suspended Metals: Those elements which are retained by a 0.45 um membrane.

3.3. Total Metals: The concentration determined on an unfiltered sample following digestion.

## 4. INTERFERENCES

Chemical and physical interferences may be encountered when analyzing samples using this method.

4.1. Potassium permanganate, which is used to breakdown organic mercury compounds also eliminates possible interferences from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of inorganic mercury from reagent water.

4.2. Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on the recovery of mercury from spiked samples.

4.3. Chlorides can cause a positive interference. Sea waters, brines and industrial effluents high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation at 253.7 nm. Care must be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This is accomplished by adding excess hydroxylamine reagent (25 mL) and purging the sample headspace before stannous chloride is added. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater using this technique.

**Note**: Sufficient addition of permanganate is apparent when the purple color persists at least 15 minutes. Some samples may require dilution prior to digestion due to extremely high concentrations of chloride.

4.4. Interference from certain volatile organic materials that absorb at this wavelength may also occur. If suspected, a preliminary run without stannous chloride can determine if this type of interference is present. While the possibility of absorption from certain organic substances present in the sample does exist, this problem is not routinely encountered. This

is mentioned only to caution the analyst of the possibility. If this condition is found to exist, the mercury concentration in the sample can be determined by subtracting the result of the sample run without the reducing reagent (stannous chloride) from that obtained with the reducing reagent.

4.5. Samples containing high concentrations of oxidizing organic materials, as evidenced by high COD levels, may not be completely oxidized by this procedure. When this occurs the recovery of mercury will be low. The problem can be eliminated by reducing the volume of original sample used.

4.6. The most common interference is laboratory contamination, which may arise from impure reagents, dirty glassware, improper sample transfers, dirty work areas, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them.

## 5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all STL North Canton associates.

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory. The following specific hazards are known:

5.3.1. The following materials are known to be **corrosive:**

hydrochloric acid, nitric acid and sulfuric acid.

5.3.2. The following materials are known to be **oxidizing agents**:

nitric acid, potassium permanganate, potassium persulfate and magnesium perchlorate.

5.3.3. Mercury is a highly toxic element that must be handled with care. The analyst must be aware of the handling and clean up techniques before working with mercury.

Since mercury vapor is toxic, precaution must be taken to avoid its inhalation, ingestion or absorption through skin. All lines should be checked for leakage and the mercury vapor must be vented into a hood or passed through a mercury absorbing media such as:

5.3.3.1. Equal volumes of 0.1 M $KMnO_4$ and 10% $H_2SO_4$, or

5.3.3.2. Iodine, 0.25%, in a 3% KI solution.

5.3.4. Magnesium sulfate is known to be a reproductive toxin (mutagen).

5.4. Exposure to chemicals must be maintained **as low as reasonably achievable.** Therefore, unless they are known to be non-hazardous, all samples should be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.5. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL North Canton associate. The situation must be reported **immediately** to a laboratory supervisor.

5.6. Do not look directly into the beam of the Hg lamp. The UV light that these lamps radiate is harmful to the eyes.

5.7. Cylinders of compressed gas must be handled with caution, in accordance with local regulations. It is recommended that, wherever possible, cylinders are located outside the laboratory and the gas led to the instrument through approved lines.

5.8. The CVAA apparatus must be properly vented to remove potentially harmful fumes generated during sample analysis.

## 6. EQUIPMENT AND SUPPLIES

6.1. Temperature controlled water bath (capable of maintaining a temperature of 90-95 °C) or autoclave that is able to obtain conditions of 15 lbs., 120 °C for 15 minutes.

6.2. Atomic Absorption Spectrophotometer equipped with:

6.2.1. Absorption Cell with quartz end windows perpendicular to the longitudinal axis. Dimensions of the cell must result in sufficient sensitivity to meet the SOP defined reporting limit. The quartz windows must be maintained to provide accurate

measurements. Any scratches or fingerprints can alter the absorption of UV radiation.

6.2.2. Mercury specific hollow cathode lamp (HCL) or electrodeless discharge lamp (EDL).

6.2.3. Peristaltic pump, which can deliver 1 L/min, air.

6.2.4. Flowmeter capable of measuring an airflow of 1 L/min.

6.2.5. Recorder or Printer.

6.2.6. Aeration Tubing: A straight glass frit having a course porosity and Tygon tubing is used for the transfer of mercury vapor from the sample bottle to the absorption cell and return.

6.2.7. Drying device (a drying tube containing magnesium perchlorate or magnesium sulfate and/or a lamp with a 60 W bulb) to prevent condensation in cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10 °C above room temperature. Other drying devices that achieve the same purpose are also acceptable (i.e., Gortex filter).

NOTE: Instruments designed specifically for the measurement of mercury using the cold vapor technique may be substituted for the atomic absorption spectrophotometer.

6.3. BOD bottles or equivalent.

6.4. Nitrogen or argon gas supply, welding grade, or equivalent.

6.5. Calibrated automatic pipettes or Class A glass volumetric pipettes.

6.6. Class A volumetric flasks.

6.7. Thermometer (capable of accurate readings at 95 °C).

6.8. Disposable cups or tubes.

## 7. REAGENTS AND STANDARDS

7.1. Reagent water must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

7.2. Stock (10 ppm) mercury standards (in 10% $HNO_3$) are purchased as custom STL North Canton solutions. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem.

7.3. Working mercury standard (0.1 ppm): Take 1 mL of the stock mercury standard (7.2) and dilute to 100 mL with reagent water. The working mercury standard must be made daily and must be prepared in a matrix of 0.15% $HNO_3$. This acid (150 uL of concentrated $HNO_3$) must be added to the flask/bottle before the addition of the stock standard aliquot.

7.4. The calibration standards listed in Table I must be prepared fresh daily from the working standard (7.3) by transferring 0, 0.2, 0.5, 1.0, 5.0 and 10.0 mL aliquots of the working mercury standard into 100 mL flasks and diluting to volume with reagent water.

**Note**: Alternate approaches to standard preparation may be taken and alternate volumes of standard may be prepared as long as the accuracy and final standard concentrations as detailed in Table I are maintained. For example, automated mercury systems do not require 100 mL of standard and therefore smaller volumes may be generated to reduce waste generation.

7.5. The initial calibration verification standard must be made from a different stock solution than that of the calibration standards.

7.6. Refer to Table I (Appendix A) for details regarding the working standard concentrations for calibration, calibration verification and spiking solutions. All standards must be processed through the entire analytical procedure including sample preparation.

7.7. Nitric acid ($HNO_3$), concentrated, trace metal grade or better.

**Note**: If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

7.8. Sulfuric acid ($H_2SO_4$), concentrated, trace metal grade or better.

7.9. Stannous sulfate solution: Add 25 g of stannous sulfate to 250 mL of 0.5 N sulfuric acid. This mixture is a suspension and should appear cloudy. This solution should be made daily and should be stirred continuously during use.

**Note**: Stannous chloride may be used in place of stannous sulfate. Prepare the stannous chloride solution according to the recommendations provided by the instrument manufacturer.

7.10. Sodium chloride-hydroxylamine hydrochloride solution: Add 12 g of sodium chloride and 12 g of hydroxylamine hydrochloride to every 100 mL of reagent water.

**Note**: Hydroxylamine sulfate may be used in place of hydroxylamine hydrochloride.

7.11. Potassium permanganate, 5% solution (w/v): Dissolve 5 g of potassium permanganate for every 100 mL of reagent water.

7.12. Potassium persulfate, 5% solution (w/v): Dissolve 5 g of potassium persulfate for every 100 mL of reagent water.

## 8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Sample holding time for mercury is 28 days from time of collection to the time of analysis.

8.2. Aqueous samples are preserved with nitric acid to a pH of <2 and may be stored in either plastic or glass. Refrigeration is not required. Preservation must be verified prior to analysis.

## 9. QUALITY CONTROL

Table II (Appendix A) provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.

9.1. Initial Demonstration of Capability

Prior to the analysis of any analyte using 7470A or the 245.1, the following requirements must be met.

9.1.1. Method Detection Limit (MDL) - An MDL must be determined for each analyte/matrix prior to the analysis of any samples. The MDL is determined using seven replicates of reagent water, spiked with all the analytes of interest, that have been carried through the entire analytical procedure. MDLs must be redetermined

on an annual basis in accordance with 40 CFR Part 136 Appendix B requirements. The spike level must be between the calculated MDL and 10X the MDL to be valid. The result of the MDL determination must be below the STL North Canton reporting limit.

9.1.2. Initial Demonstration Study - This requires the analysis of four QC check samples. The QC check sample is a well-characterized laboratory generated sample used to monitor method performance. The results of the initial demonstration study must be acceptable before analysis of samples may begin.

9.1.2.1. Four aliquots of the check sample (LCS) are prepared and analyzed using the procedures detailed in this SOP and the determinative SOPs.

9.2. Preparation Batch - A group of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The preparation batch must contain a method blank, a LCS and a matrix spike/matrix spike duplicate. In some cases, at client request, it may be appropriate to process a matrix spike and sample duplicate in place of the MS/MSD. If clients specify specific samples for MS/MSD, the batch may contain multiple MS/MSD pairs.

9.3. Sample Count - Laboratory generated QC samples (Method Blanks, LCS, and MS/MSDs) are not included in the sample count for determining the size of a preparation batch.

**9.4.** Method Blank (MB) - One method blank must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest at or above the reporting limit or at or above 10% of the measured concentration of that analyte in associated samples, whichever is higher (sample result must be a minimum of 20 times higher than the blank contamination level).

- Repreparation and reanalysis of all samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples (see exception noted above).

- If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. **Such action must be taken in consultation with the client and must be addressed in the project narrative.**

- If the above criteria are not met and reanalysis is not possible, then the sample data must be qualified. **This anomaly must be addressed in the project narrative and the client must be notified.**

9.5. Laboratory Control Sample (LCS) - One aqueous LCS must be processed with each preparation batch. The LCS is used to monitor the accuracy of the analytical process. On going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. The LCS must be carried through the entire analytical procedure. If the LCS is outside established control limits the system is out of control and corrective action must occur. Until in-house control limits are established, a control limit of 80 - 120% recovery must be applied.

- In the instance where the LCS recovery is > 120% and the sample results are < RL, the data may be reported with qualifiers. Such action must be taken in consultation with the client and must be addressed in the case narrative.

- In the event that an MS/MSD analysis is not possible, a Laboratory Control Sample Duplicate (LCSD) must be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

- Corrective action will be repreparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable.

9.6. Matrix Spike/Matrix Spike Duplicate (MS/MSD) - One MS/MSD pair must be processed for each preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MSD's. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis. Spiking levels are provided in Table I (Appendix A).

- If analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. Until in-house control limits are established, a control limit of 75 - 125 % recovery and 20% RPD must be applied to the MS/MSD. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include repreparation

and reanalysis of the batch. MS/MSD results, which fall outside the control limits, must be addressed in the narrative.

- If the native analyte concentration in the MS/MSD exceeds 4 times the spike level for that analyte, the recovery data are reported as NC (i.e., not calculated). If the reporting software does not have the ability to report NC then the actual recovery must be reported and narrated as follows: "Results outside of limits do not necessarily reflect poor method performance in the matrix due to high analyte concentrations in the sample relative to the spike level."

- If an MS/MSD is not possible due to limited sample volume, then a laboratory control sample duplicate (LCSD) should be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

9.7. Initial Calibration Verification (ICV/ICB) - Calibration accuracy is verified by analyzing a second source standard (ICV). The ICV result must fall within 10% of the true value for that solution. An ICB is analyzed immediately following the ICV to monitor low level accuracy and system cleanliness. The ICB result must fall within +/- the reporting limit (RL) from zero. If either the ICV or ICB fail to meet criteria, the analysis should be terminated, the problem corrected and the instrument recalibrated. (See Section 11.2.11 and Section 11.2.12 for required run sequence). If the cause of the ICV or ICB failure was not directly instrument related the corrective action will include repreparation of the ICV, ICB, CRA, CCV, and CCB with the calibration curve.

9.8. Continuing Calibration Verification (CCV/CCB) - Calibration accuracy is monitored throughout the analytical run through the analysis of a known standard after every 10 samples. The CCV must be a mid-range standard at a concentration other than that of the ICV. The CCV result must fall within 20% of the true value for that solution. A CCB is analyzed immediately following each CCV. (See Section 11.2.11 and 11.2.12 for required run sequence.) The CCB result must fall within +/- RL from zero. Each CCV and CCB analyzed must reflect the conditions of analysis of all associated samples. Sample results may only be reported when bracketed by valid ICV/CCV and ICB/CCB pairs.

9.9. Method of Standard Addition (MSA) -This technique involves adding known amounts of standard to one or more aliquots of the sample prior to preparation. This technique compensates for a sample interferent that may enhance or depress the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences, which cause a baseline shift. Refer to Section 11.2.13 for additional information on when full 4 point MSA is required as well as Appendix C for specific MSA requirements.

## 10. CALIBRATION AND STANDARDIZATION

10.1. Calibration standards must be processed through the preparation procedure as described in Section 11.1.

10.2. Due to the differences in preparation protocols separate calibration and calibration verification standards must be prepared for aqueous and solid matrices.

10.3. Calibration must be performed daily (every 24 hours) and each time the instrument is set up. The instrument calibration date and time must be included in the raw data.

10.4. Set up the instrument with the operating parameters recommended by the manufacturer. Allow the instrument to become thermally stable before beginning calibration (approximately 30 minutes of warm-up is required). Refer to the facility specific instrument SOP and CVAA instrument manual for detailed setup and operation protocols.

10.5. Calibrate the instrument according to instrument manufacturer's instructions, using a minimum of five standards and a blank. One standard must be at the STL North Canton reporting limit. Analyze standards in ascending order beginning with the blank. Refer to Section 7.5 and Table I for additional information on preparing calibration standards and calibration levels.

10.6. The calibration curve must have a correlation coefficient of ≥0.995 or the instrument shall be stopped and recalibrated prior to running samples. Sample results can not be reported from a curve with an unacceptable correlation coefficient.

10.7. Refer to Section 9.0 for calibration verification procedures, acceptance criteria and corrective actions.

## 11. PROCEDURE

### 11.1. Sample Preparation:

11.1.1. All calibration and calibration verification standards (ICV, ICB, CCV, CCB) are processed through the digestion procedure as well as the field samples. Transfer 0, 0.2, 0.5, 1.0, 5.0 and 10.0 mL aliquots of the working standard (7.3) into a series of 100 ml class A volumetrics, then dilute to volume . For the ICV, use a 2.5 ml aliquot of the working standard. The ICV working standard must be made from a source other than that used for the calibration standards.

11.1.2. Transfer 100 mL of well-mixed sample or standard to a clean sample digestion bottle.

**Note**: Reduced sample volumes can be used as long as a representative sample can be obtained and the reagent levels are adjusted to maintain the same sample to reagent ratio. All samples and standards must be processed similarly.

**Note**: Spiking is done before the addition of acids or reagents.

11.1.3. Add 5 mL of concentrated $H_2SO_4$ and 2.5 mL of concentrated $HNO_3$ mixing after each addition.

11.1.4. Add 15 mL of potassium permanganate solution. For samples high in organic materials or chlorides, additional permanganate may be added. Shake and add additional portions of permanganate solution until a purple color persists for at least 15 minutes. If after the addition of up to 25-mL additional permanganate the color does not persist, sample dilution prior to reanalysis may be required.

**Note**: When performing analyses using automated vs. manual techniques the sample dilution resultant from the addition of more than the original aliquot of permanganate solution must be compensated for by the addition of the same volume of permanganate to all other associated samples and standards in the run. In instances, where this is not feasible, the addition of excess reagent can be addressed through mathematical correction of the results to account for the resultant dilution effect.

11.1.5. Add 8 mL of potassium persulfate solution and heat for two hours in a water bath at 90 - 95 °C.

NOTE: Alternatively, for RCRA analyses using 7470A, samples may be digested using an autoclave for 15 minutes at 120 °C and 15 lbs.

11.1.6. Cool samples.

11.2. Sample Analysis:

11.2.1. Refer to the Appendix G of this SOP for detailed setup and operation protocols.

11.2.2. All labs are required to detail the conditions/programs utilized for each instrument within the facility specific instrument operation SOP.

11.2.3. When ready to begin analysis, add 6 mL of sodium chloride-hydroxylamine hydrochloride solution to the samples to reduce the excess permanganate (the permanganate has been reduced when no purple color remains). Add this solution in 6-mL increments until the permanganate is completely reduced.

11.2.4. Manual determination:

11.2.4.1. Treating each sample individually, purge the headspace of the sample bottle for at least one minute.

11.2.4.2. Add 5 mL of stannous chloride solution and immediately attach the bottle to the aeration apparatus.

11.2.4.3. Allow the sample to stand quietly without manual agitation while the sample is aerated (1 L/min flow). Monitor the sample absorbance during aeration. When the absorbance reaches a maximum and the signal levels off, open the bypass valve and continue aeration until the absorbance returns to its baseline level. Close the bypass valve and remove the aeration device.

11.2.4.4. Place the aeration device into 100 mL of 1% $HNO_3$ and allow to bubble rinse until the next sample is analyzed.

11.2.5. Automated determination: Follow instructions provided by instrument manufacturer.

11.2.6. Perform a linear regression analysis of the calibration standards by plotting maximum response of the standards vs. concentration of mercury. Determine the mercury concentration in the samples from the linear regression fit of the calibration curve. Calibration using computer or calculation based regression curve fitting techniques on concentration/response data is acceptable.

11.2.7. All measurements must fall within the defined calibration range to be valid. Dilute and reanalyze all samples for analytes that exceed the highest calibration standard.

11.2.8. If the sample results are negative and the absolute value of the negative result is greater than the reporting limit, the sample must be diluted and reanalyzed.

11.2.9. The samples must be allowed to cool to room temperature prior to analysis or a decrease in the response signal can occur.

11.2.10. Baseline correction is acceptable as long as it is performed after every sample or after the CCV and CCB; resloping is acceptable as long as it is immediately preceded and followed by a compliant CCV and CCB.

11.2.11. The following analytical sequence must be used with 7470A and 245.1:

Instrument Calibration
ICV
ICB
Maximum 10 samples
CCV
CCB
Repeat sequence of 10 samples between CCV/CCB pairs as required to complete run
CCV
CCB

Refer to Quality Control Section 9.0 and Table II (Appendix A) for quality control criteria to apply to Methods 7470A and 245.1.

**Note**: Samples include the method blank, LCS, MS, MSD, duplicate, field samples and sample dilutions.

11.2.12. The following run sequence is consistent with 7470A, CLP and 245.1 and may be used as an alternate to the sequence in 11.2.11. This run sequence is

recommended if multiple method requirements must be accommodated in one analytical run:

Instrument Calibration
ICV
ICB
CRA*
CCV
CCB
10 samples
CCV
CCB
Repeat sequence of 10 samples between CCV/CCB pairs as required to complete run.
CCV
CCB

Refer to the appropriate CLP SOP (CORP-MT-0006) for quality control requirements for QC samples.

* Refer to the CLP SOP for information on the CRA.

11.2.13. For TCLP samples, full four point MSA will be required if all of the following conditions are met:

1) recovery of the analyte in the matrix spike is not at least 50%,

2) the concentration of the analyte does not exceed the regulatory level, and,

3) the concentration of the analyte is within 20% of the regulatory level.

The reporting and matrix spike levels for TCLP analyses are detailed in Table I (Appendix A). Appendix E provides guidance on performing MSA analyses. For TCLP mercury determinations, MSA spikes must be added prior to sample preparation.

11.3. To facilitate the early identification of QC failures and samples requiring rerun it is strongly recommended that sample data are reviewed periodically throughout the run.

11.4. Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards, preventive maintenance and troubleshooting.

11.5. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.6. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

## 12. DATA ANALYSIS AND CALCULATIONS

12.1. ICV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(ICV)}{True(ICV)}\right)$$

12.2. CCV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(CCV)}{True(CCV)}\right)$$

12.3. Matrix spike recoveries are calculated according to the following equation:

$$\%R = 100\left(\frac{SSR - SR}{SA}\right)$$

Where:
SSR = Spike Sample Result
SR = Sample Result
SA = Spike Added

12.4. The relative percent difference (RPD) of matrix spike/matrix spike duplicates or sample duplicates are calculated according to the following equations:

$$RPD = 100\left[\frac{|MSD - MS|}{\left(\frac{MSD + MS}{2}\right)}\right]$$

Where:

MS = determined spiked sample concentration
MSD = determined matrix spike duplicate concentration

$$RPD = 100\left[\frac{|DU1 - DU2|}{\left(\frac{DU1 + DU2}{2}\right)}\right]$$

Where:

DU1 = Sample result
DU2 = Sample duplicate result

12.5. The final concentration for an aqueous sample is calculated as follows:

$$mg/L = C \times D$$

Where:

C = Concentration (mg/L) from instrument readout
D = Instrument dilution factor

12.6. The LCS percent recovery is calculated according to the following equation:

$$\%R = 100\left(\frac{Found(LCS)}{True(LCS)}\right)$$

12.7. Appropriate factors must be applied to sample values if dilutions are performed.

12.8. Sample results should be reported with up to three significant figures in accordance with the STL North Canton significant figure policy.

## 13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file for each analyte of interest as described in Section 9.0.

13.2. Method performance is determined by the analysis of method blanks, laboratory control samples, matrix spike and matrix spike duplicate samples. The matrix spike recovery should fall within +/- 25 % and the matrix spike duplicates should compare within 20% RPD. The method blanks must meet the criteria in Section 9.3. The laboratory control sample should recover within 20% of the true value until in house limits are established.

13.3. Training Qualification:

The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

## 14. POLLUTION PREVENTION

14.1. This method allows for the proportional reduction of sample and reagent volumes to decrease waste generation.

## 15. WASTE MANAGEMENT

15.1. Waste generated in the procedure must be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

## 16. REFERENCES

16.1. References

16.1.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update II, Revision I, September 1994, Method 7470A (Mercury).

16.1.2. "Methods for the Chemical Analysis of Water and Wastes", EPA-600/4-79-020, U.S.EPA, August 1983, Method 245.1.

16.1.3. U.S.EPA Statement of Work for Inorganics Analysis, ILMO3.0 and ILMO4.0.

16.1.4. Corporate Quality Management Plan (QMP), current version.

16.1.5. STL Laboratory Quality Manual (LQM), current version.

16.2. Associated SOPs and Policies, latest version

16.2.1. QA Policy, QA-003.

16.2.2. Glassware Washing, NC-QA-0014.

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018.

16.2.4. Method Detection Limits and Instrument Detection Limits, NC-QA-0021.

16.2.5. Navy/Army SOP, NC-QA-0016.

## 17. MISCELLANEOUS (TABLES, APPENDICES, ETC. . . )

17.1. Modifications/Interpretations from reference method.

17.1.1. Modifications from both 7470A and 245.1.

17.1.1.1. The 200 series methods and Chapter 1 of SW846 specify the use of reagent water with a purity equivalent to ASTM Type II water. This SOP specifies the use of a Millipore DI system or equivalent to produce reagent water. This SOP requires that reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

17.1.1.2. This SOP allows for the use of reduced sample volumes to decrease waste generation. Reagent levels are adjusted to maintain the same ratios as stated in the source methods. According to a letter from Robert Booth of EPA EMSL-Cinn to David Payne of EPA Region V, "Reduction in sample size and appropriate corresponding reduction in sample volume is not considered a significant change in the methodology."

17.1.1.3. The alternate run sequence presented in Section 11.2.12 is consistent with method requirements. An additional QC analysis (CRA) was added to accommodate the CLP protocol requirements.

17.1.2. Modifications from Method 7470A

17.1.2.1. Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the MDL. This SOP states that the

method blank must not contain any analyte of interest at or above the reporting limit.

17.1.2.2. Documentation is on file from EPA's Office of Solid Waste (Olliver Fordham 11/28/95) regarding the acceptance of the autoclave as an equivalent heating device to the water bath. In his letter, Mr. Fordham cited the CLP water protocol 245.1 CLP-M and therefore the operating parameters from that method were adopted for 7470A (15 minutes at 120 °C and 15 lbs.).

17.1.3. Modifications from 245.1

17.1.3.1. Method 245.1 Section 9.3 states concentrations should be reported as follows: Between 1 and 10 ug/L, one decimal; above 10 ug/L, to the nearest whole number. STL North Canton reports all Hg results under this SOP to two significant figures.

17.2. Modifications from previous SOP

17.2.1. Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit.

17.2.2. Documentation is on file from EPA's Office of Solid Waste (Olliver Fordham 11/28/95) regarding the acceptance of the autoclave as an equivalent heating device to the water bath. In his letter, Mr. Fordham cited the CLP water protocol 245.1 CLP-M and therefore the operating parameters from the method were adopted for 7470A (15 minutes at 120° C and 15 lbs.).

17.3. Facility Specific SOPs

Each facility shall attach a list of facility specific SOPs or approved attachments (if applicable) which are required to implement this SOP or which are used in conjunction with this SOP. If no facility specific SOPs or amendments are to be attached, a statement must be attached specifying that there are none. Refer to the Appendices for any facility specific information required to support this SOP.

17.4. Documentation and Record Management

The following documentation comprises a complete CVAA raw data package:

- Raw data (direct instrument printout)
- Run log printout from instrument software where this option is available or manually generated run log. (A bench sheet may be substituted for the run log as long as it contains an accurate representation of the analytical sequence).
- Data review checklist - See Appendix B
- Standards Documentation (source, lot, date).
- Copy of digestion log.
- Non-conformance summary (if applicable).

**Figure 1.** Aqueous Sample Preparation - Mercury

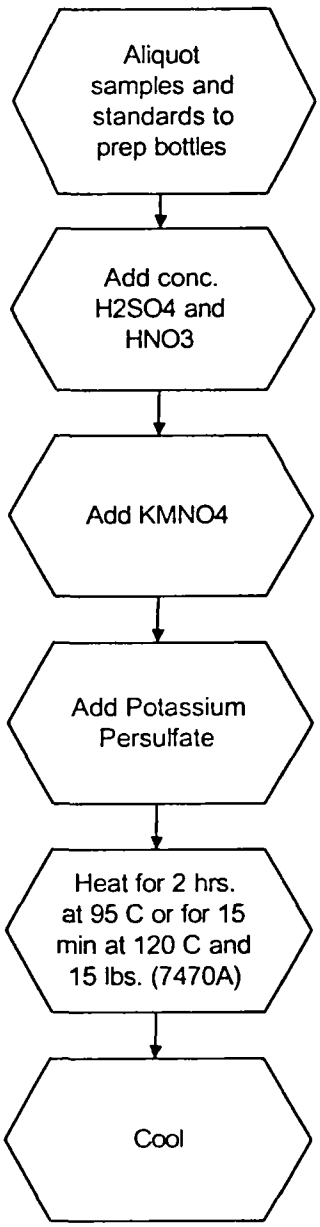
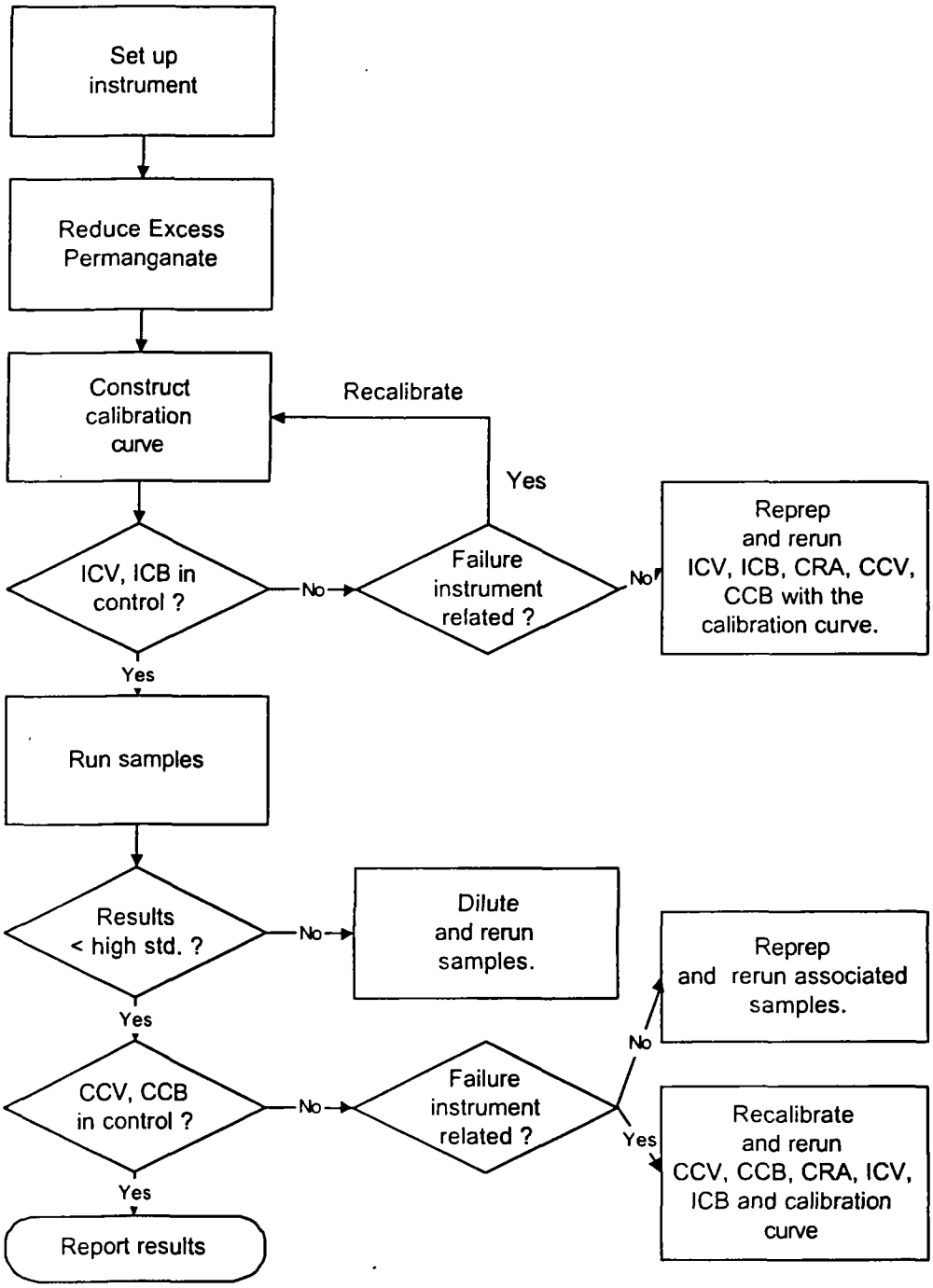


**Figure 2.** CVAA Mercury Analysis



# APPENDIX A

# TABLES

**TABLE I. MERCURY REPORTING LIMITS, CALIBRATION STANDARD*, QC STANDARD AND SPIKING LEVELS (MG/L)**

| | |
|---|---|
| Standard Aqueous RL | 0.0002 |
| TCLP RL | 0.002 |
| Std 0 | 0 |
| Std 1 | 0.0002 |
| Std 2 | 0.0005 |
| Std 3 | 0.001 |
| Std 4 | 0.005 |
| Std 5 ** | 0.010 |
| ICV | 0.001 or 0.0025 *** |
| LCS/CCV | 0.0025 or 0.005 *** |
| Aqueous MS | 0.001 |
| TCLP MS | 0.005 |

* **SOP specified calibration levels must be used unless prevented by the instrument configuration or client specific requirements. Deviations from specified calibration levels must be documented in the facility specific instrument operation SOP and must be approved by the facility technical manager and Quality Assurance Manager.**

** **Optional standard which may be used to extend the calibration range as allowed by the instrument configuration. If the instrument configuration prevents the use of 6 standards, the 2-ppb standard may be eliminated in favor of the 10 ppb standard.**

*** **Concentration level dependent on high calibration standard used. CCV must be 50% of high standard concentration and ICV must be 20-25% of high standard concentration.**

**TABLE II. Summary Of Quality Control Requirements**

| QC PARAMETER | FREQUENCY * | ACCEPTANCE CRITERIA | CORRECTIVE ACTION |
|---|---|---|---|
| ICV | Beginning of every analytical run. | 90-110 % recovery. | Terminate analysis; Correct the problem; Recalibrate or reprep with calibration curve. (See Section 9.7). |
| ICB | Beginning of every analytical run, immediately following the ICV. | The result must be within +/- RL from zero. | Terminate analysis; Correct the problem; Recalibrate or reprep with calibration curve. (See Section 9.7). |
| CCV | Every 10 samples and at the end of the run. | 80 - 120 % recovery. | Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCV or reprep with calibration curve. (See Section 9.8). |
| CCB | Immediately following each CCV. | The result must be within +/- RL from zero. | Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCB or reprep with calibration curve. (See Section 9.8). |
| Method Blank | One per sample preparation batch of up to 20 samples. | The result must be less than or equal to the RL. Sample results greater than 20x the blank concentration are acceptable. Samples for which the contaminant is < RL do not require redigestion (See Section 9.4). | Redigest and reanalyze samples.<br><br>Note exceptions under criteria section.<br><br>See Section 9.4 for additional requirements. |

*See Sections 11.2.11 and 11.2.12 for exact run sequence to be followed.

**TABLE II. Summary of Quality Control Requirements (Continued)**

| QC PARAMETER | FREQUENCY | ACCEPTANCE CRITERIA | CORRECTIVE ACTION |
|---|---|---|---|
| Laboratory Control Sample (LCS) | One per sample preparation batch of up to 20 samples. | Aqueous LCS must be within 80 - 120% recovery or in-house control limits. | Terminate analysis; Correct the problem; Redigest and reanalyze all samples associated with the LCS (see Section 9.5). |
| Matrix Spike | One per sample preparation batch of up to 20 samples. | 75 - 125 % recovery or in-house control limits. If the MS/MSD is out for an analyte, it must be in control in the LCS. | In the absence of client specific requirements, flag the data; no flag required if the sample level is > 4x the spike added. (see Section 9.6)<br><br>For TCLP see Section 11.2.13 |
| Matrix Spike Duplicate | See Matrix Spike | 75 - 125 % recovery or in-house control limits; RPD ≤ 20%. (See MS) | See Corrective Action for Matrix Spike. |

**APPENDIX B**
**EXAMPLE**
**STL NORTH CANTON Hg DATA REVIEW CHECKLIST**

## Example
## STL North Canton Hg Data Review Checklist

**Run/Project Information**

**Run Date:** _____ **Analyst:** _____ **Instrument:** _____
**Prep Batches Run:** _____

**Circle Methods used:** **7470A / 245.1** : CORP-MT-0005 Rev 1 **7471 / 245.5** : CORP-MT-0007 Rev 1
**CLP - AQ** : CORP-MT-0006 Rev 0 **CLP - SOL** : CORP-MT-0008 Rev 0

**Review Items**

| A. Calibration/Instrument Run QC | Yes | No | N/A | 2ndLevel |
|---|---|---|---|---|
| 1. Instrument calibrated per manufacturer's instructions and at SOP specified levels? | | | | |
| 2. ICV/CCV analyzed at appropriate frequency and within control limits? | | | | |
| 3. ICB/CCB analyzed at appropriate frequency and within +/- RL or +/- CRDL (CLP)? | | | | |
| 4. CRA run (CLP only)? | | | | |
| **B. Sample Results** | | | | |
| 1. Were samples with concentrations > the high calibration standard diluted and reanalyzed? | | | | |
| 2. All reported results bracketed by in control QC? | | | | |
| 3. Sample analyses done within holding time? | | | | |
| **C. Preparation/Matrix QC** | | | | |
| 1. LCS done per prep batch and within QC limits? | | | | |
| 2. Method blank done per prep batch and < RL or CRDL (CLP)? | | | | |
| 3. MS run at required frequency and within limits? | | | | |
| 4. MSD or DU run at required frequency and RPD within SOP limits? | | | | |
| **D. Other** | | | | |
| 1. Are all nonconformances documented appropriately? | | | | |
| 2. Current IDL/MDL data on file? | | | | |
| 3. Calculations and Transcriptions checked for error? | | | | |
| 4. All client/ project specific requirements met? | | | | |
| 5. Date of analysis verified as correct? | | | | |

**Analyst:** _____ **Date:** _____
**Comments:**

_____

_____

_____

**2nd Level Reviewer :** _____ **Date:** _____

_____

_____

_____

# APPENDIX C

# MSA GUIDANCE

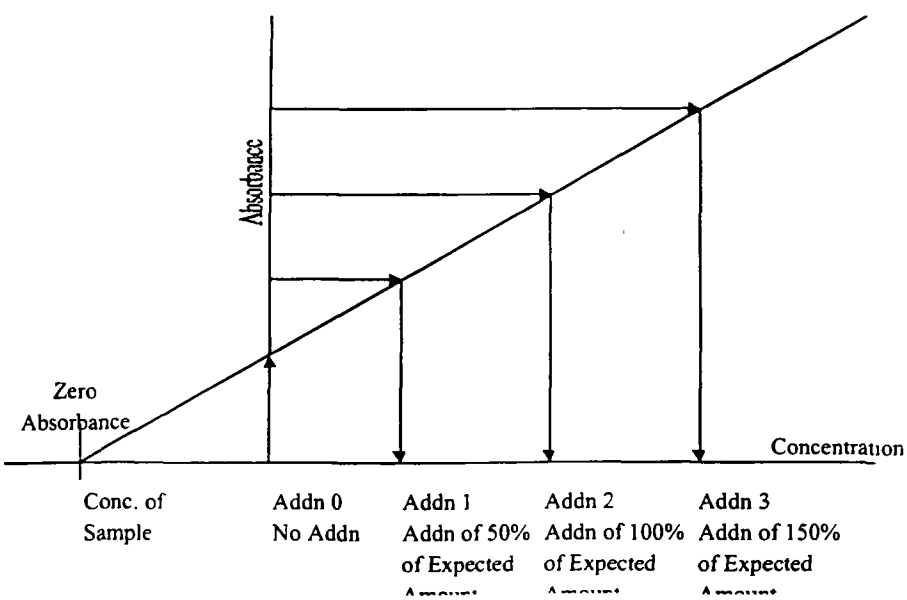
## APPENDIX C. MSA GUIDANCE

### Method of Standard Addition

Four equal volume aliquots of sample are measured and known amounts of standards are added to three aliquots. The fourth aliquot is the unknown and no standard is added to it. The concentration of standard added to the first aliquot should be 50% of the expected concentration. The concentration of standard added to the second aliquot should be 100% of the expected concentration and the concentration of standard added to the third aliquot should be 150% of the expected concentration. The volume of the unspiked and spiked aliquots should be the same (i.e., the volume of the spike added should be negligible in relation to the volume of sample).

To determine the concentration of analyte in the sample, the absorbance (or response) of each solution is determined and a linear regression performed. On the vertical axis the absorbance (or response) is plotted versus the concentrations of the standards on the horizontal axis using 0 as the concentration of the unspiked aliquot. An example plot is shown in Figure 1. When the resulting line is extrapolated back to zero absorbance, the point of interception of the horizontal axis is the concentration of the unknown. Calculate the correlation coefficient (r) and the x-intercept (where y=0) of the curve. The concentration in the digestate is equal to the negative x-intercept.

Figure 1



- For the method of standard additions to be correctly applied, the following limitations must be taken into consideration.
- The plot of the sample and standards must be linear over the concentration range of concern. For best results, the slope of the curve should be similar to that of a plot of the aqueous standard curve.
- The effect of the interference should not vary as the ratio of the standard added to the sample matrix changes.

# APPENDIX D

# TROUBLESHOOTING GUIDE

## APPENDIX D. TROUBLESHOOTING GUIDE

| Problem | Possible Cause |
|---|---|
| Poor or No Absorbance or Sensitivity Check failed | Incorrect wavelength<br>Dirty windows<br>Window loose<br>Etched or dirty optics<br>Wrong lamp<br>Bad lamp<br>Not enough or no sample introduced<br>Empty sample cup<br>Incorrectly made standards<br>Gas leak<br>EDL power supply set on "Continuous" |
| Erratic Readings | Source lamp not aligned properly<br>Lamp not prewarmed<br>Injection tip partially clogged<br>Contaminated reagents<br>Contaminated glassware<br>Drying tube saturated<br>Bad lamp<br>Injection tip hitting outside of tube<br>Injection tip coated or not set properly<br>Leak in sample tubing<br>Power fluctuations<br>Air bubbles in tubing |
| EDL Won't Light | Lamp cable not plugged in<br>Lamp power set at 0<br>Lamp is dead<br>Power supply fuse is blown<br>Short in cord |
| Standards reading twice or half normal absorbance or concentration | Incorrect standard used<br>Incorrect dilution performed<br>Dirty cell |
| Background Correction Light Blinking | Background screen or attenuator faulty |

# APPENDIX E

# CONTAMINATION CONTROL GUIDELINES

## APPENDIX E. CONTAMINATION CONTROL GUIDELINES

**The following procedures are strongly recommended to prevent contamination:**

All work areas used to prepare standards and spikes should be cleaned before and after each use.

All glassware should be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered or Latex Gloves must not be used in the metals laboratory since the powder contains silica and zinc, as well as other metallic analytes. Only vinyl or nitrile gloves should be used in the metals laboratory.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

**The following are helpful hints in the identification of the source of contaminants:**

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Separate glassware if an unusually high sample is analyzed and soak with sulfuric acid prior to routine cleaning.

# APPENDIX F

# PREVENTIVE MAINTENANCE

## APPENDIX F. PREVENTIVE MAINTENANCE

A maintenance log is used to record when maintenance is performed on instruments. When an instrument problem occurs indicate the date, time and instrument number, then identify the problem and corrective action in the maintenance log.

**The following procedures are required to ensure that that the instrument is fully operational.**

**Cold Vapor Atomic Absorption (Leeman PS 200) [1]**

| Daily | Semi-annually | Annually |
|---|---|---|
| Clean lens. | Check Hg lamp intensity. | Change Hg lamp. |
| Check aperture. | | Check liquid/gas separator. |
| Check argon flow. | | |
| Check tubing. | | |
| Check drain. | | |
| Replace drying tube. | | |

**Cold Vapor Atomic Absorption (PE 5000) [1]**

| Daily | Monthly |
|---|---|
| Clean aspirator by flushing with DI water. | Clean cell in aqua regia. |
| Check tubing and replace if needed | Clean aspirator in aqua regia. |
| Clean windows with methanol. | |
| Change silica gel in drying tube | |
| Check argon gas supply. | |
| Adjust lamp. | |

# APPENDIX G

# INSTRUMENT SET UP

# Hg Analysis (Leeman PS200II)

## SYSTEM INITIALIZATION AND WARM UP

1. F1 Menu

2. Instrument

a. TASKMASTER

b. #4 Wake System Up Enter

The warming up period takes approximately 10 minutes.

## TO SET UP INSTRUMENT FOR ANALYSIS

1. F1 Menu

2. Autosampler

   A. Rack Entry

   B. Edit (ex. Rack 1), Enter

   C. Cup ID - Enter (clears sample #'s)

   D. Extended ID- type in matrix of sample (water or solid), Enter.

   E. Press Insert Key and move cursor with arrows to cup ID and begin typing labels.

   F. F3 Print Screen

3. Press F2 Macro key and type in analyst's first name - Enter

   A. Enter folder name - ex. HG0306, Enter. If folder does not exist, type Y - Enter.

   B. Type in - "Rack 1", "Rack 2" etc. , Enter.

C. Type in : FROM CUP TO CUP

Ex. = 1 30

Do the same for position 2 if needed. If not needed, you must

press Enter 3 times to begin analysis.

**STL STANDARD OPERATING PROCEDURE**

**TITLE: CYANIDE PREPARATION METHOD**

**(SUPERSEDES: REVISION 8.1, DATED 03/20/00)**

| | | |
|---|---|---|
| Prepared by: | | 6/5/01 Date |
| Reviewed by: | Technology Specialist | 6/5/01 Date |
| Approved by: | Quality Assurance Manager | 6/5/01 Date |
| Approved by: | Environmental Health and Safety Coordinator | 6/5/01 Date |
| Approved by: | Laboratory Director | 6-5-01 Date |

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## 1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of Total, Amenable, and Free Cyanide in solids, liquids, and waters. It is based on CLP ILM03.3, CLP ILM04.0, SW 846 Method 9012A, EPA 335.1, 335.2, 335.4, Standard Method 4500-CN-I and ASTM D 4282-83. The working linear range is 0.005 - 0.1 mg/L for waters and 0.25 to 5 mg/kg for solids.

1.2. The associated method codes are CLP ILM03.0 (DV), CLP ILM04.0 (OU), SW846 Method 9012A (QP), ASTM D4282-83, EPA 335.1 and 335.2 (CG), EPA 335.4 (O2), and Standard Method 4500-CN-E (A4).

1.3. This document accurately reflects current laboratory standard operating procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary by the laboratory QA department.

## 2. SUMMARY OF METHOD

2.1. The Cyanide, as HCN, is released by distilling/refluxing the sample with strong acid and is trapped in a sodium hydroxide solution.

## 3. DEFINITIONS

3.1. Refer to the glossary in the Laboratory Quality Manual (LQM), latest version.

## 4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2. Oxyidizing agents such as chlorine will decompose most cyanides. Sulfide will distill over with the cyanide and could affect colorimetric, titrimetirc, and electrode procedures. Refer to the preparation section on how to screen and treat samples appropriately.

4.3. Aldehydes convert cyanide to cyanohydrin which could result in the lost of cyanide. If the presence of aldehydes are suspected, stabilize the sample with NaOH at the time of collection and add 2 mL 3.5% ethylenediamine solution per 100 mL of sample.

4.4. Refer to Standard Methods for further information on possible interferences and associated treatments.

## 5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all STL associates.

5.2. Eye protection that satisfies ANSI Z87.1 (per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory. The following specific hazards are known:

5.3.1. The following are known to be **corrosive: sulfamic acid, sodium hydroxide, sulfuric acid, acetic acid.**

5.3.2. Cyanide is a highly toxic compound that must be handled with care. The analyst must be aware of the handling and clean-up techniques before using this material.

5.4. Exposure to chemicals must be maintained **as low as reasonably achievable,** therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.5. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.6. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL associate. The situation must be reported **immediately** to a laboratory supervisor.

## 6. EQUIPMENT AND SUPPLIES

6.1. Cyanide Distillation Apparatus

6.2. Analytical balance, capable of accurately weighing ± 0.0001 g

6.3. Vacuum pump

6.4. Graduated cylinders: various

6.5. Volumetric flasks: various

6.6. Volumetric pipets: various

6.7. Balance: Top loading, capable of accurately weighing ± 0.01 g

6.8. Lead Acetate Indicator Paper

6.9. Potassium Iodide (KI) Indicator Paper

6.10. Erlenmeyer flasks: various

6.11. Buret: Class A 10 mL

6.12. pH strips

6.13. Boiling stones or chips

6.14. Beakers: various

6.15. Snap seal containers: 120 mL

6.16. Plastic bottles with lids: 250mL or 500mL

## 7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. Sulfamic Acid: reagent grade (not used for CLP ILM03.0)

7.1.2. Sulfamic Acid Solution: Add 100 g of sulfamic acid to 800 mL reagent water and dilute to 1 liter with reagent water (not used for CLP ILM03.0)

7.1.3. Ascorbic Acid: reagent grade

7.1.4. Sodium Hydroxide: (NaOH), high purity grade.

7.1.5. Sodium Hydroxide, 1.25 N: Add 50 g of NaOH to 900 mL and dilute to 1 liter with reagent water.

7.1.6. Sodium Hydroxide, 0.25 N: Add 10 g of to 900 mL reagent water and dilute to 1 liter with reagent water.

7.1.7. Sulfuric Acid: ($H_2SO_4$), concentrated

7.1.8. Acetic Acid Solution: Add 10 mL of glacial acetic acid to 90 mL of reagent water.

7.1.9. Magnesium Chloride: ($MgCl_2 \bullet 6H_2O$), reagent grade

7.1.10. Magnesium Chloride Solution: Add 510 g $MgCl_2 \bullet 6H_2O$ to 500 mL reagent water and dilute to 1 liter with reagent water.

7.1.11. Calcium Hypochlorite: [Ca $(OCl)_2$], reagent grade

7.1.12. Calcium Hypochlorite Solution: Add 5 g of $Ca(OCl)_2$ to 100 mL of reagent water.

7.1.13. Methyl Red Indicator: Add 0.05 g of methyl red to 50 mL of glacial acetic acid and dilute to 100 mL with reagent water.

7.1.14. Methyl red reagent grade glacial

7.1.15. Acetic Acid: ($CH_3COOH$), glacial reagent grade

7.1.16. Zinc Acetate: [$Zn(C_2H_3O_2)$], reagent grade

7.1.17. Zinc Acetate Solution: Add 100 g zinc acetate to 800 mL reagent water and dilute to 1 liter with reagent water.

7.1.18. Sodium Acetate: [$NaC_2H_3O_2 \bullet 3H_2O$] reagent grade

7.1.19. Sodium Acetate Buffer: Add 410 g of sodium acetate to 500 mL of reagent water. Adjust the pH to 4.5 using glacial acetic acid and dilute to 1 liter with reagent water.

7.1.20. Rhodanine: reagent grade

7.1.21. 0.0192 N Silver Nitrate: reagent grade

7.1.22. Bismuth nitrate [$Bi(NO_3)_3$]: Dissolve 30 g of $Bi(NO_3)_3$ in 100 mL of reagent water. While stirring, add 250 mL of glacial acetic acid. Stir until dissolved. Dilute to 1 L with reagent water.

7.1.23. Cadmium chloride [$CdCl_2$] – anhydrous : Dissolve 1.0 g $CdCl_2$ in 90 mL of reagent water. Dilute to 100 mL with reagent water to produce a 10 g/L $CdCl_2$ solution.

7.2. Standards

7.2.1. Secondary Source Cyanide Stock Standard, 1000 mg/L: Add 2.51 g of potassium ferricyanide (KCN) and 2.0 g of potassium hydroxide (KOH) to a 1000 mL volumetric flask and dilute to volume with reagent water. Mix well. Prepare fresh every 1 - 3 months.

7.2.2. Note: Cyanide stock standard must be standardized prior to use (See Section 7.3) Working Standards: Add the required amounts of 1.25 N NaOH and cyanide standards to volumetric flasks according to the suggested chart. Dilute to volume using reagent water. See chart below:

| Working Standards | | | | | |
|---|---|---|---|---|---|
| Volume 1.25 N NaOH (mL) | Std Volume (mL) | Std Conc. (mg/L) | Final Volume (mL) | Final Conc. (mg/L) | Expiration Time (Days) |
| 20 | 10 | 1000 | 100 | 100 | 14 |
| 20 | 10 | 100 | 100 | 10 | 7 |
| 20 | 10 | 10 | 100 | 1 | 1 |

7.3. Cyanide Standardization

7.3.2. Using a volumetric pipet, aliquot 10.0 mL of the 1000 ppm stock cyanide standard into an Erlenmeyer flask and add 90 mL of reagent water.

7.3.3. Add 10 drops of Rhodanine indicator.

7.3.4. Titrate with 0.0192 N Silver nitrate until the color changes from yellow to pink/orange.

7.3.5. Calculation:

$$\text{Cyanide, mg/L} = \frac{(A)\ (1000)}{\text{mL cyanide solution}\ (10)}$$

*Where:* *A = mL Titrant for standard*

7.3.6. If the cyanide concentration is not 1000 ppm, adjust concentration accordingly.

## 8. SAMPLE PRESERVATION AND STORAGE

8.1. Solid and liquid samples are not chemically preserved. Water samples are preserved with NaOH to a pH>12. All samples are stored at 4° C ± 2°C in plastic or glass containers.

8.2. The holding time is fourteen days from sampling to analysis.

NOTE: CLP samples holding time is twelve days from receipt to analysis.

## 9. QUALITY CONTROL

9.1. Batch Definition

9.1.1. A batch is a group of no greater than 20 samples excluding QC samples (LCS, Method Blank, MS, MSD) which are processed similarly, with respect to the procedure. All sample setups must be initiated within a 24 hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same process.

9.2. Method Blank (MB)

9.2.1. One method blank (MB) must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest at or above the reporting limit.

9.2.2. A blank consisting of 50 mL reagent water must be prepared and distilled (or diffused, 3 mL) with each analytical batch of samples.

9.2.3. Corrective Action for Blanks

9.2.3.1. If the analyte level in the method blank exceeds the reporting limit for the analytes of interest in the sample, all associated samples are reprepared and reanalyzed. If this is not possible due to limited sample quantity or other considerations, the corresponding sample data **must be addressed in the project narrative.**

9.2.3.2. If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. **Such action must be taken in consultation with the client and must be addressed in the project narrative.**

9.3. Laboratory Control Sample (LCS)

9.3.1. One LCS must be processed with each preparation batch. The LCS must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

9.3.2. A midrange LCS consisting of 2.0 mL of the 1.0 mg/L standard (secondary source) brought to a final volume of 50 mL must be distilled with each analytical batch of samples.

9.3.3. Corrective Action for Laboratory Control Samples

9.3.3.1. If any analyte is outside established control limits the system is out of control and corrective action must occur.

9.3.3.2. Corrective action will be repreparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable.

9.4. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.4.1. One MS/MSD pair must be processed for each batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MSD's. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis.

9.4.2. A MS/MSD consisting of 50 mL or 1.0 g of sample brought up to 50 mL with reagent water and 2.0 mL of the 1.0 mg/L standard (either source) must be distilled with each analytical batch of samples.

9.4.2.1. **Note**: MS for CLP samples require 5 mL of 1.0 mg/l standard (true 100ug/L)

9.4.3. Corrective action for MS/MSDs

9.4.3.1. If the analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch.

9.4.3.2. If the native analyte concentration in the MS/MSD exceeds 4x the spike level for that analyte, the recovery data reported as DIL (diluted out).

9.4.3.3. If an MS/MSD is not possible due to limited sample volume then a laboratory control sample duplicate (LCSD) should be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

9.5 Control Limits

9.5.1 Control limits are established by the laboratory as described in SOP, NC-QA-0018.

9.5.2 Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are listed in the Laboratory Quality Manual (LQM) and the latest is version easily accessible via the LIMs (QC Browser program).

9.6 Method Detection Limits (MDLs) and MDL Checks

9.6.1 MDLs and MDL Checks are established by the laboratory as described in SOP, NC-QA-0021.

9.6.2 MDLs are listed in the Laboratory Quality Manual (LQM) and the latest version is easily accessible via the LIMs (QC Browser program).

9.7 Nonconformance and Corrective Action

9.7.1 Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the facility QA Manager/

## 10. CALIBRATION AND STANDARDIZATION

10.1. For all non-CLP methods, a low and high standard are distilled from the same source as the calibration curve each day. Prepare the low standard (0.025 mg/L) by diluting 0.125 mL of 10.0 mg/L standard with reagent water to a final volume of 50 mL. Prepare the high standard (0.075 mg/L) by diluting 0.375 mL of a 10.0 mg/L standard with reagent water to a final volume of 50mL. Method 9012A *recommends* that the distilled standards (a high and a low) be compared to the curve with a ±10% agreement with the undistilled standards. The distilled standards are evaluated against all applicable batch QC.

## 11. PROCEDURE

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described

11.3 Summary

11.3.1. For all non-CLP methods, the sample is distilled/refluxed under acidic conditions for one hour. For CLP and EPA 335.4 methods, the samples are distilled for one and a half hours. The released HCN is trapped in 0.25 N NaOH solution.

11.4. Sample Preparation Procedure applicable for use with the Midi distillation unit.

11.4.1. Checking for Interferences (For non-CLP samples)

11.4.1.1. Using pH paper strips, check the pH of the sample and record it as >12 or <12 on the analytical logsheet. If pH is <12, the deviation **must be addressed in the project narrative.**

11.4.1.2.For ALL samples (non-CLP and CLP samples): Test each sample for the presence of sulfides using lead acetate paper. If sulfides are present, treat the sample with powdered cadmium carbonate. Yellow cadmium sulfide precipitates if the sample contains sulfide. Repeat this operation until a drop of the treated sample solution does not darken the lead acetate test paper. Filter the solution. Avoid a large excess of cadmium carbonate and long contact time in order to minimize loss by complexation or occlusion of cyanide on the precipitated material.

11.4.2. Complex Cyanide Preparation Procedure [THIS PROCESS IS PERFORMED ONLY WHEN REQUESTED BY THE CLIENT]: Add 100 mL of water sample or 2.0 g of solid sample and 100 mL reagent water to a plastic, sealable container. Add 10 g NaOH pellets. Mix or tumble for 12-16 hours. Allow solids to settle out. Transfer 50 mL of the solution to the distillation tube. Distill sample (See section 11.2.4.1).

**Note**: If the sample requires an MS/MSD or MS/Dup, double or triple the volumes as stated above. A blank and LCS should be prepared and analyzed with samples using 10 g NaOH and 100 mL reagent water.

11.4.3. Amenable Cyanide (Chlorinated Aliquot) [THIS PROCESS IS PERFORMED ONLY WHEN REQUESTED BY THE CLIENT]

11.4.3.1.Place 50 mL (waters) or 1.0 g (solids/liquids) into a beaker. Add 50 mL of reagent water to non-waters. Place the beaker on a stir plate and begin mixing. Test the pH of the solution, if less than 12 add 1.25 N NaOH, drop by drop until pH $\geq$ 12. Drop by drop, add calcium hypochlorite until an excess of chlorine is reached. Test for chlorine excess using KI paper. Allow the sample to chlorinate for one hour. At the end of the chlorination period, add about 0.1 to 0.5 g of ascorbic acid to destroy excess chlorine. Test using KI paper. Keep the addition of ascorbic acid to a minimum. Pour the sample into a distillation flask and follow the total cyanide preparation method (Section 11.2.4). Also set up an unchlorinated aliquot of sample (50 mL or 1.0 g) following the total cyanide method.

11.4.4. Total Cyanide

11.4.4.1. Add 50 mL or 1.0 g of the sample and 2 - 3 boiling chips to the distillation tube. Bring all volumes to 50 mL with reagent water. Add 50 mL of 0.25 N NaOH solution to the absorber tube and assemble the scrubber. Assemble the cyanide distillation apparatus.

NOTE: If solid samples are being prepared under the Michigan program, the initial solid weight is 2.5 g

11.4.4.2. Turn on the cooling water to "60". Turn on the vacuum source and adjust the flow such that even stream of air bubbles are in the scrubber tube approximately $^1/_4$ " of foam or 1-2 bubbles per second. At this time add any spiking solutions to the LCS or MS/MSDs samples directly into the inlet tube.

11.4.4.3. In the order stated, add 2.0 mL sulfamic acid solution (not for CLP ILM03.0 samples), 2.5 mL of concentrated sulfuric acid and 2.0 mL of magnesium chloride solution to the distillation tube. Be sure to rinse the inlet tube sparingly with reagent water between and after reagent additions.

Note: Complex cyanide samples require an additional 2.5 mL of sulfuric acid. Be sure the pH is < 2.

11.4.4.4. Flip the heater switch to "on" and turn the dial to an appropriate setting (according to manufacturer's instructions) to allow the apparatus to warm up. Be sure to adjust the air flow and water as necessary. Heat for one hour. After the heating period, the heater will turn off automatically. Allow to cool for fifteen minutes. Keep the vacuum and cooling water on.

NOTE: For CLP, heat samples for one and a half hours.

11.4.4.5. Disconnect the absorber. Pour solution into a 120 mL snap seal container. Do not rinse the scrubber tube or dilute NaOH in the snap seal. Be sure to properly label the bottles "total" or "amenable" along with sample ID, position and date.

11.4.5. Free Cyanide (Weak and Dissociable) [THIS PROCESS IS PERFORMED ONLY WHEN REQUESTED BY THE CLIENT]

11.4.5.1. Add 50 mL or 1.0 g of sample to the distillation tube. Bring all volumes up to 50 mL with reagent water. Add 50 mL of 0.25 N NaOH to the absorber tube and assemble.

11.4.5.2. Turn on cooling water to "60". Turn on the vacuum source. Add any spiking standards to the appropriate LCS or MS/MSDs at this time. Through the inlet tube, add 1.0 mL of sodium acetate buffer, 1.0 mL of zinc acetate, and 0.25 mL of methyl red indicator. Rinse the inlet tube sparingly with reagent water between and after reagent additions. If the sample is not red, carefully add 1:9 acetic acid dropwise until the sample does turn red.

11.4.5.3. Flip on the heater switch and turn the dial to "10.5" (This allows the apparatus to warm up). Adjust the air flow and water as needed. Heat for 1 hour. After the

heating period, the heater will shut off automatically. Allow the sample to cool for fifteen minutes with the air and water on.

11.4.5.4. Pour the scrubber contents into a 120 mL snap seal bottle. Do not rinse the scrubber. Label the bottle well and be sure to denote that it is a "free" sample distillate.

11.4.6 Cyanide Unit Clean-up

11.4.6.1 Cyanide distillation unit glassware is very fragile and expensive. It must be handled with care at all times.

11.4.6.2 Disassemble each set-up and rinse the sample down the drain with large amounts of water. Be sure to collect the solids in a screen and dispose of properly.

11.4.6.3 Wash each set-up with soap and hot water, and then rinse with 1:1 HCl. Rinse several times with reagent water. **After preparing samples found to be extremely high in cyanide, a subsequent rinse with 1.0N NaOH, followed by further rinsing with reagent water can help rinse away any residual cyanide.

11.4.6.4 Re-assemble the set-up.

11.4.6.5 Be sure to wash each set up as a separate unit and replace in the same position.

11.4.6.6 If a sample of known high cyanide concentration was distilled in a certain position, be sure to change the appropriate tubing on that position.

11.5 Analytical Documentation

11.5.1 Record all analytical information in the analytical logbook/logsheet, including the analytical data from standards, blanks, LCSs, MS/MSDs, and any corrective actions or modifications to the method.

11.5.2 All standards are logged into a department standard logbook. All standards are assigned an unique number for identification. Logbooks are reviewed by the supervisor or designee.

11.5.3 Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

11.5.4 Sample results and associated QC are entered into the LIMs after final technical review.

## 12. DATA ANALYSIS AND CALCULATIONS

12.1. Not applicable

## 13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file and corresponding method detection limit files.

13.2. Training Qualifications:

13.2.1. The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

13.2.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files

## 14. POLLUTION PREVENTION

14.1. Using a Midi Cyanide distillation unit saves time and requires less sample and reagents for use.

## 15. WASTE MANAGEMENT

15.1. Acid waste must be collected in clearly labeled acid waste cans.

15.2. Solid waste materials (soil, gloves, soiled paper products, etc.) are placed in the solid debris container. Do not put liquids in the solid waste container.

15.3. Refer to the Laboratory Sample and Waste Disposal plan

15.4. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of STL. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by an annual refresher training.

## 16. REFERENCES

16.1. References.

16.1.1. SW846, Test Methods for Evaluating Solid Waste, Third Edition, Total and Amenable Cyanide, Automated UV; Method 9012A.

16.1.2. EPA 600; Cyanide, Total and Cyanide, Amenable to Chlorination; Methods 335.1 and 335.2

16.1.3. Standard Methods for the Examination of Water and Wastewater, Eighteenth Edition; Weak and Dissociable Cyanide; Method 4500-CN-I

16.1.4. Standard Methods for the Examination of Water and Wastewater, Eighteenth Edition; Complex Cyanide; Method 4500-CN-E

16.1.5. USEPA CLP SOW ILM03.0 Section D-Cyanide Midi Distillation

16.1.6. Corporate Quality Management Plan (QMP), current version

16.1.7. STL Laboratory Quality Manual (LQM), current version

16.2. Associated SOPs and Policies, latest version

16.2.1. QA Policy, QA-003

16.2.2 Glassware Washing, NC-QA-0014

16.2.3 Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018

16.2.4 Method Detection Limits and Instrument Detection Limits, NC-QA-0021

16.2.5 Navy/Army SOP, NC-QA-0016

16.2.6 Cyanide, Automated Method NC-WC-0031

## 17. MISCELLANEOUS (TABLES, APPENDICES, ETC...)

17.1. BASF RFI Requirements

17.1.1. Amendments to this SOP to satisfy BASF RCRA Facility Investigation (RFI) requirements are based on comments from US EPA upon review of site requirements and laboratory procedures.

17.1.2. Amendment to the preparation of **all** samples

17.1.2.1. **Section 7.2.1**: Change 2.51 g of potassium cyanide to 2.11g potassium ferricyanide.

17.1.2.2. **Section 9.4**: The matrix spike/duplicate frequency has been increased from one per batch to one per 7 samples. Consult with the project manger for specific samples to be spiked. The goal is to spike each sampling area at the site at least once.

17.1.3. Amendment to the preparation of **Prussian blue area** samples

17.1.3.1. **Section 7.1.22**: Sodium thiocyanate (reagent grade): Prepare a spiking solution at a concentration 100X greater than the measured cyanide for the appropriate Prussian blue area samples.

17.1.3.2. **Section 9.5**: Three Prussian blue area samples will be spiked with 1 mL of the sodium thiocyanate solution (Section 17.1.3.1) in order to assess the potential impact of thiocyanate in the original samples on the measured cyanide concentration. These matrix spikes do not replace the cyanide matrix spikes mentioned above (Section 17.1.2.2). The increase (if any) in measured cyanide concentration relative to the original sample shall be reported as "percentage increase" using the following equation:

$$\%CN_{increase} = \frac{Conc_{SCN\_spike} - Conc_{unspiked}}{Conc_{unspiked}} \times 100$$

*where*

$Conc_{SCN\_spike}$ = *cyanide concentration measured in the thiocyanate spiked sample*

$Conc_{unspiked}$ = *cyanide concentration measured in the unspiked sample*

Note: Section 11.3.2.1 of NC-WC-0031 addresses sulfide testing and precipitation.

17.2. Method Deviation (9012A, 335.1, 335.2)

17.2.1. The reflux distillation apparatus used is the midi distillation.

17.2.2. The volume of sample used is reduced to 50 mL vs. 500 mL using the midi-distillation apparatus.

17.2.3. Method of Standard Addition is not performed for samples with matrix interference (sulfides).

APPENDIX A

Cyanide Distillation Form

(Example)

APPENDIX A

N:\WET-LOG\CYANIDE

QUANTERRA- NORTH CANTON
CYANIDE DISTILLATION LOGSHEET

PAGE 1 OF 2

Batch No. 0040131 waters 0040130 Leach
Prep/Anal. Date 000209 000209
Start Time: 2 30 pm

LCS&MS/MSD No. CY0117
LCS Prep Date: 000208
End Time: 3:30 pm

SDG No. —
Analyst: MFG

| Pos. | Sample No. | Type T | C | F | Sample Volume | Final Volume(mL) | pH >12 | S | Cl2 | Comments |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 C | PBK | T | C | F | 50ml | 50ml | — | — | — | D8CDF B/C |
| 2 | LCS | T | C | F | | | — | — | — | 2ml CY0117 1ppm 2° |
| 3 | LCSD | T | C | F | | | — | — | — | ↓ D8CDE 0040130 |
| 4 | .025 | T | C | F | | | — | — | — | .125ml CY0105 10ppm 1° |
| 5 | .075 | T | C | F | | | — | — | — | .375ml CY0105 10ppm 1° |
| 6 | D833X | T | C | F | | | ✓ | ✓ | ✓ | |
| 7 | D833X MS | T | C | F | | | — | — | — | 2ml CY0117 1 ppm 2° |
| 8 | D833X MSD | T | C | F | | | — | — | — | |
| *9 | D8516 MS | T | C | F | | | — | — | — | |
| *10 | D8516 MSD | T | C | F | | | — | — | — | |
| *1 A | D8516 | T | C | F | | | ✓ | ✓ | ✓ | |
| *2 | D851K | T | C | F | | | ✓ | ✓ | ✓ | |
| *3 | leach blk | T | C | F | | | ✓ | ✓ | ✓ | D8CDE 1.01 0040130 |
| 4 | D81MG | T | C | F | | | ✓ | ✓ | ✓ | |
| 5 | D81MK -- | T | C | F | | | ✓ | ✓ | ✓ | |
| 6 | D81ML | T | C | F | | | ✓ | ✓ | ✓ | |
| 7 | D83RM | T | C | F | | | ✓ | ✓ | ✓ | |
| 8 | D833H | T | C | F | | | ✓ | ✓ | ✓ | |
| 9 | D833P | T | C | F | | | ✓ | ✓ | ✓ | |
| 10 | D83R1 | T | C | F | | | ✓ | ✓ | ✓ | |

Type: T=Total C= Chlorinated F= Free
S and Cl2 column- a check mark in these columns means the sample was checked for this interference.
If the interference is present, the analyst will address this in the comments section.

* leaches came down on 2.4.00

Level Review X I II
Calibration
Calculation
Date: 2.8.00 Sign:

Level Review X I
✓ Calibration
✓ Calculation
Date: 2.8.00 Sign:

Rev 5-16-97

APPENDIX A

N:\WET-LOG\CYANIDE

QUANTERRA- NORTH CANTON
CYANIDE DISTILLATION LOGSHEET

PAGE 2 OF 2

Batch No. 0040131 waters 0040130 leaches
Prep/Anal. Date 000208 / 000209
Start Time: 2:30 pm

LCS&MS/MSD No. CN0117
LCS Prep Date: 000208
End Time: 3:30 pm

SDG No. —
Analyst: MFE

| Pos. | Sample No. | Type T | C | F | Sample Volume | Final Volume(mL) | pH >12 | S | Cl2 | Comments |
|---|---|---|---|---|---|---|---|---|---|---|
| B 1X | D83R6 | (T) | C | F | 50 ml | 50 ml | ✓ | ✓ | ✓ | |
| 2 | D83R8 | (T) | C | F | \| | \| | ✓ | ✓ | ✓ | |
| 3 | D856F | (T) | C | F | \| | \| | ✓ | ✓ | ✓ | |
| 4 | D856Q | (T) | C | F | \| | \| | ✓ | ✓ | ✓ | |
| 5 | | T | C | F | | | | | | |
| 6 | | T | C | F | | | | | | |
| 7 | | T | C | F | | | | | | |
| 8 | | T | C | F | | | | | | |
| 9 | | T | C | F | | | | | | |
| 10 | | T | C | F | | | | | | |
| 1B | | T | C | F | | | | | | |
| 2 | | T | C | F | | | | | | |
| 3 | | T | C | F | | | | | | |
| 4 | | T | C | F | MFE 000308 | | | | | |
| 5 | | T | C | F | | | | | | |
| 6 | | T | C | F | | | | | | |
| 7 | | T | C | F | | | | | | |
| 8 | | T | C | F | | | | | | |
| 9 | | T | C | F | | | | | | |
| 10 | | T | C | F | | | | | | |

Type: T=Total C= Chlorinated F= Free

S and Cl2 column- a check mark in these columns means the sample was checked for this interference.

If the interference is present, the analyst will address this in the comments section.

Level Review: X
Calibration: X
Calculation: [illegible]
Date: 2-8-00 Sign: [illegible]

Level Review: X
Calibration: ✓
Calculation: ✓
Date: 2-8-00 Sign: [illegible]

# STL NORTH CANTON STANDARD OPERATING PROCEDURE

## TITLE: CYANIDE AUTOMATED, PYRIDINE-BARBITURIC ACID METHOD

**(SUPERSEDES: REVISION 6 DATED 06/28/99)**

| | | |
|---|---|---|
| Prepared by: | | 5/31/01 Date |
| Reviewed by: | Technology Specialist | 5/31/01 Date |
| Approved by: | Quality Assurance Manager | 5/31/01 Date |
| Approved by: | Environmental Health and Safety Coordinator | 5-31-01 Date |
| Approved by: | Laboratory Director | 5-31-01 Date |

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# STL NORTH CANTON STANDARD OPERATING PROCEDURE

## TITLE: CYANIDE AUTOMATED, PYRIDINE-BARBITURIC ACID METHOD

## (SUPERSEDES: REVISION 6 DATED 06/28/99)

Prepared by: _____
Date

Reviewed by: _____
Technology Specialist Date

Approved by: _____
Quality Assurance Manager Date

Approved by: _____
Environmental Health and Safety Coordinator Date

Approved by: _____
Laboratory Director Date

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## 1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of Total, Amenable, and Free Inorganic Cyanide in solids, liquids, and waters. It is based on CLP ILM03.0, CLP ILM04.0, SW846 Method 9012A, 335.2, 335.4 and Standard Method 4500-CN-E. The working linear range is 0.005 - 0.1 mg/L for waters and 0.25 to 5 mg/kg for solids.

1.2. This document accurately reflects current laboratory standard operating procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary by the laboratory QA department.

1.3. The associated method codes are CLP ILM03.0 (DV), CLP ILM04.0 (OU), SW846 Method 9012A (QP), ASTM D4282-83, EPA 335.1 and 335.2 (CG), EPA 335.4 (O2), and Standard Method 4500-CN-E (A4).

## 2. SUMMARY OF METHOD

2.1. The Cyanide, as HCN, is released by distilling/refluxing the sample with strong acid and is trapped in a sodium hydroxide solution.

2.2. The sodium hydroxide solution is analyzed colormetrically on an autoanalyzer using the pyridine-barbituric acid method.

## 3. DEFINITIONS

3.1. Refer to the glossary in the Laboratory Quality Manual (LQM), latest version.

## 4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2. Sulfides interfere, but can be eliminated by treating the sample with cadmium carbonate prior to analysis.

## 5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all STL associates.

5.2. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned.

5.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory. The following specific hazards are known:

5.3.1. The following materials are known to be **corrosive: Sodium Hydroxide**

5.3.2. Cyanide is a highly toxic compound that must be handled with care. The analyst must be aware of the handling techniques.

5.4. Exposure to chemicals must be maintained **as low as reasonably achievable**, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.5. It is recommended that neat standards be purchased only as a last resort. The preparation of standards from neat materials and reagents {as well as glassware cleaning procedures that involved solvents such as methylene chloride} should be conducted in a fume hood with the sash closed as far as the operations will permit.

5.6. Standards in solution may be diluted in the open laboratory when syringes and the like are utilized.

5.7. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL associate. The situation must be reported **immediately** to a laboratory supervisor.

## 6. EQUIPMENT AND SUPPLIES

6.1. Traacs 800 autoanalyzer

6.2. Probe 0.016"

6.3. Flowcell 10nm

6.4. Wavelength cell 570nm

6.5. Manifold-Multitest cartridge with cyanide tubing

6.6. 125 mL Erlenmeyer flasks

6.7. 100 mL, 250 mL, 1000 mL volumetric flasks

6.8. Volumetric pipettes: various

6.9. Top loading balance: capable of accurately weighing ± 0.01g.

## 7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. Cadmium carbonate: powder

7.1.2. 1.25 N sodium hydroxide: Add 50 g of sodium hydroxide pellets (NaOH) to a 1 liter volumetric flask and dilute to volume with reagent water.

7.1.3. Phosphate buffer: Add 136 g of potassium phosphate - monobasic ($KH_2PO_4$) and 2.8 g of sodium phosphate – dibasic anhydrous ($Na_2HPO_4$) to 800 mL of reagent water in a 1 liter volumetric flask. Mix, bring to volume with reagent water. Add 3-5 drops of Brij-35 to 100 mL of Buffer prior to using.

7.1.4. Chloramine-T reagent: Add 1.0 g of chloramine-T to a 250 mL volumetric flask and dilute to volume with reagent water. Prepare fresh daily.

7.1.5. Pyridine reagent: Add 15.0 g of barbituric acid to a 1 liter volumetric flask. Add 75 mL of pyridine and 15 mL of concentrated hydrochloric acid (HCl) and mix. Bring to volume with reagent water and store at 4°C ± 2°C in an amber glass bottle.

7.1.6. 0.25 N sodium hydroxide: Add 200 mL of N NaOH to a 1 liter volumetric flask and dilute to volume with reagent water.

7.1.7. Brij-35

7.1.8. 30% Brij solution: Add 2 mL Brij-35 to 1000 mL reagent water.

7.1.9. Rhodanine indicator, purchased.

7.1.10. 0.0192 N silver nitrate, purchased

7.2. Standards

7.2.1. Primary Source Cyanide Stock Standard, 1000 mg/L: Add 2.51 g of potassium cyanide (KCN) and 2.0 g of potassium hydroxide (KOH) to a 1000 mL volumetric flask and dilute to volume with reagent water. Mix well and store in glass amber container. Stable for 1-3 months.

Note: This stock standard must be standardized prior to use. See Appendix I.

7.2.2. Secondary Source Cyanide Standard, 1000 mg/L: Follow 7.2.1 using an alternate source of Potassium Cyanide (KCN).

Note: This stock standard must be standardized prior to use. See Appendix I.

7.2.3. Calibration Standards (Water and Solid Matrices)

7.2.3.1. Pipet the appropriate amount of cyanide standard into 100 mL volumetric. Add 20 mL 1.25N NaOH to each calibration standard (except the 1.0 mg/L) and bring to volume with reagent water. Prepare weekly.

| Concentration CN- | mL CN- | Final Volume |
|---|---|---|
| 100 mg/L | 10 mL of 1000 mg/L | 100 mL |
| 10 mg/L | 10 mL of 100 mg/L | 100 mL |
| 1.0 mg/L | 10 mL of 10 mg/L | 100 mL |
| *0.1 mg/L | 10 mL of 1 mg/L | 100 mL |
| *0.05 mg/L | 5 mL of 1 mg/L | 100 mL |
| *0.025 mg/L | 25 mL of 0.1 mg/L | 100 mL |
| *0.01 mg/L | 10 mL of 0.1 mg/L | 100 mL |
| *0.005 mg/L | 10 mL of 0.05 mg/L | 100 mL |

*Denotes calibration standards

NOTE: The 1 ppm CN standard is only good for the day it is prepared and is not preserved with NaOH.

## 8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Solid and liquid samples are not chemically preserved. Water samples are preserved with NaOH to a pH > 12. All samples are stored at 4°C ± 2°C in plastic or glass containers.

8.2. The holding time is fourteen days from sampling to analysis.

*NOTE: Holding time for CLP is twelve days from receipt to analysis.

## 9. QUALITY CONTROL

9.1. Batch Definition

9.1.1. A batch is a group of no greater than 20 samples excluding QC samples (LCS, Method Blank, MS, MSD) which are processed similarly, with respect to the procedure. All sample setups must be initiated within a 24 hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same processes.

9.2. Method Blank

9.2.1. One method blank (MB) must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest at or above the reporting limit.

9.2.2. CLP

9.2.2.1. Each SDG (sample delivery group) must have one method blank (MB) processed per matrix and per twenty samples. If the SDG is distilled over multiple "racks", the method blanks must be distilled with the samples. If more than one SDG is on one rack, process one method blank per SDG and per matrix. The solid method blank is called "PBS" (prep blank solid) and the water method blank is called "PBW" (prep blank water).

**NOTE:** A "rack" is one setup of cyanide samples and QC, and can encompass 1-3 of the midi-distillation units.

9.2.3. A reagent water blank consisting of 50 mL reagent water must be distilled and analyzed with each analytical batch of samples. See SOP NC-WC-0032 for distillation instructions.

9.2.4. Corrective Action for Blanks

9.2.4.1. If the analyte level in the method blank exceeds the reporting limit for the analytes of interest in the sample, all associated samples are reprepared and reanalyzed. If this is not possible due to limited sample quantity or other considerations, the corresponding sample data **must be addressed in the project narrative.**

9.2.4.2. If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. **Such action must be taken in consultation with the client and must be addressed in the project narrative.**

9.3. Laboratory Control Sample (LCS)

9.3.1. One LCS from an independent source must be processed with each preparation batch. The LCS must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

9.3.2. A midrange LCS consisting of a 0.04 mg/L (2.0 mL of 1.0 mg/L to 50 mL) must be distilled and analyzed with each analytical batch of samples. See SOP NC-WC-0032 for distillation instruction.

9.3.3. The acceptance limits for drinking water samples is 90 – 110%. This is also the same value for CLP.

9.3.4. CLP

9.3.4.1. A LCS (which doubles as an ICV) is processed with each "rack". Even if multiple SDG's are on the "rack", only one LCS (ICV) needs to be distilled.

9.3.4.2.For solids process a solid LCS per SDG. The value for this LCS changes as the solid lot number changes each time a new one is ordered. The value is noted on the product certification. If more than one SDG is processed on a "rack", process a solid LCS for each one. If a SDG has solid sample distilled on a different "rack", then additional solid LCS's will need to be distilled.

9.3.5. Corrective Action for LCS

9.3.5.1.If any analyte is outside established control limits the system is out of control and corrective action must occur.

9.3.5.2.Corrective action will be repreparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable.

9.4. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.4.1. One MS/MSD pair must be processed for each batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MSD's. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis.

9.4.2. A MS/MSD consisting of 50 mL or 1.0 g sample and 0.04 mg/L spike (2.0 mL of 1.0 mg/L to 50 mL) will be distilled and analyzed with every batch. See SOP NC-WC-0032 for distillation instructions. This is also the same value for CLP.

9.4.3. The acceptance limits for drinking water samples is 90 – 110%.

9.4.4. Corrective action for MS/MSDs

9.4.4.1.If the analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch.

9.4.4.2.If the native analyte concentration in the MS/MSD exceeds 4x the spike level for that analyte, the recovery data is reported as DIL (diluted out).

9.4.4.3.If an MS/MSD is not possible due to limited sample volume then a laboratory control sample duplicate (LCSD) should be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

9.4.5. CLP

9.4.5.1. Each SDG must have a sample duplicate and a matrix spike processed per matrix. Sometimes this requirement is waived by the client or PM but, if uncertain, make sure that these are done. Usually , the sample to be spiked is assigned, but not always. If a MS/MSD is created in receiving, either batch the MSD and "N/A" the result or have the MSD deleted. In either case, create a sample duplicate for the sample that is spiked when batching. If processin a SDG over more than one "rack", then there is no need to process additional matrix spikes and sample duplicates from "rack" (unless specifically requested). Typically, only one spiked/duped sample is required per SDG, even if the SDG is distilled over different days.

9.4.5.2.Matrix spike for CLP consists of 50 mL or 1.0 g of sample and 100 µg/L spike (5.0 mL of 1.0 mg/L standard).

9.5. QC Acceptance Criteria

9.5.1. Control limits are established by the laboratory as described in NC-QA-0018.

9.5.2. Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are listed in the Laboratory Quality Manual (LQM) and the latest is version easily accessible via the LIMs (QC Browser program.).

9.6. Method Detection Limits (MDLs) and MDL Checks

9.6.1. MDLs and MDL Checks are established by the laboratory as described in SOP, NC-QA-0021.

9.6.2. MDLs are listed in the Laboratory Quality Manual (LQM) and the latest version is easily accessible via the LIMs (QC Browser program).

9.7. Nonconformance and Corrective Action

9.7.1. Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the facility QA Manager.

## 10. CALIBRATION AND STANDARDIZATION

10.1. Summary

10.1.1. The instrument is calibrated using five cyanide standards and a blank at the time of analysis.

10.2. Initial Calibration

10.2.1. The instrument is calibrated at the beginning of each run and is verified at the beginning of the run by using a midrange ICV. The correlation coefficient of the original curve must be $\geq$ 0.995 or recalibration is required.

10.3. Continuing Calibration

10.3.1. The run is checked every ten samples and at the end of the run using a midrange CCV to verify continued linearity. It cannot vary from the original curve by more than ± 15% or recalibration is required. The previous 10 samples must be reanalyzed and bracketed by a CCV that passes criteria. The CCV is composed of the 0.025 ppm secondary standard.

10.3.2. System cleanliness is checked every ten samples and at the end of the run using a CCB. It cannot contain the analyte of interest above the reporting limit or recalibration is required. The previous 10 samples must be reanalyzed and bracketed by a CCB that passes criteria. The CCB is 0.25N NaOH.

**NOTE**: Base and gain values may change with new reagents, standards, tubing changes, or board cleaning. These values are for reference only.

10.4. High and Low Standard

10.4.1. The distillation technique is checked by distilling a high and low standard and comparing the values obtained to the standard curve. If the percent recovery is not within ± 10%, the analyst will submit a Nonconformance Memo for the analytical run.

10.4.2. If the percent recovery is outside ±15%, the standard and samples will be redistilled and analyzed.

## 11. PROCEDURE

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.3. Sample Preparation

11.3.1. See cyanide distillation SOP: NC-WC-0032.

11.3.1.1.The sample is distilled/refluxed under acidic conditions for one hour. The released HCN is trapped in 50 mL of 0.25 N NaOH solution. EPA Method 335.4 says to reflux for one and a half hours.

NOTE: CLP samples are distilled for one and a half hours.

11.3.2. Sample Preparation Procedure

11.3.2.1.All Samples:Test each sample for the presence of sulfides using lead acetate paper. If sulfides are present, treat the sample with powdered cadmium carbonate. Yellow cadmium sulfide precipitates if the sample contains sulfide. Repeat this operation until a drop of the treated sample solution does not darken the lead acetate test paper. Filter the solution. Avoid a large excess of cadmium carbonate and long contact time in order to minimize loss by complexation or occlusion of cyanide on the precipitated material

11.4. Sample Analysis

11.4.1. Summary

11.4.1.1.The sample distillates are analyzed on the autoanalyzer for cyanide using the automated pyridine-barbituric method.

11.4.2. Recommended Instrument Conditions

11.4.2.1.See Manufacturer's information for operation instructions.

11.4.2.2.Start Up Solutions (and Wash Solutions)

11.4.2.2.1.All lines in 0.25N NaOH solution:

11.4.2.2.2.Then all lines in 30% Brij solution.

11.4.2.3.Running Solutions

11.4.2.3.1.Two DI water lines (orange/green) in 30% Brij solution

11.4.2.3.2.Red/Red in pyridine reagent

11.4.2.3.3.Orange/red in chloramine-T reagent

11.4.2.3.4.White/white in phosphate buffer solution

11.4.2.4.Base and Gain

11.4.2.4.1.Performed on the 0.1 mg/L standard

11.4.2.4.2.Approximate values: Base = 75 Gain = 150

*These values are for reference only and may change with new reagent or standard preparations.

11.4.2.5.Trouble shooting for poor Base and Gain or baseline noise

11.4.2.5.1.Place reagent lines 1-3 back in Brig solution and run on high for five minutes. Place all 5 lines (1-5) and probe line in 1.25 N NaOH solution and run on high for five minutes. Place lines back in appropriate "start-up" solutions and run on high for five minutes.

Place lines back in reagents and perform another base and gain when the baseline has stabilized.

11.4.3. Sample Analysis Procedure

11.4.3.1.See Manufacturer's information for operating instructions.

11.4.3.2.A calibration curve is analyzed at the beginning of each run. The correlation coefficient must be > 0.995 to continue.

11.4.3.3.CCV's and CCB's are analyzed at the beginning, end, and between every 10 samples. CCV's must be prepared from a secondary source.

11.4.3.4.Sample distillates higher than the highest calibration standard (0.1 mg/L) must be diluted with 0.25 N NaOH and re-analyzed.

11.4.3.5.Any samples analyzed after a high sample must be re-analyzed if carryover is suspected.

11.4.3.6.CLP

11.4.3.6.1. If more than one SDG is distilled on one rack, they may be analyzed together. Each SDG should have its own method blank(s), its own LCS-S (if samples are solids), and its own sample duplicate and matrix spike. If the SDG has been split over multiple distillation "racks", then you may not have a duped/spiked sample for each batch. You should have method blanks and, if solids, LCS's for each batch. An ICV (LCS) is distilled with each "rack". If more than one SDG is distilled on a "rack", then the ICV (LCS) distilled with that rack must be analyzed with the samples. If the samples from a multiple SDG "rack" are analyzed together, then the ICV needs to be analyzed only once; if they are analyzed on different runs, then the ICV (LCS) needs to be analyzed with each run.

11.4.3.7.Tray Protocol (Run Order)

**Normal Tray Protocol**

1. Calibration
2. ICV (CCV)
3. ICB (CCB)
4. MD
5. LCS
6. UP to 8 more samples
7. CCV
8. CCB
9. Up to 10 samples
10. CCV
11. CCb

**CLP Tray Protocol**

12. Calibration
13. Distilled ICV (LCS)
14. ICB
15. CCV
16. CCB
17. PBW
18. PBS (If solids are in SDG)

19. LCS-S (If solids are in SDG)

20. Sample

21. Sample duplicate

22. Sample MS

23. Sample MS @ 2x dilution

24. Sample A-spiked*

25. Up to 2 more samples

26. CCV

27. CCb

28. Up to ten more samples

29. CCV

30. CCb

*A-spike = 2 mL of sample + 2mL of A-spike solution

A-spike solution = 0.8 mL .25N NaOH. +3.2 mL 0.05 ppm 1° standard

11.5. Analytical Documentation

11.5.1. Record all analytical information in the analytical logbook/logsheet, including the analytical data from standards, blanks, LCSs. MS/MSDs, and any corrective actions or modifications to the method.

11.5.2. All standards are logged into a department standard logbook. All standards are assigned an unique number for identification. Logbooks are reviewed by the supervisor or designee.

11.5.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

11.5.4. Sample results and associated QC are entered into the LIMs after final technical review.

## 12. DATA ANALYSIS AND CALCULATIONS

12.1. $$\textit{Total Cyanide, mg / L} = \frac{\textit{mg / L } CN^- \textit{ from printout x 50}}{\textit{mL of sample distilled}} \textit{ x D}$$

12.2. $$\textit{Total Cyanide, mg / kg} = \frac{\textit{mg / L } CN^- \textit{ from printout x 50}}{\textit{g of sample distilled.}} \textit{ x D}$$

12.3. $$\textit{Amenable Cyanide, mg / L} = \textit{Total } CN^- \textit{ (mg / L) - Chlorinated } CN^- \textit{ (mg / L)}$$

*Where:*

*mg/L* = *can also be mg/kg*

*D* = $$\textit{Dilution Factor} = \frac{\textit{Final Volume of Dilution}}{\textit{Volume of Sample Distillate Used}}$$

*NOTE: Free cyanide has the same calculations as Total cyanide*

12.4. LCS Recovery:

$$\frac{\textit{Instrument Value}}{\textit{0.04(true)}} \textit{ x 100} = \textit{\% Recovery}$$

12.5. CCV Recovery:

$$\frac{\textit{Instrument Value}}{\textit{0.025 (true)}} \textit{ x 100} = \textit{\% Recovery}$$

*NOTE: CCV recovery must be between 85 - 115% for data to be acceptable. If CCV recovery is not within these limits, reanalysis is required 335.4 says 10%.*

12.6. *MS/MSD Recovery for Waters and solids:*

$$\frac{A - B}{0.040\ (true)} \times 100 = \%\ Recovery$$

*Where:*

*A* = *Instrument value MS/MSD*

*B* = *Sample instrument value*

## 13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file and corresponding method detection limit files.

13.2. Training Qualifications:

13.2.1. The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

13.2.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

## 14. POLLUTION PREVENTION

14.1. This method does not contain any specific modifications that serve to minimize or prevent pollution.

## 15. WASTE MANAGEMENT

15.1. All distillates can be rinsed down the drain with large amounts of water unless they contain high levels of Cyanide. If they are highly concentrated, they must be disposed of in the liquid waste container.

15.2. Solvent waste must be disposed of in clearly labeled waste cans.

15.3. Acid waste must be collected in clearly labeled acid waste containers.

15.4. Solid materials (gloves, soiled paper products, etc.) are placed in the solid debris container. Do not put liquids in the solid waste container.

15.5. Refer to the Laboratory Sample and Waste Disposal plan.

15.6. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of STL. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by an annual refresher training.

## 16. REFERENCES

16.1. References

16.1.1. SW846, Test Methods for Evaluating Solid Waste Method 9012 A, and its updates

16.1.2. EPA 600; Cyanide, Total and Cyanide, Amenable to Chlorination; Methods 335.2, March 1983

16.1.3. Standard Methods for the Examination of Water and Wastewater, Eighteenth Edition: Weak and Dissociable Cyanide; Method 4500-CN-E

16.1.4. USEPA CLP SOW ILM03.0 and ILM04.0, Section D - Cyanide Midi Distillation

16.1.5. Corporate Quality Management Plan (QMP), current version.

16.1.6. STL Laboratory Quality Manual (LQM), current version

16.2. Associated SOPs and Policies, latest version

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-0014

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018

16.2.4. Method Detection Limits and Instrument Detection Limits, NC-QA-0021

16.2.5. Navy/Army SOP, NC-QA-0016

16.2.6. NC-WC-0032, Cyanide Preparation Method

## 17. MISCELLANEOUS (TABLES, APPENDICES, ETC...)

17.1. Reporting limits

17.1.1. The reporting limit (RL) is 0.01 mg/L for waters (50 mL used) and 0.50 mg/kg for solids (1.0 g used). The reporting limit for solid samples performed only under the Michigan program is 200 µg/kg for solids (2.5 g used). The lowest level of the calibration curve can be used as the reporting limit upon request.

17.1.2. If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

17.2. Troubleshooting guide for poor Base and Gain or baseline noise

17.2.1. Place reagent lines 1-3 back in Brig solution and run on high for five minutes. Place all 5 lines (1-5) and probe line in 1.25 N NaOH solution and run on high for five minutes. Place lines back in appropriate "start-up" solutions and run on high for five minutes.

Place lines back in reagents and perform another base and gain when the baseline has been stabilized.

17.3. Method Deviation (9012A335.2)

17.3.1. Method of Standard Addition is not performed for samples with matrix interference (sulfides).

Appendix I - Cyanide Standardization

1. Pipet 10.0 mL of the 1000 ppm stock cyanide standard into a 250 mL Erlenmeyer flask and add 90 mL of reagent water.

2. Add 0.5 mL (10 drops) of Rhodanine indicator.

3. Titrate with 0.0192 N silver nitrate (using a micro burette) until the color changes from yellow to pink/orange.

4. Titrate a blank (100 mL reagent water) following steps 2 and 3.

5. Calculation:

$$\text{Cyanide, mg/L} = \frac{(A - B)\,(1000)}{\text{mL Cyanide Solution (10)}}$$

*Where:*

*A = mL titrant for standard*

*B = mL titrant for blank*

6. If the cyanide concentration is not 1000 ppm, adjust concentration accordingly.

ATTACHMENT 2

EXAMPLE FIELD FORMS

CONESTOGA-ROVERS & ASSOCIATES
JOB NAME: Waukegan Manufactured Gas and Coke Plant
JOB NO: 19023
PRESERVED? YES NO (Circle)

$HNO_3$ HCl NaOH $H_2SO_4$ NaOH/ZnOAc Other

MONTH/DAY/YEAR: _____ TIME: _____

SAMPLE ID: _____

SAMPLER'S SIGNATURE: _____

LAB SAMPLE ID: _____

# EXAMPLE SAMPLE LABEL

CRA
CONESTOGA-ROVERS & ASSOCIATES
8615 West Bryn Mawr Ave. Chicago, IL 60631

# EXAMPLE CUSTODY SEAL

**CRA**
CONESTOGA-ROVERS & ASSOCIATES
8615 W. Bryn Mawr Avenue
Chicago, Illinois 60631 (773)380-9933

# CHAIN OF CUSTODY RECORD

SHIPPED TO (Laboratory Name):

REFERENCE NUMBER:

PROJECT NAME:

SAMPLER'S SIGNATURE: _____ PRINTED NAME: _____

| SEQ. No. | DATE | TIME | SAMPLE No. | SAMPLE MATRIX | No. OF CONTAINERS | PARAMETERS | | | | | | | | | | REMARKS |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
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| | | | TOTAL NUMBER OF CONTAINERS | | | | | | | | | | | | | |

EXAMPLE

| | | | |
|---|---|---|---|
| RELINQUISHED BY: ① _____ | DATE: TIME: | RECEIVED BY: ② _____ | DATE: TIME: |
| RELINQUISHED BY: ② _____ | DATE: TIME: | RECEIVED BY: ③ _____ | DATE: TIME: |
| RELINQUISHED BY: ③ _____ | DATE: TIME: | RECEIVED BY: ④ _____ | DATE: TIME: |

METHOD OF SHIPMENT: AIR BILL No.

White —Fully Executed Copy
Yellow —Receiving Laboratory Copy
Pink —Shipper Copy
Goldenrod —Sampler Copy

SAMPLE TEAM: _____ _____

RECEIVED FOR LABORATORY BY: _____

DATE: _____ TIME: _____

5258

1001(FORMS)-OCT 24/96-REV.0-(C)(F-01)

FedEx Express USA Airbill

FedEx Tracking Number 831889446147

SPG13

Form I.D. No. 0215

**1 From** *Please print and press hard.*

Date Example

Sender's FedEx Account Number [redacted]

Sender's Name Joe Sampler Phone (773) 380-9933

Company CONESTOGA-ROVERS & ASSOC INC

Address 8615 W BRYN MAWR AVE

Dept./Floor/Suite/Room

City CHICAGO State IL ZIP 60631

**2 Your Internal Billing Reference**
First 24 characters will appear on invoice.

**3 To**

Recipient's Name Sample Receiving Phone (330) 497-0772

Company STL

Address 4101 Shuffel Drive, NW

To "HOLD" at FedEx location, print FedEx address. We cannot deliver to P.O. boxes or P.O. ZIP codes.

Dept./Floor/Suite/Room

City North Canton State OH ZIP 44720

By using this Airbill you agree to the service conditions on the back of this Airbill and in our current Service Guide, including terms that limit our liability.

**Questions? Visit our Web site at fedex.com**
or call 1.800.Go.FedEx® 800.463.3339.

0198317575

**4a Express Package Service** *Packages up to 150 lbs.*
Delivery commitment may be later in some areas.

- [x] FedEx Priority Overnight — Next business morning
- [ ] FedEx Standard Overnight — Next business afternoon
- [ ] FedEx First Overnight — Earliest next business morning delivery to select locations
- [ ] FedEx 2Day — Second business day
- [ ] FedEx Express Saver — Third business day
- [ ] FedEx Extra Hours — Later drop-off with next business afternoon delivery for select locations

FedEx Envelope rate not available. Minimum charge: One pound rate

**4b Express Freight Service** *Packages over 150 lbs.*
Delivery commitment may be later in some areas.

- [ ] FedEx 1Day Freight* — Next business day
- [ ] FedEx 2Day Freight — Second business day
- [ ] FedEx 3Day Freight — Third business day

* Call for Confirmation: _____

**5 Packaging** * Declared value limit $500

- [ ] FedEx Envelope*
- [ ] FedEx Pak* — Includes FedEx Small Pak, FedEx Large Pak, and FedEx Sturdy Pak
- [x] Other Pkg: — Includes FedEx Box, FedEx Tube, and customer pkg.

**6 Special Handling**

- [ ] SATURDAY Delivery — FedEx Priority Overnight and FedEx 2Day to select ZIP codes
- [ ] HOLD Weekday at FedEx Location — FedEx First Overnight
- [ ] HOLD Saturday at FedEx Location — FedEx Priority Overnight and FedEx 2Day to select locations

Does this shipment contain dangerous goods?

- [ ] No
- [ ] Yes — As per attached Shipper's Declaration
- [ ] Yes — Shipper's Declaration not required
- [ ] Dry Ice — Dry Ice, 9, UN 1845 _____ x _____ kg

Dangerous Goods (incl. Dry Ice) cannot be shipped in FedEx packaging or with FedEx Extra Hours service.

- [ ] Cargo Aircraft Only

**7 Payment** *Bill to:*

- [ ] Sender — Acct. No. in Section 1 will be billed.
- [ ] Recipient
- [ ] Third Party
- [ ] Credit Card
- [ ] Cash/Check

FedEx Acct No / Credit Card No _____ Exp. Date _____

| Total Packages | Total Weight | Total Declared Value† |
|---|---|---|
| | | $ _____ 00 |

†Our liability is limited to $100 unless you declare a higher value. See back for details.

FedEx Use Only

**8 Release Signature** *Sign to authorize delivery without obtaining signature.*

By signing you authorize us to deliver this shipment without obtaining a signature and agree to indemnify and hold us harmless from any resulting claims.

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