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HANFORD ENVIRONMENTAL ANALYTICAL METHODS
(METHODS AS OF MARCH 1990)

APPENDIX A3-0 AND APPENDIX A3-I

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May 1993

Prepared for
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

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HANFORD ENVIRONMENTAL ANALYTICAL METHODS
Appendix A3-0
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PNL/325: Organic

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A3-0.30	SOW 2/88 D 14/VOA	GC/MS of Volatiles	Volatile Organics
A3-0.40	SOW 2/88 D 5/SV	Sample Storage and Preparation	Semivolatile Organics
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A3-0.70	SOW 2/88 D 5/PEST	Sample Storage and Preparation	Pesticides and PCBs
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SECTION II

SAMPLE PREPARATION AND STORAGE

PART A - SAMPLE STORAGE AND HOLDING TIMES

1. Procedures for Sample Storage

- 1.1 The samples must be protected from light and refrigerated at 4°C ($\pm 2^\circ\text{C}$) from the time of receipt until analysis or extraction.

2. Contract Required Holding Times

- 2.1 VOA analysis of water or soil/sediment samples must be completed within 10 days of VTSR.

PART B - PROTOCOLS FOR HEXADECANE EXTRACTION OF VOLATILES FROM WATER AND SOIL/SEDIMENT FOR OPTIONAL SCREENING

1. Summary of Method

WATER - a 40 ml aliquot of sample is extracted with 2 ml of hexadecane. This provides a minimum quantitation limit (MQL) of:

<u>Compounds</u>	<u>MQL ug/L</u>
non-halogenated aromatics	40- 50
halogenated methanes	800-1000
halogenated ethanes	400- 500

SOIL/SEDIMENT - Forty mL of reagent water are added to 10 g (wet weight) of soil and shaken. The water phase is in turn extracted with 2 mL of hexadecane. This provides a minimum quantitation limit of approximately four times higher than those listed for water.

The hexadecane extraction and screening protocols for purgeables are optional. These protocols are included to aid the analyst in deciding whether a sample is low or medium level. The use of these or other screening protocols could prevent saturation of the purge and trap system and/or the GC/MS system. It is recommended that these or other screening protocols be used, particularly if there is some doubt about the level of organics in a sample. This is especially true in soil/sediment analysis.

2. Limitations

These extraction and preparation procedures were developed for rapid screening of water samples from hazardous waste sites. The design of the methods thus does not stress efficient recoveries or low limits of quantitation. Rather, the procedures were designed to screen at moderate recovery and sufficient sensitivity for a broad spectrum of organic chemicals. The results of the analyses thus may reflect only a minimum of the amount actually present in some samples. This is especially true if water soluble solvents are present.

3. Interferences

- 3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the total ion current profiles. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks. 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 and diversity of the site being sampled.

4. Apparatus and Materials

- 4.1 Vials and caps, 2 mL for GC auto sampler.

- 4.2 Volumetric flask, 50 mL with ground glass stopper.
- 4.3 Pasteur pipets, disposable.
- 4.4 Centrifuge tube, 50 mL with ground glass stopper or Teflon-lined screw cap.
- 4.5 Balance - Analytical, capable of accurately weighing ± 0.0001 g.

5. Reagents

- 5.1 Hexadecane and methanol - pesticide residue analysis grade or equivalent.
- 5.2 Reagent water - Reagent water is defined as water in which an interferent is not observed at the CRQL of each parameter of interest.
- 5.3 Standard mixture #1 containing benzene, toluene, ethyl benzene and xylene. Standard mixture #2 containing n-nonane and n-dodecane.
 - 5.3.1 Stock standard solutions (1.00 ug/uL)- Stock standard solutions can be prepared from pure standard materials or purchased as certified solutions.
 - 5.3.1.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in methanol dilute to volume in a 10 mL volumetric flask. Larger volumes can be used at the convenience of the analyst. If compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard.
 - 5.3.1.2 Transfer the stock standard solutions into multiple Teflon-sealed screw-cap vials. Store, with no head-space, at -10°C to -20°C , and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. These solutions must be replaced after six months, or sooner if comparison with quality control check samples indicates a problem. Standards prepared from gases or reactive compounds such as styrene must be replaced after two months, or sooner if comparison with quality control check samples indicates a problem.
 - 5.3.2 Prepare working standards of mixtures #1 and #2 at 100 ng/uL of each compound in methanol. Store these solutions as in 5.3.1.2 above.

6. Sample Extraction

6.1 Water

6.1.1 Allow the contents of the 40 mL sample vial to come to room temperature. Quickly transfer the contents of the 40 mL sample vial to a 50 mL volumetric flask. Immediately add 2.0 mL of hexadecane, cap the flask, and shake vigorously for 1 minute. Let phases separate. Open the flask and add sufficient reagent water to bring the hexadecane layer into the neck of the flask.

6.1.2 Transfer approximately 1 mL of the hexadecane layer to a 2.0 mL GC vial. If an emulsion is present after shaking the sample, break it by:

- o pulling the emulsion through a small plug of Pyrex glass wool packed in a pipet, or
- o transferring the emulsion to a centrifuge tube and centrifuging for several minutes.

6.1.3 Add 200 μ L of working standard mixture #1 and #2 to separate 40 mL portions of reagent water. Follow steps 6.1.1 - 6.1.2 beginning with the immediate addition of 2.0 mL of hexadecane.

6.2 Soil/Sediment

6.2.1 Add approximately 10 g of soil (wet weight) to 40 mL of reagent water in a 50 mL centrifuge tube with a ground glass stopper or teflon-lined cap. Cap and shake vigorously for one minute. Centrifuge the capped flask briefly. Quickly transfer supernatant water to a 50 mL volumetric flask equipped with a ground glass stopper.

6.2.2 Follow 6.1, starting with the addition of 2.0 mL of hexadecane.

7. Sample Analysis

The sample is ready for GC/FID screening. Proceed to Section III, Optional Screening of Hexadecane Extracts for Volatiles.

SECTION III

**OPTIONAL SCREENING OF HEXADECANE
EXTRACTS FOR VOLATILES**

1. Summary of Method

- 1.1 The hexadecane extracts of water and soil/sediment are screened on a gas chromatograph/flame ionization detector (GC/FID). The results of the screen will determine if volatile organics are to be analyzed by low or medium level GC/MS procedures if the sample is a soil/sediment, or to determine the appropriate dilution factor if the sample is water.

2. Apparatus and Materials

- 2.1 Gas chromatograph - An analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including syringes, analytical columns, gases, detector, and strip-chart recorder. A data system is recommended for measuring peak areas.

2.1.1 Above-described GC, equipped with flame ionization detector.

2.1.2 GC column - 3 m x 2 mm ID glass column packed with 10% OV-101 on 100-120 mesh Chromosorb W-HP (or equivalent). The column temperature should be programmed from 80°C to 280°C at 16°C/min. and held at 280°C for 10 minutes.

3. Reagents

- 3.1 Hexadecane - pesticide residue analysis grade or equivalent.

4. Limitations

- 4.1 The flame ionization detector varies considerably in sensitivity when comparing aromatics and halogenated methanes and ethanes. Halomethanes are approximately 20 X less sensitive than aromatics and haloethanes approximately 10 X less sensitive. Low molecular weight, water soluble solvents e.g. alcohols and ketones, will not extract from the water, and therefore will not be detected by the GC/FID.

- 4.2 Following are two options for interpreting the GC/FID chromatogram.

4.2.1 Option A is to use standard mixture #1 containing the aromatics to calculate an approximate concentration of the aromatics in the sample. Use this information to determine the proper dilution for purge and trap if the sample is a water or whether to use the low or medium level GC/MS purge and trap methods if the sample is a soil/sediment (see Table 1, paragraph 6.2.1.3 for guidance). This should be the best approach, however, the aromatics may be absent or obscured by higher concentrations of other purgeables. In these cases, Option B may be the best approach.

4.2.2 Option B is to use standard mixture #2 containing nonane and dodecane to calculate a factor. Use the factor to calculate a dilution for purge and trap of a water sample or to determine whether to use the low or medium level GC/MS purge and trap methods for soil/sediment samples (see Table 1, paragraph

6.2.1.3 for guidance). All purgeables of interest have retention times less than the n-dodecane.

5. Extract Screening

- 5.1 External standard calibration - Standardize the GC/FID each 12 hr. shift for half scale response. This is done by injecting 1-5 uL of the extracts that contain approximately 10 ng/uL of the mix #1 and mix #2 compounds, prepared in paragraph 5.3.1 of Section II, Part B. Use the GC conditions specified in 2.1.2.
- 5.2 Inject the same volume of hexadecane extract as the extracted standard mixture in 5.1. Use the GC conditions specified in 2.1.2.

6. Analytical Decision Point

6.1 Water

- 6.1.1 Compare the chromatograms of the hexadecane extract of the sample with those of the reagent blank and extract of the standard.
- 6.1.1.1 If no peaks are noted, other than those also in the reagent blank, analyze a 5 mL water sample by purge and trap GC/MS.
- 6.1.1.2 If peaks are present prior to the n-dodecane and the aromatics are distinguishable, follow Option A (4.2.1).
- 6.1.1.3 If peaks are present prior to the n-dodecane but the aromatics are absent or indistinguishable, use Option B as follows: If all peaks are $\leq 3\%$ of the n-nonane, analyze a 5 mL water sample by purge and trap GC/MS. If any peaks are $\geq 3\%$ of the n-nonane, measure the peak height or area of the major peak and calculate the dilution factor as follows:

$$\frac{\text{peak area of sample major peak}}{\text{peak area of n-nonane}} \times 50 = \text{dilution factor}$$

The water sample will be diluted using the calculated factor just prior to purge and trap GC/MS analysis.

6.2 Soil/Sediment

- 6.2.1 Compare the chromatograms of the hexadecane extract of the sample with those of the reagent blank and extract of the standard.
- 6.2.1.1 If no peaks are noted, other than those also in the reagent blank, analyze a 5 g sample by low level GC/MS.

- 6.2.1.2 If peaks are present prior to the n-dodecane and the aromatics are distinguishable, follow Option A (paragraph 4.2.1) and the concentration information in Table 1, paragraph 6.2.1.3, to determine whether to analyze by low or medium level method.
- 6.2.1.3 If peaks are present prior to the n-dodecane but the aromatics are absent or indistinguishable, use Option B as follows: Calculate a factor using the following formula:

$$\frac{\text{peak area of sample major peak}}{\text{peak area of n-nonane}} = X \text{ Factor}$$

Table 1 - Determination of GC/MS Purge & Trap Method

<u>X Factor</u>	<u>Analyze by</u>	<u>Approximate Concentration Range* (ug/kg)</u>
0-1.0	low level method	0-1,000
>1.0	medium level method	>1,000

* This concentration range is based on the response of aromatics to GC/FID. When comparing GC/FID responses, the concentration for halomethanes is 20X higher, and that for haloethanes 10X higher.

6.3 Sample Analysis

Proceed to Section IV, GC/MS Analysis of Volatiles.

SECTION IV

**GC/MS ANALYSIS
OF VOLATILES**

1. Summary of Methods

1.1 Water samples

An inert gas is bubbled through a 5 mL sample contained in a specifically designed purging chamber at ambient temperature. The purgeables are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the purgeables are trapped. After purging is completed, the sorbent column is heated and backflushed with the inert gas to desorb the purgeables onto a gas chromatographic column. The gas chromatograph is temperature programmed to separate the purgeables which are then detected with a mass spectrometer.

An aliquot of the sample is diluted with reagent water when dilution is necessary. A 5 mL aliquot of the dilution is taken for purging.

1.2 Soil/Sediment Samples

1.2.1 Low Level. An inert gas is bubbled through a mixture of a 5 g sample and reagent water contained in a suggested specially designed purging chamber (illustrated in Figure 5) at elevated temperatures. The purgeables are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the purgeables are trapped. After purging is completed, the sorbent column is heated and backflushed with the inert gas to desorb the purgeables onto a gas chromatographic column. The gas chromatograph is temperature programmed to separate the purgeables which are then detected with a mass spectrometer.

1.2.2 Medium Level. A measured amount of soil is extracted with methanol. A portion of the methanol extract is diluted to 5 mL with reagent water. An inert gas is bubbled through this solution in a specifically designed purging chamber at ambient temperature. The purgeables are effectively transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the purgeables are trapped. After purging is completed, the sorbent column is heated and backflushed with the inert gas to desorb the purgeables onto a gas chromatographic column. The gas chromatograph is temperature programmed to separate the purgeables which are then detected with a mass spectrometer.

2. Interferences

2.1 Impurities in the purge gas, organic compounds out-gassing from the plumbing ahead of the trap, and solvent vapors in the laboratory account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks as described in Exhibit E. The use of non-TFE tubing, non-TFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

- 2.2 Samples can be contaminated by diffusion of volatile organics (particularly fluorocarbons and methylene chloride) through the septum seal into the sample during storage and handling. A holding blank prepared from reagent water and carried through the holding period and the analysis protocol serves as a check on such contamination. One holding blank per case should be analyzed. Data must be retained by laboratory and made available for inspection during on-site evaluations.
- 2.3 Contamination by carry-over can occur whenever high level and low level samples are sequentially analyzed. To reduce carryover, the purging device and sampling syringe must be rinsed with reagent water between sample analyses. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of reagent water to check for cross contamination. For samples containing large amounts of water soluble materials, suspended solids, high boiling compounds or high purgeable levels, it may be necessary to wash out the purging device with a detergent solution, rinse it with distilled water, and then dry it in a 105°C oven between analyses. The trap and other parts of the system are also subject to contamination; therefore, frequent bakeout and purging of the entire system may be required.
- 2.4 The laboratory where volatile analysis is performed should be completely free of solvents.
3. Apparatus and Materials
- 3.1 Micro syringes - 25 μ L and larger, 0.006 inch ID needle.
- 3.2 Syringe valve - two-way, with Luer ends (three each), if applicable to the purging device.
- 3.3 Syringe - 5 mL, gas tight with shut-off valve.
- 3.4 Balance-Analytical, capable of accurately weighing ± 0.0001 g. and a top-loading balance capable of weighing ± 0.1 g.
- 3.5 Glassware
- 3.5.1
- o Bottle - 15 mL, screw cap, with Teflon cap liner.
 - o Volumetric flasks - class A with ground-glass stoppers.
 - o Vials - 2 mL for GC autosampler.
- 3.6 Purge and trap device - The purge and trap device consists of three separate pieces of equipment; the sample purger, trap and the desorber. Several complete devices are now commercially available.
- 3.6.1 The sample purger must be designed to accept 5 mL samples with a water column at least 3 cm deep. The gaseous head space between the water column and the trap must have a total volume of less than 15 mL. 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. The sample purger, illustrated in Figure 1, meets these design criteria. Alternate sample purge devices may be utilized provided equivalent performance is demonstrated.

- 3.6.2 The trap must be at least 25 cm long and have an inside diameter of at least 0.105 inch. The trap must be packed to contain the following minimum lengths of absorbents: 15 cm of 2,6-diphenylene oxide polymer (Tenax-GC 60/80 mesh) and 8 cm of silica gel (Davison Chemical, 35/60 mesh, grade 15, or equivalent). The minimum specifications for the trap are illustrated in Figure 2.
- 3.6.3 The desorber should be capable of rapidly heating the trap to 180°C. The polymer section of the trap should not be heated higher than 180°C and the remaining sections should not exceed 220°C during bakeout mode. The desorber design, illustrated in Figure 2, meets these criteria.
- 3.6.4 The purge and trap device may be assembled as a separate unit or be coupled to a gas chromatograph as illustrated in Figures 3 and 4.
- 3.6.5 A heater or heated bath capable of maintaining the purge device at 40°C $\pm$ 1°C.

3.7 GC/MS system

- 3.7.1 Gas chromatograph - An analytical system complete with a temperature programmable gas chromatograph suitable for on-column injection and all required accessories including syringes, analytical columns, and gases.
- 3.7.2 Column - 6 ft long x 0.1 in ID glass, packed with 1 $\frac{1}{2}$ SP-1000 on Carbopack B (60/80 mesh) or equivalent. NOTE: Capillary columns may be used for analysis of volatiles, as long as the Contractor uses the instrumental parameters in EPA Method 524.2 as guidelines, uses the internal standards and surrogates specified in this contract, and demonstrates that the analysis meets all of the performance and QA/QC criteria contained in this contract.
- 3.7.3 Mass spectrometer - Capable of scanning from 35 to 260 amu every 3 seconds or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode and producing a mass spectrum which meets all the criteria in Table 2 when 50 ng of 4-bromofluorobenzene (BFB) is injected through the gas chromatograph inlet.
- 3.7.4 GC/MS interface - Any gas chromatograph to mass spectrometer interface that gives acceptable calibration points at 50 ng or less per injection for each of the parameters of interest and achieves all acceptable performance criteria (Exhibit E) may be used. Gas chromatograph to mass spectrometer interfaces

constructed of all-glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane.

- 3.7.5 Data system - A computer system must be interfaced to the mass spectrometer 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 abundance in any EICP between specified time or scan number limits.

4. Reagents

- 4.1 Reagent water - Reagent water is defined as water in which an interferent is not observed at or above the CRQL of the parameters of interest.
- 4.1.1 Reagent water may be generated by passing tap water through a carbon filter bed containing about 453 g of activated carbon (Calgon Corp., Filtrasorb-300 or equivalent).
- 4.1.2 A water purification system (Millipore Super-Q or equivalent) may be used to generate reagent water.
- 4.1.3 Reagent water may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the temperature at 90°C, bubble a contaminant-free inert gas through the water for one hour. While still hot, transfer the water to a narrow-mouth screw-cap bottle and seal with a Teflon-lined septum and cap.
- 4.2 Sodium thiosulfate - (ACS) Granular.
- 4.3 Methanol - Pesticide quality or equivalent.
- 4.4 Stock standard solutions - Stock standard solutions may be prepared from pure standard materials or purchased and must be traceable to EMSL/LV supplied standards. Prepare stock standard solutions in methanol using assayed liquids or gases as appropriate.
- 4.4.1 Place about 9.8 mL of methanol into a 10.0 mL tared ground glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes or until all alcohol wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.
- 4.4.2 Add the assayed reference material as described below.
- 4.4.2.1 Liquids - Using a 100 uL syringe, immediately add two or more drops of assayed reference material to the flask then reweigh. The liquid must fall

directly into the alcohol without contacting the neck of the flask.

- 4.4.2.2 Gases - To prepare standards for any of the four halocarbons that boil below 30°C (bromomethane, chloroethane, chloromethane, and vinyl chloride), fill a 5 mL valved gas-tight syringe with the reference standard to the 5.0 mL mark. Lower the needle to 5 mm above the methanol meniscus. Slowly introduce the reference standard above the surface of the liquid. The heavy gas rapidly dissolves in the methanol. This may also be accomplished by using a lecture bottle equipped with a Hamilton Lecture Bottle Septum (#86600). Attach Teflon tubing to the side-arm relief valve and direct a gentle stream of gas into the methanol meniscus.
- 4.4.3 Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in micrograms per microliter from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared standards may be used at any concentration if they are certified by the manufacturer. Commercial standards must be traceable to EMSL/LV-supplied standards.
- 4.4.4 Transfer the stock standard solution into multiple Teflon-sealed screw-cap bottles. Store with no headspace at -10°C to -20°C and protect from light. Once one of the bottles containing the standard solution has been opened, it may be used for at most one week.
- 4.4.5 Prepare fresh standards every two months for gases or for reactive compounds such as styrene. All other standards must be replaced after six months, or sooner if comparison with check standards indicates a problem.
- 4.5 Secondary dilution standards - Using stock standard solutions, prepare secondary dilution standards in methanol that contain the compounds of interest, either singly or mixed together. (See GC/MS Calibration in Exhibit E). Secondary dilution standards should be stored with minimal headspace and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.
- 4.6 Surrogate standard spiking solution. Prepare stock standard solutions for toluene-d₈, p-bromofluorobenzene, and 1,2-dichloroethane-d₄ in methanol as described in paragraph 4.4. Prepare a surrogate standard spiking solution from these stock standards at a concentration of 250 ug/10 mL in methanol.

4.7 Purgeable Organic Matrix Standard Spiking Solution

- 4.7.1 Prepare a spiking solution in methanol that contains the following compounds at a concentration of 250 ug/10.0 mL:

Purgeable Organics
1,1-dichloroethene
trichloroethene
chlorobenzene
toluene
benzene

- 4.7.2 Matrix spikes also serve as duplicates; therefore, add an aliquot of this solution to each of two portions from one sample chosen for spiking.

- 4.8 BFB Standard - Prepare a 25 ng/uL solution of BFB in methanol.

- 4.9 Great care must be taken to maintain the integrity of all standard solutions. Store all standard solutions at -10°C to -20°C in screw-cap amber bottles with teflon liners.

5. Calibration

- 5.1 Assemble a purge and trap device that meets the specification in paragraph 3.6. Condition the trap overnight at 180°C in the purge mode with an inert gas flow of at least 20 cm³/min. Daily, prior to use, condition the traps for 10 minutes while backflushing at 180°C with the column at 220°C.

- 5.2 Connect the purge and trap device to a gas chromatograph. The gas chromatograph must be operated using temperature and flow rate parameters equivalent to those in paragraph 7.1.2. Calibrate the purge and trap-GC/MS system using the internal standard technique (paragraph 5.3).

- 5.3 Internal standard calibration procedure. The three internal standards are bromochloromethane, 1,4-difluorobenzene, and chlorobenzene-d₅, at 50 ug/L at time of purge. Separate initial and continuing calibrations must be performed for water samples, and medium level soil samples.

- 5.3.1 Prepare calibration standards at a minimum of five concentration levels for each TCL parameter and each surrogate compound. The concentration levels are specified in Exhibit E. Standards may be stored up to 24 hours, if held in sealed vials with zero headspace at -10°C to -20°C and protected from light. If not so stored, they must be discarded after an hour.

- 5.3.2 Prepare a spiking solution containing each of the internal standards using the procedures described in paragraphs 4.4 and 4.5. It is recommended that the secondary dilution standard be prepared at a concentration of 25 ug/mL of each internal standard compound. The addition of 10 uL of this standard to

5.0 mL of sample or calibration standard would be equivalent of 50 ug/L.

- 5.3.3 Tune the GC/MS system to meet the criteria in Exhibit E by injecting BFB. Analyze each calibration standard, according to paragraph 7, adding 10 uL of internal standard spiking solution directly to the syringe. Tabulate the area response of the characteristic ions against concentration for each compound and internal standard and calculate relative response factors (RRF) for each compound using equation 1.

$$\text{EQ. 1} \quad \text{RRF} = \frac{A_x}{A_{Is}} \times \frac{C_{Is}}{C_x}$$

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 from Exhibit E.

C_{Is} - Concentration of the internal standard.

C_x - Concentration of the compound to be measured.

- 5.3.4 The average relative response factor ($\overline{\text{RRF}}$) must be calculated for all compounds. A system performance check must be made before this calibration curve is used. Five compounds (the system performance check compounds) are checked for a minimum average relative response factor. These compounds (the SPCC) are chloromethane, 1,1-dichloroethane, bromoform, 1,1,2,2-tetrachloroethane, and chlorobenzene. Six compounds (the calibration check compounds, CCC) are used to evaluate the curve. These compounds (the CCC) are 1,1-Dichloroethene, Chloroform, 1,2-Dichloropropane, Toluene, Ethylbenzene, and Vinyl Chloride. Calculate the % Relative Standard Deviation (%RSD) of RRF values over the working range of the curve. A minimum %RSD for each CCC must be met before the curve is valid.

$$\% \text{RSD} = \frac{\text{Standard deviation}}{\text{mean}} \times 100$$

See instructions for Form VI, Initial Calibration Data for more details.

- 5.3.5 Check of the calibration curve must be performed once every 12 hours. These criteria are described in detail in the instructions for Form VII, Continuing Calibration Check. (see Exhibit B, Section III). The minimum relative response factor for the system performance check compounds must be checked. If this criteria is met, the relative response factor of all

compounds are calculated and reported. A percent difference of the daily relative response factor (12 hour) compared to the average relative response factor from the initial curve is calculated. The maximum percent difference allowed for each compound flagged as 'CCC' in Form VII is checked. Only after both these criteria are met can sample analysis begin.

- 5.3.6 Internal standard responses and retention times in all standards must be evaluated during or immediately after data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the latest daily (12 hour) calibration standard, the chromatographic system must be inspected for malfunctions, and corrections made as required. The extracted ion current profile (EICP) of the internal standards must be monitored and evaluated for each standard. If the EICP area for any internal standard changes by more than a factor of two (-50% to +100%), the mass spectrometric system must be inspected for malfunction and corrections made as appropriate. When corrections are made, re-analysis of samples analyzed while the system was malfunctioning is necessary.

6: GC/MS Operating Conditions

- 6.1 These performance tests require the following instrumental parameters:

Electron Energy:	70 Volts (nominal)
Mass Range:	35 - 260
Scan Time:	to give at least 5 scans per peak and not to exceed 3 seconds per scan.

7. Sample Analysis

7.1 Water Samples

- 7.1.1 All samples and standard solutions must be allowed to warm to ambient temperature before analysis.
- 7.1.2 Recommended operating conditions for the gas chromatograph
Packed column conditions: Carbowax B (60/80 mesh) with 1% SP-1000 packed in a 6 foot by 2 mm ID glass column with helium carrier gas at a flow rate of 30 cm³/min. Column temperature is isothermal at 45°C for 3 minutes, then programmed at 8°C per minute to 220°C and held for 15 minutes. Injector temperature is 200-225°C. Source temperature is set according to the manufacturer's specifications. Transfer line temperature is 250-300°C. The recommended carrier gas is helium at 30 cm³/sec. (See EPA Method 5.2.4.2 for capillary column condition.)
- 7.1.3 After achieving the key ion abundance criteria, calibrate the system daily as described in Exhibit E.

- 7.1.4 Adjust the purge gas (helium) flow rate to 25-40 cm³/min. Variations from this flow rate may be necessary to achieve better purging and collection efficiencies for some compounds, particularly chloromethane and bromoform.
- 7.1.5 Remove the plunger from a 5 mL syringe and attach a closed syringe valve. Open the sample or standard bottle which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. This process of taking an aliquot destroys the validity of the sample for future analysis so if there is only one VOA vial, the analyst should fill a second syringe at this time to protect against possible loss of sample integrity. This second sample is maintained only until such a time when the analyst has determined that the first sample has been analyzed properly. Filling one 20 mL syringe would allow the use of only one syringe. If a second analysis is needed from the 20 mL syringe, it must be analyzed within 24 hours. Care must also be taken to prevent air from leaking into the syringe.
- 7.1.6 The purgeable organics screening procedure (Section III), if used, will have shown the approximate concentrations of major sample components. If a dilution of the sample was indicated, this dilution shall be made just prior to GC/MS analysis of the sample. All steps in the dilution procedure must be performed without delays until the point at which the diluted sample is in a gas tight syringe.
- 7.1.6.1 The following procedure will allow for dilutions near the calculated dilution factor from the screening procedure:
- 7.1.6.1.1 All dilutions are made in volumetric flasks (10 mL to 100 mL).
- 7.1.6.1.2 Select the volumetric flask that will allow for the necessary dilution. Intermediate dilutions may be necessary for extremely large dilutions.
- 7.1.6.1.3 Calculate the approximate volume of reagent water which will be added to the volumetric flask selected and add slightly less than this quantity of reagent water to the flask.
- 7.1.6.1.4 Inject the proper aliquot from the syringe prepared in paragraph 7.1.5 into the volumetric flask. Aliquots of less than 1 mL increments are prohibited. Dilute the flask to the

mark with reagent water. Cap the flask, invert, and shake three times.

- 7.1.6.1.5 Fill a 5 mL syringe with the diluted sample as in paragraph 7.1.5.
- 7.1.6.1.6 If this is an intermediate dilution, use it and repeat above procedure to achieve larger dilutions.
- 7.1.7 Add 10.0 μ L of the surrogate spiking solution (4.6) and 10.0 μ L of the internal standard spiking solution (5.3.2) through the valve bore of the syringe, then close the valve. The surrogate and internal standards may be mixed and added as a single spiking solution. The addition of 10 μ L of the surrogate spiking solution to 5 mL of sample is equivalent to a concentration of 50 μ g/L of each surrogate standard.
- 7.1.8 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber.
- 7.1.9 Close both valves and purge the sample for 11.0 ± 0.1 minutes at ambient temperature.
- 7.1.10 At the conclusion of the purge time, attach the trap to the chromatograph, adjust the device to the desorb mode, and begin the gas chromatographic temperature program. Concurrently, introduce the trapped materials to the gas chromatographic column by rapidly heating the trap to 180°C while backflushing the trap with an inert gas between 20 and 60 cm^3/min for four minutes. If this rapid heating requirement cannot be met, the gas chromatographic column must be used as a secondary trap by cooling it to 30°C (or subambient, if problems persist) instead of the recommended initial temperature of 45°C.
- 7.1.11 While the trap is being desorbed into the gas chromatograph, empty the purging chamber. Wash the chamber with a minimum of two 5 mL flushes of reagent water to avoid carryover of pollutant compounds.
- 7.1.12 After desorbing the sample for four minutes, recondition the trap by returning the purge and trap device to the purge mode. Wait 15 seconds, then close the syringe valve on the purging device to begin gas flow through the trap. The trap temperature should be maintained at 180°C. Trap temperatures up to 220°C may be employed, however the higher temperature will shorten the useful life of the trap. After approximately seven minutes, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When cool, the trap is ready for the next sample.
- 7.1.13 If the initial analysis of a sample or a dilution of a sample has concentration of TCL compounds that exceeds the initial

calibration range, the sample must be reanalyzed at a higher dilution. **Note:** For total xylenes, where three isomers are quantified as two peaks, the calibration range of each peak should be considered separately, e.g., a diluted analysis is not required for total xylenes unless the concentration of either peak separately exceeds 200 ug/L. Secondary ion quantitation is only allowed when there are sample interferences with the primary ion. If secondary ion quantitation is used, document the reasons in the Case Narrative. When a sample is analyzed that has saturated ions from a compound, this analysis must be followed by a blank reagent water analysis. If the blank analysis is not free of interferences, the system must be decontaminated. Sample analysis may not resume until a blank can be analyzed that is free of interferences.

- 7.1.14 For water samples, add 10 uL of the matrix spike solution (paragraph 4.7) to the 5 mL of sample purged. Disregarding any dilutions, this is equivalent to a concentration of 50 ug/L of each matrix spike standard.
- 7.1.15 All dilutions must keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

7.2 Soil/Sediment Samples

Two approaches may be taken to determine whether the low level or medium level method may be followed.

- o Assume the sample is low level and analyze a 5 g sample.
- o Use the X factor calculated from the optional hexadecane screen (Section III, paragraph 6.2.1.3).

If peaks are saturated from the analysis of a 5 g sample, a smaller sample size must be analyzed to prevent saturation. However, the smallest sample size permitted is 1 g. If smaller than 1 g sample size is needed to prevent saturation, the medium level method must be used.

7.2.1 Low Level Soil Method

The low level soil method is based on purging a heated sediment/ soil sample mixed with reagent water containing the surrogate and internal standards. Analyze all reagent blanks and standards under the same conditions as the samples.

Use 5 grams of sample or use the X Factor to determine the sample size for purging.

- o If the X Factor is 0 (no peaks noted on the hexadecane screen), analyze a 5 g sample.
- o If the X Factor is between 0 and 1.0, analyze a minimum of a 1 g sample.

- 7.2.1.1 The GC/MS system should be set up as in 7.1.2-7.1.4. This should be done prior to the preparation of the sample to avoid loss of volatiles from standards and sample. A heated purge calibration curve must be prepared and used for the quantitation of all samples analyzed with the low-level method. Follow the initial and daily calibration instructions (5.3) except for the addition of a 40°C purge temperature.
- 7.2.1.2 To prepare the reagent water containing the surrogates and internal standards, remove the plunger from a 5 mL "Luerlock" type syringe equipped with a syringe valve and fill until overflowing with reagent water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to 5.0 mL. Add 10 µL each of the surrogate spiking solution (4.6) and the internal standard solution to the syringe through the valve. (Surrogate spiking solution and internal standard solution may be mixed together). The addition of 10 µL of the surrogate spiking solution to 5 g of soil/sediment is equivalent to 50 µg/kg of each surrogate standard.
- 7.2.1.3 The sample (for volatile organics) consists of the entire contents of the sample container. Do not discard any supernatant liquids. Mix the contents of the sample container with a narrow metal spatula. Weigh the amount determined in 7.2.1 into a tared purge device. Use a top loading balance. Note and record the actual weight to the nearest 0.1 g.
- 7.2.1.4 Immediately after weighing the sample, weigh 5-10 g of the sediment into a tared crucible. Determine the percent moisture by drying overnight at 105°C. Allow to cool in a desiccator before weighing. Concentrations of individual analytes will be reported relative to the dry weight of sediment.

$$\frac{\text{Percent moisture}}{\text{g of sample-g of dry sample}} \times 100 = \% \text{ moisture}$$

- 7.2.1.5 Add the spiked reagent water to the purge device and connect the device to the purge and trap system. **Note:** Prior to the attachment of the purge device, steps 7.2.1.2 and 7.2.1.3 must be performed rapidly to avoid loss of volatile organics. These steps must be performed in a laboratory free of solvent fumes.
- 7.2.1.6 Heat the sample to 40°C ± 1°C and purge the sample for 11.0 ± 0.1 minutes.

- 7.2.1.7 Proceed with the analysis as outlined in 7.1.10 7.1.13. Use 5 mL of the same reagent water as the reagent blank.
- 7.2.1.8 For low level soils/sediment add 10 μ L of the matrix spike solution (4.7) to the 5 mL of water (7.2.1.2). The concentration for a 5 g sample would be equivalent to 50 μ g/kg of each matrix spike standard.

7.2.2 Medium Level Soil Method

The medium level soil method is based on extracting the soil/sediment sample with methanol. An aliquot of the methanol extract is added to reagent water containing the surrogate and internal standards. This is purged at ambient temperature. All samples with an X Factor >1.0 should be analyzed by the medium level method. If saturated peaks occurred or would occur when a 1 g sample was analyzed, the medium level method must be used.

- 7.2.2.1 The GC/MS system should be set up as in 7.1.2 - 7.1.4. This should be done prior to the addition of the methanol extract to reagent water. Initial and continuing calibrations (5.3) are performed by adding standards in methanol to reagent water and purging at ambient temperature.
- 7.2.2.2 The sample (for volatile organics) consists of the entire contents of the sample container. Do not discard any supernatant liquids. Mix the contents of the sample container with a narrow metal spatula. Weigh 4 g (wet weight) into a tared 15 mL vial. Use a top loading balance. Note and record the actual weight to the nearest 0.1 g. Determine the percent moisture as in 7.2.1.4.
- 7.2.2.3 Quickly add 9.0 mL of methanol, then 1.0 mL of the surrogate spiking solution to the vial. Cap and shake for 2 minutes. NOTE: Steps 7.2.2.1 and 7.2.2.2 must be performed rapidly to avoid loss of volatile organics. These steps must be performed in a laboratory free of solvent fumes.
- 7.2.2.4 Using a disposable pipette, transfer approximately 1 mL of extract into a GC vial for storage. The remainder may be disposed of. Transfer approximately 1 mL of the reagent methanol to a GC vial for use as the method blank for each case or set of 20 samples, whichever is more frequent. These extracts may be stored in the dark at 4°C ($\pm 2^\circ\text{C}$) prior to analysis.

The addition of a 100 uL aliquot of each of these extracts in paragraph 7.2.2.6 will give a concentration equivalent to 6,200 ug/kg of each surrogate standard.

7.2.2.5 The following table can be used to determine the volume of methanol extract to add to the 5 mL of reagent water for analysis. If the Hexadecane screen procedure was followed, use the X factor (Option B) or the estimated concentration (Option A) to determine the appropriate volume. Otherwise, estimate the concentration range of the sample from the low level analysis to determine the appropriate volume. If the sample was submitted as a medium level sample, start with 100 uL.

All dilutions must keep the response of the major constituents (previously saturated peaks) in the upper half of linear range of the curve.

<u>X Factor</u>	<u>Estimated Concentration Range</u> ¹ ug/kg	<u>Take this Volume of Methanol Extract</u> ² uL
0.25 - 5.0	500 - 10,000	100
0.5 - 10.0	1000 - 20,000	50
2.5 - 50.0	5000 - 100,000	10
12.5 - 250	25,000 - 500,000	100 of 1/50 dilution ³

Calculate appropriate dilution factor for concentrations exceeding the table.

- ¹ Actual concentration ranges could be 10 to 20 times higher than this if the compounds are halogenated and the estimates are from GC/FID.
- ² The volume of methanol added to the 5 mL of water being purged should be kept constant. Therefore, add to the 5 mL syringe whatever volume of methanol is necessary to maintain a volume of 100 uL added to the syringe.
- ³ Dilute an aliquot of the methanol extract and then take 100 uL for analysis.

7.2.2.6 Remove the plunger from a 5 mL "Luerlock" type syringe equipped with a syringe valve and fill until overflowing with reagent water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to 4.9 mL. Pull the plunger back to 5 mL to allow volume for the addition of sample and standards. Add 10 uL of the internal standard solution. Also add the volume of methanol extract determined in 7.2.2.5 and a volume of methanol solvent to total 100 uL (excluding methanol in standards).

- 7.2.2.7 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valve and inject the water/methanol sample into the purging chamber.
- 7.2.2.8 Proceed with the analysis as outlined in 7.1.9 - 7.1.13. Analyze all reagent blanks on the same instrument as the samples. The standards should also contain 100 μ L of methanol to simulate the sample conditions.
- 7.2.2.9 For a matrix spike in the medium level sediment/soil samples, add 8.0 mL of methanol, 1.0 mL of surrogate spike solution (4.6), and 1.0 mL of matrix spike solution (4.7) in paragraph 7.2.2.2. This results in a 6,200 μ g/kg concentration of each matrix spike standard when added to a 4 g sample. Add a 100 μ L aliquot of this extract to 5 mL of water for purging (as per paragraph 7.2.2.6).

8. Qualitative Analysis

- 8.1 The compounds listed in the Target Compound List (TCL), Exhibit C, shall be identified by an analyst competent in the interpretation of mass spectra (see Bidder Responsibility description) by comparison of the sample mass spectrum to the mass spectrum of a standard of the suspected compound. Two criteria must be satisfied to verify the identifications: (1) elution of the sample component at the same GC relative retention time as the standard component, and (2) correspondence of the sample component and standard component mass spectra.
- 8.1.1 For establishing correspondence of the GC relative retention time (RRT), the sample component RRT must compare within ± 0.06 RRT units of the RRT of the standard component. For reference, the standard must be run on the same shift as the sample. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions unique to the component of interest.
- 8.1.2 For comparison of standard and sample component mass spectra, mass spectra obtained on the Contractor's GC/MS are required. Once obtained, these standard spectra may be used for identification purposes, only if the Contractor's GC/MS meets the daily tuning requirements for BFB. These standard spectra may be obtained from the run used to obtain reference RRTs.
- 8.1.3 The requirements for qualitative verification by comparison of mass spectra are as follows:
- 8.1.3.1 All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant

ion in the spectrum equals 100%) must be present in the sample spectrum.

8.1.3.2 The relative intensities of ions specified in 8.1.3.1 must agree within plus or minus 20% 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 30 and 70 percent).

8.1.3.3 Ions greater than 10% in the sample spectrum but not present in the standard spectrum must be considered and accounted for by the analyst making the comparison. In Task III, the verification process should favor false negatives. All compounds meeting the identification criteria must be reported with their spectra. For all compounds below the CRQL report the actual value followed by a "J", e.g., "3J."

8.1.4 If a compound cannot be verified by all of the criteria in 8.1.3.3, but in the technical judgement of the mass spectral interpretation specialist, the identification is correct, then the Contractor shall report that identification and proceed with quantification in 9.

8.2 A library search shall be executed for non-TCL sample components for the purpose of tentative identification. For this purpose, the 1985 release of the National Bureau of Standards Mass Spectral Library (or more recent release), containing 42,261 spectra, shall be used. Computer generated library search routines must not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

8.2.1 Up to 10 nonsurrogate organic compounds of greatest apparent concentration not listed in Exhibit C for the purgeable organic fraction shall be tentatively identified via a forward search of the NBS mass spectral library. (Substances with responses less than 10% of the internal standard are not required to be searched in this fashion). Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification. Computer generated library search routines must not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

8.2.2 Guidelines for making tentative identification:

8.2.2.1 Relative intensities of major ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum.

8.2.2.2 The relative intensities of the major ions should agree within $\pm 20\%$. (Example: For an ion with an

abundance of 50 percent of the standard spectra, the corresponding sample ion abundance must be between 30 and 70 percent.)

- 8.2.2.3 Molecular ions present in reference spectrum should be present in sample spectrum.
- 8.2.2.4 Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.
- 8.2.2.5 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 co-eluting compounds. Data system library reduction programs can sometimes create these discrepancies.

8.2.3 If in the technical judgement of the mass spectral interpretation specialist, no valid tentative identification can be made, the compound should be reported as unknown. The mass spectral specialist should give additional classification of the unknown compound, if possible (i.e. unknown aromatic, unknown hydrocarbon, unknown acid type, unknown chlorinated compound). If probable molecular weights can be distinguished, include them.

9. Quantitative Analysis

9.1 TCL components identified shall be quantified by the internal standard method. The internal standard used shall be that which is listed in Exhibit E, Table 2.1. The EICP area of the characteristic ions of analytes listed in Tables 2 and 3 in this Section are used.

9.2 Internal standard responses and retention times in all standards must be evaluated during or immediately after data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the latest daily (12 hour) calibration standard, the chromatographic system must be inspected for malfunctions, and corrections made as required. The extracted ion current profile (EICP) of the internal standards must be monitored and evaluated for each sample, blank, matrix spike and matrix spike duplicate. If the EICP area for any internal standard changes by more than a factor of two (-50% to +100%), the mass spectrometric system must be inspected for malfunction and corrections made as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is necessary.

9.2.1 If after re-analysis, the EICP areas for all internal standards are inside the contract limits (-50% to +100%), then the problem with the first analysis is considered to have been within the control of the laboratory. Therefore, only submit data from the analysis with EICPs within the contract limits.

This is considered the initial analysis and must be reported as such on all data deliverables.

9.2.2 If the re-analysis of the sample does not solve the problem, i.e., the EICP areas are outside the contract limits for both analyses, then submit the EICP data and sample data from both analyses. Distinguish between the initial analysis and the re-analysis on all data deliverables, using the sample suffixes specified in Exhibit B. Document in the Case Narrative all inspection and corrective actions taken.

9.3 The relative response factor (RRF) from the daily standard analysis is used to calculate the concentration in the sample. Use the relative response factor as determined in paragraph 5.3.3 and the equations below. When TCL compounds are below contract required quantitation limits (CRQL) but the spectra meet the identification criteria, report the concentration with a "J." For example, if CRQL is 10 ug/L and concentration of 3 ug/L is calculated, report as "3J."

Water

$$\text{Concentration} \quad \text{ug/L} = \frac{(A_x)(I_s)}{(A_{I_s})(RRF)(V_o)}$$

Where:

- A_x - Area of the characteristic ion for the compound to be measured
- A_{I_s} - Area of the characteristic ion for the specific internal standard from Exhibit E.
- I_s - Amount of internal standard added in nanograms (ng)
- V_o - Volume of water purged in milliliters (mL) (take into account any dilutions)

Sediment/Soil (medium level)

$$\text{Concentration} \quad \text{ug/kg} = \frac{(A_x)(I_s)(V_e)}{(A_{I_s})(RRF)(V_i)(W_s)(D)}$$

Sediment/Soil (low level)

$$\text{Concentration} \quad \text{ug/kg} = \frac{(A_x)(I_s)}{(A_{I_s})(RRF)(W_s)(D)}$$

(Dry weight basis)

Where:

- A_x, I_s, A_{I_s} - same as for water, above
- V_e - Volume of total extract (uL) (use 10,000 uL or a factor of this when dilutions are made)

V_1 - Volume of extract added (uL) for purging
 D - $\frac{100 - \% \text{ moisture}}{100}$
 W_s - Weight of sample extracted (g) or purged

9.4 An estimated concentration for non-TCL components tentatively identified shall be quantified by the internal standard method. For quantification, the nearest internal standard free of interferences shall be used.

9.4.1 The formula for calculating concentrations is the same as in paragraph 9.3. Total area counts (or peak heights) from the total ion chromatograms are to be used for both the compound to be measured and the internal standard. A relative response factor (RRF) of one (1) is to be assumed. The value from this quantitation shall be qualified as estimated. This estimated concentration should be calculated for all tentatively identified compounds as well as those identified as unknowns.

9.5 Xylenes (o-, m-, & p- isomers) are to be reported as Xylenes (total). Since o- and p-Xylene overlap, the Xylenes must be quantitated as m-Xylene. The concentration of all Xylene isomers must be added together to give the total.

9.6 1,2-Dichloroethane (trans and cis stereoisomers) are to be reported as 1,2-Dichloroethane (total). The concentrations of both isomers must be added together to give the total.

9.7 Calculate surrogate standard recovery on all samples, blanks and spikes. Determine if recovery is within limits and report on appropriate form.

9.7.1 Calculation for surrogate recovery.

$$\text{Percent Surrogate Recovery} = \frac{Q_d}{Q_a} \times 100\%$$

Where:

Q_d - quantity determined by analysis

Q_a - quantity added to sample

9.7.2 If recovery is not within limits, the following is required:

- o Check to be sure there are no errors in calculations, surrogate solutions, and internal standards. Also, check instrument performance.
- o Reanalyze the sample if none of the above reveal a problem.

9.7.3 If the reanalysis of the sample solves the problem, then the problem was within the laboratory's control. Therefore, only

submit data from the analysis with surrogate spike recoveries within the contract limits. This shall be considered the initial analysis and shall be reported as such on all data deliverables.

- 9.7.4 If the reanalysis of the sample does not solve the problem, i.e., surrogate recoveries are outside the contract limits for both analyses, then submit the surrogate spike recovery data and the sample data from both analyses. Distinguish between the initial analysis and the reanalysis on all data deliverables, using the sample suffixes specified in Exhibit B.
- 9.7.5 If the sample with surrogate recoveries outside the limits is the sample used for the matrix spike and matrix spike duplicate, and the surrogate recoveries of the matrix spike and matrix spike duplicate show the same pattern (i.e., outside the limits), then the sample, matrix spike, and matrix spike duplicate do not require reanalysis. Document in the narrative the similarity in surrogate recoveries.

Table 2

Characteristic Ions for Surrogate and
Internal Standards for Volatile Organic Compounds

Compound	Primary Ion	Secondary Ion(s)
<u>SURROGATE STANDARDS</u>		
4-Bromofluorobenzene	95	174, 176
1,2-Dichloroethane d-4	65	102
Toluene d-8	98	70, 100
<u>INTERNAL STANDARDS</u>		
Bromochloromethane	128	49, 130, 51
1,4-Difluorobenzene	114	63, 88
Chlorobenzene d-5	117	82, 119

Table 3
Characteristic Ions for Volatile TCL Compounds

Parameter	Primary Ion*	Secondary Ion(s)
Chloromethane	30	52
Bromomethane	94	96
Vinyl chloride	62	64
Chloroethane	64	66
Methylene chloride	84	49, 51, 86
Acetone	43	58
Carbon disulfide	76	78
1,1-Dichloroethane	96	61, 98
1,1-Dichloroethane	63	63, 83, 85, 98, 100
1,2-Dichloroethane	96	61, 98
Chloroform	83	85
1,2-Dichloroethane	62	64, 100, 98
2-Butanone	72	57
1,1,1-Trichloroethane	97	99, 117, 119
Carbon tetrachloride	117	119, 121
Vinyl acetate	43	86
Bromodichloromethane	83	85
1,1,2,2-Tetrachloroethane	83	85, 131, 133, 166
1,2-Dichloropropane	63	65, 114
trans-1,3-Dichloropropene	75	77
Trichloroethane	130	95, 97, 132
Dibromochloromethane	129	208, 206
1,1,2-Trichloroethane	97	83, 85, 99, 132, 134
Benzene	78	-
cis-1,3-Dichloropropene	75	77
Bromoform	173	171, 175, 250, 252, 254, 256
2-Hexanone	43	58, 57, 100
4-Methyl-2-pentanone	43	58, 100
Tetrachloroethane	164	129, 131, 166
Toluene	92	91
Chlorobenzene	112	114
Ethyl benzene	106	91
Styrene	104	78, 103
Total xylenes	106	91

* The primary ion should be used unless interferences are present, in which case, a secondary ion may be used.

Figure 1. Purging device

Figure 2. Trap packings and construction to include desert capability

Figure 3. Schematic of purge and trap device — purge mode

Figure 4. Schematic of purge and trap device — desorb mode

Figure 5. Low Soils Impinger

SECTION II

SAMPLE PREPARATION AND STORAGE

PART A - SAMPLE STORAGE AND HOLDING TIMES

1. Procedures for Sample Storage

- 1.1** The samples must be protected from light and refrigerated at 4°C ($\pm 2^\circ\text{C}$) from the time of receipt until extraction and analysis.
- 1.2** After analysis, extracts and unused sample volume must be protected from light and refrigerated at 4°C ($\pm 2^\circ\text{C}$) for the periods specified in the contract schedule.

2. Contract Required Holding Times

- 2.1** If separatory funnel or sonication procedures are employed for extractions for semivolatile analyses, extraction of water samples shall be completed within 5 days of VTSR (Validated Time of Sample Receipt), and extraction of soil/sediment samples shall be completed within 10 days of VTSR. If continuous liquid-liquid extraction procedures are employed, extraction of water samples shall be started within 5 days of VTSR.

Extracts of either water or soil/sediment samples must be analyzed within 40 days following extraction.

PART B - SAMPLE PREPARATION FOR EXTRACTABLE SEMIVOLATILES (BNA) IN WATER

1. Summary of Method

A measured volume of sample, approximately one liter, is serially extracted with methylene chloride at a pH greater than 11 and again at pH less than 2, using a separatory funnel or a continuous extractor. The methylene chloride extracts are dried and concentrated separately to a volume of 1 mL.

2. Interferences

- 2.1 Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing hardware, that lead to discrete artifacts and/or elevated baselines in the total ion current profiles (TICPs). All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks. 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.

3. Apparatus and Materials

- 3.1 Glassware (Brand names and catalog numbers are included for illustration purposes only).

- 3.1.1 Separatory funnel - 2,000 mL, with teflon stopcock.
- 3.1.2 Drying column - 19 mm ID chromatographic column with coarse frit. (Substitution of a small pad of Pyrex glass wool for the frit will prevent cross contamination of sample extracts.)
- 3.1.3 Concentrator tube - Kuderna-Danish, 10 mL, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of extracts.
- 3.1.4 Evaporative flask - Kuderna-Danish, 500 mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.
- 3.1.5 Snyder column - Kuderna-Danish, Three-ball macro (Kontes K-503000-0121 or equivalent).
- 3.1.6 Snyder column - Kuderna-Danish, Two-ball micro (Kontes K569001-0219 or equivalent).
- 3.1.7 Vials - Amber glass, 2 mL capacity with Teflon-lined screw cap.
- 3.1.8 Continuous liquid-liquid extractors - Equipped with Teflon or glass connecting joints and stopcocks requiring no lubrication (Hershberg-Wolf Extractor-Ace Glass Company, Vineland, NJ P/N 6841-10 or equivalent.)

- 3.2 Silicon carbide boiling chips - approximately 10/40 mesh. Heat to 400°C for 30 minutes or Soxhlet extract with methylene chloride.
- 3.3 Water bath - Heated, with concentric ring cover, capable of temperature control ($\pm 2^\circ\text{C}$). The bath should be used in a hood.
- 3.4 Balance - Analytical, capable of accurately weighing ± 0.0001 g.
- 3.5 Nitrogen evaporation device equipped with a water bath that can be maintained at 35-40°C. The N-Evap by Organomation Associates, Inc., South Berlin, MA (or equivalent) is suitable.
4. **Reagents**
- 4.1 Reagent water - Reagent water is defined as a water in which an interferent is not observed at or above the CRQL of each parameter of interest.
- 4.2 Sodium hydroxide solution (10N) - Dissolve 40 g NaOH in reagent water and dilute to 100 mL.
- 4.3 Sodium thiosulfate - (ACS) Granular.
- 4.4 Sulfuric acid solution (1+1) - Slowly add 50 mL of H_2SO_4 (sp gr. 1.84) to 50 mL of reagent water.
- 4.5 Acetone, methanol, methylene chloride - Pesticide quality or equivalent.
- 4.6 Sodium sulfate - (ACS) Powdered, anhydrous. Purify by heating at 400°C for four hours in a shallow tray, cool in a desiccator and store in a glass bottle. Baker anhydrous powder, catalog #73898 or equivalent.
- 4.7 Surrogate standard spiking solution.
- 4.7.1 Surrogate standards are added to all samples and calibration solutions; the compounds specified for this purpose are phenol- d_6 ; 2,4,6 tribromophenol; 2-fluorophenol; nitrobenzene- d_5 ; terphenyl- d_{14} and 2-fluorobiphenyl. Two additional surrogates, one base/neutral and one acid, may be added.
- 4.7.2 Prepare a surrogate standard spiking solution that contains the base/neutral compounds at a concentration of 100 ug/mL, and the acid compounds at 200 ug/mL. Store the spiking solutions at 4°C ($\pm 2^\circ\text{C}$) in Teflon-sealed containers. The solutions should be checked frequently for stability. These solutions must be replaced after twelve months, or sooner if comparison with quality control check samples indicates a problem.
- 4.8 BNA Matrix standard spiking solution. The matrix spike solution consists of:

Base/Neutrals

1,2,4-trichlorobenzene
acenaphthene
2,4-dinitrotoluene
pyrene
N-nitroso-di-n-propylamine
1,4-dichlorobenzene

Acids

pentachlorophenol
phenol
2-chlorophenol
4-chloro-3-methylphenol
4-nitrophenol

Prepare a spiking solution that contains each of the base/neutral compounds above at 100 ug/1.0 mL in methanol and the acid compounds at 200 ug/1.0 mL in methanol. Analyze duplicate aliquots of a sample spiked with BNA matrix spiking solution.

5. Sample Extraction - Separatory Funnel

- 5.1 Samples may be extracted using separatory funnel techniques. If emulsions prevent acceptable solvent recovery with separatory funnel extraction, continuous extraction (paragraph 6.) may be used. The separatory funnel extraction scheme described below assumes a sample volume of 1-liter.
- 5.2 Using a 1-liter graduated cylinder, measure out a 1-liter sample aliquot and place it into a 2-liter separatory funnel. Pipet 1.0 mL surrogate standard spiking solution into the separatory funnel and mix well. Check the pH of the sample with wide range pH paper and adjust to pH >11 with 10N sodium hydroxide. Add 1.0 mL of BNA matrix spiking solution to each of two 1-liter portions from the sample selected for spiking.
- 5.3 Add 60 mL methylene chloride to the separatory funnel and extract the sample by shaking the funnel for two minutes, with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the volume 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.
- Collect the methylene chloride extract in a 250-mL Erlenmeyer flask. If the emulsion cannot be broken (recovery of less than 80% of the methylene chloride, corrected for the water solubility of methylene chloride), transfer the sample, solvent and emulsion into the extraction chamber of a continuous extractor. Proceed as described in paragraph 6.3.
- 5.4 Add a second 60-mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner. Label the combined extract as the base/neutral fraction.
- 5.5 Adjust the pH of the aqueous phase to less than 2 using sulfuric acid (1 + 1). Serially extract three times with 60-mL aliquots of methylene

chloride, as per paragraph 5.3. Collect and combine the extracts in a 250-mL Erlenmeyer flask and label the combined extract as the acid fraction.

- 5.6 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D, if equivalency is demonstrated for all extractable organics listed in Exhibit C.
- 5.7 Transfer the individual base/neutral and acid fractions by pouring extracts through separate drying columns containing about 10 cm of anhydrous granular sodium sulfate, and collect the extracts in the separate K-D concentrators. Rinse the Erlenmeyer flasks and columns with 20 to 30 mL of methylene chloride to complete the quantitative transfer.
- 5.8 Add one or two clean boiling chips and attach a three-ball Snyder column to the evaporative flask. Pre-wet the Snyder column by adding about 1 mL methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80° to 90°C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10 to 15 minutes. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of methylene chloride. A 5-mL syringe is recommended for this operation.
- 5.9 Micro Snyder column technique - Add another one or two clean boiling chips to the concentrator tube and attach a two-ball micro Snyder column. Pre-wet the Snyder column by adding about 0.5 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80° to 90°C) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5 to 10 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches about 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain for at least 10 minutes while cooling. Remove the Snyder column and rinse its flask and its lower joint into the concentrator tube with 0.2 mL of methylene chloride. Adjust the final volume to 1.0 mL with methylene chloride. If GC/MS analysis will not be performed immediately, stopper the concentrator tube and store refrigerated. If the extracts will be stored longer than two days, they should be transferred to individual Teflon-sealed screw cap bottles and labeled base/neutral or acid fraction, as appropriate.

5.10 Nitrogen blowdown technique (taken from ASTM Method D3086)

The following method may be used for final concentration, instead of the procedure outlined in paragraph 5.9. Place the concentrator tube in a warm water bath (35°C) and evaporate the solvent volume to just below 1 mL using a gentle stream of clean, dry nitrogen filtered through a column of activated carbon). **Caution:** New plastic tubing must not be used between the carbon trap and the sample, as it may introduce interferences. The internal wall of the tube must be rinsed down several times with methylene chloride during the operation and the final volume brought to 1 mL with methylene chloride. During evaporation, the tube solvent level must be kept below the water level of the bath. The extract must never be allowed to become dry.

6. Sample Extraction - Continuous Liquid-Liquid Extractor

6.1 Check the pH of the sample with wide-range pH paper and adjust to pH 11 with 10 N sodium hydroxide. Transfer a 1-liter sample aliquot to the continuous extractor; using a pipet, add 1 mL of surrogate standard spiking solution and mix well.

6.2 Add 500 mL of methylene chloride to the distilling flask. Add sufficient reagent water to ensure proper operation and extract for 18 hours. Allow to cool, then detach the boiling flask and dry. Concentrate the extract as in paragraphs 5.6 through 5.8. Hold the concentrated extract for combining with the acid extract (see paragraph 6.4).

6.3 Add 500 mL of methylene chloride to a clean distilling flask and attach it to the continuous extractor. Carefully adjust the pH of the aqueous phase to less than 2 using sulfuric acid (1 + 1). Extract for 18 hours. Dry and concentrate the extract as described in paragraphs 5.6 through 5.8. Hold the concentrated extract and label as the acid extract.

6.3.1 If the base/neutral and/or acid extracts cannot be concentrated to a final volume of 1 mL, dilute the more concentrated extract to the final volume of the least concentrated extract.

7. The samples extracts are ready for GC/MS analysis. Proceed to Section IV, GC/MS Analysis of Semivolatiles. If high concentrations are suspected (e.g., highly colored extracts), the optional GC/FID screen in Section III is recommended.

PART C - PROTOCOLS FOR SOIL/SEDIMENT

It is mandatory that all soil/sediment samples be characterized as to concentration level so that the appropriate analytical protocol is chosen to ensure proper quantitation limits for the sample. Note that the terms "low level" and "medium level" are not used here as a judgement of degree of contamination but rather as a description of the concentration ranges that are encompassed by the "low" and "medium" level procedures.

The laboratory is at liberty to determine the method of characterization. The following two screening methods may be used for soil/sediment sample characterization:

- o Screen an aliquot from the "low level" 30 g extract or an aliquot from the "medium level" 1 g extract.
- o Screen using either GC/FID or GC/MS as the screening instrument.

The concentration ranges covered by these two procedures may be considered to be approximately 330 ug/kg - 20,000 ug/kg for the low level analysis and >20,000 ug/kg for medium level analysis for BNA extractables. For soils only, the extract for pesticide/PCB analysis may be prepared from an aliquot of the extract for semivolatiles, or in a separate extraction procedure. If it is prepared from the semivolatile extract, refer to Exhibit D PEST for the procedures for extraction of pesticides/PCBs.

Screen from the Medium Level Method

Take 5.0 mL from the 10.0 mL total extract and concentrate to 1.0 mL and screen. If the sample concentration is >20,000 ug/kg proceed with GC/MS analysis of the organics. If the sample concentration is <20,000 ug/kg discard the medium level extract and follow the low level method.

Screen from Low Level Method

Take 5.0 mL from the 300 mL (approximate) total extract from the 30 g sample and concentrate to 1.0 mL and screen. If the concentration is >20,000 ug/kg in the original sample, discard the 30 g extract and follow the medium level methods for organics, using medium level surrogates. If the sample concentration is <20,000 ug/kg, proceed with concentration and the remainder of the low level method.

1. Medium Level Preparation for Screening and Analysis of Semivolatiles (BNA)

1.1 Scope and Application

This procedure is designed for the preparation of sediment/soil samples which may contain organic chemicals at a level greater than 20,000 ug/kg.

- 1.1.1. The extracts and sample aliquots prepared using this method are screened by GC/MS or FID, using capillary columns for base/neutral and acid priority pollutants, and related organic chemicals. The results of these screens will determine whether

sufficient quantities of pollutants are present to warrant analysis by low or medium protocol.

- 1.1.2 If the screenings indicate no detectable pollutants at the lower limits of quantitation, the sample should be prepared by the low level protocol in Section II, Part C, paragraph 2.

1.2 Summary of Method

- 1.2.1. Approximately 1 g portions of sediment/soil are transferred to vials and extracted with methylene chloride. The methylene chloride extract is screened for extractable organics by GC/FID or GC/MS.
- 1.2.2 If organic compounds are detected by the screen, the methylene chloride extract is analyzed by GC/MS for extractable organics.
- 1.2.3 If no organic compounds are detected by the medium level screen, then a low level sample preparation is required.

1.3 Interferences

- 1.3.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the total ion current profiles. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks. 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.

1.4 Limitations

- 1.4.1. The procedure is designed to allow quantitation limits for screening purposes as low as 20,000 ug/kg for extractable organics. For analysis purposes, the quantitation limits are 20,000 ug/kg for extractable organics. If peaks are present based on the GC/FID screen, the sample is determined to require a medium level analysis by GC/MS. Some samples may contain high concentrations of chemicals that interfere with the analysis of other components at lower levels; the quantitation limits in those cases may be significantly higher.
- 1.4.2 These extraction and preparation procedures were developed for rapid and safe handling of high concentration hazardous waste samples. The design of the methods thus does not stress efficient recoveries or low limits of quantitation of all components. Rather, the procedures were designed to screen at moderate recovery and sufficient sensitivity, a broad spectrum of organic chemicals. The results of the analyses thus may reflect only a minimum of the amount actually present in some samples.

1.5 Reagents

1.5.1. Sodium Sulfate - anhydrous powdered reagent grade, heated at 400°C for four hours, cooled in a desiccator, and stored in a glass bottle Baker anhydrous powder, catalog # 73898 or equivalent.

1.5.2. Methylene chloride. Pesticide residue analysis grade or equivalent.

1.5.3. Methanol. Pesticide residue analysis grade or equivalent.

1.5.4. Acetone. Pesticide residue analysis grade or equivalent.

1.5.5. Base/Neutral and Acid Surrogate Standard Spiking Solution

The compounds specified are phenol-d₆, 2,4,6-tribromophenol, 2-fluorophenol, nitrobenzene-d₅, terphenyl-d₁₄ and 2-fluorobiphenyl. Prepare a solution containing these compounds for base/neutral surrogates at a concentration of 100 ug/1.0 mL, and for acid surrogate standards at a concentration of 200 ug/1.0 mL in methanol. Store the spiking solutions at 4°C (±2°C) in Teflon-sealed containers. The solutions should be checked frequently for stability. These solutions must be replaced after twelve months, or sooner, if comparison with quality control check samples indicates a problem.

1.5.6. Base/Neutral and Acid Matrix Standard Spiking solution.

Prepare a spiking solution in methanol that contains the following compounds at a concentration of 100 ug/1.0 mL for base/neutrals and 200 ug/1.0 mL for acids. Store the spiking solutions at 4°C (±2°C) in Teflon-sealed containers. The solutions should be checked frequently for stability. These solutions must be replaced after twelve months, or sooner, if comparison with quality control check samples indicates a problem.

Base Neutrals

1,2,4-trichlorobenzene
acenaphthene
2,4-dinitrotoluene
pyrene
N-nitroso-di-n-propylamine
1,4-dichlorobenzene

Acids

pentachlorophenol
phenol
2-chlorophenol
4-chloro-3-methylphenol
4-nitrophenol

1.6 Equipment

1.6.1. Glass scintillation vials, at least 20 mL, with screw cap and teflon or aluminum foil liner.

1.6.2. Spatula. Stainless steel or Teflon.

- 1.6.3 Balance capable of weighing 100 g to ± 0.01 g.
- 1.6.4 Vials and caps, 2 mL for GC auto sampler.
- 1.6.5 Disposable pipets, Pasteur; glass wool rinsed with methylene chloride.
- 1.6.6 15-mL concentrator tubes.
- 1.6.7 Ultrasonic cell disruptor, Heat Systems Ultrasonics, Inc., Model W-385 SONICATOR (475 Watt with pulsing capability, No. 200 1/2 inch tapered disruptor horn plus No. 207 3/4 inch tapered disruptor horn, and No. 419 1/8 inch standard tapered MICROTIP probe), or equivalent device with a minimum of 375 Watt output capability. NOTE: In order to ensure that sufficient energy is transferred to the sample during extraction, the MICROTIP probe must be replaced if the tip begins to erode. Erosion of the tip is evidenced by a rough surface.
- 1.6.8 Sonabox acoustic enclosure - recommended with above disruptors for decreasing cavitation sound.
- 1.6.9 Test tube rack.
- 1.6.10 Oven, drying.
- 1.6.11 Desiccator.
- 1.6.12 Crucibles, porcelain.
- 1.7 Medium Level Sample Preparation.
 - 1.7.1. Transfer the sample container into a fume hood. Open the sample vial. Decant and discard any water layer and then mix the sample. Transfer approximately 1 g (record weight to the nearest 0.1 g) of sample to a 20-mL vial. Wipe the mouth of the vial with a tissue to remove any sample material. Record the exact weight of sample taken. Cap the vial before proceeding with the next sample to avoid any cross-contamination.
 - 1.7.1.1 Transfer 50 g of soil/sediment to 100 mL beaker. Add 50 mL of water and stir for 1 hour. Determine pH of sample with glass electrode and pH meter while stirring. Report pH value on appropriate data sheets. If the pH of the soil is greater than 11 or less than 5, contact the Deputy Project Officer cited in the contract for instructions on how to handle the sample. Document the instructions in the Case Narrative. Discard this portion of sample.
 - 1.7.2 Immediately after weighing the sample for extraction, weigh 5-10 g of the sediment into a tared crucible. Determine the percent moisture by drying overnight at 105°C. Allow to cool

in a desiccator before weighing. Concentrations of individual analytes will be reported relative to the dry weight of sediment.

$$\frac{\text{g of sample} - \text{g of dry sample}}{\text{g of sample}} \times 100 = \% \text{ moisture}$$

- 1.7.3 Add 2.0 g of anhydrous powdered sodium sulfate to sample in the 20 mL vial from paragraph 1.7.1 and mix well.
 - 1.7.4 Surrogate Standards are added to all samples, spikes, and blanks. Add 1.0 mL of surrogate spiking solution to sample mixture.
 - 1.7.5 Add 1.0 mL of matrix standard spiking solution to each of two 1 g portions from the sample chosen for spiking.
 - 1.7.6 Immediately add 9.0 mL of methylene chloride to the sample and disrupt the sample with the 1/8 inch tapered MICROTIP ultrasonic probe for 2 minutes at output control setting 5, in continuous mode. (If using a sonicator other than Models W-375 or W-385, contact the Project Officer for appropriate output settings). Before extraction, make certain that the sodium sulfate is free flowing and not a consolidated mass. As required, break up large lumps with a clean spatula, or very carefully with the tip of the unenergized probe.
 - 1.7.6.1. Add only 8.0 mL of methylene chloride to the matrix spike samples to achieve a final volume of 10 mL.
 - 1.7.7 Loosely pack disposable Pasteur pipets with 2-3 cm glass wool plugs. Filter the extract through the glass wool and collect 5.0 mL in a concentrator tube.
 - 1.7.8 Concentrate the extract to 1.0 mL by the nitrogen blowdown technique described in paragraph 2.7.3.
 - 1.7.9 Transfer the concentrate to an autosampler vial for GC/FID or GC/MS capillary column screening. If the concentrate is screened, the quantitation limits should be approximately 20,000 ug/kg.
 - 1.7.10 Proceed to Section III, paragraph 1.
2. Low Level Preparation for Screening and Analysis of Semivolatiles (BNA)
 - 2.1 Summary of Method

A 30 gram portion of sediment is mixed with anhydrous powdered sodium sulfate and extracted with 1:1 methylene chloride/acetone using an ultrasonic probe. If the optional low level screen is used, a portion of this dilute extract is concentrated fivefold and is screened by GC/FID or GC/MS. If peaks are present at greater than 20,000 ug/kg, discard the extract and prepare the sample by the medium level method.

If no peaks are present at greater than 20,000 ug/kg, the extract is concentrated. An optional gel permeation column cleanup may be used before analysis.

2.2 Interferences

Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the total ion current profiles.

All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks. 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.

2.3 Apparatus and Materials

2.3.1 Apparatus for determining percent moisture

2.3.1.1 Oven, drying

2.3.1.2 Desiccator

2.3.1.3 Crucibles, porcelain

2.3.2 Disposable Pasteur glass pipets, 1 mL

2.3.3 Ultrasonic cell disruptor, Heat Systems - Ultrasonics, Inc. Model 385 SONICATOR (475 Watt with pulsing capability, No. 305 3/4 inch tapered high gain "Q" disruptor horn or No. 208 3/4 inch standard solid disruptor horn), or equivalent device with a minimum of 375 Watt output capability. NOTE: In order to ensure that sufficient energy is transferred to the sample during extraction, the horn must be replaced if the tip begins to erode. Erosion of the tip is evidenced by a rough surface.

2.3.3.1 Sonabox acoustic enclosure - recommended with above disruptors for decreasing cavitation sound.

2.3.4 Beakers, 400 mL

2.3.5 Vacuum filtration apparatus

2.3.5.1 Buchner funnel.

2.3.5.2 Filter paper, Whatman No. 41 or equivalent.

2.3.6 Kuderna-Danish (K-D) apparatus.

2.3.6.1 Concentrator tube - 10 mL, graduated (Kontes K-570040-1025 or equivalent).

- 2.3.6.2 Evaporative flask - 500 mL (Kontes K-570001-0500 or equivalent).
- 2.3.6.3 Snyder column - three-ball macro (Kontes K-503000-0121 or equivalent).
- 2.3.6.4 Snyder column - two-ball micro (Kontes K-569001-0219) or equivalent).
- 2.3.7 Silicon carbide boiling chips - approximately 10/40 mesh. Heat to 400°C for 30 minutes or Soxhlet extract with methylene chloride.
- 2.3.8 Water bath - heated, with concentric ring cover, capable of temperature control ($\pm 2^\circ\text{C}$). The bath should be used in a hood.
- 2.3.9 Balance, capable of accurately weighing ± 0.01 g.
- 2.3.10 Vials and caps, 2 mL for GC auto sampler.
- 2.3.11 Balance - Analytical, capable of accurately weighing ± 0.0001 g.
- 2.3.12 Nitrogen evaporation device equipped with a water bath that can be maintained at 35-40°C. The N-Evap by Organomation Associates, Inc., South Berlin, MA (or equivalent) is suitable.
- 2.3.13 Gel permeation chromatography (GPC) cleanup device. NOTE: GPC cleanup is highly recommended for all extracts for low level soils.
 - 2.3.13.1 Automated system
 - 2.3.13.1.1 Gel permeation chromatograph Analytical Biochemical Labs, Inc. GPC Autoprep 1002 or equivalent including:
 - 2.3.13.1.2 25 mm ID X 600 - 700 mm glass column packed with 70 g of Bio-Beads SX-3.
 - 2.3.13.1.3 Syringe, 10 mL with Luer-Lock fitting.
 - 2.3.13.1.4 Syringe filter holder and filters - stainless steel and TFE, Gelman 4310 or equivalent.
 - 2.3.13.2 Manual system assembled from parts. (Wise, R.H., Bishop, D.F., Williams, R.T. & Austern, B.M. "Gel Permeation Chromatography in the GC/MS Analysis of Organics in Sludges" U.S. EPA, Municipal Environmental Research Laboratory - Cincinnati, Ohio 45268)

- 2.3.13.2.1 25 mm ID X 600 - 700 mm heavy wall glass column packed with 70 g of BIO-Beads SX-3.
- 2.3.13.2.2 Pump: Altex Scientific, Model No. 1001A, semipreparative, solvent metering system. Pump capacity = 28 mL/min.
- 2.3.13.2.3 Detector: Altex Scientific, Model No. 153, with 254 nm UV source and 8-ul semi-preparative flowcells (2-mm pathlengths)
- 2.3.13.2.4 Microprocessor/controller: Altex Scientific, Model No. 420, Microprocessor System Controller, with extended memory.
- 2.3.13.2.5 Injector: Altex Scientific, Catalog No. 201-56, sample injection valve, Tefzel, with 10 mL sample loop.
- 2.3.13.2.6 Recorder: Linear Instruments, Model No. 385, 10-inch recorder.
- 2.3.13.2.7 Effluent Switching Valve: Teflon slider valve, 3-way with 0.060" ports.
- 2.3.13.2.8 Supplemental Pressure Gauge with connecting Tee: U.S. Gauge, 0-200 psi, stainless steel. Installed as a "downstream" monitoring device between column and detector.

Flow rate was typically 3 mL/min. of methylene chloride. Recorder chart speed was 0.50 cm/min.

2.3.14 Pyrex glass wool.

2.3.15 Pasteur pipets, disposable.

2.4 Reagents

- 2.4.1 Sodium Sulfate - anhydrous powdered reagent grade, heated at 400°C for four hours, cooled in a desiccator, and stored in a glass bottle. Baker anhydrous powder, catalog #73898 or equivalent.
- 2.4.2 Methylene chloride, methanol, acetone, isooctane, 2-propanol and benzene pesticide quality or equivalent.

2.4.3 Reagent water - Reagent water is defined as a water in which an interferent is not observed at or above the CRQL of each parameter of interest.

2.4.4 GPC calibration solutions:

2.4.4.1 Corn oil - 200 mg/mL in methylene chloride.

2.4.4.2 Bis(2-ethylhexylphthalate) and pentachlorophenol 4.0 mg/mL in methylene chloride.

2.4.5 Sodium Sulfite, reagent grade.

2.4.6 Surrogate standard spiking solution.

2.4.6.1 Base/neutral and acid surrogate solution.

2.4.6.1.1 Surrogate standards are added to all samples, blanks, matrix spikes, matrix spike duplicates, and calibration solutions; the compounds specified for this purpose are phenol- d_6 , 2,4,6-tribromophenol, 2-fluorophenol, nitrobenzene- d_5 , terphenyl- d_{14} and 2-fluorobiphenyl. Two additional surrogates, one base/neutral and one acid may be added.

2.4.6.1.2 Prepare a surrogate standard spiking solution at a concentration of 100 ug/1.0 mL for base/ neutral and 200 ug/1.0 mL for acids in methanol. Store the spiking solutions at 4°C ($\pm 2^\circ\text{C}$) in Teflon-sealed containers. The solutions must be replaced after twelve months, or sooner if comparison with quality control check samples indicate a problem.

2.4.7 Matrix standard spiking solutions.

2.4.7.1 Base/neutral and acid matrix spiking solution consists of:

Base/Neutrals (100 ug/1.0 mL)

1,2,4-trichlorobenzene
acenaphthene
2,4-dinitrotoluene
pyrene
N-nitroso-di-n-propylamine
1,4-dichlorobenzene

Acids (200 ug/1.0 mL)

pentachlorophenol
phenol
2-chlorophenol
4-chloro-3-methylphenol
4-nitrophenol

Prepare a spiking solution that contains each of the above in methanol. Store the spiking solutions at 4°C (±2°C) in Teflon-sealed containers. The solutions should be checked frequently for stability. These solutions must be replaced after twelve months, or sooner if comparison with quality control check samples indicate a problem.

Matrix spikes also serve as duplicates, therefore, add volume specified in Sample Extraction section to each of two 30-g portions from one sample chosen for spiking.

2.5 Low Level Sample Preparation

2.5.1 Decant and discard any water layer on a sediment sample. Mix samples thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.

2.5.1.1 Transfer 50 g of soil/sediment to 100 mL beaker. Add 50 mL of water and stir for 1 hour. Determine pH of sample with glass electrode and pH meter while stirring. Report pH value on appropriate data sheets. If the pH of the soil is greater than 11 or less than 5, contact the Deputy Project Officer cited in the contract for instructions on how to handle the sample. Document the instructions in the Case Narrative. Discard this portion of sample.

2.5.2 The following steps should be performed rapidly to avoid loss of the more volatile extractables. Weigh approximately 30 g of sample to the nearest 0.1 g into a 400-mL beaker and add 60 g of anhydrous powdered sodium sulfate. Mix well. The sample should have a sandy texture at this point. Immediately, add 100 mL of 1:1 methylene chloride - acetone to the sample, then add the surrogates according to paragraph 2.5.2.3.

2.5.2.1 Immediately after weighing the sample for extraction, weigh 5-10 g of the sediment into a tared crucible. Determine the percent moisture by drying overnight at 105°C. Allow to cool in a desiccator before weighing. Concentrations of individual analytes will be reported relative to the dry weight of sediment.

$$\frac{\text{g of sample} - \text{g of dry sample}}{\text{g of sample}} \times 100 = \% \text{ moisture}$$

2.5.2.2 Weigh out two 30 g (record weight to nearest 0.1 g) portions for use as matrix and matrix spike duplicates according to 2.5.2. When using GPC cleanup, add 2.0 mL of the base/neutral and acid matrix spike to each of two portions. When not

using GPC cleanup, add 1.0 mL of base/neutral and acid matrix spike to each of the other two portions.

- 2.5.2.3 When using GPC, add 1.0 mL of base/neutral and acid surrogate standard to the sample. When not using GPC, add 0.5 mL of BNA surrogate standard to the sample.
- 2.5.3 Place the bottom surface of the tip of the 3/4 inch disruptor horn about 1/2 inch below the surface of the solvent but above the sediment layer.
- 2.5.4 Sonicate for 1 1/2 minutes with the W-385 (or 3 minutes with the W-375), using No. 208 3/4 inch standard disruptor horn with output control knob set at 10 (or No. 305 3/4 inch tapered high gain "Q" disruptor horn at 5) and mode switch on "1 sec. pulse" and duty cycle knob set at 50%. Do NOT use MICROTIP probe. (If using a sonicator other than Models W-375 or W-385, contact the Project Officer for appropriate output settings).
- 2.5.5 Decant and filter extracts through Whatman #41 filter paper using vacuum filtration or centrifuge and decant extraction solvent.
- 2.5.6 Repeat the extraction two more times with 2 additional 100 mL portions of 1:1 methylene chloride - acetone. Before each extraction, make certain that the sodium sulfate is free flowing and not a consolidated mass. As required, break up large lumps with a clean spatula, or very carefully with the tip of the probe. Decant off the extraction solvent after each sonication. On the final sonication, pour the entire sample into the Buchner funnel and rinse with 1:1 methylene chloride - acetone.
- 2.5.6.1 If the sample is to be screened from the low level method, take 5.0 mL and concentrate to 1.0 mL following paragraph 2.7.2 or 2.7.3. Note that the sample volume in this case is 5.0 mL not 10.0 mL as given in 2.7.2. Screen the extract as per Section III, paragraph 1., "Screening of Extractable Organic Extracts." Transfer the remainder of the 1 mL back to the total extract from paragraph 2.5.6 after GC/FID or GC/MS screening. (CAUTION: To minimize sample loss, autosamplers which pre-flush samples through the syringe should not be used.)
- 2.5.7 Transfer the extract to a Kuderna-Danish (K-D) concentrator consisting of a 10 mL concentrator tube and a 500 mL evaporative flask. Other concentration devices or techniques may be used if equivalency is demonstrated for all extractable compounds listed in Exhibit C.
- 2.5.8 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Pre-wet the Snyder column

by adding about 1 mL methylene chloride to the top. Place the K-D apparatus on a hot water bath (80 to 90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10 to 15 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes, and make up to 10 mL volume with methylene chloride.

2.5.9 If GPC cleanup is not used proceed to paragraph 2.7.

2.6. Extract Cleanup

2.6.1 GPC Setup and Calibration

2.6.1.1 Packing the column - Place 70 g of Bio Beads SX-3 in a 400 mL beaker. Cover the beads with methylene chloride; allow the beads to swell overnight (before packing the columns). Transfer the swelled beads to the column and start pumping solvent through the column, from bottom to top, at 5.0 mL/min. After approximately 1 hour, adjust the pressure on the column to 7 to 10 psi and pump an additional 4 hours to remove air from the column. Adjust the column pressure periodically as required to maintain 7 to 10 psi.

2.6.1.2 Calibration of the column - Load 5 mL of the corn oil solution into sample loop No. 1 and 5 mL of the phthalatephenol solution into loop No. 2. Inject the corn oil and collect 10 mL fraction (i.e., change fraction at 2-minute intervals) for 36 minutes. Inject the phthalate-phenol solution and collect 15 mL fractions for 60 minutes. Determine the corn oil elution pattern by evaporation of each fraction to dryness followed by a gravimetric determination of the residue. Analyze the phthalate-phenol fractions by GC/FID on the DB-5 capillary column, a UV spectrophotometer or a GC/MS system. Plot the concentration of each component in each fraction versus total eluent volume (or time) from the injection points. Choose a "dump time" which allows $\geq 85\%$ removal of the corn oil and $\geq 85\%$ recovery of the bis(2-ethylhexyl)-phthalate. Choose the "collect time" to extend at least 10 minutes after the elution of pentachlorophenol. Wash the column at least 15 minutes between samples. Typical parameters selected are: Dump time, 30 minutes (150 mL), collect time, 36 minutes (180 mL) and wash time, 15 minutes (75 mL). The column can also be

calibrated by the use of a 254 nm UV detector in place of gravimetric and GC analyses of fractions. Measure the peak areas at various elution times to determine appropriate fractions.

The SX-3 Bio Beads column may be reused for several months, even if discoloration occurs. System calibration usually remains constant over this period of time if column flowrate remains constant.

2.6.2 GPC Extract Cleanup

Prefilter or load all extracts via the filter holder to avoid particulates that might stop the flow. Load one 5.0 mL aliquot of the extract onto the GPC column. Do not apply excessive pressure when loading the GPC. Purge the sample loading tubing thoroughly with solvent between extracts. After especially dirty extracts, run a GPC blank (methylene chloride) to check for carry-over. Process the extracts using the dump, collect and wash parameters determined from the calibration and collect the cleaned extracts in 400 mL beakers tightly covered with aluminum foil. The phthalate-phenol calibration solution shall be taken through the cleanup cycle with each set of 23 extracts loaded into the GPC. The recovery for each compound must be $\geq 85\%$. This must be determined on a GC/FID, using a DB-5 capillary column, a UV recording spectrophotometer or a GC/MS system. A copy of the printouts of standard and check solution are required as deliverables with each case. Show % recovery on the copy.

2.6.3 Concentrate the extract as per paragraphs 2.5.7 and 2.5.8.

2.7 Final Concentration of Extract with Optional Extract Splitting Procedure

If the extract in 2.5.8 is to be used only for semivolatile analysis, it must be concentrated to a volume of 1.0 mL, following the procedure in 2.7.2.1.

If the extract in 2.5.8 is to be used for both semivolatile and pesticide/PCB analyses, then it must be split into two portions. In that case, follow the procedure in 2.7.1 to obtain the pesticide portion, and follow that with the procedure in 2.7.2.2 to obtain the semivolatile portion.

Refer to Exhibit D PEST for specific instructions regarding the treatment of extracts for pesticide analysis.

- 2.7.1 If the same extract is used for both semivolatile and pesticide/PCB analyses, to split out the pesticide extract, transfer 0.5 mL of the 10 mL methylene chloride extract from 2.5.8 to a separate concentrator tube. Add 5 mL of hexane and a silicon carbide boiling chip and mix using vortex mixer. Attach a two-ball micro-Snyder column. Pre-wet the Snyder

column by adding 0.5 mL of hexane to the top of the column. Place the K-D apparatus on a hot water bath (80 - 90°C) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5 to 10 minutes. Concentrate the extract to an apparent volume of less than 1 mL. Use Nitrogen blowdown (see 2.7.3) to reduce the volume to 0.5 mL. Add 0.5 mL of acetone. The pesticide extract must now be passed through an alumina column to remove the BNA surrogates and polar interferences. Proceed to paragraph 2.8 of the pesticide/PCB method (Exhibit D PEST).

2.7.2 Concentration of the semivolatile extract.

2.7.2.1 If the extract in 2.5.8 was not split to obtain a portion for pesticide analysis, reattach the micro-Snyder column to the concentrator tube used in 2.5.8 which contains the 10 mL extract and add a fresh silicon carbide boiling chip to the concentrator tube. Pre-wet the Snyder column with 0.5 mL of methylene chloride. Place the K-D apparatus on the hot water bath (80 - 90°C) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5 to 10 minutes. When the apparent volume of the liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain for at least 10 minutes while cooling. Remove the Snyder column and rinse the lower joint into the concentrator tube with 0.2 mL of methylene chloride. Adjust the final volume to 1.0 mL with methylene chloride. If GPC cleanup was used, this 1.0 mL represents a two-fold dilution to account for only half of the extract going through the GPC.

2.7.2.2 If the extract in 2.5.8 was split in 2.7.1 to obtain a portion for pesticide analysis, reattach the micro-Snyder column to the concentrator tube used in 2.5.8 which contains the 9.5 mL extract and add a fresh silicon carbide boiling chip to the concentrator tube. Pre-wet the Snyder column with 0.5 mL of methylene chloride. Place the K-D apparatus on the hot water bath (80 - 90°C) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5 to 10 minutes. When the apparent volume of the liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain for at least 10 minutes while cooling. Remove the Snyder column and rinse the lower joint into the concentrator tube with 0.2 mL

of methylene chloride. Adjust the final volume to 0.95 mL with methylene chloride. If GPC cleanup was used, this 0.95 mL represents a twofold dilution to account for only half of the extract going through the GPC, and therefore, the sample detection limit for the sample would be 2x CRQL (see Exhibit B).

- 2.7.3 Nitrogen blowdown technique (taken from ASTM Method D 3086). The following method may be used for final concentration of the BNA extract instead of the procedures in paragraph 2.7.2. Place the concentrator tube in a warm water bath (35°C) and evaporate the solvent volume to below 1 mL using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon). Caution: New plastic tubing must not be used between the carbon trap and the sample, since it may introduce interferences.

The internal wall of the tube must be rinsed down several times with methylene chloride during the operation. During evaporation, the tube solvent level must be kept below the water level of the bath. The extract must never be allowed to become dry.

If the extract in 2.5.8 was not split for both semivolatile and pesticide analyses, bring the final volume of the extract to 1.0 mL with methylene chloride. This represents a ten-fold concentration. If the extract in 2.5.8 was split in 2.7.1, then bring the final volume of the semivolatile portion to 0.95 mL with methylene chloride. This represents a similar ten-fold concentration. In either case, if GPC cleanup techniques were employed, the final volume (1.0 or 0.95 mL) represents a two-fold dilution to account for the fact that only half the extract went through the GPC.

- 2.7.4 Store all extracts at 4°C ($\pm 2^\circ\text{C}$) in the dark in Teflon-sealed containers.

SECTION III

**SCREENING OF SEMIVOLATILE
ORGANIC EXTRACTS**

1. Summary of Method

- 1.1 The solvent extracts of water and sediment/soil are screened on a gas chromatograph/flame ionization detector (GC/FID) using a fused silica capillary column (FSCC). The results of the screen will determine the concentration of extract taken for GC/MS analysis.

2. Apparatus and Materials

- 2.1 Gas chromatograph - An analytical system complete with a temperature programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases. The injection port must be designed for on-column injection when using packed columns and for splitless injection when using capillary columns.

2.1.1 Above GC equipped with flame ionization detector.

2.1.2 GC column - 30 m x 0.32 mm, 1 micron film thickness, silicone coated, fused silica capillary column (J & W Scientific DB-5 or equivalent).

3. Reagents

- 3.1 Methylene chloride - pesticide residue analysis grade or equivalent.

- 3.2 GC calibration standard. Prepare a standard solution containing phenol, phenanthrene and di-n-octylphthalate.

3.2.1 Stock standard solutions (1.00 ug/ μ L)-Stock standard solutions can be prepared from pure standard materials or purchased solutions.

3.2.1.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in pesticide quality methylene chloride and dilute to volume in a 10 mL volumetric flask. Larger volumes may be used at the convenience of the analyst. If compound purity is assayed at 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source and are traceable to EMSL/LV-supplied standards.

3.2.1.2 Transfer the stock standard solutions into Teflon sealed screw-cap bottles. Store at -10°C to -20°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. Stock standard solutions must be replaced after six months or sooner if comparison with quality control

check samples indicates a problem. Standards prepared from gases or reactive compounds such as styrene must be replaced after two months, or sooner if comparison with quality control check samples indicates a problem.

- 3.2.2 Prepare a working standard mixture of the three compounds in methylene chloride. The concentration must be such that the volume injected equals 50 ng of each compound. The storage and stability requirements are the same as specified in 3.2.1.2.

4. GC Calibration

- 4.1 At the beginning of each 12 hour shift, inject the GC calibration standard. The following criteria must be:

- 4.1.1 Standardized for half scale response from 50 ng of phenanthrene.
- 4.1.2 Adequately separates phenol from the solvent front.
- 4.1.3 Minimum of quarter scale response for 50 ng of di-n-octylphthalate.

5. GC/FID Screening

- 5.1 Suggested GC operating conditions:

Initial Column Temperature Hold - 50°C for 4 minutes

Column Temperature Program - 50 - 280°C at 8 degrees/min.

Final Column Temperature Hold - 280°C for 8 minutes

Injector - Grob-type, splitless

Sample Volume - 1 μ L - 2 μ L

Carrier Gas - Helium at 30 cm^3/sec

- 5.2 Inject the GC calibration standard and ensure the criteria specified in 4. are met before injecting samples. Estimate the response for 10 ng of phenanthrene.

- 5.3 Inject the appropriate extracts from Section II, including blanks.

6. Interpretation of Chromatograms

6.1 Water

- 6.1.1 If no sample peaks are detected, or all are less than full scale deflection, the undiluted extract is analyzed on GC/MS.

- 6.1.2 If any sample peaks are greater than full scale deflection, calculate the dilution necessary to reduce the major peaks to between half and full scale deflection. Use this dilution factor to dilute the extract for GC/MS analysis.

6.2 Soil/Sediment

- 6.2.1 If no sample peaks from the extract (from low or medium level preparation) are detected, or all are less than 10% full scale deflection, the sample must be prepared by the low level protocol, Section II, Part C, paragraph 2.

- 6.2.2 Peaks are detected at greater than 10% full scale deflection and less than or equal to full scale deflection.

- 6.2.2.1 If the screen is from the medium level extract, proceed with GC/MS analysis of this extract with appropriate dilution if necessary.

- 6.2.2.2 If screen is from the low level extract, discard extract and prepare sample by medium level method for GC/MS analysis.

- 6.2.3 Peaks are detected at greater than full scale deflection:

- 6.2.3.1 If the screen is from the medium level preparation, calculate the dilution necessary to reduce the major peaks to between half and full scale deflection. Use this dilution factor to dilute the extract. This dilution is analyzed by GC/MS for extractable organics.

- 6.2.3.2 If the screen is from the low level preparation, discard the extract and prepare a sample by the medium level method for GC/MS analysis.

7. GC/MS Analysis

- 7.1 Use the information from 6. to perform the GC/MS analysis of extractables in Section IV, GC/MS Analysis of Semivolatiles, paragraph 1.

SECTION IV

GC/MS ANALYSIS OF SEMI-VOLATILES

1. Summary of Method

This method is to be used for the GC/MS analysis of semivolatiles screened by Section III protocols and for confirmation of pesticides/PCBs identified by GC/EC, if concentrations permit.

2. Apparatus and Materials

2.1 Gas chromatograph/mass spectrometer system.

- 2.1.1 Gas chromatograph - An analytical system complete with a temperature programmable gas chromatograph suitable for splitless injection and all required accessories including syringes, analytical columns and gases.
- 2.1.2 Column - 30 m x 0.25 mm ID (or 0.32 mm) bonded-phase silicone coated fused silica capillary column (J&W Scientific DB-5 or equivalent). A film thickness of 1.0 micron is recommended because of its larger capacity. A film thickness of 0.25 micron may be used.
- 2.1.3 Mass Spectrometer - Capable of scanning from 35 to 500 amu every 1 second or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode and producing a mass spectrum which meets all required criteria when 50 ng of decafluorotriphenylphosphine (DFTFP) is injected through the GC inlet. NOTE: DFTFP criteria must be met before any sample extracts are analyzed. Any samples analyzed when DFTFP criteria have not been met will require reanalysis at no cost to the Government.
- 2.1.4 Data system - A computer system must be interfaced to the mass spectrometer 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 specific 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 abundance in any EICP between specified time or scan number limits.

3. Reagents

- 3.1 Internal standards - 1,4 dichlorobenzene-d₄, naphthalene-d₈, acenaphthene-d₁₀, phenanthrene-d₁₀, chrysene-d₁₂, perylene-d₁₂.

An internal standard solution can be prepared by dissolving 200 ng of each compound in 50 µL of methylene chloride. It may be necessary to use 5 to 10 percent benzene or toluene in this solution and a few minutes of ultrasonic mixing in order to dissolve all the constituents. The resulting solution will contain each standard at a concentration of 4000 ng/µL. A 10 µL portion of this solution should be added to each 1

mL of sample extract. This will give a concentration of 40 ng/uL of each constituent.

- 3.2 Prepare calibration standards at a minimum of five concentration levels. Each calibration standard should contain each compound of interest and each surrogate standard. (See GC/MS calibration in Exhibit E for calibration standard concentration.) Great care must be taken to maintain the integrity of all standard solutions. Store all standard solutions at -10°C to -20°C in screw-cap amber bottles with teflon liners. Fresh standards should be prepared every twelve months at a minimum. The continuing calibration standard should be prepared weekly and stored at 4°C ($\pm 2^\circ\text{C}$).

4. Calibration

- 4.1 Each GC/MS system must have the hardware tuned to meet the criteria listed in Exhibit E for a 50 ng injection of decafluorotriphenyl phosphine (DFTFP). No sample analyses can begin until all these criteria are met. This criteria must be demonstrated each 12 hour shift. DFTFP has to be injected to meet this criterion. Post-acquisition manipulation of abundances is not acceptable.
- 4.2 The internal standards selected in paragraph 2.3.1 should permit most components of interest in a chromatogram to have retention times of 0.80 to 1.20 relative to the internal standards (see instructions for Form VI, Initial Calibration Data). Use the base peak ion from the specific internal standard as the primary ion for quantification, found in Exhibit E, Table 2.2. If interferences are noted, use the next most intense ion as the secondary ion, i.e. For 1,4-dichlorobenzene- d_4 use m/z 152 for quantification.
- 4.2.1 The internal standards are added to all calibration standards and all sample extracts just prior to analysis by GC/MS. A 10 uL aliquot of the internal standard solution should be added to a 1 mL aliquot of calibration standards.
- 4.3 Analyze 1 uL of each calibration standard and tabulate the area of the primary characteristic ion against concentration for each compound including the surrogate compounds. Calculate relative response factors (RRF) for each compound using Equation 1.

$$RRF = \frac{A_x}{A_{IS}} \times \frac{C_{IS}}{C_x} \quad \text{Equation 1.}$$

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 from Exhibit E.
- C_{IS} - Concentration of the internal standard (ng/uL).
- C_x - Concentration of the compound to be measured (ng/uL).

- 4.3.1 The average relative response factor (RRF) should be calculated for all compounds. A system performance check must be made before this calibration curve is used. Four compounds (the system performance check compounds) are checked for a minimum average relative response factor. These compounds (the SPCC) are N-nitroso-di-n-propylamine, hexachlorocyclopentadiene, 2,4-dinitrophenol, 4-nitrophenol. See instructions in Exhibit E for Form VI, Initial Calibration Data for more details.
- 4.3.2 A $\pm$ Relative Standard Deviation ($\pm$ RSD) is calculated for thirteen compounds labeled the Calibration Check Compounds (CCC) on Form VI SV and in Table 2.3, Exhibit E, III SV. A maximum $\pm$ RSD is also specified for these compounds. These criteria must be met for the calibration curve to be valid.
- 4.4 A check of the calibration curve must be performed once every 12 hours during analysis. These criteria are described in detail in the instructions for Form VII, Calibration Check. The minimum relative response factor for the system performance check compounds must be checked. If this criteria is met, the relative response factors of all compounds are calculated. A percent difference of the daily (12 hour) relative response factor compared to the average relative response factor from the initial curve is calculated. A maximum percent difference is allowed for each compound flagged as 'CCC' on Form VII. Only after both these criteria are met can sample analysis begin.
- 4.5 Internal standard responses and retention times in all standards must be evaluated during or immediately after data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the latest daily (12 hour) calibration standard, the chromatographic system must be inspected for malfunctions, and corrections made as required. The extracted ion current profile (EICP) of the internal standards must be monitored and evaluated for each standard. If EICP area for any internal standard changes by more than a factor of two (-50% to +100%), the mass spectrometric system must be inspected for malfunction and corrections made as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is necessary.

5. GC/MS Analysis

- 5.1 The following instrumental parameters are required for all performance tests and for all sample analyses:
- Electron Energy - 70 volts (nominal)
Mass Range - 35 to 500 amu
Scan Time - not to exceed 1 second per scan
- 5.2 Combine 0.5 mL of the base/neutral extract and 0.5 mL of acid from the water extract prior to analysis.
- 5.3 Internal standard solution is added to each sample extract. For water and/or medium soil extracts, add 10 μ L of internal standard solution to each accurately measured 1.0 mL of sample extract. If the low soil

extracts required a pesticide split (see Section II, Part C, paragraph 2.7), add 9.5 μ L of internal standard solution to each accurately measured 0.95 mL of sample extract. Analyze the 1.0 mL extract by GC/MS using a bonded-phase silicone-coated fused silica capillary column. The recommended GC operating conditions to be used are as follows:

Initial Column Temperature Hold	-	40°C for 4 minutes
Column Temperature Program	-	40-270°C at 10 degrees/min.
Final Column Temperature Hold	-	270°C for 10 minutes
Injector Temperature	-	250-300°C
Transfer Line Temperature	-	250-300°C
Source Temperature	-	according to manufacturer's specifications
Injector	-	Grob-type, splitless
Sample Volume	-	1 - 2 μ L
Carrier Gas	-	Helium at 30 cm^3/sec

NOTE: Make any extract dilution indicated by characterization prior to the addition of internal standards. If any further dilutions of water or soil/sediment extracts are made, additional internal standards must be added to maintain the required 40 ng/ μ L of each constituent in the extract volume. If the concentration on the column of any compound exceeds the initial calibration range, the extract must be diluted and reanalyzed. See Exhibit E, Section III, SV, Part 6. Secondary ion quantitation is only allowed when there are sample interferences with the primary ion. If secondary ion quantitation is performed, document the reasons in the Case Narrative.

6. Qualitative Analysis

- 6.1** The compounds listed in the Target Compound List (TCL), Exhibit C, shall be identified by an analyst competent in the interpretation of mass spectra (see PreAward Bid Confirmation description) by comparison of the sample mass spectrum to the mass spectrum of a standard of the suspected compound. Two criteria must be satisfied to verify the identifications: (1) elution of the sample component at the GC relative retention time as the standard component, and (2) correspondence of the sample component and standard component mass spectra.

- 6.1.1** For establishing correspondence of the GC relative retention time (RRT), the sample component RRT must compare within ± 0.06 RRT units of the RRT of the standard component. For reference, the standard must be run on the same shift as the sample. If coelution of interfering components prohibits accurate

assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions unique to the component of interest.

- 6.1.2 For comparison of standard and sample component mass spectra, mass spectra obtained on the contractor's GC/MS are required. Once obtained, these standard spectra may be used for identification purposes, only if the contractor's GC/MS meets the DFTPP daily tuning requirements. These standard spectra may be obtained from the run used to obtain reference RRTs.
- 6.1.3 The requirements for qualitative verification by comparison of mass spectra are as follows:
 - 6.1.3.1 All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum.
 - 6.1.3.2 The relative intensities of ions specified in (1) must agree within plus or minus 20% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample ion abundance must be between 30 and 70 percent.)
 - 6.1.3.3 Ions greater than 10% in the sample spectrum but not present in the standard spectrum must be considered and accounted for by the analyst making the comparison. In Task III, the verification process should favor false positives. All compounds meeting the identification criteria must be reported with their spectra. For all compounds below the CRQL report the actual value followed by "J", e.g. "3J."
- 6.1.4 If a compound cannot be verified by all of the criteria in 6.1.3, but in the technical judgement of the mass spectral interpretation specialist, the identification is correct, then the Contractor shall report that identification and proceed with quantification in 7.
- 6.2 A library search shall be executed for non-TCL sample components for the purpose of tentative identification. For this purpose, the 1985 release of the National Bureau of Standards Mass Spectral Library (or more recent release), containing 42,261 spectra, shall be used.
 - 6.2.1 Up to 20 nonsurrogate organic compounds of greatest apparent concentration not listed in Exhibit C for the combined base/neutral/acid fraction shall be tentatively identified via a forward search of the NBS mass spectral library. (Substances with responses less than 10% of the nearest internal standard are not required to be searched in this fashion). Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist

assign a tentative identification. NOTE: Computer generated library search routines must not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

6.2.2 Guidelines for making tentative identification:

6.2.2.1 Relative intensities of major ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum.

6.2.2.2 The relative intensities of the major ions should agree within $\pm 20\%$. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample ion abundance must be between 30 and 70 percent.)

6.2.2.3 Molecular ions present in reference spectrum should be present in sample spectrum.

6.2.2.4 Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.

6.2.2.5 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 compounds. NOTE: Data system library reduction programs can sometimes create these discrepancies.

6.2.3 If in the technical judgement of the mass interpretation spectral specialist, no valid tentative identification can be made, the compound should be reported as unknown. The mass spectral specialist should give additional classification of the unknown compound, if possible (i.e., unknown phthalate, unknown hydrocarbon, unknown acid type, unknown chlorinated compound). If probable molecular weights can be distinguished, include them.

7. Quantitation

7.1 TCL components identified shall be quantified by the internal standard method. The internal standard used shall be the one nearest the retention time to that of a given analyte (see Exhibit E, Tables 2.1 and 2.2). The EICP area of characteristic ions of analytes listed in Tables 4, 5 and 6 are used.

Internal standard responses and retention times in all samples must be evaluated during or immediately after data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the latest daily (12 hour) calibration standard, the chromatographic system must be inspected for malfunctions, and

corrections made as required. The extracted ion current profile (EICP) of the internal standards must be monitored and evaluated for each sample, blank, matrix spike and matrix spike duplicate. The criteria are described in detail in the instructions for Form VIII, Internal Standard Area Summary. If the EICP area for any internal standard changes by more than a factor of two (-50% to +100%), the mass spectrometric system must be inspected for malfunction and corrections made as appropriate. If the analysis of a subsequent sample or standard indicates that the system is functioning properly, then corrections may not be required. The samples or standards with EICP areas outside the limits must be re-analyzed, and treated according to 7.1.1 and 7.1.2 below. If corrections are made, then the laboratory must demonstrate that the mass spectrometric system is functioning properly. This must be accomplished by the analysis of a standard or sample that does meet the EICP criteria. After corrections are made, the re-analysis of samples analyzed while the system was malfunctioning is required.

7.1.1 If after re-analysis, the EICP areas for all internal standards are inside the contract limits (-50% to +100%), then the problem with the first analysis is considered to have been within the control of the laboratory. Therefore, only submit data from the analysis with EICPs within the contract limits. This is considered the initial analysis and must be reported as such on all data deliverables.

7.1.2 If the re-analysis of the sample does not solve the problem, i.e., the EICP areas are outside the contract limits for both analyses, then submit the EICP data and sample data from both analyses. Distinguish between the initial analysis and the re-analysis on all data deliverables, using the sample suffixes specified in Exhibit B. Document in the Case Narrative all inspection and corrective actions taken.

7.2 The relative response factor (RRF) from the daily standard analysis is used to calculate the concentration in the sample. Secondary ions may be used if interferences are present. The area of a secondary ion cannot be substituted for the area of a primary ion unless a relative response factor is calculated using the secondary ion. When TCL Compounds are below contract required quantitation limits (CRQL) but the spectra meets the identification criteria, report the concentration with a "J." For example, if CRQL is 10 ug/L and concentration of 3 ug/L is calculated, report as "3J."

7.2.1 Calculate the concentration in the sample using the relative response factor (RRF) as determined in paragraph 4.3 and the following equation:

Water

$$\text{Concentration ug/L} = \frac{(A_x)(I_s)(V_c)}{(A_{IS})(RRF)(V_o)(V_i)}$$

A_x - Area of the characteristic ion for the compound to be measured

A_{IS} - Area of the characteristic ion for the internal standard

I_s - Amount of internal standard injected in nanograms (ng)

V_o - Volume of water extracted in milliliters (mL)

V_i - Volume of extract injected (uL)

V_c - Volume of total extract

(Use 2000 uL or a factor of this when dilutions are made. The 2,000 uL is derived from combining half of the 1 mL BN extract and half of the 1 mL A extract.)

Soil/Sediment

$$\text{Concentration ug/kg (Dry weight basis)} = \frac{(A_x)(I_s)(V_c)}{(A_{IS})(RRF)(V_i)(W_s)(D)}$$

Where:

A_x, I_s, A_{IS} - Same as given for water, above

V_c - Volume of low level total extract (Use 1000 uL or a factor of this when dilutions are made. If GPC cleanup is used, the volume is 2,000 uL. The 1000 uL is derived from concentrating the 9.5 mL extract to 0.95 mL.)

- OR -

V_c - Volume of medium level extract (Use 2,000 uL or a factor of this when dilutions are made. The 2,000 uL is derived from concentrating 5 mL of the 10 mL extract to 1 mL.)

V_i - Volume of extract injected (uL)

D - $\frac{100 - \% \text{ moisture}}{100}$

W_s - Weight of sample extracted (grams)

- 7.3 An estimated concentration for non-TCL components tentatively identified shall be quantified by the internal standard method. For quantification, the nearest internal standard free of interferences shall be used.
- 7.3.1 The formula for calculating concentrations is the same as in paragraph 7.2.1. Total area counts (or peak heights) from the total ion chromatograms are to be used for both the compound to be measured and the internal standard. A relative response factor (RRF) of one (1) is to be assumed. The value from this quantitation shall be qualified as estimated. This estimated concentration should be calculated for all tentatively identified compounds as well as those identified as unknowns.
- 7.4 Calculate surrogate standard recovery on all samples, blanks and spikes. Determine if recovery is within limits and report on appropriate form.
- 7.4.1 If recovery is not within limits (i.e., if two surrogates from either base/neutral or acid fractions are out of limits or if recovery of any one surrogate in either fraction is below 10%), the following is required.
- o Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
 - o Reanalyze the sample if none of the above reveal a problem.
- 7.4.2 If the reanalysis of the sample solves the problem, then the problem was within the laboratory's control. Therefore, only submit data from the analysis with surrogate spike recoveries within the contract windows. This shall be considered the initial analysis and shall be reported as such on all data deliverables.
- 7.4.3 If none of the steps in 7.4.1 or 7.4.2 solve the problem, then reextract and reanalyze the sample. If the reextraction and reanalysis of the sample solves the problem, then the problem was within the laboratory's control. Therefore, only submit data from the analysis with surrogate spike recoveries within the contract windows. This shall be considered the initial analysis and shall be reported as such on all data deliverables.
- 7.4.4 If the reextraction and reanalysis of the sample does not solve the problem, i.e., the surrogate recoveries are outside the contract limits for both analyses, then submit the surrogate spike recovery data and the sample analysis data from analysis of both sample extracts. Distinguish between the initial analysis and the reanalysis on all data deliverables, using the sample suffixes specified in Exhibit B.

7.4.3 If the sample with surrogate recoveries outside the limits is the sample used for the matrix spike and matrix spike duplicate and the surrogate recoveries of the matrix spike and matrix spike duplicate show the same pattern (i.e., outside the limits), then the sample, matrix spike and matrix spike duplicate do not require re-analysis.

Document in the narrative the similarity in surrogate recoveries.

Table 4.

Characteristic Ions for Semivolatile TCL Compounds

Parameter	Primary Ion	Secondary Ion(s)
Phenol	94	63, 66
bis(-2-Chloroethyl)Ether	93	63, 95
2-Chlorophenol	128	64, 130
1,3-Dichlorobenzene	146	148, 113
1,4-Dichlorobenzene	146	148, 113
Benzyl Alcohol	108	79, 77
1,2-Dichlorobenzene	146	148, 113
2-Methylphenol	108	107
bis(2-chloroisopropyl)Ether	43	77, 79
4-Methylphenol	108	107
N-Nitroso-Di-Propylamine	70	42, 101, 130
Hexachloroethane	117	201, 199
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	128	129, 127
4-Chloroaniline	127	129
Hexachlorobutadiene	225	223, 227
4-Chloro-3-Methylphenol	107	144, 142
2-Methylnaphthalene	142	141
Hexachlorocyclopentadiene	237	235, 272
2,4,6-Trichlorophenol	196	198, 200
2,4,5-Trichlorophenol	196	198, 200
2-Chloronaphthalene	162	164, 127
(continued)		

Table 4. (continued)
Characteristic Ions for Semivolatile TCL Compounds

Parameter	Primary Ion	Secondary Ion(s)
2-Nitroaniline	65	92, 138
Dimethyl Phthalate	163	194, 164
Acenaphthylene	152	151, 153
3-Nitroaniline	138	108, 92
Acenaphthene	153	152, 154
2,4-Dinitrophenol	184	63, 154
4-Nitrophenol	109	139, 65
Dibenzofuran	168	139
2,4-Dinitrotoluene	163	63, 182
2,6-Dinitrotoluene	163	89, 121
Diethylphthalate	149	177, 150
4-Chlorophenyl-phenylether	204	206, 141
Fluorene	166	163, 167
4-Nitroaniline	138	92, 108
4,6-Dinitro-2-Methylphenol	198	182, 77
N-Nitrosodiphenylamine	169	168, 167
4-Bromophenyl-phenylether	248	250, 141
Hexachlorobenzene	284	142, 249
Pentachlorophenol	266	264, 268
Phenanthrene	178	179, 176
Anthracene	178	179, 176
Di-N-Butylphthalate	149	150, 104
Fluoranthene	202	101, 100
Pyrene	202	101, 100
Butylbenzylphthalate	149	91, 206
3,3'-Dichlorobenzidine	252	254, 126
Benzo(a)Anthracene	228	229, 226
bis(2-Ethylhexyl)Phthalate	149	167, 279
Chrysene	228	226, 229
Di-N-Octyl Phthalate	149	-
Benzo(b)Fluoranthene	252	253, 125
Benzo(k)Fluoranthene	252	253, 125
Benzo(a)Pyrene	252	253, 125
Indeno(1,2,3-cd)Pyrene	276	138, 227
Dibenz(a, h)Anthracene	278	139, 279
Benzo(g, h, i)Perylene	276	138, 277

Table 5.

Characteristic Ions for Pesticides/PCBs

Parameter	Primary Ion	Secondary Ion(s)
Alpha-BHC	183	181, 109
Beta-BHC	181	183, 109
Delta-BHC	183	181, 109
Gamma-BHC (Lindane)	183	181, 109
Heptachlor	100	272, 274
Aldrin	66	263, 220
Heptachlor Epoxide	353	355, 351
Endosulfan I	195	339, 341
Dieldrin	79	263, 279
4,4'-DDE	246	248, 176
Endrin	263	82, 81
Endosulfan II	337	339, 341
4,4'-DDD	235	237, 165
Endosulfan Sulfate	272	387, 422
4,4'-DDT	235	237, 165
Methoxychlor	227	228
Chlordane (alpha and/or gamma)	373	375, 377
Toxaphene	159	231, 233
Aroclor-1016	222	260, 292
Aroclor-1221	190	222, 260
Aroclor-1232	190	222, 260
Aroclor-1242	222	256, 292
Aroclor-1248	292	362, 326
Aroclor-1254	292	362, 326
Aroclor-1260	360	362, 394
Endrin Ketone	317	67, 319

Table 6.

Characteristic Ions for Surrogates and
Internal Standards for Semivolatile Compounds

<u>SURROGATES</u>	<u>Primary Ion</u>	<u>Secondary Ion(s)</u>
Phenol-d ₃	99	42, 71
2-Fluorophenol	112	64
2,4,6-Tribromophenol	330	332, 141
d-5 Nitrobenzene	82	128, 54
2-Fluorobiphenyl	172	171
Terphenyl	244	122, 212
<u>INTERNAL STANDARDS</u>		
1,4-Dichlorobenzene-d ₄	132	115
Naphthalene-d ₈	136	68
Acenaphthene-d ₁₀	164	162, 160
Phenanthrene-d ₁₀	188	94, 80
Chrysene-d ₁₂	240	120, 236
Perylene-d ₁₂	264	260, 265

SECTION II
SAMPLE PREPARATION AND STORAGE

PART A - SAMPLE STORAGE AND HOLDING TIMES

1. Procedures for Sample Storage

- 1.1 The samples must be protected from light and refrigerated at 4°C ($\pm$ 2°C) from the time of receipt until extraction and analysis.
- 1.2 After analysis, extracts and unused sample volume must be protected from light and refrigerated at 4° C ($\pm$ 2° C) for the periods specified in the contract schedule.

2. Contract Required Holding Times

- 2.1 If separatory funnel or sonication procedures are employed for extractions for pesticide/ PCB analyses, extraction of water samples shall be completed within 5 days of VTSR (Validated Time of Sample Receipt), and extraction of soil/ sediment samples shall be completed within 10 days of VTSR. If continuous liquid-liquid extraction procedures are employed, extraction of water samples shall be started within 5 days of VTSR.
- 2.2 Extracts of either water or soil/sediment samples must be analyzed within 40 days following extraction.

PART B - SAMPLE PREPARATION FOR PESTICIDES/PCBs IN WATER

1. Summary of Method

A measured volume of sample, approximately one-liter, is solvent extracted with methylene chloride using a separatory funnel or a continuous extractor. The methylene chloride extract is dried, exchanged to hexane and adjusted to a final volume of 10 mL.

2. Interferences

- 2.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks. Interferences by phthalate esters can pose a major problem in pesticide analysis when using the electron capture detector. These compounds generally appear in the chromatogram as broad eluting peaks. Common flexible plastics contain varying amounts of phthalates. These phthalates are easily extracted or leached from such materials during laboratory operations. Cross-contamination of clean glassware routinely occurs when plastics are handled. Interferences from phthalates can best be minimized by avoiding the use of plastics in the laboratory. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination.
- 2.2 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 and diversity of the site being sampled. The cleanup procedures in paragraphs 7.1 thru 7.5 must be used to overcome such interferences to attempt to achieve the CQLs. The cleanup procedures in paragraph 8.1 through 8.5 may be used to remove sulfur interferences.

3. Apparatus and Materials

- 3.1 Glassware (Brand names and catalog numbers included for illustration purposes only).
- 3.1.1 Separatory funnel - 2000 mL with Teflon stopcock.
- 3.1.2 Drying column - Chromatographic column approximately 400 mm long x 19 mm ID, with coarse frit. (Substitution of a small pad of disposable Pyrex glass wool for the frit will help prevent cross-contamination of sample extracts.)
- 3.1.3 Concentrator tube - Kuderna-Danish, 10 mL, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of extracts.
- 3.1.4 Evaporative flask - Kuderna-Danish, 500 mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.

- 3.1.5 Snyder column - Kuderna-Danish, Three-ball macro (Kontas K-503000-0121 or equivalent).
- 3.1.6 Snyder column - Kuderna-Danish, Two-ball micro (Kontas K-569001-0219 or equivalent).
- 3.1.7 Continuous liquid-liquid extractors - Equipped with Teflon or glass connecting joints and stopcocks requiring no lubrication. (Harshberg-Wolf Extractor-Ace Glass Company, Vineland, NJ P/N 6841-10, or equivalent.)
- 3.1.8 Vials - Amber glass, 10 to 15 mL capacity, with Teflon-lined screw cap.
- 3.1.9 Bottle or test tube - 50 mL with Teflon-lined screw cap for sulfur removal.
- 3.1.10 Chromatographic column for alumina - 8 mL (200 mm X 8 mm ID) Polypropylene column (Kontas K-420160 or equivalent) or 6 mL (150 mm x 8 mm ID) glass column (Kontas K-420155 or equivalent) or 5 mL serological pipettes plugged with a small piece of Pyrex glass wool in the tip. The Kontas columns may be plugged with Pyrex glass wool or a polyethylene porous disk (Kontas K-420162).
- 3.2 Pyrex glass wool - Pre-rinse glass wool with appropriate solvents to ensure its cleanliness.
- 3.3 Silicon carbide boiling chips - Approximately 10/40 mesh. Heat to 400°C for 30 minutes or Soxhlet extract with methylene chloride.
- 3.4 Water bath - Heated, with concentric ring cover, capable of temperature control ($\pm 2^\circ\text{C}$). The bath should be used in a hood.
- 3.5 Balance - Analytical, capable of accurately weighing ± 0.0001 g.
- 3.6 Nitrogen evaporation device equipped with a water bath that can be maintained at 35-40°C. The N-Evap by Organomation Associates, Inc. South Berlin, MA (or equivalent) is suitable.
- 4. Reagents
- 4.1 Reagent water - Reagent water is defined as a water in which an interferent is not observed at or above the CRQL of each parameter of interest.
- 4.2 Acetone, hexane, isooctane (2,2,4-trimethylpentane), methylene chloride Pesticide quality or equivalent.
- 4.3 Sodium sulfate - (ACS) granular, anhydrous. Purify by heating at 400°C for 4 hours in a shallow tray.
- 4.4 Alumina - Neutral, Super I Woelm (Universal Scientific, Incorporated, Atlanta, Georgia) or equivalent. Prepare activity III by adding 7%

(v/v) reagent water to the Super I neutral alumina. Tumble or shake in a wrist action shaker for a minimum of 2 hours or preferably overnight. There should be no lumps present. Store in a tightly sealed glass container. A 25 cycle soxhlet extraction of the alumina with methylene chloride is required if a solvent blank analyzed by the pesticide technique indicates any interferences for the compounds of interest.

- 4.4.1 **Alumina Equivalency Check.** Test the alumina by adding the BNA surrogates (see Exhibit D SV) in 1:1 acetone/hexane to the alumina and following paragraph 7.1. The tribromophenol should not be detected by GC/EC if the alumina and its activation are acceptable. Also check recovery of all single component pesticides following the same procedure. The percent recovery for all single component pesticides must be $\geq 80\%$, except for endosulfan sulfate which must be $\geq 60\%$ and endrin aldehyde which is not recovered. The data must be retained by the laboratory and made available for inspection during on-site evaluations. If the alumina deactivated with 7% (v/v) reagent water does not prove adequate to remove the BNA surrogates and other interferences, the alumina may be deactivated with as much as 9% reagent water, so long as the criteria for tribromophenol and the recovery of all single component pesticides can be met.
- 4.5 **Sodium hydroxide solution (10N)-(ACS).** Dissolve 40 g NaOH in reagent water and dilute to 100 mL.
- 4.6 **Tetrabutylammonium (TBA) - Sulfite reagent.** Dissolve 3.39 g tetrabutylammonium hydrogen sulfate in 100 mL distilled water. To remove impurities, extract this solution three times with 20 mL portions of hexane. Discard the hexane extracts, and add 25 g sodium sulfite to the water solution. Store the resulting solution, which is saturated with sodium sulfite, in an amber bottle with a Teflon-lined screw cap. This solution can be stored at room temperature for at least one month.
- 4.7 **Pesticide surrogate standard spiking solution.**
- 4.7.1 The surrogate standard is added to all samples and calibration solutions; the compound specified for this purpose is dibutylchlorodate.
- 4.7.2 Prepare a surrogate standard spiking solution at a concentration of 1 ug/1.00 mL in acetone. Store the spiking solutions at 4°C ($\pm 2^\circ\text{C}$) in Teflon-sealed containers. The solutions should be checked frequently for stability. These solutions must be replaced after twelve months, or sooner, if comparison with quality control check samples indicates a problem.
- 4.8 **Sulfuric acid solution (1+1)-(ACS).** Slowly, add 50 mL H_2SO_4 (sp. gr. 1.84) to 50 mL of reagent water.

- 4.9 Pesticide matrix standard spiking solution. Prepare a spiking solution of acetone or methanol that contains the following pesticides in the concentrations specified.

<u>Pesticide</u>	<u>ug/1.0 mL</u>
Lindane	0.2
Heptachlor	0.2
Aldrin	0.2
Dieldrin	0.5
Endrin	0.5
4,4' DDT	0.5

Matrix spikes are also to serve as duplicates by spiking two 1-liter portions from the one sample chosen for spiking.

- 4.10 See Exhibit A for a summary of the quality control requirements of this contract. See Exhibit E for contract-required quality assurance/quality control procedures.

5. Sample Extraction - Separatory Funnel

- 5.1 Samples may be extracted using separatory funnel techniques. If emulsions prevent acceptable solvent recovery with separatory funnel extractions, continuous liquid-liquid extraction (paragraph 6.1) may be used. The separatory funnel extraction scheme described below assumes a sample volume of one liter.
- 5.2 Using a 1-liter graduated cylinder, measure out a 1-liter sample aliquot and place it into a 2-liter separatory funnel. Check the pH of the sample with wide range pH paper and adjust to between 5 and 9 pH with 10 N sodium hydroxide and/or 1:1 sulfuric acid solution. (NOTE: Recovery of dibutylchlorodate will be low if pH is outside this range. Alpha-BHC, gamma-BHC, Endosulfan I and II and Endrin are subject to decomposition under alkaline conditions and therefore may not be detected if the pH is above 9.) Pipet 1.0 mL surrogate standard spiking solution into the separatory funnel and mix well. Add 1.0 mL of pesticide matrix spiking solution to each of two 1-liter portions from the sample selected for spiking.
- 5.3 Add 60 mL methylene chloride to the separatory funnel and extract the sample by shaking the funnel for two minutes, with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the volume 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 means. Drain methylene chloride into a 250 mL Erlenmeyer flask.
- 5.4 Add a second 60 mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner.

- 5.5 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D if equivalency is demonstrated for all pesticides listed in Exhibit C.
- 5.6 Pour the combined extract through a drying column containing about 10 cm of anhydrous granular sodium sulfate, and collect the extract in the K-D concentrator. Rinse the Erlenmeyer flask and column with 20 to 30 mL of methylene chloride to complete the quantitative transfer.
- 5.7 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL methylene chloride to the top. Place the K-D apparatus on a hot water bath (80 to 90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10 to 15 minutes. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus. Allow it to drain and cool for at least 10 minutes.
- 5.8 Momentarily remove the Snyder column, add 50 mL of hexane and a new boiling chip and re-attach the Snyder column. Pre-wet the column by adding about 1 mL of hexane to the top. Concentrate the solvent extract as before. The elapsed time of concentration should be 5 to 10 minutes. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool at least 10 minutes.
- 5.9 Remove the Snyder column, rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of hexane. If sulfur crystals are a problem, proceed to paragraph 8.1; otherwise continue to paragraph 5.10.
- 5.10 Nitrogen blowdown technique (taken from ASTM Method D 3086)
- Place the concentrator tube in a warm water bath (35°C) and evaporate the solvent volume to 0.5 mL using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon). Caution: New plastic tubing must not be used between the carbon trap and the sample, as it may introduce interferences. The internal wall of the tube must be rinsed down several times with hexane during the operation and the final volume brought to 0.5 mL. During evaporation, the tube solvent level must be kept below the water level of the bath. The extract must never be allowed to become dry.
- 5.11 Dilute the extract to 1 mL with acetone and proceed to 7.1 (Alumina Column Cleanup).

6. Sample Extraction - Continuous Liquid-Liquid Extractor

- 6.1 When experience with a sample from a given source indicates that a serious emulsion problem will result, or if an emulsion is encountered

in paragraph 5.3 using a separatory funnel, a continuous extractor should be used.

- 6.2 Using a 1-liter graduated cylinder, measure out a 1-liter sample aliquot and place it into the continuous extractor. Pipet 1.0 mL surrogate standard spiking solution into the continuous extractor and mix well. Check the pH of the sample with wide range pH paper and adjust to between 5 and 9 pH with 10N sodium hydroxide and/or 1:1 sulfuric acid solution.
- 6.3 Add 500 mL of methylene chloride to the distilling flask. Add sufficient reagent water to ensure proper operation and extract for 18 hours. Allow to cool, then detach the boiling flask and dry. Concentrate the extract as in paragraphs 5.5 through 5.11.

7. Alumina Column Cleanup

- 7.1 Add 3 g of activity III neutral alumina to the 10-mL chromatographic column. Tap the column to settle the alumina. Do not pre-wet the alumina.
- 7.2 Transfer the 1 mL of hexane/acetone extract from paragraph 5.11 to the top of the alumina using a disposable Pasteur pipet. Collect the eluate in a clean 10-mL concentrator tube.
- 7.3 Add 1 mL of hexane to the original extract concentrator tube to rinse it. Transfer these rinsings to the alumina column. Elute the column with an additional 9 mL of hexane. Do not allow the column to go dry during the addition and elution of the sample.
- 7.4 Adjust the extract to a final volume of 10 mL using hexane.
- 7.5 The pesticide/PCB fraction is ready for analysis. Proceed to Section IV, paragraph 3. Store the extracts at 4°C ($\pm 2^\circ\text{C}$) in the dark in Teflon-sealed containers until analyses are performed.

8. Optional Sulfur Cleanup

- 8.1 Concentrate the hexane extract from paragraph 5.9 to 1 mL.
- 8.2 Transfer the 1 mL to a 50 mL clear glass bottle or vial with a Teflon-lined screw cap. Rinse the concentrator tube with 1 mL of hexane, adding the rinsings to the 50 mL bottle.
- 8.3 Add 1 mL TBA-sulfite reagent and 2 mL 2-propanol, cap the bottle, and shake for at least 1 min. If the sample is colorless or if the initial color is unchanged, and if clear crystals (precipitated sodium sulfite) are observed, sufficient sodium sulfite is present. If the precipitated sodium sulfite disappears, add more crystalline sodium

sulfite in approximately 100 mg portions until a solid residue remains after repeated shaking.

- 8.4 Add 5 mL distilled water and shake for at least 1 minute. Allow the sample to stand 5-10 minutes. Transfer the hexane layer (top) to a concentrator ampule and go back to paragraph 5.10.

PART C - PROTOCOLS FOR SOIL/SEDIMENT

It is mandatory that all soil/sediment samples be characterized as to concentration level so that the appropriate analytical protocol may be chosen to ensure proper quantitation limits for the sample.

The use of GC/EC methods is recommended for screening soil/sediment samples for pesticides/PCBs, however, the Contractor is at liberty to determine the specific method of characterization.

Note that the terms "low level" and "medium level" are not used here as a judgement of degree of contamination but rather as a description of the concentration ranges that are encompassed by the "low" and "medium" level procedures.

The concentration range covered by the low level analysis may be considered to be less than 1000 ug/kg of pesticides/PCBs. The concentration range covered by the medium level analysis is greater than 1000 ug/kg.

1. Medium Level Preparation for Analysis of Pesticides/PCBs in Soil/Sediment

1.1 Scope and Application

This procedure is designed for the preparation of sediment/soil samples which may contain pesticides/PCBs at a level greater than 1,000 ug/kg.

- 1.1.1 Samples to be prepared and analyzed by this method should have been screened by GC/EC techniques. The results of those screens will determine whether sufficient quantities of pesticides/PCBs are present to warrant analysis by the medium level protocol.
- 1.1.2 If the screenings indicate no detectable pollutants at a level of quantitation of 1000 ug/kg, the sample should be prepared by the low level protocol in this Section.
- 1.1.3 If the extract for pesticide/PCB analysis is to be prepared from an aliquot of the semivolatile extract, also refer to the specific instructions in Exhibit D SV.

1.2 Summary of Method

- 1.2.1 Portions of soil/sediment are extracted and screened by methods of the Contractor's choice.
- 1.2.2 If pesticides/PCBs are detected in the screen at levels above approximately 1000 ug/kg, a 1 g sample is extracted with 10.0 mL of hexane for analysis by GC/EC.
- 1.2.3 If no pesticides/PCBs are detected above 1000 ug/kg, then the sample shall be prepared by the low level protocol.

1.3 Interferences

- 1.3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the total ion current profiles. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks. 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.

1.4 Limitations

- 1.4.1 The procedure is designed to allow quantitation limits as low as 1000 ug/kg for pesticides/PCBs. If peaks are present based on GC screen, the sample is determined to require a medium level analysis by GC/EC. Some samples may contain high concentrations of chemicals that interfere with the analysis of other components at lower levels; the quantitation limits in these cases may be significantly higher.

1.5 Reagents

- 1.5.1 Sodium Sulfate - anhydrous powdered reagent grade, heated at 400°C for four hours, cooled in a desiccator and stored in a glass bottle Baker anhydrous powder, catalog # 73898 or equivalent.
- 1.5.2 Methylene chloride. Pesticide residue analysis grade or equivalent.
- 1.5.3 Hexane. Pesticide residue analysis grade or equivalent.
- 1.5.4 Methanol. Pesticide residue analysis grade or equivalent.
- 1.5.5 Acetone. Pesticide residue analysis grade or equivalent.
- 1.5.6 Pesticide/PCB Surrogate Standard Spiking solution.
- 1.5.6.1 The compound specified is dibutylchlorodata. Prepare a solution at a concentration of 20 ug/1.0 mL in methanol. Store the spiking solutions at 4°C ($\pm 2^\circ\text{C}$) in Teflon-sealed containers. The solutions should be checked frequently for stability. These solutions must be replaced after twelve months, or sooner, if comparison with quality control check samples indicates a problem.
- 1.5.7 Pesticide/PCB Matrix Standard Spiking solution
- 1.5.7.1 Prepare a spiking solution in methanol that contains the following pesticides in the concentrations specified below. Store the spiking solutions at 4°C

($\pm 2^{\circ}\text{C}$) in Teflon-sealed containers. The solutions should be checked frequently for stability. These solutions must be replaced after twelve months, or sooner, if comparison with quality control check samples indicates a problem.

<u>Pesticide</u>	<u>ug/1.0mL</u>
lindane	2.0
heptachlor	2.0
aldrin	2.0
dieldrin	5.0
endrin	5.0
4,4' DDT	5.0

- 1.5.8 Alumina - neutral, super I Woelm (Universal Scientific, Atlanta, GA) or equivalent. Prepare activity III by adding 7% (v/v) reagent water to the Super I neutral alumina. Tumble or shake on a wrist action shaker for a minimum of 2 hours or preferably overnight. There should be no lumps present. Store in a tightly sealed glass container. A 25 cycle soxhlet extraction of the alumina with methylene chloride is required if a solvent blank analyzed by the pesticide techniques indicates any interferences for the compounds of interest.

- 1.5.8.1 Alumina Equivalency Check. Test the alumina by adding the BNA surrogates (see Exhibit D SV) in 1:1 acetone/hexane to the alumina and following paragraph 2.8.1. The tri-bromophenol should not be detected by GC/EC if the alumina and its activation are acceptable. Also check recovery of all single component pesticides following the same procedure. The percent recovery for all single component pesticides must be $\geq 80\%$, except for endosulfan sulfate which must be $\geq 60\%$ and endrin aldehyde which is not recovered. The data must be retained by the laboratory and made available for inspection during on-site evaluations. If the alumina deactivated with 7% (v/v) reagent water does not prove adequate to remove the BNA surrogates and other interferences, the alumina may be deactivated with as much as 9% reagent water, so long as the criteria for tribromophenol and the recovery of all single component pesticides can be met.

- 1.5.9 Reagent Water - Reagent water is defined as water in which an interferent is not observed at or above the CRQL of each parameter of interest.

1.6 Equipment

- 1.6.1 Glass scintillation vials, at least 20 mL, with screw cap and teflon or aluminum foil liner.
- 1.6.2 Spatula. Stainless steel or Teflon.

- 1.6.3 Balance capable of weighing 100 g to the nearest 0.01 g.
- 1.6.4 Vials and caps, 2 mL for GC auto sampler.
- 1.6.5 Disposable pipettes, Pasteur; glass wool rinsed with methylene chloride.
- 1.6.6 15-mL concentrator tubes.
- 1.6.7 Ultrasonic cell disruptor, Heat Systems-Ultrasonics, Inc., Model W-385 SONICATOR (475 Watt with pulsing capability, No. 200 1/2 inch tapered disruptor horn, and No. 419 1/8 inch standard tapered MICROTIP probe), or equivalent device with a minimum of 375 Watt output capability. NOTE: In order to ensure that sufficient energy is transferred to the sample during extraction, the MICROTIP probe must be replaced if the tip begins to erode. Erosion of the tip is evidenced by a rough surface.
- 1.6.8 Sonabox acoustic enclosure - recommended with above disruptors for decreasing cavitation sound.
- 1.6.9 Test tube rack.
- 1.6.10 Oven, drying.
- 1.6.11 Desiccator.
- 1.6.12 Crucibles, porcelain.
- 1.6.13 Chromatography column for alumina. 8 mL (200 mm x 8 mm ID) Polypropylene column (Kontes K-420160 or equivalent) or 6 mL (150 mm x 8 mm ID) glass column (Kontes K-420155 or equivalent) or 5 mL serological pipettes plugged with a small piece of Pyrex glass wool in the tip. (Pyrex glass wool shall be pre-rinsed with appropriate solvents to insure its cleanliness). The Kontes columns may be plugged with Pyrex glass wool or a polyethylene porous disk (Kontes K-420162).

1.7 Sample Preparation

- 1.7.1 Medium Level preparation for analysis of Pesticide/PCBs (Determine results of GC/EC screen before proceeding.)
 - 1.7.1.1 Transfer the sample container into a fume hood. Open the sample vial and mix the sample. Transfer approximately 1 g (record weight to nearest 0.1 g) of sample to a 20 mL vial. Wipe the mouth of the vial with a tissue to remove any sample material. Record the exact weight of the sample taken. Cap the vial before proceeding with the next sample to avoid any cross contamination.

- 1.7.1.1.1 Transfer 50 g of soil/sediment to 100 mL beaker. Add 50 mL of water and stir for 1 hour. Determine pH of sample with glass electrode and pH meter while stirring. Report pH value on appropriate data sheets. If the pH of the soil is greater than 11 or less than 5, contact the Deputy Project Officer cited in the contract for instructions on how to handle the sample. Document the instructions in the Case Narrative. Discard this portion of sample. NOTE: Recovery of dibutylchlorodate will be low if pH is outside this range.
- 1.7.1.2 Add at least 2 g of anhydrous powdered sodium sulfate to the sample and mix well.
- 1.7.1.3 Surrogate standards are added to all samples, spikes and blanks. Add 50 uL of surrogate spiking solution to the sample mixture.
- 1.7.1.4 Add 1.0 mL of matrix standard spiking solution to each of two 1 g portions from the sample chosen for spiking.
- 1.7.1.5 Immediately add 10.0 mL (only 9.0 mL for the matrix spike sample) of hexane to the sample and disrupt the sample with the 1/8 inch tapered MICROTIP ultrasonic probe for 1 minute with the W-385 (or 2 minutes with the W-375) with output control setting at 5 and mode switch on "1 sec. pulse" and duty cycle set at 50%. (If using a sonicator other than Models W-375 or W-385, contact the Project Officer for appropriate output settings.) Before extraction, make certain that the sodium sulfate is free flowing and not a consolidated mass. As required, break up large lumps with a clear spatula, or very carefully with the tip of the unenergized probe.
- 1.7.1.6 Loosely pack disposable Pasteur pipettes with 2-3 cm glass wool plugs. Filter the extract through the glass wool and collect at approximately 5 mL in a concentrator tube.
- 1.7.1.7 Transfer 1.0 mL of the hexane extract to a glass concentrator tube and concentrate to 0.5 mL using Nitrogen blowdown. Add 0.5 mL of acetone to 0.5 mL of hexane extract. Swirl to mix. The pesticide extract must now be passed through an alumina column to remove polar interferences.

- 1.7.1.8 Follow the procedures for low level soil sediment preparation outlined in paragraphs 2.8.1.1 through 2.8.3.3 for alumina cleanup and sulfur removal.

2. Low Level Preparation for Analysis of Pesticides/PCBs in Soil/Sediment

2.1 Summary of Method.

- 2.1.1 If based on the results of a GC/EC screen, no pesticides/PCBs are present in the sample above 1000 ug/kg, a 30 gram portion of soil/ sediment is mixed with anhydrous powdered sodium sulfate and extracted with 1:1 methylene chloride/acetone using an ultrasonic probe. The extract is concentrated and an optional gel permeation column cleanup may be used. The extract is cleaned up using a micro alumina column and analyzed by GC/EC for pesticides.

2.2 Interferences

- 2.2.1 Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the total ion current profiles. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks. 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.

2.3 Apparatus and Materials

2.3.1 Apparatus for determining percent moisture

- 2.3.1.1 Oven, drying.
- 2.3.1.2 Desiccator.
- 2.3.1.3 Crucibles, porcelain.

2.3.2 Disposable Pasteur glass pipettes, 1 mL

- 2.3.3 Ultrasonic cell disruptor, Heat Systems - Ultrasonics, Inc. Model W-385 SONICATOR (475 watt with pulsing capability, No. 305 3/4 inch tapered high gain "Q" disruptor horn or No. 208 3/4 inch standard solid disruptor horn), or equivalent device with a minimum of 375 watt output capability. NOTE: In order to ensure that sufficient energy is transferred to the sample during extraction, the probe must be replaced if the tip begins to erode. Erosion of the tip is evidenced by a rough surface.

- 2.3.3.1 Sonabox acoustic enclosure - recommended with above disruptors for decreasing cavitation sound.

2.3.4 Beakers, 400 mL

- 2.3.5 Vacuum filtration apparatus
 - 2.3.5.1 Buchner funnel.
 - 2.3.5.2 Filter paper, Whatman No. 41 or equivalent.
- 2.3.6 Kuderna-Danish (K-D) apparatus.
 - 2.3.6.1 Concentrator tube - 10 mL, graduated (Kontas K-570040-1025 or equivalent).
 - 2.3.6.2 Evaporative flask - 500 mL (Kontas K-570001-0500 or equivalent).
 - 2.3.6.3 Snyder column - three-ball macro (Kontas K-503000-0121 or equivalent).
 - 2.3.6.4 Snyder column - two-ball micro (Kontas K-569001-0219) or equivalent).
- 2.3.7 Silicon carbide boiling chips - approximately 10/40 mesh. Heat to 400°C for 30 minutes or Soxhlet extract with methylene chloride.
- 2.3.8 Water bath - heated, with concentric ring cover, capable of temperature control ($\pm 2^\circ\text{C}$). The bath should be used in a hood.
- 2.3.9 Balance, capable of accurately weighing ± 0.01 g.
- 2.3.10 Vials and caps, 2 mL for GC auto sampler.
- 2.3.11 Balance - Analytical, capable of accurately weighing ± 0.0001 g.
- 2.3.12 Nitrogen evaporation device equipped with a water bath that can be maintained at 35-40°C. The N-Evap by Organomation Associates, Inc. South Berlin, MA (or equivalent) is suitable.
- 2.3.13 Gel permeation chromatography (GPC) cleanup device. NOTE: GPC cleanup is highly recommended for all extracts for low level soils.
 - 2.3.13.1 Automated system
 - 2.3.13.1.1 Gel permeation chromatograph Analytical Biochemical Labs, Inc. GPC Autoprep 1002 or equivalent including:
 - 2.3.13.1.2 25 mm ID X 600 - 700 mm glass column packed with 70 g of Bio-Beads SX-3.
 - 2.3.13.1.3 Syringe, 10 mL with Luer-Lock fitting.

- 2.3.13.1.4 Syringe filter holder and filters - stainless steel and TFE, Gelman 4310 or equivalent.
- 2.3.13.2 Manual system assembled from parts. (Wise, R.H., Bishop, D.F., Williams, R.T. & Austern, B.M. "Gel Permeation Chromatography in the GC/MS Analysis of Organics in Sludges" U.S. EPA, Municipal Environmental Research Laboratory - Cincinnati, Ohio 45268.)
 - 2.3.13.2.1 25 mm ID X 600 - 700 mm heavy wall glass column packed with 70 g of BIO-Beads SX-3.
 - 2.3.13.2.2 Pump: Altex Scientific, Model No. 1001A, semipreparative, solvent metering system. Pump capacity = 28 mL/min.
 - 2.3.13.2.3 Detector: Altex Scientific, Model No. 153, with 254 nm UV source and 8-ul semi-preparative flowcells (2-mm pathlengths)
 - 2.3.13.2.4 Microprocessor/controller: Altex Scientific, Model No. 420, Microprocessor System Controller, with extended memory.
 - 2.3.13.2.5 Injector: Altex Scientific, catalog No. 201-56, sample injection valve, Tefzel, with 10 mL sample loop.
 - 2.3.13.2.6 Recorder: Linear Instruments, Model No. 385, 10-inch recorder.
 - 2.3.13.2.7 Effluent Switching Valve: Teflon slider valve, 3-way with 0.060" ports.
 - 2.3.13.2.8 Supplemental Pressure Gauge with connecting Tee: U.S. Gauge, 0-200 psi, stainless steel. Installed as a "downstream" monitoring device between column and detector. Flow rate was typically 5 mL/min. of methylene chloride. Recorder chart speed was 0.50 cm/min.
- 2.3.14 Chromatography column for alumina. 8 mL (200 mm & 8 mm ID) Polypropylene column (Kontes K-420160 or equivalent) or 6 mL (150 mm X 8 mm ID) glass column (Kontes K-420155 or equivalent) or 5 mL serological pipettes plugged with a small piece of Pyrex glass wool in the tip. (Pyrex glass wool shall be

pre-rinsed with appropriate solvents to ensure its cleanliness). The Kontas columns may be plugged with Pyrex glass wool or a polyethylene porous disk (Kontas K-420162).

2.3.15 Pyrex glass wool.

2.3.16 Bottle or test tube, 50 mL with Teflon-lined screw cap for sulfur removal.

2.3.17 Pasteur pipettes, disposable.

2.4 Reagents

2.4.1 Sodium Sulfate - anhydrous powdered reagent grade, heated at 400°C for four hours, cooled in a desiccator, and stored in a glass bottle. Baker anhydrous powder, catalog #73898 or equivalent.

2.4.2 Methylene chloride, hexane, acetone, isooctane, 2-propanol and benzene - pesticide quality or equivalent.

2.4.3 Alumina - neutral, super I Woelm (Universal Scientific, Atlanta, GA) or equivalent. Prepare activity III by adding 7% (v/v) reagent water to the Super I neutral alumina. Tumble or shake on a wrist action shaker for a minimum of 2 hours or preferably overnight. There should be no lumps present. Store in a tightly sealed glass container. A 25 cycle soxhlet extraction of the alumina with methylene chloride is required if a solvent blank analyzed by the pesticide techniques indicate any interferences for the compounds of interest.

2.4.3.1 Alumina Equivalency Check. Test the alumina by adding the RNA surrogates (see Exhibit D SV) in 1:1 acetone/hexane to the alumina and following paragraph 2.8.1. The tribromophenol should not be detected by GC/EC if the alumina and its activation are acceptable. Also check recovery of all single component pesticides following the same procedure. The percent recovery for all single component pesticides must be $\geq 80\%$, except for endosulfan sulfate which must be $\geq 60\%$ and endrin aldehyde which is not recovered. The data must be retained by the Contractor and made available for inspection during on-site evaluations. If the alumina deactivated with 7% (v/v) reagent water does not prove adequate to remove the RNA surrogates and other interferences, the alumina may be deactivated with as much as 9% reagent water, so long as the criteria for tribromophenol and the recovery of all single component pesticides can be met.

2.4.4 Reagent water - Reagent water is defined as water in which an interferent is not observed at or above the CRQL of each parameter of interest.

- 2.4.5 Tetrabutylammonium (TBA) - sulfite reagent. Dissolve 3.39 g tetrabutylammonium hydrogen sulfate in 100 mL distilled water. To remove impurities, extract this solution three times with 20 mL portions of hexane. Discard the hexane extracts and add 25 g sodium sulfite to the water solution. Store the resulting solution, which is saturated with sodium sulfite, in an amber bottle with a Teflon-lined screw cap. This solution can be stored at room temperature for at least one month.
- 2.4.6 GPC calibration solutions:
- 2.4.6.1 Corn oil - 200 mg/mL in methylene chloride.
- 2.4.6.2 Bis(2-ethylhexylphthalate) and pentachlorophenol - 4.0 mg/mL in methylene chloride.
- 2.4.7 Sodium Sulfite, reagent grade.
- 2.4.8 Surrogate standard spiking solution.
- 2.4.8.1 Pesticide surrogate standard spiking solution.
- 2.4.8.1.1 The surrogate standard is added to all samples, blanks, matrix spike, matrix spike duplicates and calibrations solutions; the compound specified for this purpose is dibutylchlorodate.
- 2.4.8.1.2 Prepare a surrogate standard spiking solution at a concentration of 20 ug/1.0 mL in methanol. Store the spiking solutions at 4°C ($\pm 2^\circ\text{C}$) Teflon-sealed containers. The solutions should be checked frequently for stability. These solutions must be replaced after twelve months, or sooner if comparison with quality control check samples indicates a problem.
- 2.4.9 Matrix standard spiking solutions.
- 2.4.9.1 Pesticide matrix standard spiking solution. Prepare a spiking solution in methanol that contains the following pesticides in the concentrations specified below. Store spiking solutions at 4°C ($\pm 2^\circ$) in Teflon-sealed containers. These solutions should be checked frequently for stability. These solutions must be replaced after twelve months, or sooner if comparison with quality control check samples indicate a problem.

Pesticide	ug/1.0 mL
lindane	2.0
heptachlor	2.0
aldrin	2.0
dieldrin	5.0
endrin	5.0
4,4' DDT	5.0

Matrix spikes are also to serve as duplicates, therefore, add volume specified in Sample Extraction section to each of two 30 g portions from one sample chosen for spiking.

2.5 Sample Extraction

2.5.1 Decant and discard any water layer on a sediment sample. Mix samples thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves and rocks.

2.5.1.1 Transfer 50 g of soil/sediment to 100 mL beaker. Add 50 mL of water and stir for 1 hour. Determine pH of sample with glass electrode and pH meter while stirring. Report pH value on appropriate data sheets. If the pH of the soil is greater than 11 or less than 5, contact the Deputy Project Officer cited in the contract for instructions on how to handle the sample. Document the instructions in the Case Narrative. Discard this portion of sample. NOTE: Recovery of dibutylchlorodate will be low if pH is outside this range.

2.5.2 The following step should be performed rapidly to avoid loss of the more volatile extractables. Weigh approximately 30 g of sample to the nearest 0.1 g into a 400-mL beaker and add 60 g of anhydrous powdered sodium sulfate. Mix well. The sample should have a sandy texture at this point. Immediately, add 100 mL of 1:1 methylene chloride - acetone to the sample.

2.5.2.1 Immediately after weighing the sample for extraction, weigh 5-10 g of the sediment into a tared crucible. Determine the percent moisture by drying overnight at 105°C. Allow to cool in a desiccator before weighing. Concentrations of individual analytes will be reported relative to the dry weight of sediment.

$$\frac{\text{g of sample} - \text{g of dry sample}}{\text{g of sample}} \times 100 = \% \text{ moisture}$$

2.5.2.2 Weigh out two 30 g (record weight to nearest 0.1 g) portions for use as matrix and matrix spike duplicates. Follow 2.5.2. When using GPC cleanup, add 800 uL of the pesticide matrix spike to each of

the other two portions. When not using GPC cleanup, add 400 μ L of the pesticide matrix spike to each of the two portions.

- 2.5.2.3 When using GPC, add 200 μ L of pesticide surrogate to the sample. When not using GPC, add 100 μ L of pesticide surrogate to the sample.
- 2.5.3 Place the bottom surface of the tip of the 3/4 inch disruptor horn about 1/2 inch below the surface of the solvent but above the sediment layer.
- 2.5.4 Sonicate for 1 1/2 minutes with the W-385 (or 3 minutes with the W-375), using No. 208 3/4 inch standard disruptor horn with output control knob set at 10 (or No. 305 3/4 inch tapered high gain "Q" disruptor horn at 5) and mode switch on "1 sec. pulse" and duty cycle knob set at 50%. Do NOT use MICROTIP probe. (If using a sonicator other than Models W-375 or W-385, contact the Project Officer for appropriate output settings).
- 2.5.5 Decant and filter extracts through Whatman #41 filter paper using vacuum filtration or centrifuge and decant extraction solvent.
- 2.5.6 Repeat the extraction two more times with 2 additional 100 mL portions of 1:1 methylene chloride - acetone. Before each extraction, make certain that the sodium sulfate is free flowing and not a consolidated mass. As required, break up large lumps with a clean spatula, or very carefully with the tip of the unenergized probe. Decant off the extraction solvent after each sonication. On the final sonication, pour the entire sample into the Buchner funnel and rinse with 1:1 methylene chloride - acetone.
- 2.5.7 Transfer the extract to a Kuderna-Danish (K-D) concentrator consisting of a 10 mL concentrator tube and a 500 mL evaporative flask. Other concentration devices or techniques may be used if equivalency is demonstrated for all extractable and pesticide compounds listed in Exhibit C.
- 2.5.8 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL methylene chloride to the top. Place the K-D apparatus on a hot water bath (80 to 90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10 to 15 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes, and make up to 10 mL volume with methylene chloride.

2.5.9 If GPC cleanup is not used proceed to paragraph 2.7.

2.6. Extract Cleanup

2.6.1 GPC Setup and Calibration

2.6.1.1 Packing the column - Place 70 g of Bio Beads SX-3 in a 400 mL beaker. Cover the beads with methylene chloride; allow the beads to swell overnight (before packing the columns). Transfer the swelled beads to the column and start pumping solvent through the column, from bottom to top, at 3.0 mL/min. After approximately 1 hour, adjust the pressure on the column to 7 to 10 psi and pump an additional 4 hours to remove air from the column. Adjust the column pressure periodically as required to maintain 7 to 10 psi.

2.6.1.2 Calibration of the column - Load 5 mL of the corn oil solution into sample loop No. 1 and 5 mL of the phthalate-phenol solution into loop No. 2. Inject the corn oil and collect 10 mL fraction (i.e., change fraction at 2-minute intervals) for 36 minutes. Inject the phthalate-phenol solution and collect 15 mL fractions for 60 minutes. Determine the corn oil elution pattern by evaporation of each fraction to dryness followed by a gravimetric determination of the residue. Analyze the phthalate-phenol fractions by GC/FID on the DB-5 capillary column, a UV spectrophotometer or a GC/MS system. Plot the concentration of each component in each fraction versus total eluent volume (or time) from the injection points. Choose a "dump time" which allows $\geq 85\%$ removal of the corn oil and $\geq 85\%$ recovery of the bis(2-ethylhexyl)-phthalate. Choose the "collect time" to extend at least 10 minutes after the elution of pentachlorophenol. Wash the column at least 15 minutes between samples. Typical parameters selected are: Dump time, 30 minutes (150 mL), collect time, 36 minutes (180 mL), and wash time, 15 minutes (75 mL). The column can also be calibrated by the use of a 254 nm UV detector in place of gravimetric and GC analyses of fractions. Measure the peak areas at various elution times to determine appropriate fractions.

The SX-3 Bio Beads column may be reused for several months, even if discoloration occurs. System calibration usually remains constant over this period of time if column flow rate remains constant.

2.6.2 GPC Extract Cleanup

Prefilter or load all extracts via the filter holder to avoid particulates that might stop the flow. Load one 5.0 mL aliquot of the extract onto the GPC column. Do not apply excessive pressure when loading the GPC. Purge the sample loading tubing thoroughly with solvent between extracts. After especially dirty extracts, run a GPC blank (methylene chloride) to check for carry-over. Process the extracts using the dump, collect and wash parameters determined from the calibration and collect the cleaned extracts in 400 mL beakers tightly covered with aluminum foil. The phthalate-phenol calibration solution shall be taken through the cleanup cycle with each set of 23 extracts loaded into the GPC. The recovery for each compound must be $\geq 85\%$. This must be determined on a GC/FID, using a DB-5 capillary column, a UV recording spectrophotometer or a GC/MS system. A copy of the printouts of standard and check solution are required as deliverables with each case. Show % recovery on the copy.

2.6.2.1 If GPC cleanup of samples is required because of poor GC/ EC chromatography in Section IV, dilute the extract to 10 mL with methylene chloride and perform GPC cleanup as per paragraph 2.6.2. The reagent blank accompanying the samples should be included, unless only one or a partial group of samples requires cleanup. In this case, set up a new reagent blank with 10 mL of methylene chloride and appropriate surrogate standard added.

2.6.3 Concentrate the extract as per paragraphs 2.5.7 and 2.5.8.

2.7 Final Concentration of Extract with Optional Extract Splitting Procedure

If the extract in 2.5.8 is to be used only for pesticide/PCB analysis, it must be concentrated to a volume of 1.0 mL, following the procedure in 2.7.1.

If the extract in 2.5.8 is to be used for both semivolatile and pesticide/ PCB analyses, then it must be split into two portions. In that case, follow the procedure in 2.7.1 to obtain the pesticide portion, and follow that with the procedure in 2.7.2 to obtain the semivolatile portion. Refer to Exhibit D SV for specific instructions regarding the treatment of extracts for semivolatile analysis.

2.7.1 If the extract is to be used only for the pesticide/PCB analysis, or if the same extract is used for both semivolatile and pesticide/ PCB analyses, to split out the pesticide/PCB extract, transfer 0.5 mL of the 10 mL methylene chloride extract to a separate concentrator tube. Add 5 mL of hexane and a silicon carbide boiling chip and mix using vortex mixer. Attach a two-ball micro-Snyder column. Pre-wet the Snyder column by adding 0.5 mL of hexane to the top of the column.

Place the K-D apparatus on a hot water bath (80 - 90°C) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5 to 10 minutes. Concentrate the extract to an apparent volume of less than 1 mL. Use Nitrogen blowdown (see 2.7.3) to reduce the volume to 0.5 mL. Add 0.5 mL of acetone. The pesticide extract must now be passed through an alumina column to remove the BNA surrogates and polar interferences. Proceed to paragraph 2.8.

2.7.2 If the extract in 2.5.8 was split in 2.7.1 to obtain a portion for pesticides analysis, the portion for semivolatile analysis must be treated according to the procedures in Exhibit D SV, Section II, Part C, paragraph 2.7.2.2.

2.7.3 Nitrogen blowdown technique (taken from ASTM Method D 3086). Place the concentrator tube in a warm water bath (35°C) and evaporate the solvent volume to below 1 mL using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon). Caution: New plastic tubing must not be used between the carbon trap and the sample, since it may introduce interferences.

The internal wall of the tube must be rinsed down several times with hexane during the operation. During evaporation, the tube solvent level must be kept below the water level of the bath. The extract must never be allowed to become dry. If GPC cleanup techniques were employed, the 0.5 mL volume represents a two-fold dilution to account for the fact that only half the extract went through the GPC, and therefore, the sample detection limit would be 2x CRQL (see Exhibit B).

2.7.4 Store all extracts at 4°C ($\pm 2^\circ\text{C}$) in the dark in Teflon-sealed containers until all analyses are performed.

2.8 Pesticide/PCB

2.8.1 Alumina Column Cleanup

All samples prepared from the same extract as used for the semivolatile analysis must be taken through this cleanup technique to eliminate BNA surrogates that will interfere in the GC/EC analysis.

2.8.1.1 Add 3 g of activity III neutral alumina to the 10 mL chromatographic column. Tap the column to settle the alumina. Do not pre-wet the alumina.

2.8.1.2 Transfer the 1.0 mL of hexane/acetone extract from paragraph 2.7.1 to the top of the alumina using a disposable Pasteur pipette. Collect the eluate in a clean, 10 mL concentrator tube.

- 2.8.1.3 Add 1 mL of hexane to the original extract concentrator tube to rinse it. Transfer these rinsings to the alumina column. Elute the column with an additional 9 mL of hexane. Do not allow the column to go dry during the addition and elution of the sample.
- 2.8.1.4 Concentrate the extract to 1.0 mL following either paragraph 2.7.1 or 2.7.3, using hexane where methylene chloride is specified. When concentrating medium level extracts, the Nitrogen blowdown technique should be used to avoid contaminating the micro Snyder column.
- 2.8.2 Observe the appearance of the extract.
- 2.8.2.1 If crystals of sulfur are evident or sulfur is expected to be present, proceed to paragraph 2.8.3.
- 2.8.2.2 If the sulfur is not expected to be a problem, transfer the 1.0 mL to a GC vial and label as Pesticide/PCB fraction. The extract is ready for GC/EC analysis. Proceed to Section IV. Store the extracts at 4°C ($\pm 2^\circ\text{C}$) in the dark until analyses are performed.
- 2.8.3 Optional Sulfur Cleanup
- 2.8.3.1 Transfer the 1.0 mL from paragraph 2.8.2 to a 50 mL clear glass bottle or vial with a Teflon-lined screw cap. Rinse the concentrator tube with 1.0 mL of hexane, adding the rinsings to the 50 mL bottle. If only a partial set of samples requires sulfur cleanup, set up a new reagent blank with 1.0 mL of hexane and take it through the sulfur cleanup. Include the surrogate standards.
- 2.8.3.2 Add 1 mL TBA-sulfite reagent and 1 mL 2-propanol, cap the bottle, and shake for at least 1 min. If the sample is colorless or if the initial color is unchanged, and if clear crystals (precipitated sodium sulfite) are observed, sufficient sodium sulfite is present. If the precipitated sodium sulfite disappears, add more crystalline sodium sulfite in approximately 100 mg portions until a solid residue remains after repeated shaking.
- 2.8.3.3 Add 5 mL distilled water and shake for at least 1 min. Allow the sample to stand for 5-10 min. and remove the hexane layer (top) for analysis. Concentrate the hexane to 1.0 mL as per paragraphs

2.7.1 and 2.7.3 using hexane where methylene chloride is specified. The temperature for the water bath should be about 80°C for the micro Snyder column technique. Continue as outlined in paragraph 2.8.2.2.

SECTION III

SCREENING OF PESTICIDE/PCB EXTRACTS

1. It is mandatory that all soil/sediment samples be characterized as to concentration level so that the appropriate analytical protocol may be chosen to ensure proper quantitation limits for the sample.

The use of GC/EC methods is recommended for screening soil/sediment samples for pesticides/PCBs. The contractor is at liberty to determine the specific method of characterization. The protocols for sample preparation (Section II) and sample analysis (Section IV) are broken down by concentration level.

2. The terms "low level" and "medium level" are not used as a judgement of the degree of contamination, but rather as a description of the concentration ranges that are encompassed by the "low" and "medium" protocols.

The concentration range encompassed by the low level protocols may be considered to be appropriate for those samples with less than 1000 ug/kg of pesticides/PCBs. The concentration range encompassed by the medium level protocols may be considered to appropriate for those samples with more than 1000 ug/kg of pesticides/PCBs.

SECTION IV

GC/EC ANALYSIS OF PESTICIDES/PCBs

1. Summary of Method

- 1.1 The hexane extracts of water and soil/sediment are analyzed on a gas chromatograph/electron capture detector (GC/EC). If pesticides or PCBs are tentatively identified, a second GC/EC analysis is required using an alternate column. Quantitation must be on a packed column, whereas, confirmation can be on either a packed or a capillary column. NOTE: To determine that no pesticides/PCBs are present at or above the contract required quantitation limit is a form of quantitation.

2. Interferences

- 2.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory method blanks.

3. Apparatus and Materials

- 3.1 Gas chromatograph - An analytical system complete with gas chromatograph and all required accessories including syringes, analytical columns, gases, electron capture detector and strip-chart recorder with recording integrator. A data system is required for measuring peak areas or peak heights and recording retention times. An electrolytic conductivity detector is also acceptable if the required quantitation limits are met. Overlapping peaks on chromatograms are not acceptable.

3.1.1 Quantitation and/or confirmation columns.

- 3.1.1.1 Column 1 - Gas Chrom Q (100/120 mesh) or equivalent coated with 1.5% OV-17/1.95% OV-210 or equivalent packed in a 1.8 m long x 4 mm ID (6 mm OD) glass column.

NOTE: The 2mm ID column cited in Table 7 as Column 1 will not adequately separate dibutylchlorodate and endrin ketone.

- 3.1.1.2 Column 2 - Gas Chrom Q (100/120 mesh) or equivalent coated with 3% OV-1 or equivalent packed in a 1.8 m long x 2 mm ID (6 mm OD) glass column.

- 3.1.1.3 Column 3 - Gas Chrom Q (80/100 mesh) or equivalent coated with 5% OV-210 or equivalent packed in a 1.8 m long x 2 mm ID (6 mm OD) glass column.

- 3.1.2 Confirmation column only. Column - 30 m X 0.25 mm ID, 0.25 micron film thickness, bonded-phase silicone coated, fused silica capillary column (J&W Scientific DB-5 or DB-1701 or equivalent). NOTE: DB-1701 provides better separation of TCL

pesticides. Column 10 m x 0.32 mm ID, 1 micron film thickness has been used.

3.2 Balance - analytical, capable of accurately weighing ± 0.0001 g.

4. Reagents

4.1 Isooctane (2,2,4-trimethylpentane), hexane and toluene - Pesticide quality or equivalent.

4.2 Stock standard solutions (1.00 ug/uL) - Stock standard solution can be prepared from pure standard materials or purchased as certified solutions.

4.2.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in toluene, dilute to volume in a 10 mL volumetric flask with isooctane. Larger volumes can be used at the convenience of the analyst. If compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are traceable to EHS/LV supplied standards.

4.2.2 Transfer the stock standard solutions into a bottle/vial with Teflon-lined septa. Store at 4°C ($\pm 2^\circ\text{C}$) and protect from light. Stock standard solutions must be replaced after twelve months, or sooner if comparison with check standards indicate a problem.

4.3 Working standards solutions - Prepare mixtures of standards diluted with hexane that will provide approximately half scale response for all the compounds of interest. This should be at the attenuation setting capable of achieving the contract-required quantitation limits (Exhibit C). (This would be approximately 0.01 ng/uL for aldrin.) Two mixtures of the individual component standards are recommended to prevent co-elution of components on packed columns. However, all individual component standards may be included in one mixture on packed or capillary columns if the laboratory demonstrates that the components may be separated with no overlap of peaks. Include dibutylchlorodata in all standard mixtures. All multicomponent standards, i.e., PCB Aroclors and toxaphene must be in separate solutions with the exception of Aroclors 1016/1260. Include dibutylchlorodata in all multicomponent standard mixtures.

4.3.1 Evaluation Standard Mixtures - Prepare working standard mixtures diluted with hexane containing aldrin, endrin, 4,4' DDT and dibutylchlorodata to evaluate the GC column. Prepare three concentration levels to provide the following criteria:

4.3.1.1 Low level will be approximately 20% above base line (Evaluation Standard Mix A).

- 4.3.1.2 Mid level will be approximately half scale (Evaluation Standard Mix B).
- 4.3.1.3 High level will be approximately full scale (Evaluation Standard Mix C). (Dibutylchlorodato must be 0.1 ng/uL to correspond with 100% surrogate recovery in 10 mL final volume. This may be slightly greater than full scale but should still be in linear range).

4.3.2 Individual Standard Mixtures - These include all single component TCL pesticides plus alpha chlordane, gamma chlordane, endrin ketone, endrin aldehyde and dibutylchlorodato (see paragraph 6.1.4 for suggested mixtures). Alpha and gamma chlordane should be in Mixture B to avoid overlap with other pesticides.

5. Calibration

5.1 The gas chromatographic system must be calibrated using the external standard technique for all packed columns used for quantitation.

5.2 External standard calibration procedure:

5.2.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with hexane. One of the external standards should be at a concentration near, but above, the CRQL and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector. This should be done on each quantitation column and each instrument at the beginning of the contract period and each time a new column is installed. The data must be retained by the laboratory and made available for inspection during on-site evaluations.

5.2.2 Using injections of 2 to 5 uL of each calibration standard, tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each compound.

6. GC/EC Primary Analysis (Quantitation may be performed on primary or confirmation analyses.)

Adjust oven temperature and carrier gas flow rates so that the retention time for 4,4'-DDT is equal to or greater than 12 minutes.

Table 7 provides examples of operating conditions for the gas chromatograph. Separation should be $\geq 25\%$ resolution between peaks. Percent resolution is calculated by dividing the height of the valley by the peak height of the smaller peak being resolved, multiplied by 100. This criterion must be considered when determining whether to quantitate on the Primary Analysis or the Confirmation Analysis. When

this criterion cannot be met, quantitation is adversely affected because of the difficulty in determining where to establish the baseline.

- 6.1 Inject 2 to 5 μ L of the sample or standard extract using the solvent-flush technique or auto sampler. Smaller (1.0 μ L) volumes can be injected only if automatic devices are employed. Record the volume injected to the nearest 0.05 μ L and the total extract volume. NOTE: Dibutylchlorodate recovery may be calculated from a capillary or packed column GC/EC meeting all QC requirements for quantitation. However, matrix spike duplicates must be quantitated on a packed column.

- 6.1.1 Inject Individual Standard Mix A and B and all multiresponse pesticides/PCBs at the beginning of each 72 hour sequence. (See paragraph 6.1.3.5) To establish the RT window within each 72-hour sequence for the pesticide/PCB of interest, use the absolute RT from the above chromatograms as the mid-point, and $\pm$ three times the standard deviation calculated in Exhibit E for each compound. Individual Standard Mix A and B are analyzed alternately and intermittently throughout the analysis as shown in 6.1.3.5. Any pesticide outside of its established retention time window requires immediate investigation and correction before continuing the analysis. The laboratory must reanalyze all affected samples.

- 6.1.2 Sample analysis of extracts from Section II, Sample Preparation, can begin when linearity and degradation QA/QC requirements specified in Exhibit E have been met.

NOTE: The 10.0% RSD linearity criterion is only required on the column(s) being used for pesticide/PCBs quantitation. If a column is used for surrogate quantitation only, the 10.0% RSD is required only for dibutylchlorodate.

Analyze samples in groups of no more than 5 samples. After the analysis of the first group of up to 5 samples, analyze Evaluation Mix B. Analyze another group of up to 5 samples, followed by the analysis of Individual Mix A or B. Subsequent groups of up to 5 samples may be analyzed by repeating this sequence, alternately analyzing Evaluation Mix B and Individual Mix A or B between the groups as shown in 6.1.3.5. The Pesticide/PCB analytical sequence must end with Individual Mix A and B regardless of the number of samples analyzed (see 6.1.3.5).

If a multiresponse pesticide/PCB is detected in either of the preceding groups of 5 samples, the appropriate multiresponse pesticide/PCB may be substituted for Individual Mix A or B. All standards listed in 6.1.3.5 must be included for every Case and must be analyzed within the same 72-hour period as the samples, with the exception of Aroclors 1221 and 1232 which are analyzed at a minimum of once per month (see footnote in 6.1.3.5). If the samples are split between 2 or more instruments, the

complete set of standards must be analyzed on each instrument with the same 72-hour requirement. All standards must be analyzed prior to the samples to avoid the effects of poor chromatography caused by the unsuspected injection of a highly concentrated sample.

- 6.1.3 Paragraphs 6.1.3.1 - 6.1.3.5 contain GC performance criteria. If it is determined during the course of a 72-hour sequence that one or more of the criteria have been violated, stop the run and take corrective action (see Exhibit E, Section III, PEST, 4.3.3.8). After the corrective action has been taken, the 72-hour sequence may be restarted as follows. If a standard violated the criterion, restart the sequence with that standard, determine that the criteria have been met and continue with sample analyses, according to 6.1.3.5. If a sample violated the criterion, restart the sequence with the standard that would have followed that group of samples (thereby preserving the sequence of standards in 6.1.3.5), determine that the criteria have been met and continue with sample analyses, according to 6.1.3.5.

If it is determined after the completion of a 72-hour sequence that one or more of the criteria have been violated, proceed as follows. If a standard violated the criterion, all samples analyzed after that standard must be re-analyzed as part of a new 72-hour sequence. If a subsequent standard in the original sequence met all the criteria, then only those samples analyzed between the standard that did not meet the criterion and the standard that did meet the criterion must be re-analyzed as part of a new 72-hour sequence. If only samples violated the criteria, then those samples must be re-analyzed as part of a new 72-hour sequence.

- 6.1.3.1 Differences in the Calibration Factors for each standard in Individual Standard Mix A and B must not exceed 20.0% (15.0% for any standard compound used for quantitation) during the 72-hour Primary Analysis. Calculate the % difference using the initial Individual Standard Mix versus all subsequent Individual Standard Mixes analyzed during the 72-hour sequence. (The equations for calculation of Calibration Factor and % difference are in Exhibit E, Section III PEST, paragraph 4:3.4.2.) NOTE: To determine that no pesticides/PCBs are present at or above the contract required quantitation limit is a form of quantitation.

The retention time shift of dibutylchlorodate in any standard or sample must be less than 2.0% difference for packed columns, less than 1.5% difference for wide bore capillary columns (ID greater than 0.32 mm) and less than 0.3% difference

for narrow bore capillary columns (ID less than 0.32 mm).

- 6.1.3.2 Samples must also be repeated if the degradation of DDT and/or endrin exceeds 20.0% respectively on the intermittent analysis of Evaluation Standard Mix B.
- 6.1.3.3 All pesticide standards must fall within the established 72-hour retention time windows.
- 6.1.3.4 Highly colored extracts may require a dilution.
- 6.1.3.5 The 72-hour sequence must be as follows.

72-Hour Sequence for Pesticide/PCB Analysis:

1. Evaluation Standard Mix A
2. Evaluation Standard Mix B
3. Evaluation Standard Mix C
4. Individual Standard Mix A*
5. Individual Standard Mix B*
6. Toxaphene
7. Aroclors 1016/1260
8. Aroclor 1221**
9. Aroclor 1232**
10. Aroclor 1242
11. Aroclor 1248
12. Aroclor 1254
13. 5 samples
14. Evaluation Standard Mix B
15. 5 samples
16. Individual Standard Mix A or B
17. 5 samples
18. Evaluation Standard Mix B
19. 5 samples
20. Individual Standard Mix A or B
(whichever not run in step 16)
21. 5 samples
22. Repeat the above sequence starting with Evaluation Standard Mix B (step 14 above).
23. Pesticide/PCB analysis sequence must end with the analyses of both Individual Standard Mix A and B regardless of number of samples analyzed.

*These may be combined into one mixture (see paragraph 4.3).

**Aroclors 1221 and 1232 must be analyzed on each instrument and each column at a minimum of once per month.

Copies of these chromatograms must be submitted for sample analyses performed during the applicable month.

- 6.1.4 Suggested groups of compounds and concentrations for Individual Standard Mix A and B follow, which are recommended to prevent overlap of compounds on the two packed columns (3% OV-1 and 1.5% OV-17/1.95% OV-210). Some of the compounds overlap on the 5% OV-210 column (see Table 7). The concentration is based on a 5 uL injection.

<u>Individual Standard Mix A</u>	<u>ng/uL</u>	<u>Individual Standard Mix B</u>	<u>ng/uL</u>
gamma-BHC	0.005	alpha-BHC	0.005
heptachlor	0.010	beta-BHC	0.010
aldrin*	0.010	delta-BHC	0.010
heptachlor epoxide	0.010	aldrin*	0.010
endosulfan I	0.010	p,p'-DDE	0.010
dieldrin	0.010	endrin	0.010
p,p'-DDT	0.020	p,p'-DDD	0.020
endrin aldehyde	0.025	endosulfan sulfate	0.020
endosulfan II	0.020	endrin ketone	0.020
methoxychlor	0.100	alpha chlordane	0.010
dibutylchlorodate	0.050	gamma chlordane	0.010
		dibutylchlorodate	0.050

*For RET determination.

- 6.1.5 Inject the method blank (extracted with each set of samples) on every instrument and GC column on which the samples are analyzed.

6.2 Evaluation of Chromatograms.

- 6.2.1 Consider the sample negative when its peaks, depending on the pesticide's response factor, result in concentrations less than the required quantitation level. The sample is complete at this point. Confirmation is not required.
- 6.2.2 Tentative identification is made when the unknown's retention time matches the retention time of a corresponding standard that was chromatographed on the same instrument within a 72-hour period.
- 6.2.3 Determine if any pesticides/PCBs listed in Exhibit C are present. Pattern recognition techniques, based on chromatograms of standards, are recommended for the identification of PCB compounds.
- 6.2.3.1 If the response for any of these compounds is 100% or less of full scale, the extract is ready for confirmation and quantitation.

- 6.2.3.2 If the response for any compound is greater than full scale, dilute the extract so that the peak will be between 50 and 100% full scale and reanalyze on the packed column. Use this dilution also for confirmation and quantitation.
- 6.2.3.3 For dilution >10 fold. Also inject an aliquot of a dilution 10 fold more concentrated to determine if other compounds of interest are present at lower concentrations.
- 6.2.3.4 Computer reproductions of chromatograms manipulated to ensure all peaks are on scale over a 100 fold range are an accepted substitute. However, this can be no greater than a 100 fold range. This is to prevent retention time shifts by column or detector overload. Linearity must be demonstrated over the 100 fold range using higher concentrations of the evaluation mixture.
- 6.2.4 Quantitation may be performed on the primary analysis, with the exception of toxaphene and possibly the DDT series. If DDT exceeds the 10.0% RSD linearity criterion, then quantitations for any DDE, DDD and DDT in a sample must be on the confirmation analysis. Toxaphene must always be quantitated on the confirmation analysis. See Exhibit E for special QC requirements for quantitation.
- 6.2.5 If identification of compounds of interest are prevented by the presence of interferences, further cleanup is required. If sulfur is evident go to Sulfur Cleanup (Section II, Part B, paragraph 8.). If unknown interferences or poor chromatography are noted only in the sample chromatogram, it is recommended that gel permeation chromatography cleanup (Section II, Part C, paragraph 2.6) be applied.
- 6.2.6 When selecting a GC column for confirmation and/or quantitation, be sure that none of the compounds to be confirmed/quantitated overlap, i.e., do not select the 3% OV-1 column if DDE and dieldrin are to be confirmed and/or quantitated. When samples are very complex, it may be necessary to use all three packed columns to achieve adequate separation ($\geq 25\%$ resolution) of all compounds being quantitated.

7. GC/EC Confirmation Analysis

- 7.1 Confirmation Analysis is to confirm the presence of all compounds tentatively identified in the Primary Analysis. Therefore, the only standards that are required are the Evaluation Standard Mixes (to check linearity and degradation criteria) and standards of all compounds to be confirmed. The linearity criterion on the confirmation column for pesticides is not required unless the column is used for quantitation. The 72-hour sequence in 6.1.3.5 is, therefore, modified

to fit each case. Quantitation may be performed on the confirmation analysis. If toxaphene or DDT is to be quantitated, additional linearity requirements are specified in 7.3.1.

- 7.2 Table 7 provides examples of operating conditions for the gas chromatograph. Separation should be $\geq 25\%$ resolution between peaks. Percent resolution is calculated by dividing the height of the valley by the peak height of the smaller peak being resolved, multiplied by 100. This criterion must be considered when determining whether to quantitate on the Primary Analysis or the Confirmation Analysis. When this criterion cannot be met, quantitation is adversely affected because of the difficulty in determining where to establish the baseline.

For a fused silica capillary column (FSCC) confirmation, there must be ≥ 25 percent resolution (valley) between the following pesticide pairs:

- o beta-BHC and delta-BHC
- o Dieldrin and 4,4'-DDT
- o 4,4'-DDD and Endrin Aldehyde
- o Endosulfan Sulfate and 4,4'-DDT

All QC requirements specified in Exhibit E must be adhered to, i.e., the ≥ 12 min. retention time for 4,4'-DDT, the criteria for 4,4'-DDT and endrin degradation, linearity, calibration factor for standards and retention time shift for dibutylchlorodate. The retention time criterion for 4,4'-DDT does not have to be met if the confirmation column is OV-1 or OV-101. Apply instructions from 6.1.3 to the confirmation analysis.

- 7.3 Inject 2 to 5 μ L (1-2 μ L for capillary columns) of the sample extract and standards using the solvent-flush technique or auto samplers. A volume of 1 μ L can be injected only if automatic devices are employed. Record the volume injected to the nearest 0.05 μ L and the total extract volume. The detector attenuation must provide peak response equivalent to the Primary Analysis response for each compound to be confirmed.

- 7.3.1 Begin the Confirmation Analysis GC sequence with the three concentration levels of Evaluation Standard Mixes A, B and C. The exception to this occurs when toxaphene and/or DDT series are to be confirmed and quantitated. There are four combinations of pesticides that could occur, therefore, the following sequences must be followed depending on the situation.

- 7.3.1.1 Toxaphene only - Begin the sequence with Evaluation Mix B to check degradation, followed by three concentration levels of toxaphene. Check linearity by calculating $\pm$ RSD.

If $\leq 10.0\%$ RSD, use the appropriate equation in paragraph 8 for calculation. If $> 10.0\%$ RSD, plot a standard curve and determine the ng for each sample in that set from the curve.

- 7.3.1.2 DDT, DDE, DDD only - Begin the sequence with Evaluation Mix B. Then inject three concentration levels of a standard containing DDE, DDD and DDT. Calculate linearity and follow the requirements specified in 7.3.1.1 for each compound to be quantitated.
- 7.3.1.3 DDT series and toxaphene - Begin the sequence with Evaluation Mix B. Then inject three concentration levels of toxaphene and another three levels of the DDT series. Calculate linearity and follow the requirements specified in 7.3.1.1 for each compound to be quantitated. NOTE: Capillary quantitation would be allowed only in this situation.
- 7.3.1.4 Other pesticides/PCBs plus DDT series and/or toxaphene - Begin the sequence with Evaluation Standard Mixes A, B and C. Calculate linearity on the four compounds in the Evaluation Standard Mixes. If DDT and/or one or more of the other compounds are >10.0% RSD and/or degradation exceeds the criterion, corrective maintenance as outlined in Exhibit E, Section III PEST, paragraph 4.3.3.8, should be performed before repeating the above chromatography evaluations. If only DDT exceeds the linearity criterion and one or more of the DDT series is to be quantitated, follow 7.3.1.2 (do not repeat Evaluation Mix B).

If none of the DDT series is to be quantitated and DDT exceeds the 10.0% RSD, simply record the % RSD on the proper form. Any time toxaphene is to be quantitated, follow 7.3.1.1.

- 7.3.2 After the linearity standards required in 7.3.1 are injected, continue the confirmation analysis sequence by injecting standards for all compounds tentatively identified in the primary analysis, to establish the 72-hour retention time windows. (See paragraph 6.1.1.) Analyze all confirmation standards for a case at the beginning, at intervals specified in 7.3.3 and at the end. Any pesticide outside of its established retention time window requires immediate investigation and correction before continuing the analysis. The laboratory must reanalyze all samples which follow the standard that exceeds the criterion.
- 7.3.3 After injection of the appropriate standards (see 7.3.2), begin injection of samples. Analyze groups of 5 samples. Analyze Evaluation Mix B after the first group of 5 samples. After the second group of 5 samples, analyze a standard pertaining to the samples in the preceding groups (i.e., substitute standards pertaining to the preceding samples for Individual Mix A or B in 6.1.3.5). Continue analyzing groups of 5 samples, alternately analyzing Evaluation Mix B and standards pertaining

to the preceding samples between groups of 5 samples. The alternating standard's calibration factors must be within 15.0% of each other if quantitation is performed. Deviations larger than 15.0% require the laboratory to repeat the analyses of samples which were analyzed after the standard that exceeded the criterion. The 15.0% criterion only pertains to compounds being quantitated.

If more than one standard is required to confirm all compounds tentatively identified in the Primary Analysis, alternate the standards with Evaluation Mix B. Samples must also be repeated if the degradation of either DDT and/or endrin exceeds 20.0% on the Intermittent Evaluation Standard Mix B.

If the samples are split between 2 or more instruments, all standards and blanks pertaining to those samples must be analyzed on each instrument.

- 7.3.4 Inject the method blank (extracted with each set of samples) on every GC and GC column on which the samples are analyzed.

7.4 Evaluation of Chromatograms

- 7.4.1 A compound tentatively identified in the primary analysis is confirmed if the retention time from the confirmation analysis falls within the retention time window of a corresponding standard that was chromatographed on the same instrument within a 72-hour period.

- 7.4.2 Quantitation should be on the packed column chromatogram (primary or confirmation) that provides the best separation from interfering peaks. NOTE: To determine that no pesticides/PCBS are present at or above the contract required quantitation limit is a form of quantitation.

- 7.4.2.1 Quantitation of Chlordane - Because weathering and/or different formulations of chlordane usually modify the pattern exhibited by technical chlordane, this method is not appropriate for determining technical chlordane. Instead, standards for alpha chlordane and gamma chlordane are used for quantitation, and each isomer of chlordane is reported separately.

- 7.4.3 Computer reproductions of chromatograms that are attenuated to ensure all peaks are on scale over a 100 fold range are acceptable. However, this can be no greater than a 100 fold range. This is to prevent retention time shifts by column or detector overload. Also, peak response must be >25% of full scale deflection to allow visual pattern recognition of multicomponent compounds, and individual compounds must be visible.

- 7.4.4 If identification of compounds of interest are prevented by the presence of interferences, further cleanup is required. If sulfur is evident, go to Sulfur Cleanup (Section II, Part B, paragraph 8).

If unknown interferences or poor chromatography are noted only in the sample chromatogram, it is recommended that gel permeation chromatography cleanup (Section II, Part C, paragraph 2.6) be applied.

- 7.4.5 Calculate surrogate standard recovery on all samples, blanks and spikes unless the surrogate was diluted out. Determine if recovery is within limits and report on Form II. See formula for calculation in 8.3.
- 7.4.6 If TCL pesticide/PCB compounds were identified in the unspiked sample from which the matrix spike and matrix spike duplicate were prepared, confirmation analysis is required for the matrix spike and matrix spike duplicate. If TCL pesticide/PCB compounds were not identified in the unspiked sample, confirmation of the matrix spike and matrix spike duplicate is not required. Calculate matrix spike duplicate recoveries and report on Form III (see Exhibit B, Section III).

8. Calculations

- 8.1 Calculate the concentration in the sample using the following equation for external standards. Response can be measured by the manual peak height technique or by automated peak height or peak area measurements from an integrator.

8.1.1 Water

$$\text{Concentration ug/L} = \frac{(A_x)(I_s)(V_e)}{(A_s)(V_i)(V_s)}$$

Where:

- A_x = Response for the parameter to be measured.
 A_s = Response for the external standard.
 V_e = Volume of total extract (uL) (take into account any dilutions)
 I_s = Amount of standard injected in nanograms (ng)
 V_i = Volume of extract injected (uL)
 V_s = Volume of water extracted (mL)

8.1.2 Sediment/Soil

$$\text{Concentration ug/kg (Dry weight basis)} = \frac{(A_x)(I_s)(V_e)}{(A_s)(V_i)(W_s)(D)}$$

Where:

A_x, I_s, A_s, V_1 - same as given above in 8.1.1

V_t - Volume of low level total extract
(Use 20,000 μ L or a factor of this when dilutions are made other than those accounted for below):
o 1/20 total extract taken for pesticide analysis (derived from 0.5 mL of 10 mL extract)
o final concentration to 1.0 mL for pesticide analysis

- or -

V_t - Volume of medium level total extract
(Use 10,000 μ L or a factor of this when dilutions are made.)

D - $\frac{100 - \% \text{ moisture}}{100}$ (% moisture from Section II, Part C)

W_s - Weight of sample extracted (g)

8.2 For multicomponent mixtures (chlordanes, toxaphene and PCBs) match retention times of peaks in the standards with peaks in the sample. Quantitate every identifiable peak (>50% of the total area must be used) unless interference with individual peaks persist after cleanup. Add peak height or peak area of each identified peak in the chromatogram. Calculate as total response in the sample versus total response in the standard.

8.3 Calculation for surrogate and matrix spike recoveries.

$$\text{Percent Recovery} = \frac{Q_d}{Q_s} \times 100\%$$

where,

Q_d - quantity determined by analysis

Q_s - quantity added to sample.

Be sure all dilutions are taken into account. Soil/Sediment has a 20-fold dilution factor built into the method when accounting for one-twentieth of extract taken for pesticide analysis and final dilution to 1 mL.

8.4 Report results in micrograms per liter or micrograms per kilogram without correction for recovery data.

9. GC/MS Confirmation of Pesticides

9.1 Any compounds confirmed by two columns must also be confirmed by GC/MS if the concentration is sufficient for detection by GC/MS. The following paragraphs should be used as guidance when determining if a pesticide/PCB compound can be confirmed by GC/MS.

9.1.1 The GC/MS analysis normally requires a minimum concentration of 10 ng/ul in the final extract, for each single component compound. For the BNA extract of a water sample, a concentration of 10 ng/ul in extract is approximately 20 ug/L (ppb) in the sample. For the BNA extract of a low level soil sample, the equivalent sample concentration would be approximately 170 ug/Kg if no GPC was performed. For the BNA extract of a medium soil, the equivalent sample concentration is on the order of 10,000 ug/Kg.

9.1.2 The pesticide extract and associated blank should be analyzed by GC/MS as per Exhibit D SV, Section IV, paragraph 3.

9.1.3 The confirmation may be from the GC/MS analysis of the semivolatile extracts (sample and blank). However, if the compounds are not detected in the semivolatile extract even though the concentration is high enough, a GC/MS analysis of the pesticide extract is required.

9.1.4 A reference standard for the compound must also be analyzed by GC/MS. The concentration of the reference standard must be at a level that would demonstrate the ability to confirm the pesticides/PCBs identified by GC/EC. Use the sample concentration calculated from the GC/EC results as guidance. The concentration of the reference standards must be no greater than the sample ~~extract~~ concentration predicted from the GC/EC sample concentration. For instance, as in paragraph 9.1.1 above, a 20 ug/L sample result from GC/EC requires a 10 ng/ul GC/MS reference standards in order to demonstrate adequate sensitivity for a water sample.

9.1.5 In the event the GC/MS does not confirm the presence of the pesticides/PCBs identified by GC/ECD, those compounds should be reported as not detected. The minimum quantitation limits ("U" values) should be adjusted to reflect the interferences. The inability to confirm the compounds by GC/MS must be noted in the Case Narrative.

9.1.6 For GC/MS confirmation of multicomponent pesticides and PCBs, required deliverables are spectra of 3 major peaks of multicomponent compounds from samples and standards.

9.1.7 Quantitation by GC/MS must use the characteristic quantitation ions for pesticides/PCBs given in Table 5 of Exhibit D SV.

Table 7

Examples of Orders of Elution of Pesticides/PCBs

Parameter	Column 1	Column 2	Column 3
alpha-BHC	1.45	1.64	1.86
gamma-BHC	1.86	1.94	2.37
beta-BHC	2.18	1.76	2.75
Heptachlor	2.27	3.21	2.55
delta-BHC	2.55	2.01	2.80
Aldrin	2.76	4.01	2.93
Heptachlor epoxide	4.31	4.98	5.53
Endosulfan I	5.46	6.26	7.08
4,4'-DDE	6.37	7.51	6.03
Dieldrin	6.74	7.38	8.59
Endrin	8.25	8.35	10.14
4,4'-DDD	10.08	9.53	10.57
Endosulfan II	10.14	8.35	12.88
4,4'-DDT	12.06	12.75	11.55
Endrin aldehyde	13.64	9.53	21.11
Endosulfan sulfate	16.73	11.09	31.27
Endrin ketone	22.70	-	33.16
gamma Chlordane	4.77	5.74	5.25
alpha Chlordane	5.24	6.39	5.70
Toxaphene	nr	nr	nr
Aroclor-1016	nr	nr	nr
Aroclor-1221	nr	nr	nr
Aroclor-1232	nr	nr	nr
Aroclor-1242	nr	nr	nr
Aroclor-1248	nr	nr	nr
Aroclor-1254	nr	nr	nr
Aroclor-1260	nr	nr	nr
methoxychlor	24.07	19.60	18.12
dibutylchloredate	21.80	27.21	22.26

nr = multiresponse compounds.

Column 1 conditions: Gas Chrom Q (80/100 mesh) or equivalent coated with 1.5% OV-17/1.95% OV-210 or equivalent packed in a 1.8 m long x 2 mm ID (6 mm OD) glass column with 5% methane/95% argon carrier gas at a flow rate of 30 mL/min. (HP 5880) Column temperature, isothermal at 192°C. 2 mm ID column with 80/100 mesh does not adequately resolve dibutyl chloredate and endrin ketone.

Column 2 conditions: Gas Chrom Q (100/120 mesh) or equivalent coated with 3% OV-1 or equivalent packed in a 1.8 m long x 2 mm ID (6 mm OD) glass column with 5% methane/95% argon carrier gas at a flow rate of 30 mL/min. (30 mL/min makeup gas). (Tracor 222). Column temperature, isothermal at 194°C.

Table 7 (continued)

Column 3 conditions: Gas Chrom Q (80/100 mesh) or equivalent coated with 5% OV-210 packed in a 1.8 m x 2 mm ID (6 mm OD) glass column with 5% methane/95% argon carrier gas at a flow rate of 30 mL/min. (30 mL/min. make-up gas). HP5840. Column temperature, isothermal at 183°C.

Capillary column 1 conditions: 30 m x 0.25 mm ID, 0.25 micron film thickness, fused silica DB-5 (or equivalent) splitless mode

Helium carrier gas: 4 mL/min at 280°C and 25 PSI

Septum purge: 15 mL/min

Split vent: none

Initial temperature: 160°C, initial hold - 2 min

Program at 5°C/min

Final temperature: 270°C, final hold - 4 min

Injection port temperature: 225°C

Capillary column 2 conditions: 10 m x 0.32 mm ID, 1 micron film thickness, fused silica DB-1701, splitless mode

Helium carrier gas: 4 mL/min at 280°C and 25 PSI

Septum purge: 15 mL/min

Split vent: none

Initial temperature: 160°C, initial hold - 3 min

Program at 10°C/min to 240°C

Program from 240 to 270°C at 5°C/min

Final Hold: 4 min

Injection port temperature: 235°C

HANFORD ENVIRONMENTAL ANALYTICAL METHODS MANUAL
Appendix A3-1
Table of Contents

PNL/325 Laboratory: Inorganic

Appendix Number	Lab Number	Method Name	Analytes
A3-I.10	PNL-SP-6-R0-3	ICP Analysis using Jarrell Ash in 3720 Building	Metals
A3-I.20	PNL-SP-12	Potassium Hydroxide Fusion	
A3-I.30	HWVP-1	Sample Preparation for Chemical Analysis	
A3-I.40	PNL-SP-7	ICP Analysis (325 Building)	Metals
A3-I.50	PNL-SP-11-R0-1	Atomic Absorption Using the Perkin-Elmer Model 5000 Spectrophotometer and Graphite Furnace	Metals
A3-I.60	HTA-4-16, Rev. 3	Solutions Analysis: Uranium by Laser-Excited Fluorescence	Total U
A3-I.70	PNL-MA-597-7-40.8 Rev. 0	Solutions Analysis: Anions by Ion Chromatography	Metals
A3-I.80	PNL-MA-597-7.40-7 Rev. 0	Solutions Analysis: Carbon	C
A3-I.85	ESM D-449	Determination of Inorganic Ions in Aqueous and Solid Samples by Ion Chromatography	F ⁻ , Cl ⁻ , PO ₄ ³⁻ , NO ₃ ⁻ , NO ₂ ⁻ , SO ₄ ²⁻

HANFORD ENVIRONMENTAL ANALYTICAL METHODS MANUAL
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PNL/325 Laboratory: Inorganic

Appendix Number	Lab Number	Method Name	Analytes
A3-I.90	HWVP-2	Fluoride Ion in Aqueous Samples	Fl
A3-I.100	Inorganic CLP Exhibit D Sec. III SOW 7/88 Sec. III Part A + B	Sample Preparation	Metals
A3-I.110	Inorganic CLP SOW 7/88, Exhibit D, Sec. IV, Part D	Cold Vapor Methods for Mercury Analysis	Metals
A3-I.120	Inorganic CLP SOW 7/88, Sec. IV, Part F	Percent Solids Determination Procedure	Total Solids

TCid Rm
Dana Thon
10-27-87

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INTERIM CHANGE NOTICE (ICN)

ICN No. PNL-SP-6-RO-3
Page 1 of 2

A. Doc. No. PNL-SP-6 Rev. No. 0 Doc. Title ICP Analysis Using Jarrell Ash in 3720 Bldg.
Document's Author FT Hara
Requested by Dana Widrig / Jeff Smith Date Issued 9-17-87

B. Type of Change Approvals:

☒ Minor Change QAD Concurrence SL English Date 9-25-87
Approval SL English Date 9-28-87
JM Latkovich

☐ Major Change QAD Concurrence _____ Date _____
Approval _____ Date _____
Reviews, _____ Date _____
Approvals & Dates _____

C. Reason for Change:
Procedure needs to specify the matrix matching and spectral correction that normally occur when the situation merits.

D. Description of Change:

Insert the new sections: 5.6.7 Matrix Matching
5.6.8 Spectral Corrections
(see attached)

PLACE THIS ICN AT THE FRONT OF THE SUBJECT DOCUMENT

Insert

- 5.6.7 Matrix Matching: When the concentration of the total dissolved solid in the sample is very high (10g/l) and there is very little change in concentration of the major elements in the samples (e.g. saturated brine) the major elements exceeded in the samples are added to the standards used to calibrate the spectrometer. Since the concentration of major elements in the sample and standards are essentially the same, the matrix in the sample and standards are matched and thus any spectral interferences are compensated for.
- 5.6.8 Spectral Correction: Frequently a sample may contain a few elements which are significantly higher in concentration than the trace elements to be analyzed. The emission spectra of certain elements such as iron or rare earths, are quite complex. When the concentration of these elements with complex spectra are significantly greater than the trace elements to be analyzed, a standard containing only one element is analyzed and the single element standard is used to correct for spectral overlap in each of the samples.

INTERIM CHANGE NOTICE (ICN)

ICN No. PNL-SP-6-R0-2
Page 1 of 1

A. Doc. No. PNL-SP-6 Rev. No. 0 Doc. Title ICP Analysis Using the Jarrell-Ash O/O Atom Comp Model 975 (3720 Building)

Document's Author F.T. Hara

Requested by F.T. Hara

Date Issued 06/08/87

B. Type of Change and Approvals:

☒ Minor Change QAD Concurrence H. English Date 6-2-87

☐ Major Change QAD Concurrence _____ Date _____

Approval _____ Date _____

Reviews, _____

Approvals & Dates _____

Sponsor concurrence documented by _____

C. Reason for Change:

To fulfill the requirements for "Specific Qualification" in Section 4.2.1 of PAP-901.

D. Description of Change (old text versus requested text):

Add
5.6.6 in calibration and the process is in control.

Add
5.6.7 Specific Qualification - refer to 5.6.6 above.

PLACE THIS ICN AT THE FRONT OF THE SUBJECT DOCUMENT

INTERIM CHANGE REQUEST/NOTICE (ICR/N)

ICR/N No. PNL-SP-6-1

Page 1 of 1

ICP Analysis using the Jarrell-Ash
Atom Comp Model 975 (3720 Bldg.)

Doc. No. PNL-SP-6

Rev. No. 0

Doc. Title

Document's Author Frank Hara

Requested by Carrie Matsuzaki

Date Issued 11-18-86

Type of Change (Check the most appropriate method of change):

1. ☐ Revision Required Approved _____ Date _____
2. ☒ Minor Change QAD Approval KVP 11/24/86 (Ref. PAP-602, 5.2.3)
3. ☐ Major Change Reviews, & _____
Approvals _____
(Ref. PAP-602, 5.3.3) Sponsor concurrence documented
by: _____

Reason for Change:

Change in Exhibit 2 to streamline program and make sure all values are
set to zero before a new calculation is made.

Description of Change (old text vs. requested text):

New Exhibit 2 attached. Most of changes made in section 5.

** PLACE THIS ICR/N AT THE FRONT OF THE SUBJECT DOCUMENT **

MESS LA 2

LAB NO=?
ALIST

1,1 % ICP CALCULATION FOR MESS PROGRAM F HARA REV 2 1 OCT 86

1,9 SET I=36

1,10 A X(1)

1,11 A Y(36)

1,12 A Z(36)

1,13 FOR I=1,36;SET X(1)=0

1,20 SET S1=1;"LAB NO=?

1,21 SET C1=" CUSTOMER'S SAMPLE NO=?

1,22 SET WT=1;"SAMPLE WEIGHT=?

1,23 SET FU=" FUSION METHOD=?

1,24 SET RF=" SAMPLE DILUTION=?

1,45 SET F1=(.0001*RF)/WT

1,46 VIEW I;"FACTOR TO CONVERT PPM VALUES TO WT 1=?F1

2,1 SET X(1)=1;"AL=?;SET X(2)=", AS=?;SET X(3)=", R=?;SET X(4)=", BA="

?;SET X(33)=", RE=?;SET X(15)=", (A=?

2,5 SET X(6)=1;"CU=?;SET X(7)=", (E=?;SET X(8)=", CO=?;SET X(9)=", CR="

"?;SET X(10)=", (U=?;SET X(11)=", (V=?

2,9 SET X(12)=1;"EU=?;SET X(13)=", FE=?;SET X(14)=", GU=?;SET X(15)=",

LA=?;SET X(16)=", LA=?

2,13 SET X(17)=1;"LI=?;SET X(18)=", MO=?;SET X(19)=", NH=?;SET X(20)="

, NO=?;SET X(21)=", NA=?

2,17 SET X(22)=1;"ND=?;SET X(23)=", NI=?;SET X(24)=", P=?;SET X(25)=",

FE=?;SET X(26)=", RU=?

2,21 SET X(34)=1;"SB=?;SET X(27)=", SI=?;SET X(28)=", SR=?;SET X(29)="

, TE=?;SET X(30)=", TI=?

2,25 SET X(35)=1;"V=?;SET X(36)=", I=?;SET X(31)=", ZH=?;SET X(32)=",

ZK=?

2,50 IF X(1)<.03 SET X(1)=-.03

2,51 IF X(2)<.15 SET X(2)=-.15

2,52 IF X(3)<.02 SET X(3)=-.02

2,53 IF X(4)<.005 SET X(4)=-.005

2,54 IF X(5)<.01 SET X(5)=-.01

2,55 IF X(6)<.008 SET X(6)=-.008

2,56 IF X(7)<.05 SET X(7)=-.05

2,57 IF X(8)<.02 SET X(8)=-.02

2,59 IF X(9)<.02 SET X(9)=-.02

2,60 IF X(10)<.01 SET X(10)=-.01

2,61 IF X(11)<.01 SET X(11)=-.01

2,62 IF X(12)<.005 SET X(12)=-.005

2,63 IF X(13)<.01 SET X(13)=-.01

2,64 IF X(14)<.1 SET X(14)=-.1

2,65 IF X(15)<.3 SET X(15)=-.3

```

2,69 IF X(19)<.005 SET X(19)=-.005
2,70 IF X(20)<.02 SET X(20)=-.02
2,71 IF X(21)<.01 SET X(21)=-.01
2,72 IF X(22)<.02 SET X(22)=-.02
2,73 IF X(23)<.02 SET X(23)=-.02
2,74 IF X(24)<.2 SET X(24)=-.2
2,75 IF X(25)<.1 SET X(25)=-.1
2,76 IF X(26)<.1 SET X(26)=-.1
2,77 IF X(27)<.02 SET X(27)=-.02
2,78 IF X(28)<.005 SET X(28)=-.005
2,79 IF X(29)<.1 SET X(29)=-.1
2,80 IF X(30)<.005 SET X(30)=-.005
2,81 IF X(31)<.04 SET X(31)=-.04
2,82 IF X(32)<.01 SET X(32)=-.01
2,83 IF X(33)<.002 SET X(33)=-.002
2,84 IF X(34)<.1 SET X(34)=-.1
2,85 IF X(35)<.01 SET X(35)=-.01
2,86 IF X(36)<.007 SET X(36)=-.007

```

```

3,30 FOR J=1,36 ;SET Y(J)=X(J)*F1

```

```

4,1 SET Z(1)=Y(1)*1.889;SET Z(2)=Y(2)*1.32;SET Z(3)=Y(3)*3.22;SET Z(4)=Y
(4)*1.116
4,2 SET Z(33)=Y(33)*2.775
4,5 SET Z(5)=Y(5)*1.399;SET Z(6)=Y(6)*1.142;SET Z(7)=Y(7)*1.228;SET Z(8)
=Y(8)*1.407
4,9 SET Z(9)=Y(9)*1.461;SET Z(10)=Y(10)*1.252;SET Z(11)=Y(11)*1.148;SET
Z(12)=Y(12)*1.158
4,13 SET Z(13)=Y(13)*1.43;SET Z(14)=Y(14)*1.153;SET Z(15)=Y(15)*1.205;SE
T Z(16)=Y(16)*1.173
4,17 SET Z(17)=Y(17)*2.153;SET Z(18)=Y(18)*1.658;SET Z(19)=Y(19)*1.583;S
ET Z(20)=Y(20)*1.50
4,21 SET Z(21)=Y(21)*1.348;SET Z(22)=Y(22)*1.166;SET Z(23)=Y(23)*1.275;S
ET Z(24)=Y(24)*2.292
4,25 SET Z(25)=Y(25)*1.08;SET Z(26)=Y(26)*1.316;SET Z(27)=Y(27)*2.14;SET
Z(28)=Y(28)*1.18
4,29 SET Z(29)=Y(29)*1.251;SET Z(30)=Y(30)*1.668;SET Z(31)=Y(31)*1.245;S
ET Z(32)=Y(32)*1.351
4,30 SET Z(34)=Y(34)*1.197;SET Z(35)=Y(35)*1.471;SET Z(36)=Y(36)*1.270
4,50 VIEW !"PERCENT BY WEIGHT - NEGATIVE NUMBERS ARE LESS THAN VALUES"
4,51 VIEW !"NEGATIVE NUMBERS DO NOT APPLY TO K/N1 OR NA/ZR FUSED SAMPLES
"
```

```

5,1 VIEW !"AL= "Y(1)" UT Z, AL203= "Z(1)" UT Z"
5,2 VIEW !"AS= "Y(2)" UT Z, AS203= "Z(2)" UT Z"
5,3 VIEW !"B = "Y(3)" UT Z, B203 = "Z(3)" UT Z"
5,4 VIEW !"BA= "Y(4)" UT Z, BA0 = "Z(4)" UT Z"
5,5 VIEW !"C = "Y(33)" UT Z, C00 = "Z(33)" UT Z"
5,8 VIEW !"D= "Y(5)" UT Z, DA0 = "Z(5)" UT Z"
5,9 VIEW !"E= "Y(6)" UT Z, EA0 = "Z(6)" UT Z"

```

```

5,11 VIEW !"CU="Y(8)" UT Z,
5,12 VIEW !"CR="Y(9)" UT Z,
5,16 VIEW !"CU="Y(10)" UT Z,
5,17 VIEW !"CY="Y(11)" UT Z,
5,18 VIEW !"EZ="Y(12)" UT Z,
5,19 VIEW !"FE="Y(13)" UT Z,
5,20 VIEW !"GD="Y(14)" UT Z,
5,23 VIEW !"K="Y(15)" UT Z,
5,24 VIEW !"LA="Y(16)" UT Z,
5,25 VIEW !"LI="Y(17)" UT Z,
5,26 VIEW !"MG="Y(18)" UT Z,
5,27 VIEW !"MN="Y(19)" UT Z,
5,30 VIEW !"ND="Y(20)" UT Z,
5,31 VIEW !"NA="Y(21)" UT Z,
5,32 VIEW !"ND="Y(22)" UT Z,
5,33 VIEW !"NI="Y(23)" UT Z,
5,34 VIEW !"P="Y(24)" UT Z,
5,39 VIEW !"PB="Y(25)" UT Z,
5,40 VIEW !"RU="Y(26)" UT Z,
5,41 VIEW !"SB="Y(27)" UT Z,
5,42 VIEW !"SI="Y(28)" UT Z,
5,43 VIEW !"SR="Y(29)" UT Z,
5,44 VIEW !"IE="Y(30)" UT Z,
5,46 VIEW !"II="Y(31)" UT Z,
5,47 VIEW !"V="Y(32)" UT Z,
5,48 VIEW !"Y="Y(33)" UT Z,
5,49 VIEW !"ZN="Y(34)" UT Z,
5,50 VIEW !"ZR="Y(35)" UT Z,
5,51 SET K=36
5,52 FOR K=1,36;IF Y(K)<.0 SET Y(K)=0
5,53 SET L=36
5,54 FOR L=1,36;IF Z(L)<.0 SET Z(L)=0

6,1 SET S1=Y(1)+Y(2)+Y(3)+Y(4)+Y(5)+Y(6)+Y(7)+Y(8)+Y(9)+Y(10)
6,2 SET S2=Y(11)+Y(12)+Y(13)+Y(14)+Y(15)+Y(16)+Y(17)+Y(18)+Y(19)+Y(20)
6,3 SET S3=Y(21)+Y(22)+Y(23)+Y(24)+Y(25)+Y(26)+Y(27)+Y(28)+Y(29)+Y(30)
6,4 SET S4=Y(31)+Y(32)+Y(33)+Y(34)+Y(35)+Y(36)
6,10 SET I1=Z(1)+Z(2)+Z(3)+Z(4)+Z(5)+Z(6)+Z(7)+Z(8)+Z(9)+Z(10)
6,11 SET I2=Z(11)+Z(12)+Z(13)+Z(14)+Z(15)+Z(16)+Z(17)+Z(18)+Z(19)+Z(20)
6,12 SET I3=Z(21)+Z(22)+Z(23)+Z(24)+Z(25)+Z(26)+Z(27)+Z(28)+Z(29)+Z(30)
6,13 SET I4=Z(31)+Z(32)+Z(33)+Z(34)+Z(35)+Z(36)
6,20 VIEW !"TOTAL ELEMENT="S1+S2+S3+S4" UT Z"
6,21 VIEW !"TOTAL OXIDE ="I1+I2+I3+I4" UT Z"

```

7,1 GO 1,9

Battelle

Pacific Northwest Laboratories

Project Number _____

Internal Distribution

File/LB

Date August 28, 1985
To Distribution
From J. E. Mendel, Manager MCC Program
Subject Restricted Use, PNL Technical Service Group Procedure No. PNL-SP-6

The attached technical service procedure is written to meet requirements for providing analytical support service to license-related projects as specified in PNL-MA-60, Quality Assurance Manual for License-Related Projects. It is approved for use on all license-related work except the Basalt Waste Isolation Program (BWIP).

Copies of this procedure have been submitted to BWIP for their concurrence. This memorandum shall remain attached to the procedure until the requested BWIP concurrence is received at which time a change notice withdrawing this restriction will be issued.

JEM/chb

TRANSMITTED

OCT 31 1985

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2. DOCUMENT TRANSMITTED

Doc. No.	Rev. No.	Document Title	Replaces Doc. No./Rev.
PNL-SP-6	0	ICP Analysis using the Jarrell-Ash Atom Comp Model 975 (3720 Building)	-

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This procedure is approved for use on all license-related work except for the Basalt Waste Isolation Program (BWIP). A separate procedure applying to the BWIP is in preparation.			

PNL STANDARD PROCEDURE

TITLE: ICP ANALYSIS USING THE JARRELL-ASH ATOM COMP MODEL 975 (3720 BUILDING)

1.0 OBJECTIVE

The objective of this procedure is to ensure that inorganic ions analyzed with the Jarrell-Ash inductively coupled plasma/atomic emission spectrometer (ICP/AES) are performed in a controlled, reproducible manner.

2.0 APPLICABILITY

The Jarrell-Ash Atom Comp Model 975 ICP/AES is an automated direct reading spectrometer which can analyze up to 33 elements simultaneously in aqueous solutions. Solid samples (e.g., glass samples) are fused with an alkaline hydroxide flux, cooled to room temperature, leached with water, acidified and diluted to volume. A suitable aliquot of this solution is analyzed by the ICP/AES method.

3.0 DEFINITIONS

- 3.1 RF Generator - The crystal controlled 27.12 MHz radiofrequency generator has a controlled power output from 700 to 2500 watts.
- 3.2 Source Stand - The source stand consists of the quartz plasma torch, the nebulizer, the spray chamber, the argon gas flow controller, the working coil, and the manually turning matchbox which converts the power from the RF generator into a very stable argon plasma.
- 3.3 Spectrometer - A 0.75 meter Roland Circle spectrometer using a grating with 2400 grooves per mm spacing. The system has 33 channels mounted on the direct reader array.
- 3.4 Computer - A Digital Data PDP-8a computer which is an integral part of the system and is used for the control of the system during the accumulation of the data, the calibration of the system, and the computation of the results.
- 3.5 Matrix - The user created computer program which controls the operational parameters used during data accumulation, system calibration and the calculation of the results.

QAO Approval <i>KE Thompson</i> 5-23-85		Approved (Line Manager) <i>WHD</i>	
Prepared by F. T. Hara <i>Frank P Hara</i>		Technical Review <i>Roy K</i> 4/15/85	
Procedure No. PNL-SP-6	Revision No. 0	Date Issued JUL 19 1985	Page <u>1</u> of <u>7</u>

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- 3.6 Sample Log - This log contains the lab serial number, customer identification, date, work order number, and analysis required.
- 3.7 Report of Analysis Cards - The sample cards shall contain the lab serial number and the customer's sample information which is required for unique identification. The analyses required are also listed on this card.
- 3.8 Analytical Reports - These reports contain the laboratory serial number, results of the required analyses, plus computer-generated data, if appropriate.

4.0 RESPONSIBILITIES

4.1 Line Manager

- Ensure that all affected staff members have been trained in the use of this procedure.

4.2 Responsible Scientist

- Implement this procedure for the analysis of samples requiring ICP analyses
- Direct supervision of the individual responsible for the analysis of the samples
- Review, sign, and date the data before transmission of results to the task leader.

4.3 Cognizant Staff

- Follow this procedure.

5.0 PROCEDURE

5.1 Summary of Method

The ICP is an argon plasma formed by the interaction of an RF field and an ionized argon gas stream. This spatially stable, chemically inert plasma is reported to reach a temperature as high as 10,000°K. The argon carrier gas nebulizes the liquid sample into the spray chamber. It also transports the smaller sample droplets into the plasma. The high temperature in the plasma desolvates the droplets and dissociates the sample material into individual atoms and ions which are excited to emit light at wavelengths characteristic of the elements in the sample. The spectrometer sorts the various wavelengths and measures the intensity of specific spectral lines. The photomultiplier tubes convert the

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PNL STANDARD PROCEDURE

emitted light to an electrical signal which is proportional to the intensity of the spectral line. The digitized signals are converted by the computer into mg/L units which are printed directly on the input/output terminal.

5.2 Starting the Jarrell-Ash ICP

The stepwise procedure for starting the Jarrell-Ash ICP is:

- 5.2.1 Open the needle valve on the argon line at the pressure reduction valve.
- 5.2.2 Switch lines 1 and 2 on the Matheson Multiple Flow Controller to the control mode. Line 1 is to read "70" and line 2 to read "37.5."
- 5.2.3 Turn the line and control breakers on at the front of the RF regulator console.
- 5.2.4 Turn on the peristaltic pump and place the sample uptake tube in demineralized water.
- 5.2.5 Set the RF coupler potentiometer dial (on the side of the hood) to 4.8.
- 5.2.6 Set the power control switch to manual mode.
- 5.2.7 Turn the VSWR potentiometer knob to the minimum value which is full counterclockwise.
- 5.2.8 Turn the RF generator power knob to the minimum value which is full counterclockwise.
- 5.2.9 When the "RF OFF" pushbutton (blue in color) is lit, open the Hoke valve to bleed the argon gas from the carrier gas line.
- 5.2.10 Now, press the "RF ON" Button (red button).
- 5.2.11 Turn the power potentiometer clockwise until the incident RF Powermeter reads 0.6 kilowatts power. Press the ignitor button momentarily.
- 5.2.12 Continue increasing the RF power until the plasma has ignited. Once the plasma has ignited, quickly proceed through steps 5.2.13, 5.2.14, and 5.2.15 or one could ruin the torch.
- 5.2.13 Turn the RF coupler potentiometer dial to 4.28.
- 5.2.14 Turn the power switch to "auto" mode.

PNL STANDARD PROCEDURE

- 5.2.15 Close the Hoke valve on the argon carrier gas line.
- 5.2.16 Turn the RF power potentiometer to its full clockwise position.
- 5.2.17 Adjust the RF coupler potentiometer so the reflected power is at a minimum value (about 10 or 15 watts).
- 5.2.18 Turn the VSWR potentiometer to the position marked on the panel.
- 5.2.19 Let the RF plasma source run for at least 1/2 hour before beginning the profile and calibration procedure.

5.3 Profiling of the ICP

The instrument is profiled each morning. The stepwise procedure for profiling is outlined below.

- 5.3.1 Place the sample uptake tubing in the cobalt sample (about 20 $\mu\text{g/mL}$).
- 5.3.2 Enter the profile command of control P RETURN on the keyboard located on the printer.
- 5.3.3 Adjust the refractor plate micrometer so the signal on the profile meter is about 1/2 the maximum deflection. Write this reading on the sheet posted on the spectrometer.
- 5.3.4 Adjust the profile micrometer over the maximum deflection point to the 1/2 maximum deflection signal on the other side of the Gaussian-shaped signal peak. Write this dial reading on the sheet referred to in step 5.3.3.
- 5.3.5 Sum the two values obtained in steps 5.3.3 and 5.3.4, and divide this value by 2.
- 5.3.6 Adjust the profile micrometer dial to the value obtained in step 5.3.5.

5.4 Calibration of the ICP

The cycle of at least 30 second rinse with demineralized water and a 1-minute preburn aspiration of sample prior to the analyses is used for both the standardization and the sample analysis. The stepwise procedure for the calibration of the instrument is given below:

- 5.4.1 Enter the time and date each morning into the computer by typing T, RETURN, at the keyboard. The RETURN key will produce <. This (<) prompt requires the operator to specify a 24-hour time. The second return key will give a second (<) prompt. The operator

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PNL STANDARD PROCEDURE

will specify the date, month, and year followed by the operator's initials. (An example would be 210384 DR, which would read March 21, 1984 by Don Rinehart.)

- 5.4.2 Place the sample uptake tube in the first standard and start the stop watch to time the preburn cycle.
- 5.4.3 Type ON into the keyboard, and when the 60 second preburn time has elapsed hit the RETURN KEY. Now the system will perform three burns and type the concentrations, the average intensity, and the average concentration on the printer and type ENTER STD ID. Our standard ID is either STD1, STD2, STD3, STD4, or STD5.
- 5.4.4 Place the sample uptake tube in demineralized water to rinse the system for 30 seconds.
- 5.4.5 After rinsing the nebulizer system, repeat steps 2 and 3 with the appropriate standard required.
- 5.4.6 After analyzing the last standard required for this standardization, type S, and RETURN. The system will now ask you to enter the LCN (logical channel numbers) to be calibrated. If one desires to calibrate all channels, press RETURN key.
- 5.4.7 Repeat the calibration procedure to determine whether the system is properly calibrated.
- 5.4.8 Once the system has been calibrated, store the current calibration data on the system disk by typing CONTROL W and RETURN on the keyboard.

5.5 Sample Logging Procedure

- 5.5.1 Log the sample in the sample log. Series of similar liquid samples which requires no special sample preparations except sample dilution can be logged under one laboratory number. Series of samples are identified by the customer identification.
- 5.5.2 For each laboratory number, prepare the "Report of Analysis" card which uniquely identifies each customer sample. These cards follow the sample during analysis. Any sample with weighing or unique identification required during special sample preparation (e.g., fusion) are written on the back of the analysis card. These entries are to be dated and signed when the person performs the analyses. Upon completion of analyses, the cards are filed in the office by the laboratory serial number.

PNL STANDARD PROCEDURE

5.5.3 The analytical reports are prepared by either the responsible scientist or the cognizant staff. The analytical report shall be dated and signed by the responsible scientist before sending the results to the customer.

5.6 Analysis of Samples

Once the system has been profiled and calibrated in the morning, the system is prepared for sample analysis. The stepwise procedure for sample analysis of aqueous solutions is:

5.6.1 When the Q string of EHGGGVAIHAC is entered into the computer, the complete cycle for the analysis is obtained by typing 0 into the keyboard.

5.6.2 Place the sample uptake tube in the sample.

5.6.3 Start the stop watch and begin timing the preburn cycle.

5.6.4 Type 0 into the keyboard and press the RETURN key after aspirating the sample for 60 seconds. (Note: If one wants to label that sample at the keyboard, type 0/. The / informs the computer that all data typed after it is not an execution command; thus, one can type sample labels on the printout sheet).

5.6.5 Repeat steps 2, 3, and 4 with the next sample.

5.6.6 During the analysis of a series of samples, intersperse one of the calibration standards periodically (usually after 4 or 5 samples) to ascertain that the system is still in calibration.

5.7 Reporting of Data *6.7 & 5.6.3 see ICN PNL-SP-6-R0-3*

The data from the ICP printout are transcribed onto a separate reporting form. A copy of this form is attached as Exhibit 1. Liquid samples are generally reported in milligram per liter (or microgram per millileter). If a dilution is made on liquid samples in the laboratory, the final reported element concentrations are corrected for our dilution, and the dilution factor recorded on the tabulation sheet.

For solid samples, a computer program is used to convert the concentration of each element analyzed by ICP to a weight percent element and a weight percent oxide. A listing of this program is in the laboratory notebook used for the 3720 Building ICP. The listing is also attached as Exhibit 2. If this calculation is performed manually, the calculation steps are:

$$\frac{A \times D.F. \times 10^{-6} \text{ } \mu\text{g/g} \times 100}{\text{g sample}} = \text{wt\% element}$$

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PNL STANDARD PROCEDURE

where $A = \mu\text{g/mL}$ value from the ICP data and D.F. = dilution of the sample in mL.

If the results are reported as metal oxide, the values used to calculate the oxides are the same as the values on the computer program listed in Exhibit 2.

6.0 REFERENCED DOCUMENT

Refer to the latest revision of these documents.

6.1 The Jarrell-Ash Operation Manual, Atom. Comp. Model 975.

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LAB NO. _____

NOTE: All tabulated values have been corrected for our lab dilution. () values are near the detection limit.

LISTING OF COMPUTER PROGRAM FOR CONVERTING ICP CONCENTRATION
DATA TO WEIGHT PERCENT ELEMENT OR WEIGHT PERCENT OXIDE

1.1 % ICP CALCULATION FOR WEST PROGRAM

1.10 A X(35)
1.11 A Y(35)
1.12 A Z(35)
1.20 SET S1=!!"LAB NO="?"
1.21 SET C1=!!"CUSTOMER'S SAMPLE NO="?"
1.22 SET WT=!!"SAMPLE WEIGHT="?"
1.23 SET FU=" FUSION METHOD="?11
1.24 SET DF=!!"SAMPLE DILUTION="?"
1.45 SET F1=(.0001*DF)/WT
1.46 VIEW !!"FACTOR TO CONVERT PPM VALUES TO WT %="F1

2.1 SET X(1)=!!"PPM AL="";SET X(2)=" , PPM AS="";SET X(3)=" , PPM B="";SET X(4)=" ,
PPM BA="?"
2.5 SET X(5)=!!"PPM CA="";SET X(6)=" , PPM CD="";SET X(7)=" , PPM CE="";SET X(8)=" ,
PPM CO="?"
2.9 SET X(9)=!!"PPM CR="";SET X(10)=" , PPM CU="";SET X(11)=" , PPM DY="";SET
X(12)=" , PPM EU="?"
2.13 SET X(13)=!!"PPM FE="";SET X(14)=" , PPM GD="";SET X(15)=" , PPM K="";SET
X(16)=" , PPM LA="?"
2.17 SET X(17)=!!"PPM LI="";SET X(18)=" , PPM MG="";SET X(19)=" , PPM MN="";SET
X(20)=" , PPM MO="?"
2.21 SET X(21)=!!"PPM NA="";SET X(22)=" , PPM ND="";SET X(23)=" , PPM NI="";SET
X(24)=" , PPM P="?"
2.25 SET X(25)=!!"PPM PB="";SET X(26)=" , PPM RU="";SET X(27)=" , PPM SI="";SET
X(28)=" , PPM SR="?"
2.29 SET X(29)=!!"PPM TE="";SET X(30)=" , PPM TI="";SET X(31)=" , PPM ZN="";SET
X(32)=" , PPM ZR="?"
2.50 IF X(1)<.03 SET X(1)=-.03
2.51 IF X(2)<.15 SET X(2)=-.15
2.52 IF X(3)<.02 SET X(3)=-.02
2.53 IF X(4)<.005 SET X(4)=-.005
2.54 IF X(5)<.01 SET X(5)=-.01
2.55 IF X(6)<.008 SET X(6)=-.008
2.56 IF X(7)<.05 SET X(7)=-.05
2.57 IF X(8)<.02 SET X(8)=-.02
2.59 IF X(9)<.02 SET X(9)=-.02
2.60 IF X(10)<.01 SET X(10)=-.01
2.61 IF X(11)<.01 SET X(11)=-.01
2.62 IF X(12)<.005 SET X(12)=-.005
2.63 IF X(13)<.01 SET X(13)=-.01
2.64 IF X(14)<.1 SET X(14)=-.1
2.65 IF X(15)<.3 SET X(15)=-.3
2.66 IF X(16)<.01 SET X(16)=-.01
2.67 IF X(17)<.01 SET X(17)=-.01
2.68 IF X(18)<.06 SET X(18)=-.06
2.69 IF X(19)<.005 SET X(19)=-.005
2.70 IF X(20)<.02 SET X(20)=-.02
2.71 IF X(21)<.01 SET X(21)=-.01
2.72 IF X(22)<.02 SET X(22)=-.02

2.73 IF X(23)<.02 SET X(23)=-.02
2.74 IF X(24)<.2 SET X(24)=-.2
2.75 IF X(25)<.1 SET X(25)=-.1
2.76 IF X(26)<.1 SET X(26)=-.1
2.77 IF X(27)<.02 SET X(27)=-.02
2.78 IF X(28)<.005 SET X(28)=-.005
2.79 IF X(29)<.1 SET X(29)=-.1
2.80 IF X(30)<.005 SET X(30)=-.005
2.81 IF X(31)<.04 SET X(31)=-.04
2.82 IF X(32)<.01 SET X(32)=-.01

3.30 FOR J=1,32;SET Y(J)=X(J)*F1

4.1 SET Z(1)=Y(1)*1.889;SET Z(2)=Y(2)*1.32;SET Z(3)=Y(3)*3.22;SET
Z(4)=Y(4)*1.116
4.5 SET Z(5)=Y(5)*1.399;SET Z(6)=Y(6)*1.142;SET Z(7)=Y(7)*1.228;SET
Z(8)=Y(8)*1.407
4.9 SET Z(9)=Y(9)*1.461;SET Z(10)=Y(10)*1.252;SET Z(11)=Y(11)*1.148;SET
Z(12)=Y(12)*1.158
4.13 SET Z(13)=Y(13)*1.43;SET Z(14)=Y(14)*1.153;SET Z(15)=Y(15)*1.205;SET
Z(16)=Y(16)*1.173
4.17 SET Z(17)=Y(17)*2.153;SET Z(18)=Y(18)*1.658;SET Z(19)=Y(19)*1.583;SET
Z(20)=Y(20)*1.50
4.21 SET Z(21)=Y(21)*1.348;SET Z(22)=Y(22)*1.166;SET Z(23)=Y(23)*1.275;SET
Z(24)=Y(24)*2.292
4.25 SET Z(25)=Y(25)*1.08;SET Z(26)=Y(26)*1.316;SET Z(27)=Y(27)*2.14;SET
Z(28)=Y(28)*1.18
4.29 SET Z(29)=Y(29)*1.251;SET Z(30)=Y(30)*1.668;SET Z(31)=Y(31)*1.245;SET
Z(32)=Y(32)*1.351
4.50 VIEW !"PERCENT BY WEIGHT - NEGATIVE NUMBERS ARE LESS THAN VALUES"
4.51 VIEW !"NEGATIVE NUMBERS DOES NOT APPLY TO K AND NI OR NA AND ZR FUSED
SAMPLES"

5.1 VIEW !"AL= "Y(1)" WT %,	AL203= "Z(1)" WT %
5.2 VIEW !"AS= "Y(2)" WT %,	AS203= "Z(2)" WT %
5.3 VIEW !"B = "Y(3)" WT %,	B203 = "Z(3)" WT %
5.4 VIEW !"BA= "Y(4)" WT %,	BAO = "Z(4)" WT %
5.5 VIEW !"CA= "Y(5)" WT %,	CAO = "Z(5)" WT %
5.6 VIEW !"CD= "Y(6)" WT %,	CDO = "Z(6)" WT %
5.7 VIEW !"CE= "Y(7)" WT %,	CE02 = "Z(7)" WT %
5.8 VIEW !"CO= "Y(8)" WT %,	CO203= "Z(8)" WT %
5.9 VIEW !"CR= "Y(9)" WT %,	CR203= "Z(9)" WT %
5.10 VIEW !"CU= "Y(10)" WT %,	CUO = "Z(10)" WT %
5.11 VIEW !"DY= "Y(11)" WT %,	DY203= "Z(11)" WT %
5.12 VIEW !"EU= "Y(12)" WT %,	EU203= "Z(12)" WT %
5.13 VIEW !"FE= "Y(13)" WT %,	FE203= "Z(13)" WT %
5.14 VIEW !"GD= "Y(14)" WT %,	GD203= "Z(14)" WT %
5.15 VIEW !"K = "Y(15)" WT %,	K20 = "Z(15)" WT %
5.16 VIEW !"LA= "Y(16)" WT %,	LA203= "Z(16)" WT %
5.17 VIEW !"LI= "Y(17)" WT %,	LI20 = "Z(17)" WT %
5.18 VIEW !"MG= "Y(18)" WT %,	MGO = "Z(18)" WT %
5.19 VIEW !"MN= "Y(19)" WT %,	MNO2 = "Z(19)" WT %
5.20 VIEW !"MO= "Y(20)" WT %,	MOO3 = "Z(20)" WT %

```

5.21 VIEW !"NA= "Y(21)" WT %,      NA2O = "Z(21)" WT %
5.22 VIEW !"ND= "Y(22)" WT %,      ND2O3= "Z(22)" WT %
5.23 VIEW !"NI= "Y(23)" WT %,      NIO  = "Z(23)" WT %
5.24 VIEW !"P = "Y(24)" WT %,      P2O5 = "Z(24)" WT %
5.25 VIEW !"PB= "Y(25)" WT %,      PBO  = "Z(25)" WT %
5.26 VIEW !"RU= "Y(26)" WT %,      RUO2 = "Z(26)" WT %
5.27 VIEW !"SI= "Y(27)" WT %,      SiO2 = "Z(27)" WT %
5.28 VIEW !"SR= "Y(28)" WT %,      SRO  = "Z(28)" WT %
5.29 VIEW !"TE= "Y(29)" WT %,      TeO2 = "Z(29)" WT %
5.30 VIEW !"TI= "Y(30)" WT %,      TiO2 = "Z(30)" WT %
5.31 VIEW !"ZN= "Y(31)" WT %,      ZNO  = "Z(31)" WT %
5.32 VIEW !"ZR= "Y(32)" WT %,      ZRO2 = "Z(32)" WT %

5.51 IF Y(1)<.0 SET Y(1)=0; IF Z(1)<.0 SET Z(1)=0
5.52 IF Y(2)<.0 SET Y(2)=0; IF Z(2)<.0 SET Z(2)=0
5.53 IF Y(3)<.0 SET Y(3)=0; IF Z(3)<.0 SET Z(3)=0
5.54 IF Y(4)<.0 SET Y(4)=0; IF Z(4)<.0 SET Z(4)=0
5.55 IF Y(5)<.0 SET Y(5)=0; IF Z(5)<.0 SET Z(5)=0
5.56 IF Y(6)<.0 SET Y(6)=0; IF Z(6)<.0 SET Z(6)=0
5.57 IF Y(7)<.0 SET Y(7)=0; IF Z(7)<.0 SET Z(7)=0
5.58 IF Y(8)<.0 SET Y(8)=0; IF Z(8)<.0 SET Z(8)=0
5.59 IF Y(9)<.0 SET Y(9)=0; IF Z(9)<.0 SET Z(9)=0
5.60 IF Y(10)<.0 SET Y(10)=0; IF Z(10)<.0 SET Z(10)=0
5.61 IF Y(11)<.0 SET Y(11)=0; IF Z(11)<.0 SET Z(11)=0
5.62 IF Y(12)<.0 SET Y(12)=0; IF Z(12)<.0 SET Z(12)=0
5.63 IF Y(13)<.0 SET Y(13)=0; IF Z(13)<.0 SET Z(13)=0
5.64 IF Y(14)<.0 SET Y(14)=0; IF Z(14)<.0 SET Z(14)=0
5.65 IF Y(15)<.0 SET Y(15)=0; IF Z(15)<.0 SET Z(15)=0
5.66 IF Y(16)<.0 SET Y(16)=0; IF Z(16)<.0 SET Z(16)=0
5.67 IF Y(17)<.0 SET Y(17)=0; IF Z(17)<.0 SET Z(17)=0
5.68 IF Y(18)<.0 SET Y(18)=0; IF Z(18)<.0 SET Z(18)=0
5.69 IF Y(19)<.0 SET Y(19)=0; IF Z(19)<.0 SET Z(19)=0
5.70 IF Y(20)<.0 SET Y(20)=0; IF Z(20)<.0 SET Z(20)=0
5.71 IF Y(21)<.0 SET Y(21)=0; IF Z(21)<.0 SET Z(21)=0
5.72 IF Y(22)<.0 SET Y(22)=0; IF Z(22)<.0 SET Z(22)=0
5.73 IF Y(23)<.0 SET Y(23)=0; IF Z(23)<.0 SET Z(23)=0
5.74 IF Y(24)<.0 SET Y(24)=0; IF Z(24)<.0 SET Z(24)=0
5.75 IF Y(25)<.0 SET Y(25)=0; IF Z(25)<.0 SET Z(25)=0
5.76 IF Y(26)<.0 SET Y(26)=0; IF Z(26)<.0 SET Z(26)=0
5.77 IF Y(27)<.0 SET Y(27)=0; IF Z(27)<.0 SET Z(27)=0
5.78 IF Y(28)<.0 SET Y(28)=0; IF Z(28)<.0 SET Z(28)=0
5.79 IF Y(29)<.0 SET Y(29)=0; IF Z(29)<.0 SET Z(29)=0
5.80 IF Y(30)<.0 SET Y(30)=0; IF Z(30)<.0 SET Z(30)=0
5.81 IF Y(31)<.0 SET Y(31)=0; IF Z(31)<.0 SET Z(31)=0
5.82 IF Y(32)<.0 SET Y(32)=0; IF Z(32)<.0 SET Z(32)=0

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6.1 SET S1=Y(1)+Y(2)+Y(3)+Y(4)+Y(5)+Y(6)+Y(7)+Y(8)+Y(9)+Y(10)
6.2 SET S2=Y(11)+Y(12)+Y(13)+Y(14)+Y(15)+Y(16)+Y(17)+Y(18)+Y(19)+Y(20)
6.3 SET S3=Y(21)+Y(22)+Y(23)+Y(24)+Y(25)+Y(26)+Y(27)+Y(28)+Y(29)+Y(30)
6.4 SET S4=Y(31)+Y(32)

6.10 SET T1=Z(1)+Z(2)+Z(3)+Z(4)+Z(5)+Z(6)+Z(7)+Z(8)+Z(9)+Z(10)
6.11 SET T2=Z(11)+Z(12)+Z(13)+Z(14)+Z(15)+Z(16)+Z(17)+Z(18)+Z(19)+Z(20)
6.12 SET T3=Z(21)+Z(22)+Z(23)+Z(24)+Z(25)+Z(26)+Z(27)+Z(28)+Z(29)+Z(30)
6.13 SET T4=Z(31)+Z(32)

```

6.20 VIEW !"TOTAL ELEMENT="S1+S2+S3+S4" WT %"
6.21 VIEW !"TOTAL OXIDE ="T1+T2+T3+T4" WT %"

7.1 GO !1.20

A. Doc. No. PNL-SP-12 Rev. No. 0 Doc. Title Potassium Hydroxide Fusion
Document's Author E T Hara *(Signature)* FOR E T HARA 7/21/88
Requested by A.C. Leaf Date Issued 7/21/88

B. Type of Change and Approvals:

☒ Minor Change QAD Concurrence *Spethridge* Date 7/21/88
☐ Major Change QAD Concurrence _____ Date _____
Approval _____ Date _____
Reviews _____
Approvals & Dates _____
Sponsor concurrence documented by _____

C. Reason for Change:

Eliminate nitrate in order to enhance the measurement of sulfate by ion chromatography. These changes are specific to Zeolite fusion but may be applicable to other materials as determined by testing.

D. Description of Change (old text versus requested test):

3.0 Definitions

- 5.2.3 "Add about 2.5 g of potassium hydroxide and about 0.1 g potassium nitrate to crucible and melt the flux on a hot plate", change to "add potassium hydroxide two times the weight of sample plus 1 ml of deionized water to dissolve the potassium hydroxide. Take to dryness on a hot plate".
- 5.2.4 "400 ± 50°C for 10 minutes", change to "500 ± 50°C for 30 minutes."

••PLACE THIS ICN AT THE FRONT OF THE SUBJECT DOCUMENT••

INTERIM CHANGE NOTICE (ICN)

ICN No. PNL-SP-12-R0-1
Page 1 of 1

A. Doc. No. PNL-SP-12 Rev. No. 0 Doc. Title Potassium Hydroxide Fusion

Document's Author F.T. Hara

Requested by F.T. Hara Date Issued 06/08/87

B. Type of Change and Approvals:

☒ Minor Change QAD Concurrence S.L. English Date 6-2-87

☐ Major Change QAD Concurrence _____ Date _____

Approval _____ Date _____

Reviews, _____

Approvals & Dates _____

Sponsor concurrence documented by _____

C. Reason for Change:

To fulfill the requirement for "Specific Qualification" in Section 4.2.1 of PAP-901.

D. Description of Change (old text versus requested test):

Add

5.3 SPECIFIC QUALIFICATION - None required

The fusion method is used to decompose solid and slurry samples so they are soluble in an aqueous solution. The specific qualification for this procedure is that the sample is completely solubilized in a dilute acid solution. This procedure is for preparation of a sample that will be analyzed by some other controlled method.

PLACE THIS ICN AT THE FRONT OF THE SUBJECT DOCUMENT

Battelle

Pacific Northwest Laboratories

Project Number _____

Internal Distribution

File/LB

Date August 28, 1985

To Distribution

From J. E. Mendenhall, Manager MCC Program

Subject Restricted Use, PNL Technical Service Group Procedure No. PNL-SP-12

The attached technical service procedure is written to meet requirements for providing analytical support service to license-related projects as specified in PNL-MA-60, Quality Assurance Manual for License-Related Projects. It is approved for use on all license-related work except the Basalt Waste Isolation Program (BWIP).

Copies of this procedure have been submitted to BWIP for their concurrence. This memorandum shall remain attached to the procedure until the requested BWIP concurrence is received at which time a change notice withdrawing this restriction will be issued.

JEM/chb

TRANSMITTED

OCT 31 1985

NOT RECORDED

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- d. Return this transmittal form to Document Control
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John E. Bender 7-19-85
Signature/date (distribution authority)

2. DOCUMENT TRANSMITTED

Doc. No.	Rev. No.	Document Title	Replaces Doc. No./Rev.
PNL-SP-12	0	Potassium Hydroxide Fusion	-

3. DISTRIBUTION LIST

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008	DW Felix	325/300	
009	PNL Records Center c/o CM Smyser	ESB	
<p>This procedure is approved for use on all license-related work except for the Basalt Waste Isolation Program (BWIP). A separate procedure applying to the BWIP is in preparation.</p>			

PNL STANDARD PROCEDURE

TITLE: POTASSIUM HYDROXIDE FUSION

1.0 OBJECTIVE

The objective of this procedure is to ensure that the potassium hydroxide fusion on samples are performed in a controlled, reproducible manner.

2.0 APPLICABILITY

The potassium hydroxide fusion can be used for most solid samples which do not require potassium analyses. If potassium must be analyzed, the fusion can be performed using sodium hydroxides as the fusion compound. The potassium hydroxide fusion is generally made in a nickel metal crucible. If nickel analyses are required, the fusion can be made in a zirconium metal crucible. Liquid slurry sample is dried in the metal crucible and the dried sample treated as a solid sample.

3.0 DEFINITIONS

3.1 Dilute Hydrochloric Acid - The hydrochloric acid is diluted to 30 vol% with demineralized water. Dilute hydrochloric acid is used rather than concentrated acid to decrease acid fumes during sample acidification.

4.0 RESPONSIBILITIES

4.1 Responsible Scientist

- Implement this procedure for the fusion of the sample
- Supervision of the individual responsible for the fusion of the sample.

4.2 Cognizant Staff

- Follow this procedure.

QAQ Approval <i>KE Thompson</i> 5-21-85		Approved (Line Manager) <i>W. D. L.</i>	
Prepared by F. T. Hara <i>Paul P. Hara</i>		Technical Review <i>DM Richardson</i> 4-16-85	
Procedure No. PNL-SP-12	Revision No. 0	Date Issued JUL 19	Page <u>1</u> of <u>3</u>

PNL STANDARD PROCEDURE

5.0 PROCEDURE^(a)

5.1 Summary of Method

Finely ground samples are fused with potassium hydroxide in either a nickel or zirconium metal crucible. The fused samples are then leached with demineralized water, acidified, and diluted to volume. The samples are then analyzed by the appropriate method used in this laboratory.

5.2 Fusion Procedure

- 5.2.1 Finely ground solid sample is analyzed by weighing between 0.25 to 0.50 g of sample to within 0.001 g and transferring the powder to the appropriate metal crucible. Proceed to step 5.2.3.
- 5.2.2 Liquid slurry sample is analyzed by weighing between 1 to 3 g of sample in the appropriate metal crucible. If the sample is acidic, neutralize the sample with potassium hydroxide. Dry the sample under a heat lamp and proceed with step 5.2.3.
- 5.2.3 Add about 2.5 g of potassium hydroxide and about 0.1 g of potassium nitrate to crucible and melt the flux on a hot plate.
- 5.2.4 Complete the fusion by heating the sample on the Meeker burner. The fusion can also be done in a muffle furnace by heating the sample at $400 \pm 50^{\circ}\text{C}$ for 10 minutes.
- 5.2.5 Cool the melt to room temperature.
- 5.2.6 Leach the melt with demineralized water and transfer the sample into a suitable container. Rinse the crucible with 30% HCl and water to obtain a quantitative transfer. Transfer the solution into a 250 mL volumetric flask and add 30% HCl to a total volume of 50 mL.
- 5.2.7 If necessary, gently heat the solution to aid in dissolving the sample.
- 5.2.8 Cool the solution and dilute to volume with demineralized water. This solution or a suitable aliquot is used for sample analyses.

(a) The 1984 Annual Book of ASTM Standards, Section 5, Volume 05.05, pages 366-367, was consulted in preparing this procedure.

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PNL STANDARD PROCEDURE

6.0 REFERENCED DOCUMENT

Refer to the latest revision of this document.

6.1 1984 Annual Book of ASTM Standards, Section 5, Volume 05.05, pages 366-367

Procedure No.
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Revision No.
0

Date Issued
JUL 19 1985

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PNL TEST PROCEDURE

1740 4325-
0 4.2

TITLE: HWVP-1; SAMPLE PREPARATION FOR CHEMICAL ANALYSIS

1.0 APPLICABILITY

This procedure defines the method of sample preparation for the analysis of water soluble, acid soluble and/or total ion concentrations utilizing the various analytical methods available to this laboratory.

2.0 DEFINITION

None

3.0 RESPONSIBLE STAFF

Responsible scientist
Cognizant staff

4.0 PROCEDURE

4.1 Summary of Method

The method of sample preparation depends on the type of sample to be analyzed, the method of sample collection, the amount of sample available for analysis, the type and concentration of the various compounds in the sample, the analysis required, and the methods to be used for the analysis. Since the analytical requirements and the chemistry of each set of sample are usually unique, a general method of sample preparation is outlined in this procedure. The procedure shall consist of a water dissolution step, an acid dissolution step, and a potassium hydroxide and/or a sodium peroxide fusion step. Although this procedure consists of these three steps, depending on the type of sample and the analysis required, the sample preparation method may consist of only one of the outlined steps or all three of the steps.

4.2 Specific qualification

4.2.1 Procedure

None required since this procedure is only for sample preparation and not analysis.

Concurrence: <i>[Signature]</i> D. L. Widrig		Date 6/21/88	Approved: <i>[Signature]</i> J. J. McCown		Date 6/21/88
Prepared by T. T. Hara <i>[Signature]</i>		Date 6/21/88	QAD Concurrence L. J. Ethridge <i>[Signature]</i>		Date 6/21/88
Procedure No. HWVP-1	Revision No. 0	Effective Date 6/21/88	Page 1	of 3	

PNL TEST PROCEDURE

4.2.2 A RESPONSIBLE SCIENTIST shall determine which steps of section 4.4 are to be performed and supervise the individual performing the analysis.

4.2.3 The COGNIZANT STAFF shall follow the steps to be performed in this procedure.

4.3 Reagent

4.3.1 Reagent grade acid as required.

4.3.2 Reagent grade potassium hydroxide or sodium peroxide as required.

4.4 Sample Preparation

4.4.1 The RESPONSIBLE SCIENTIST shall determine which steps of Section 4.4 shall be followed by the COGNIZANT STAFF.

4.4.2 Depending on the type of sample, either weigh a portion of the sample or place the entire sample into a suitable container. Measure a known amount of demineralized water and leach the sample with agitation for at least four hours.

4.4.3 Let the suspended solids settle from the sample (if the solids settle very slowly, centrifuge or filter the solution) and remove a measured aliquot for analysis.

4.4.4 If one has sufficient sample, weigh a second sample into a suitable container for the determination of the acid soluble species. Add the required acid (the acid concentration to be at least 5% by volume) to the sample and dissolve the acid soluble species. Heat the solution if required.

4.4.4 If the entire sample was used in step 4.4.2, add a measured volume of dilute acid to the sample container. The final acid concentration of the solution in the container is to be at least 5 % by volume. Leach the sample for at least four hours. Let the solids settle and remove a suitable aliquot of the solution for sample analyses.

4.4.5 If there are undissolved solids in the container after the acid dissolution, filter the sample using a 0.45 μ membrane filter and fuse the sample with either potassium hydroxide or sodium peroxide.

4.4.6 Leach the fused sample with demineralized water. Transfer the leached sample into a volumetric flask, acidify the sample and analyze as required.

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HWVP-1	0	6/21/88	2	3

PNL TEST PROCEDURE

4.4.7 As mentioned previously, the sample may consist of only a water leach if only the water soluble species are requested by the customer.

4.5 Calculation

Since this procedure is a sample preparation method, there are no calculations involved.

Procedure No.	Revision No.	Effective Date	Page	of
HWVP-1	0	6/21/88	3	3

INTERIM CHANGE NOTICE (ICN)

ICN No. PNL-SP-7-R0-2
Page 1 of 1

A. Doc. No. PNL-SP-7 Rev. No. 0 Doc. Title ICP Analysis (325 Building)
Document's Author C.I. Matsuzaki
Requested by F.T. Hara Date Issued 06/08/87

B. Type of Change and Approvals:

☒ Minor Change QAD Concurrence *St. English* Date 6-2-87

☐ Major Change QAD Concurrence _____ Date _____
Approval _____ Date _____
Reviews, _____
Approvals & Dates _____
Sponsor concurrence documented by _____

C. Reason for Change:

To fulfill the requirement for "Specific Qualification" in Section 4.2.1 of PAP-901.

D. Description of Change (old text versus requested text):

Add
5.4.5 ... is in calibration and the process is in control.

Add
5.4.6 Specific Qualification - refer to 5.4.5 above.

PLACE THIS ICN AT THE FRONT OF THE SUBJECT DOCUMENT

Battelle

Pacific Northwest Laboratories

Project Number _____

Internal Distribution

File/LB

Date August 28, 1985

To Distribution

From J. E. Mendenhall, Manager MCC Program

Subject Restricted Use, PNL Technical Service Group Procedure No. PNL-SP-7

The attached technical service procedure is written to meet requirements for providing analytical support service to license-related projects as specified in PNL-MA-60, Quality Assurance Manual for License-Related Projects. It is approved for use on all license-related work except the Basalt Waste Isolation Program (BWIP).

Copies of this procedure have been submitted to BWIP for their concurrence. This memorandum shall remain attached to the procedure until the requested BWIP concurrence is received at which time a change notice withdrawing this restriction will be issued.

JEM/chb

TRANSMITTED

OCT 31 1985

PNL RECORDS CENTER

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John E. Burke 8/14/85
Signature/date (distribution authority)

2. DOCUMENT TRANSMITTED

<u>Doc. No.</u>	<u>Rev. No.</u>	<u>Document Title</u>	<u>Replaces Doc. No./Rev.</u>
PNL-SP-7	0	ICP Analysis (325 Building)	-

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<p>This procedure is approved for use on all license-related work except for the Basalt Waste Isolation Program (BWIP). A separate procedure applying to the BWIP is in preparation.</p>			

PNL STANDARD PROCEDURE

TITLE: ICP ANALYSIS (325 BUILDING)

1.0 OBJECTIVE

The objective of this procedure is to ensure that inorganic ions analyzed with the Applied Research Laboratory (ARL) inductively coupled plasma/atomic emission spectrometer (ICP/AES) are performed in a controlled, reproducible manner.

2.0 APPLICABILITY

The Applied Research Laboratory Model 3580 ICP/AES is an automated direct reading spectrometer coupled with a sequential system dedicated to the analysis of radioactive aqueous solutions. The sequential reader can analyze wavelengths greater than 200 nanometers. Solid samples (e.g., glass samples) are fused with an alkaline hydroxide flux (following PNL-SP-12), cooled to room temperature, leached with water, acidified and diluted to volume. A suitable aliquot of this solution is analyzed by the ICP/AES method.

3.0 DEFINITIONS

- 3.1 RF Generator - The crystal controlled radiofrequency generator at 27.12 MHz has a controlled power output from 700 to 2500 watts.
- 3.2 Source Stand - The source stand consists of the quartz plasma torch, the nebulizer, the spray chamber, the argon gas flow controller, the working coil, and the autotuned matchbox which converts the power from the RF generator into a very stable argon plasma.
- 3.3 Spectrometer - A 1.0 meter Roland Circle Spectrometer using a grating with 1080 grooves per mm spacing. The system has 26 channels mounted on the direct reader array.
- 3.4 Computer - A PDP-1103 with a Winchester and a floppy disk drive which is an integral part of the system and is used for the control of the system during the accumulation of the data, the calibration of the system, the computation of the results, and data storage/management.

QA0 Approval <i>LE Hampton</i> 6-10-85		Approved (Line Manager) <i>W. J. [Signature]</i>	
Prepared by C. L. Matsuzaki <i>C. L. Matsuzaki</i>		Technical Review <i>Ray Fe</i> 4/15/85	
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PNL STANDARD PROCEDURE

4.0 RESPONSIBILITIES

4.1 Line Manager

- Assure that all affected staff members have been trained in the use of this procedure.

4.2 Responsible Scientist

- Implement this procedure for sample analyses
- Direct supervision of the individual responsible for sample analyses
- Review and sign the data before transmission of results to the customer.

4.3 Cognizant Staff

- Follow this procedure.

5.0 PROCEDURE

5.1 Summary of Method

The ICP is an argon plasma formed by the interaction of an RF field and an ionized argon gas stream. This spatially stable, chemically inert plasma is reported to reach a temperature as high as 10,000°K.

The argon carrier gas aspirates the liquid sample into the spray chamber and transports the smaller sample droplets into the plasma. The high temperature in the plasma desolvates the droplets and dissociates the sample material into individual atoms and ions which are excited to emit light at wavelengths characteristic of the elements in the sample. The spectrometer sorts the various wavelengths and measures the intensity of specific spectral lines. The photomultiplier tubes convert the emitted light to an electrical signal which is proportional to the intensity of the spectral line. The digitized signals are converted by the computer into mg/L (µg/mL) units which are printed directly on the input/output terminal.

5.2 Starting the ARL ICP

The stepwise procedure for starting the ARL ICP is:

- 5.2.1 Check the water saturator and tip wash reservoirs to ensure that water is filled to the proper levels. Fill if necessary.
- 5.2.2 Open the valve on the argon tank; check to make sure that the regulator is set at 80 psi.

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PNL STANDARD PROCEDURE

- 5.2.3 Turn on the RF generator main power.
- 5.2.4 Turn on the water circulating bath that cools the torch.
- 5.2.5 Turn on the plasma control box.
- 5.2.6 Turn on the mass flow controller.
- 5.2.7 Hook up the tubing on the peristaltic pump and turn the pump on, making sure that there is an adequate supply of water in the rinse reservoir.
- 5.2.8 Profile the sequential spectrometer (see 5.3.1) before lighting the torch.
- 5.2.9 Light the torch by pressing the green "start" button.

5.3 Profiling the ICP

5.3.1 Profiling the Sequential Spectrometer

Use the command "POS" to initiate the scanner calibration. Once the calibration is complete, use the command "RPOS" to send the position data to the ICS.

(Note: This procedure should be done when the torch is NOT lit.)

5.3.2 Profiling the Simultaneous Spectrometer

Use the command "IPROF" and a manganese solution of approximately 20 ppm. Follow the directions given by the system, using a 2 second integration. Print a graph of the manganese profile for the log book.

5.4 Sample Analysis

The ARL ICP allows the user to select the elements of interest for analysis according to the needs of the customer. Various programs can be stored for different applications. The responsible scientist or cognizant staff selects the lines and analytical conditions, establishes a calibration curve, calibrates the system, and then performs the sample analyses. Refer to the ARL Spectrometer Automation and Data Processing System (SAS/DPS) operation manuals for a detailed stepwise procedure. The SAS/DPS is a computer program that operates the spectrometer and processes the data.

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PNL STANDARD PROCEDURE

5.4.1 Line Selection/Analytical Condition Selection

Use the "PSETUP" command to establish a user-defined program (name of the program can be up to six alpha/numeric characters). Follow the menu provided to select the lines, the analytical conditions (preflush, integration time, etc.).

5.4.2 Calibration Curve

Use the "CSETUP" command to establish a user-defined calibration curve for the program named in 5.4.1. Follow the menu provided to enter the standards selected for calibration. Enter the standards from lowest to highest concentrations.

5.4.3 Initial Normalization

Use the command "NSETUP XXXXXX" (name of program defined in 5.4.1) to establish the initial normalization data. This command establishes a two point calibration that aids in correcting for instrument drift. If the calibration curve established in 5.4.2 is only a two point curve, this NSETUP step is not used.

5.4.4 Run Calibration Standards

Use the command "CALIB XXXXXX" (name of program) to run the calibration standards defined in 5.4.2. Follow the system prompts to run the standards in the proper order.

5.4.5 Sample Analysis

Use the command "NORM XXXXXX" (name of program) to calibrate the system on a routine basis before sample analysis. If an NSETUP file was not established, do 5.4.4 (calibration) before sample analysis. Use the command "SAMPLE XXXXXX" (name of program) to begin sample analysis once the system is calibrated. Follow the prompts to enter sample name, sample number, etc. During the analysis of a series of samples, run at least one of the calibration standards periodically (usually after 5 or 6 samples) to ascertain that the system is still in calibration.

5.5 Reporting of Data

The data from the ICP printout are transcribed onto a separate reporting form. A copy of this form is attached as Exhibit 1. Liquid samples are generally reported in milligrams per liter (or micrograms per milliliter). If a dilution is made on liquid samples in the laboratory, the final reported element concentrations are corrected for our dilution, and the dilution factor recorded on the tabulation sheet. For solid samples, a computer program is used to convert the concentration of each

PNL STANDARD PROCEDURE

element analyzed by ICP to a weight percent element and a weight percent oxide. A copy of the listing of this program is attached as Exhibit 2.

If this calculation is performed manually, the calculation steps are:

$$\frac{A \times D.F. \times 10^{-6} \text{ } \mu\text{g/g} \times 100}{\text{g sample}} = \text{wt\% element}$$

where A = $\mu\text{g/mL}$ value from the ICP data and D.F. = dilution of the sample in mL. If the results are reported as metal oxide, the values used for hand calculation of the oxides are the same as the values on the computer program listed in Exhibit 2.

In addition to the data reported, each report must include the following entries:

- signature of preparer and date
- instrument identification (control or calibration number)
- sample(s) identification.

6.0 REFERENCED DOCUMENTS

Refer to the latest revision of these documents.

6.1 The Applied Research Laboratory SAS/DPS Operation Manuals

6.2 PNL-SP-12, Potassium Hydroxide Fusion

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325 BUILDING ICP
ANALYTICAL RESULTS

CALCULATION OF ELEMENT CONCENTRATION IN SOLID SAMPLES

L131

1,1 Z OXIDE CALCULATION 325 BLDG REVISION 1 CL MATSUZAKI 04 JUNE 85
1,10 A X(35)
1,11 A Y(35)
1,12 A Z(35)
1,20 SET S1="LAB NO=?"
1,21 SET C1="CUSTOMER'S SAMPLE NO=?"
1,22 SET UT="SAMPLE WEIGHT=?"
1,23 SET FU=" FUSION METHOD=?11
1,24 SET DF="SAMPLE DILUTION=?"
1,45 SET F1=(.0001*DF)/UT
1,46 VIEW 1"FACTOR TO CONVERT PPM VALUES TO WT Z="F1

2,1 SET X(1)="PPH AL=?";SET X(3)=", PPM B=?";SET X(4)=", PPM BA=?";SET
X(5)=", PPM CA=?"
2,5 SET X(7)="PPH CE=?";SET X(9)=", PPM CR=?";SET X(11)=", PPM DY=?";SE
T X(13)=", PPM FE=?"
2,13 SET X(15)="PPH K=?";SET X(16)=", PPM LA=?";SET X(17)=", PPM LI=?";
SET X(18)=", PPM MG=?"
2,17 SET X(19)="PPH MN=?";SET X(20)=", PPM MO=?";SET X(21)=", PPM NA=?"
;SET X(22)=", PPM ND=?"
2,21 SET X(23)="PPH NI=?";SET X(24)=", PPM P=?";SET X(25)=", PPM RH=?";
SET X(26)=", PPM RU=?";SET X(27)=", PPM SI=?"
2,25 SET X(28)="PPH SR=?";SET X(29)=", PPM TE=?";SET X(30)=", PPM TI=?"
;SET X(31)=", PPM ZN=?"
2,29 SET X(32)="PPH ZR=?"
2,50 IF X(1)<.09 SET X(1)=-.09
2,51 IF X(2)<.15 SET X(2)=-.15
2,52 IF X(3)<.02 SET X(3)=-.02
2,53 IF X(4)<.003 SET X(4)=-.003
2,54 IF X(5)<.01 SET X(5)=-.01
2,55 IF X(6)<.008 SET X(6)=-.008
2,56 IF X(7)<.12 SET X(7)=-.12
2,57 IF X(8)<.02 SET X(8)=-.02
2,59 IF X(9)<.01 SET X(9)=-.01
2,60 IF X(10)<.01 SET X(10)=-.01
2,61 IF X(11)<.02 SET X(11)=-.02
2,62 IF X(12)<.005 SET X(12)=-.005
2,63 IF X(13)<.006 SET X(13)=-.006
2,64 IF X(14)<.1 SET X(14)=-.1
2,65 IF X(15)<.6 SET X(15)=-.6
2,66 IF X(16)<.01 SET X(16)=-.01
2,67 IF X(17)<.006 SET X(17)=-.006
2,68 IF X(18)<.003 SET X(18)=-.003
2,69 IF X(19)<.003 SET X(19)=-.003
2,70 IF X(20)<.015 SET X(20)=-.015
2,71 IF X(21)<.06 SET X(21)=-.06
2,72 IF X(22)<.06 SET X(22)=-.06
2,73 IF X(23)<.015 SET X(23)=-.015
2,74 IF X(24)<1.0 SET X(24)=-1.0
2,75 IF X(25)<.09 SET X(25)=-.09

2,76 IF X(26)<.06 SET X(26)=-.06
2,77 IF X(27)<.09 SET X(27)=-.09
2,78 IF X(28)<.003 SET X(28)=-.003
2,79 IF X(29)<.09 SET X(29)=-.09
2,80 IF X(30)<.003 SET X(30)=-.003
2,81 IF X(31)<.02 SET X(31)=-.02
2,82 IF X(32)<.02 SET X(32)=-.02

3,30 FOR J=1,32;SET Y(J)=X(J)*F1

4,1 SET Z(1)=Y(1)*1.889;SET Z(2)=Y(2)*1.32;SET Z(3)=Y(3)*3.22;SET Z(4)=Y(4)*1.116
4,5 SET Z(5)=Y(5)*1.399;SET Z(6)=Y(6)*1.142;SET Z(7)=Y(7)*1.228;SET Z(8)=Y(8)*1.407
4,9 SET Z(9)=Y(9)*1.461;SET Z(10)=Y(10)*1.252;SET Z(11)=Y(11)*1.148;SET Z(12)=Y(12)*1.158
4,13 SET Z(13)=Y(13)*1.43;SET Z(14)=Y(14)*1.153;SET Z(15)=Y(15)*1.205;SET Z(16)=Y(16)*1.173
4,17 SET Z(17)=Y(17)*2.153;SET Z(18)=Y(18)*1.658;SET Z(19)=Y(19)*1.583;SET Z(20)=Y(20)*1.50
4,21 SET Z(21)=Y(21)*1.348;SET Z(22)=Y(22)*1.166;SET Z(23)=Y(23)*1.275;SET Z(24)=Y(24)*2.292
4,25 SET Z(25)=Y(25)*1.311;SET Z(26)=Y(26)*1.316;SET Z(27)=Y(27)*2.14;SET Z(28)=Y(28)*1.18
4,29 SET Z(29)=Y(29)*1.251;SET Z(30)=Y(30)*1.668;SET Z(31)=Y(31)*1.245;SET Z(32)=Y(32)*1.351
4,50 VIEW ! "PERCENT BY WEIGHT - NEGATIVE NUMBERS ARE LESS THAN VALUES"
4,51 VIEW ! "NEGATIVE NUMBERS DO NOT APPLY TO KOH/NI OR NA2O2/ZR FUSED SAMPLES"

5,1 VIEW ! "AL= "Y(1)" UT Z,
5,3 VIEW ! "B = "Y(3)" UT Z,
5,4 VIEW ! "BA= "Y(4)" UT Z,
5,5 VIEW ! "CA= "Y(5)" UT Z,
5,7 VIEW ! "CE= "Y(7)" UT Z,
5,9 VIEW ! "CR= "Y(9)" UT Z,
5,11 VIEW ! "DY= "Y(11)" UT Z,
5,13 VIEW ! "FE= "Y(13)" UT Z,
5,15 VIEW ! "K = "Y(15)" UT Z,
5,16 VIEW ! "LA= "Y(16)" UT Z,
5,17 VIEW ! "LI= "Y(17)" UT Z,
5,18 VIEW ! "MG= "Y(18)" UT Z,
5,19 VIEW ! "MN= "Y(19)" UT Z,
5,20 VIEW ! "MO= "Y(20)" UT Z,
5,21 VIEW ! "NA= "Y(21)" UT Z,
5,22 VIEW ! "ND= "Y(22)" UT Z,
5,23 VIEW ! "NI= "Y(23)" UT Z,
5,24 VIEW ! "P = "Y(24)" UT Z,
5,25 VIEW ! "RH= "Y(25)" UT Z,
5,26 VIEW ! "RU= "Y(26)" UT Z,
5,27 VIEW ! "SI= "Y(27)" UT Z,
5,28 VIEW ! "SR= "Y(28)" UT Z,
5,29 VIEW ! "TE= "Y(29)" UT Z,
5,30 VIEW ! "TI= "Y(30)" UT Z,

AL203= "Z(1)" UT Z"
B2O3 = "Z(3)" UT Z"
BAO = "Z(4)" UT Z"
CAO = "Z(5)" UT Z"
CEO2 = "Z(7)" UT Z"
CR2O3= "Z(9)" UT Z"
DY2O3= "Z(11)" UT Z"
FE2O3= "Z(13)" UT Z"
K2O = "Z(15)" UT Z"
LA2O3= "Z(16)" UT Z"
Li2O = "Z(17)" UT Z"
MgO = "Z(18)" UT Z"
MnO2 = "Z(19)" UT Z"
MOO3 = "Z(20)" UT Z"
NA2O = "Z(21)" UT Z"
ND2O3= "Z(22)" UT Z"
NiO = "Z(23)" UT Z"
P2O5 = "Z(24)" UT Z"
RH2O = "Z(25)" UT Z"
RUO2 = "Z(26)" UT Z"
SiO2 = "Z(27)" UT Z"
SRU = "Z(28)" UT Z"
TEO2 = "Z(29)" UT Z"
TiO2 = "Z(30)" UT Z"

```

5,31 VIEW !"ZN= "Y(31)" WT Z,      ZN0 = "Z(31)" WT Z"
5,32 VIEW !"ZR= "Y(32)" WT Z,      ZR02 = "Z(32)" WT Z"
5,51 IF Y(1)<.0 SET Y(1)=0;IF Z(1)<.0 SET Z(1)=0
5,52 IF Y(2)<.0 SET Y(2)=0;IF Z(2)<.0 SET Z(2)=0
5,53 IF Y(3)<.0 SET Y(3)=0;IF Z(3)<.0 SET Z(3)=0
5,54 IF Y(4)<.0 SET Y(4)=0;IF Z(4)<.0 SET Z(4)=0
5,55 IF Y(5)<.0 SET Y(5)=0;IF Z(5)<.0 SET Z(5)=0
5,56 IF Y(6)<.0 SET Y(6)=0;IF Z(6)<.0 SET Z(6)=0
5,57 IF Y(7)<.0 SET Y(7)=0;IF Z(7)<.0 SET Z(7)=0
5,58 IF Y(8)<.0 SET Y(8)=0;IF Z(8)<.0 SET Z(8)=0
5,59 IF Y(9)<.0 SET Y(9)=0;IF Z(9)<.0 SET Z(9)=0
5,60 IF Y(10)<.0 SET Y(10)=0;IF Z(10)<.0 SET Z(10)=0
5,61 IF Y(11)<.0 SET Y(11)=0;IF Z(11)<.0 SET Z(11)=0
5,62 IF Y(12)<.0 SET Y(12)=0;IF Z(12)<.0 SET Z(12)=0
5,63 IF Y(13)<.0 SET Y(13)=0;IF Z(13)<.0 SET Z(13)=0
5,64 IF Y(14)<.0 SET Y(14)=0;IF Z(14)<.0 SET Z(14)=0
5,65 IF Y(15)<.0 SET Y(15)=0;IF Z(15)<.0 SET Z(15)=0
5,66 IF Y(16)<.0 SET Y(16)=0;IF Z(16)<.0 SET Z(16)=0
5,67 IF Y(17)<.0 SET Y(17)=0;IF Z(17)<.0 SET Z(17)=0
5,68 IF Y(18)<.0 SET Y(18)=0;IF Z(18)<.0 SET Z(18)=0
5,69 IF Y(19)<.0 SET Y(19)=0;IF Z(19)<.0 SET Z(19)=0
5,70 IF Y(20)<.0 SET Y(20)=0;IF Z(20)<.0 SET Z(20)=0
5,71 IF Y(21)<.0 SET Y(21)=0;IF Z(21)<.0 SET Z(21)=0
5,72 IF Y(22)<.0 SET Y(22)=0;IF Z(22)<.0 SET Z(22)=0
5,73 IF Y(23)<.0 SET Y(23)=0;IF Z(23)<.0 SET Z(23)=0
5,74 IF Y(24)<.0 SET Y(24)=0;IF Z(24)<.0 SET Z(24)=0
5,75 IF Y(25)<.0 SET Y(25)=0;IF Z(25)<.0 SET Z(25)=0
5,76 IF Y(26)<.0 SET Y(26)=0;IF Z(26)<.0 SET Z(26)=0
5,77 IF Y(27)<.0 SET Y(27)=0;IF Z(27)<.0 SET Z(27)=0
5,78 IF Y(28)<.0 SET Y(28)=0;IF Z(28)<.0 SET Z(28)=0
5,79 IF Y(29)<.0 SET Y(29)=0;IF Z(29)<.0 SET Z(29)=0
5,80 IF Y(30)<.0 SET Y(30)=0;IF Z(30)<.0 SET Z(30)=0
5,81 IF Y(31)<.0 SET Y(31)=0;IF Z(31)<.0 SET Z(31)=0
5,82 IF Y(32)<.0 SET Y(32)=0;IF Z(32)<.0 SET Z(32)=0

```

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6,1 SET S1=Y(1)+Y(2)+Y(3)+Y(4)+Y(5)+Y(6)+Y(7)+Y(8)+Y(9)+Y(10)
6,2 SET S2=Y(11)+Y(12)+Y(13)+Y(14)+Y(15)+Y(16)+Y(17)+Y(18)+Y(19)+Y(20)
6,3 SET S3=Y(21)+Y(22)+Y(23)+Y(24)+Y(25)+Y(26)+Y(27)+Y(28)+Y(29)+Y(30)
6,4 SET S4=Y(31)+Y(32)
6,10 SET T1=Z(1)+Z(2)+Z(3)+Z(4)+Z(5)+Z(6)+Z(7)+Z(8)+Z(9)+Z(10)
6,11 SET T2=Z(11)+Z(12)+Z(13)+Z(14)+Z(15)+Z(16)+Z(17)+Z(18)+Z(19)+Z(20)
6,12 SET T3=Z(21)+Z(22)+Z(23)+Z(24)+Z(25)+Z(26)+Z(27)+Z(28)+Z(29)+Z(30)
6,13 SET T4=Z(31)+Z(32)
6,20 VIEW !"TOTAL ELEMENT="S1+S2+S3+S4" WT Z"
6,21 VIEW !"TOTAL OXIDE ="T1+T2+T3+T4" WT Z"

```

6,1 GO !!!!!!!!!!!!!.20

INTERIM CHANGE NOTICE (ICN)

ICN No. PNL-SP-11-R0-1
Page 1 of 1

A. Doc. No. <u>PNL-SP-11</u> Rev. No. <u>0</u> Doc. Title <u>Atomic Absorption Using the Perkin-Elmer Model 5000 Spectrophotometer and Graphite Furnace</u>	
Document's Author <u>F.T. Hara</u>	
Requested by <u>F.T. Hara</u>	Date Issued <u>06/08/87</u>
B. Type of Change and Approvals:	
☒ Minor Change	QAD Concurrence <u>S.L. English</u> Date <u>6-2-87</u>
☐ Major Change	QAD Concurrence _____ Date _____
	Approval _____ Date _____
	Reviews, _____
	Approvals & Dates _____
	Sponsor concurrence documented by _____
C. Reason for Change:	
To fulfill the requirement for "Specific Qualification" in Section 4.2.1 of IAP-901.	
D. Description of Change (old text versus requested test):	
Add	
5.1	If the recovery of the cesium spike added to a sample or set of samples of similar types is greater than 80%, the process is in control.
Add	
5.3	Specific Qualification - refer to Section 5.1 shown above.
PLACE THIS ICN AT THE FRONT OF THE SUBJECT DOCUMENT	

66X. Lee / James

BATTELLE Project Management Division
505 King Avenue
Columbus, Ohio 43201-2693

August 2, 1985

Mr. Max Kreiter, Manager
Geologic Repository Deployment
Nuclear Fuel Cycle Program Office
Battelle Pacific Northwest Laboratory
Post Office Box 999
Richland, Washington 99352

Dear Mr. Kreiter:

PNL WASTE PACKAGE PROGRAM PROCEDURES

The following procedures have been reviewed and approved by ONWI.

PNL-SP-7, Draft A, dated 7-23-85, "ICP Analysis (325 Building)."

PNL-SP-11, Draft B, dated 7-23-85, "Atomic Absorption Spectrophotometry Using the Perkin-Elmer Model 5000 Spectrophotometer and Graphite Furnace."

This is a tentative approval, subject to confirmation by SRPO. If you do not hear otherwise by August 12, 1985, you can assume these have complete approval.

If you have any questions, please call J. Perrin at FTS 976-4408.

Sincerely,

A handwritten signature in cursive script that reads "James S. Perrin".

James S. Perrin
Senior Project Manager
Engineering Department

JSP:mo

cc: WP File
DJ Bradley, PNL

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From J. E. Mendenhall, Manager MCC Program

Subject Restricted Use, PNL Technical Service Group Procedure No. PNL-SP-11

The attached technical service procedure is written to meet requirements for providing analytical support service to license-related projects as specified in PNL-MA-60, Quality Assurance Manual for License-Related Projects. It is approved for use on all license-related work except the Basalt Waste Isolation Program (BWIP).

Copies of this procedure have been submitted to BWIP for their concurrence. This memorandum shall remain attached to the procedure until the requested BWIP concurrence is received at which time a change notice withdrawing this restriction will be issued.

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<u>Doc. No.</u>	<u>Rev. No.</u>	<u>Document Title</u>	<u>Replaces Doc. No./Rev.</u>
PNL-SP-11	0	Atomic Absorption Spectrophotometry using the Perkin-Elmer Model 5000 Spectrophotometer and Graphite Furnace	-

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PNL STANDARD PROCEDURE

TITLE: ATOMIC ABSORPTION SPECTROPHOTOMETRY USING THE PERKIN-ELMER MODEL 5000 SPECTROPHOTOMETER AND GRAPHITE FURNACE

1.0 OBJECTIVE

The objective of this procedure is to describe the method of analysis for cesium in aqueous solutions using the atomic absorption spectrophotometry graphite furnace method in the Spectrometry Laboratory in 3720 Building.

2.0 APPLICABILITY

The graphite furnace method of atomization of the sample for atomic absorption analysis is used when the solution to be analyzed does not contain chlorides, and cesium is either below the optimum concentration of the flame method (<0.1 mg/mL) or the sample volume is insufficient to perform the analyses required using the flame method.

3.0 DEFINITIONS

- 3.1 Perkin-Elmer Model 5000 Atomic Absorption Spectrophotometer - The spectrophotometer is a microprocessor-controlled unit in which all mechanical, electrical, and optical functions are electronically controlled and activated. This enables the analytical conditions to be set either manually via the keyboard or from preprogrammed magnetic cards. Analyses performed on a routine basis are stored on magnetic cards.
- 3.2 Graphite Furnace - The electrothermal graphite device which can heat the sample in a graphite tube in a controlled manner to the desired temperature.
- 3.3 Graphite Furnace Programmer - The microprocessor controlled, programmable high current power supply which controls the duration and temperature for the drying, ashing, and atomization cycles of the graphite furnace. This microprocessor is also equipped with a magnetic card reader for storage and recall of analyses performed on a routine basis.
- 3.4 AS-40 - The programmer for the AS-40 Autosampler Sequencer functions as the system controller. Both the graphite furnace controller and the Model 5000 Spectrophotometer obeys its instruction. Thus, all the sample parameters, spectrometer (INST) program, and the Graphite Furnace (HGA) program are entered on the AS-40 keyboard.

QAO Approval <i>E. Thompson</i> 6-5-85		Approved (Line Manager)	
Prepared by F. T. Hara <i>F. T. Hara</i>		Technical Review <i>John C. [Signature]</i>	
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3.5 Argon Gas - The inert gas which is passed through the graphite furnace which is used to purge the inert matrix during the drying and charring cycle, and to control oxidation of the graphite tube during the oxidation cycle.

3.6 Light Source - The source of a reference spectrum for the analysis, generally either a hollow cathode lamp or an electrodeless discharge lamp.

4.0 RESPONSIBILITIES

4.1 Line Manager

- Assure that affected staff are trained in the use of this procedure.

4.2 Responsible Scientist

- Implement this procedure for the analysis of the sample
- Direct supervision of the individual responsible for the analysis of the sample
- Review, sign, and date the data before transmission of the results to the task leader.

4.3 Cognizant Staff

- Follow this procedure.

5.0 PROCEDURE

5.1 Summary of Method

Atomic absorption is the process that occurs when a ground state atom absorbs light at a specific wavelength and is elevated to an excited state. The amount of light absorbed is proportional to the concentration of the ground state atoms of the analyte in the light path.

The basic components for analysis by atomic absorption are a light source, a device for atomizing the specimen solution, a monochromator to isolate the specific wavelength, a detector to measure the light energy, and the electronics to convert the light energy into a measurable form.

A thermal source is used to produce free atoms of the analyte material from the sample. When the sample is introduced as an aerosol, the heat energy desolvates the fine droplets and forms free atoms in the ground

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state. The heat source is aligned to intersect the spectrometer light-path so that the atomic absorption of the light by free atoms can be measured by the spectrophotometer.

For the analysis of cesium the graphite furnace is used to atomize the sample. The graphite furnace method is used on a solution not containing chlorides, and where the concentration of the cesium sample is less than 0.1 mg/mL or the volume of the sample is less than 10 mL and other analyses are requested. The laboratory uses the instrument parameters set as listed in the Perkin-Elmer instruction manuals. It is the laboratory practice to perform spike recovery analyses periodically on samples, even when that type of sample has been analyzed previously.

5.2 Analytical Procedure

5.2.1 Sample Logging

A laboratory log number is assigned to each sample or series of similar samples. At this time, a "Report of Analysis" card is prepared, and the required analyses written onto the card.

5.2.2 The Model 5000 Spectrophotometer

The standby/run switch on the left front of the spectrophotometer is switched to the run position which will activate the keyboard to the microprocessor. The Perkin-Elmer "Model 5000 Analytical Methods for Atomic Absorption Spectrometry Manual" explains the procedure for entering the instrument parameters at the keyboard. Since our system is equipped with a magnetic card reader, these stored parameters are recalled from the system memory or the appropriate magnetic card.

5.2.3 HGA-500 Graphite Furnace

The programmer is activated by pressing the standby button. This will activate the indicator and display lights on the front panel of the programmer. The method for programming the microprocessor controlling the graphite furnace is outlined in the Perkin-Elmer "HGA-500 Graphite Furnace Operator's Manual." The detailed procedure for the optical alignment of the furnace for the Model 5000 AA spectrophotometer is also given. The parameters for setup of the furnace for the elements analyzed are recorded in the "Applications Data Sheets for the HGA Graphite Furnace" which is in the folder labeled "HGA-500 Graphite Furnace." Since this programmer is also equipped with a magnetic card reader, elements which are frequently analyzed are recalled from the appropriate magnetic cards.

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5.2.4 AS-40 Sequencer

The programmer to the AS-40 Autosampler Sequencer functions as the system controller. Since this programmer is connected to the HGA Programmer and the spectrometer, instructions for the entire system are entered by the AS-40 keyboard. The sample analyses performed in this laboratory are by Method 1. The determination using Method 1 is outlined on pages 7.2 through 7.4, Perkin-Elmer "AS-40 Autosampler Sequencer Version Operator's Manual." Since the operation of the Perkin-Elmer Atomic Absorption System is covered by five separate manuals, no attempt is made in reproducing a complete step-by-step procedure. A very abbreviated outline of the procedure is as follows:

5.2.4.1 Recall the appropriate magnetic card for the element to be analyzed into spectrophotometer and the HGA programmer.

5.2.4.2 Follow the setup outlined in the Perkin-Elmer "AS-40 Autosampler Sequencer Version Operator's Manual" on pages 7.2, 7.3, and 7.4. (Note: The spectrometer is set for two standards. The concentrations of the standards for a particular element analysis are recorded on the "Application Data Sheet for the Graphite Furnace.")

5.2.4.3 Referring to the "Application Data Sheet for the Graphite Furnace," if a zero range time is used for the atomization temperature, the temperature sensor must be calibrated. The method for calibration of the maximum power heating temperature is outlined on page 5-3 and 5-4 in the "HGA-500, Graphite Furnace Operator's Manual."

5.2.4.4 Using the standards referenced to in Step 2, the mg/L values are printed directly. The sample value is obtained by multiplying this value by the dilution factor. If the sample was diluted with the concentrations of the two standards referenced in 5.2.4.2, the instrument will perform a calibration and print the sample results in mg/L. If the sample was diluted prior to the analysis, the concentration of the element in the sample is calculated by multiplying the printed sample result by the appropriate dilution factor.

6.0 REFERENCED DOCUMENTS

Refer to the latest revision of these documents.

6.1 Perkin-Elmer HGA 500 Graphite Furnace Operator's Manual

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- 6.2 Perkin-Elmer Analytical Methods for Furnace Atomic Absorption Spectroscopy
- 6.3 Perkin-Elmer Operator's Manual for the AA Spectrometer
- 6.4 Perkin-Elmer Model 5000 Analytical Methods for Atomic Absorption Spectrophotometry
- 6.5 Perkin-Elmer AS-40 Autosampler Sequencer Version Operator's Manual

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PNL TEST PROCEDURE

TITLE: HTA-4-16, SOLUTIONS ANALYSIS: URANIUM BY LASER-EXCITED FLUORESCENCE

1.0 APPLICABILITY

This procedure applies to the laser-excitation fluorimetry method of determining uranium concentration in test solutions.

The form of this procedure may not comply with all the requirements of PAP-501 due to the conversion from Westinghouse Hanford Co. format to PNL format. Exceptions to PAP-501 will be addressed during the next revision of this procedure.

2.0 DEFINITIONS

None.

3.0 EQUIPMENT AND MATERIALS

- Uranium analyzer, Scintrex UA-3, Scintrex Ltd, Concord, Ontario, Canada..
- Sample cell, UV-quartz, 1 x 2 x 4.5 cm with ~7-mL volume.
- Analytical balance, 0.1-mg resolution.
- Micropipets, replaceable plastic tip, Eppendorff-type.
- Magnetic stirrer with magnetic stir bar for sample cell (optional).
- Fluorescence enhancement buffer, FLURAN, Scintrex Ltd, Concord, Ontario, Canada.
- Uranium standard, NBS SRM 960.
- Deionized water, greater than 10-megohm resistance, as indicated by the deionizer meter readout.

Concurrence <i>NA</i>		Date		Approved <i>[Signature]</i>		Date <i>7/2/87</i>	
Prepared by <i>[Signature]</i>		Date <i>7/1/87</i>		QAD Concurrence <i>B.O. BARNES</i>		Date <i>6/30/87</i>	
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4.0 PROCEDURE

4.1 Calibration

Calibration is performed as part of the determination using the standard addition technique described in Section 4.2. The standard is prepared by dissolving about 10 g (record actual weight to the nearest 0.1 mg) of NBS SRM 960 uranium metal in a minimal volume of 8 M HNO_3 . The solution is diluted to about 500 g (record actual weight to the nearest 0.1 mg) with 1 M H_2SO_4 . About 0.5 g (record actual weight to the nearest 0.1 mg) of this solution is diluted to 100 mL with deionized water, giving a nominal 100 $\mu\text{g/mL}$ uranium. The high-range standard is prepared by accurately diluting the 100 $\mu\text{g/mL}$ solution 1-to-100 with 0.1 N HNO_3 , giving a nominal 1 $\mu\text{g/mL}$ solution; and the low-range standard is prepared by diluting the 1 $\mu\text{g/mL}$ solution 1-to-10 or 11, giving a nominal 0.1 $\mu\text{g/mL}$ solution. The bottles used to store the two working trace-level standards are conditioned by repeatedly adding freshly prepared standards over a period of time until the standards' concentrations stabilize. This may require several weeks.

4.2 Method

Trace-level concentrations of uranium in aqueous solutions containing a buffered complexing reagent are determined by measuring the emitted green luminescence upon excitation with a UV-emitting pulsed nitrogen laser. Discrimination against fluorescing organics is provided by using a green filter and a gated detection circuit that measures the long-lived uranium fluorescence after the short-lived organic fluorescence has decayed. Correction for interference by quencher constituents is accomplished by the standard addition method. The fluorescence of the sample is determined and a known amount of uranium is added. The increase in signal due to the standard addition is then related to the sample signal to calculate the sample uranium. The assumption that the solution matrix quenching effect on the added uranium is the same as on the sample uranium should be valid.

4.3 Sample Analysis

- Step 1) Prepare the analyzer. Switch POWER on. Wait until the READY light comes on and switch LASER on. Wait 30 minutes for the laser to stabilize. Set RANGE to LOW. Zero the meter with the ZERO control, allowing 4 seconds for the meter to respond each time between adjustments.
- Step 2) Place the cell in its holder on the cell compartment door.
- Step 3) Pipet 5 mL of deionized water into the sample cell and 10 μL of sample into the deionized water. Stir the solution with the pipet tip and close the door.
- Step 4) Turn on the photomultiplier tube (PMT) with the PMT switch.
CAUTION: NEVER open the door with the PMT switch on.

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- Step 5) Zero the meter with the BALANCE control. If the meter goes off-scale, there may be too much uranium or acid. Dilution or neutralization may be required, after which the meter can be zeroed upon repeating this step. If not, sample purification may be required. The method of purification will depend on the sample.
- Step 6) Turn off the PMT, open the door, and pipet 500 μL of FLURAN into the sample. Stir the solution by working the plunger several times. Alternately, a magnetic stir bar can be placed in the cell and the cell removed to a magnetic stirrer.
- Step 7) Return the cell to its compartment (if removed), close the cell door, and turn on the PMT. Record the meter reading (R_1). If the reading is too low, add more sample to the cell (if the sample matrix does not cause a zero shift). A large initial balance adjustment in Step 5 should indicate this problem. Otherwise, the procedure must be repeated, starting at Step 2. If the reading is off-scale, switch to HIGH RANGE. If the reading is too high, dilute the sample and repeat the procedure starting at Step 2.
- Step 8) Turn off the PMT and open the cell door. Add sufficient standard (0.1 $\mu\text{g/mL}$ for the low range or 1 $\mu\text{g/mL}$ for the high range) to cause an increase in meter reading of about the same amount as the sample reading. Use enough standard to give at least 0.05 meter units. **NOTE:** Do these steps rapidly to prevent significant solution temperature changes that affect fluorescent intensity. Record the meter reading (R_2).
- Step 9) Calculate the results according to Section 4.4.

4.4 Calculations

For small volume change with standard addition:

$$U = \frac{R_1 SK}{(R_2 - R_1)V}$$

where: U = uranium concentration ($\mu\text{g/mL}$)
 R_1 = initial meter reading for sample uranium
 R_2 = final meter reading for sample plus standard uranium
 S = standard concentration ($\mu\text{g/mL}$)
 K = standard volume (mL)
 V = Sample volume (mL).

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4.5 Data Recording

- 4.5.1 The identity of the sample is entered on an analytical report card along with a serial number. The serial number may be the analysis requester's identification number or the analytical laboratory's assigned laboratory number for that sample.
- 4.5.2 Meter reading values R_1 and R_2 are recorded on the buff part of the analytical report card.
- 4.5.3 Results are calculated on the analytical report card using the equation in Section 4.4.
- 4.5.4 The analysis results are recorded on the Results section of the card and the white copy is sent to the analysis requester.
- 4.5.5 The buff section of the card is filed in the designated repository file.

4.6 Records

Records will be maintained and controlled so as to conform with requirements of PAP-1701. Laboratory notebooks provide a mechanism for control of most records.

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PNL TEST PROCEDURE

TITLE: 7-40.8, SOLUTIONS ANALYSIS: ANIONS BY ION CHROMATOGRAPHY

1.0 APPLICABILITY

This procedure provides instructions for analysis of anions in solutions using the ion chromatography method. The suppressor column method is used with the conductimetric detection.

2.0 DEFINITIONS

None.

3.0 RESPONSIBLE STAFF

Staff responsible for implementing this procedure are:

- Cognizant Scientist
- Analyst

4.0 PROCEDURE

4.1 Equipment and Materials

- Ion chromatograph, Dionex Models 12, 2000 Series or equivalent, equipped with appropriate separator and suppressor columns and with a conductimetric (and electrochemical, if needed) detector.
- Strip chart recorder, multi-speed, multi-range, and/or
- Chromatographic peak integrator, Spectro Physics SP4270, Dionex AI300, HP3393 or equivalent.
- Glass and plastic laboratory ware, including volumetric flasks, graduate cylinders, disposable pipet tips, syringes and beakers.
- Balance, top loader, readable to 1-mg.
- Autosampler, Dionex, low volume, pressure delivery, or equivalent (optional item).
- Micropipets, Eppendorf-type with disposable tips.
- Deionized water, greater than 15 megohm, as indicated by the deionizer meter readout.

Concurrence	Date	Approved	Date
		<i>J. M. Town</i>	3/31/88
Prepared by	Date	QAD Concurrence	Date
<i>W. H. Hornath</i>	3/31/88	<i>L. E. Thridge</i>	3/31/88
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- Eluant, 0.00175 M NaHCO_3 - 0.00185 M Na_2CO_3 (or other, as recommended by Dionex Corporation, depending on the anions to be determined and the columns used).
- Regenerant solution for suppressor: 0.5 M H_2SO_4 for the column suppressor or 0.025 M for the fiber and membrane suppressors, or other acid concentration as recommended by Dionex Corporation.
- Standard stock solutions, commercial source with 100 or 1000 ($\pm 1\%$) ug/ml concentrations for the anions of interest. Upon opening a new bottle, verify the solution anion concentration using appropriate diluted standard solutions. Agreement shall be within ± 3 percent relative of the assigned value. If not, determine the source of the problem and take corrective action.
- Multi-element standards; appropriate amounts of stock standards are added with micropipets to deionized water solution containing a hundred-fold dilution of the eluant concentrate. The anion concentrations depend on their concentration levels in the sample. Standard solutions should be made up as similar as possible to the sample to reduce matrix effects. Standards containing anion concentrations less than 100 ug/ml should be made up daily. The micropipets shall be checked before use by weighing the amount of water delivered. Delivery accuracy shall be within $\pm 1.5\%$.

4.2 Method

Ion chromatography is a rapid method of multi-ion analysis for anions and some cations in a single solution sample. The two-column technique utilized in this method is based on separation of the anions in an anion exchange column, suppression of eluant conductivity on an acid form cation exchange column, and conductimetric detection of the separated anions as they pass through a small conductivity cell. The increase in conductivity caused by each anion is recorded on a strip chart recorder or peak integrator, and anion concentrations are determined by comparisons with the detector responses from standard solutions. In addition, anions such as cyanide, sulfide and iodide can be determined using an electrochemical detector, the cell of which is inserted between the separator and suppressor columns (the suppressor column is not needed). The common anions can usually be identified from the amount of time required for the peak to appear from the time of the sample injection.

4.3 Ion Chromatographic Peak Measurements

Detector response is measured on a strip chart recorder and/or a peak integrator in terms of peak heights or areas. The analyst determines the peak height on the strip chart recorder by interpretation of the distance of the peak to the baseline (or interpolated baseline). This measurement is difficult if the baseline is complicated (sloping, adjacent peak, etc.), and an experienced analyst is required. The integrator determines peak heights (or

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areas) from the distance of the peak from the instrument's interpretation of the baseline. An experienced analyst is needed to check the validity of the integrator's baseline selection for complex chromatograms.

It is often useful to record chromatograms with both a multi-pen recorder and an integrator simultaneously. For example, the detector output is 0 to 1 volt, and if the integrator input is set at 1 volt and a 2-channel recorder is set at 0.5 and 2 volt, the chance of recording otherwise too small and off-scale peaks without changing the detector range is improved.

4.4 Calibration

- Step 1) The ion chromatograph, chromatographic columns, eluant(s), water, regeneration acid, and integrator shall be set up according to the instrument manuals.
- Step 2) To calibrate the instrument, run ion chromatograms with multi-element standard solutions according to the operating manuals (see Section 4.5). If the detector response for a given detector range is linear with concentration and there is essentially zero response for zero concentration, a single-point calibration can be used. Multi-level standards should be used if the detector response is not linear with concentration for a given detector response range or if the curve does not pass through the origin.
- Step 3) In a single-point calibration using the strip chart recorder, the peak heights are measured according to Section 4.3 and converted to conductance (see Section 4.6). Calibration factors for the anions are calculated by dividing anion concentration by peak conductance for each anion (see Section 4.6). A similar factor is calculated automatically using an integrator. In a multi-level calibration, the detector response is plotted as a function of concentration for each anion. Most integrators can be used for multi-level calibrations, and are able to calibrate with either linear or nonlinear data. The detector ranges on some ion chromatographs are not linear, in which case calibrations are made for each detector range used.
- Step 4) Frequency of the calibrations depends primarily on the suppressor column used and should be determined for each system. Run a standard at least twice before calibration to demonstrate instrument stability.
- Step 5) Verify the calibration by analyzing a calibration solution. Results shall be within ± 10 percent relative of the assigned values. If not, repeat calibration using freshly prepared calibration solution(s).

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4.5 Sample Analysis

- Step 1) Dilute an aliquot of the sample as appropriate, and if the integrator can not compensate for the water dip or if the system resolution is too poor to resolve the fluoride peak from the water dip, add enough eluant concentrate to the solution to make a 1 to 100 dilution of it. The amount of sample dilution required depends on the anion concentrations and the calibration ranges of the anions. The measured anion concentrations should be within the calibration range up to 25% over range and under range is permissible for linear or near linear calibrations if the calibration curve passes through the origin.
- Step 2) Set the system controller to the program or the schedule to be used. (See instrument manual for details of operation.) Set pump, chromatography and detector modules on REMOTE. Allow the baseline to stabilize.
- Step 3) Load the sample (or standard) by injecting a minimum of 1-ml into the sample port. A volume of 0.5 ml can be used for subsequent replicates. The Dionex Autosampler can be used, and requires less sample volume. If using 0.5 ml vials use 0.7 ml rinse step between different samples.
- Step 4) Press START. This initiates the analysis; the sample in the sample loop (about 0.05 ml) is injected into the eluant stream, and the integrator is started. When the analysis is complete, the ion chromatograph returns to its reset condition, and is ready for the next injection. The integrator prints out solution concentration results, or results are interpreted from a strip chart recording as described in Sections 4.3 and 4.6. Repeat Steps 3 and 4 for each run (if the autosampler is used the sample rinse, load and start steps are automatic).
- Step 5) Calculate undiluted anion concentrations by correcting for the dilution (following Section 4.6).

4.6 Calculations

- Conversion from strip chart peak height to conductance peak height, if an integrator is not used:

$$h_1 = r_1 \times r_2 \times P_1$$

where: r_1 = Detector range (umho/V)

r_2 = Recorder range (V)

P_1 = Peak height (fraction of full-scale recorder range)

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h_1 = Peak height (umho)

- Single-point calibration factor:

$$f_1 = s_1/h_1$$

where: s_1 = Standard solution anion concentration (ug/ml)

f_1 = Calibration factor (ug/ml/umho)

- Dilution factor:

$$d = v_2/v_1$$

where: v_1 = initial volume

v_2 = final volume

- Solution concentration from calibration factor:

$$C_1 = f_1 h_1 d$$

where: C_1 = Solution anion concentration

- Solution concentration from multi-level plot or integrator:

$$C_1 = d a_1$$

where: a_1 = Solution concentration (read from calibration plot or from integrator readout)

4.7 Records

Records will be controlled according to PAP-1701. Laboratory notebooks shall be controlled according to PAP-1704.

4.8 Procedure Qualification

None required. This procedure is self-qualifying due to its dependence on analytical standards.

5.0 REFERENCES

- System 21101 Operator's Manual, Dionex Corporation, Sunnyvale, CA.
- Ion Chromatographs Operations and Maintenance, Dionex Corporation, Sunnyvale, CA.
- SP4270 Operations Manual, Spectro Physics, Autolab Division, San Jose, CA

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- EPA Test Method 300.0, "The Determination of Inorganic Anions in Water by Ion Chromatography," EPA-600/4-84-017 (March 1984).
- ASTM Standard Test Method D4327-84, "Anions in Water by Ion Chromatography," (1984).

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PNL TEST PROCEDURE

TITLE: 7-40.7, SOLUTIONS ANALYSIS: CARBON

1.0 APPLICABILITY

This procedure provides instructions for the analysis of aqueous solutions for total organic carbon, inorganic carbon and total carbon using the UV light catalyzed oxidation method.

2.0 DEFINITIONS

None.

3.0 RESPONSIBLE STAFF

Staff responsible for implementing this procedure are:

- Cognizant Scientist
- Analyst

4.0 PROCEDURE

4.1 Equipment and Materials

- Carbon analyzer (procedure based on Dohrmann DC80 total organic carbon analyzer).
- Hypodermic syringes (25, 50, 250 and 1000 ul).
- Carbon standards (10, 400 and 2000 ug/ml carbon) in aqueous solutions of potassium acid phthalate -- The 2000 ug/ml standard is purchased from the manufacturer or prepared as follows: dissolve 425 (± 1) mg NBS SRM-84 potassium acid phthalate in 15 M or better deionized water as determined by the deionizer readout, add 0.1 ml concentrated phosphoric acid and dilute the solutions to 100 ml. The 10 and 400 ug/ml standards are prepared by diluting the 2000 ug/ml standard. The 10 ug/ml standard should be prepared fresh the day it is used.
WARNING: Because of the potential for biodegradation of the standard, it is to be stored in a refrigerator to minimize the biodegradation process. Before use, the solution shall be checked visually; and if any precipitation is observed, a new 2000 ug/ml standard shall be prepared.
- Oxidizing reagent (2 to 3.5 wt% $K_2S_2O_8$ in 0.2 vol% concentrated H_3PO_4).

Concurrence	Date	Approved	Date
		<i>J. H. Town</i>	3/31/88
Prepared by	Date	QAD Concurrence	Date
<i>R. H. Town</i>	3/31/88	<i>L. E. Thridge</i>	3/31/88
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PNL TEST PROCEDURE

4.2 Method

Total carbon is determined by injecting the sample into an acidic oxidizing reagent that flows through an ultraviolet light catalyzed reactor. All the carbon is converted to CO_2 , which is measured by a nondispersive infrared detector. Detector response is converted electronically to carbon concentration in the sample. Total organic carbon is determined by acidifying the sample, purging the CO_2 from the solution, and injecting the inorganic carbon-free sample into the analyzer.

Inorganic carbon can be measured indirectly by subtracting the results of the total organic carbon from the results of the total carbon measurement. A direct determination of inorganic carbon is made by injecting the sample into the analyzer after replacing the oxidizing solution with acid or turning off the ultraviolet light in the analyzer and allowing the reactor solution to cool.

4.3 Calibration

Perform the following steps according to the instrument's operating manual (see Section 5.0).

- Step 1) Turn on detector and reaction module power, UV lamp, pump, and oxygen. Allow detector current to stabilize.
- Step 2) Set the instrument to the appropriate range: 1-ml for the 10 ppm calibration, 200- μ l for 400 ppm or 40 μ l for 2000 ppm.
- Step 3) Inject the standard into the instrument and depress START immediately. When the determination is completed, the READY light will glow.
- Step 4) Repeat the determinations until two successive results are within 1% relative.
- Step 5) Depress the CALIBRATE switch.

4.4 Sample Analysis

- Step 1) Set the instrument to the concentration range used for the calibration (Section 4.3).
- Step 2) To determine total carbon inject the sample (sample volume is set according to instrument range used) and press START as in Section 4.3.
- Step 3) To determine inorganic carbon turn off the UV lamp and wait 10 minutes, inject sample as in Step 2 and press START.

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PNL TEST PROCEDURE

Step 4) To determine total organic carbon place about 5-ml (or less) in test tube and acidify with concentrated phosphoric acid. Place a drop of the acidified solution on pH indicator paper; if the pH is $\leq$ than about 3: continue as follows otherwise add more acid and repeat acidity check. Place the sample on the external sparger, and bubble gas through the sample 5-min. Then inject the sample and press START.

Step 5) If a dilution is used it may be necessary to determine a diluent blank.

4.5 Calculations

If an undiluted sample is analyzed, record the instrument readout, R. If a diluted sample is analyzed, use the following equations.

$$C = \frac{V_2}{V_1} [R - (\frac{V_2 - V_1}{V_2}) B]$$

where, C = carbon concentration, ppm
V₂ = final volume, ml
V₁ = initial volume, ml
R = carbon reading in sample, ppm
B = carbon reading in blank, ppm

4.6 Records

Records will be controlled according to PAP-1701. Laboratory notebooks will be controlled according to PAP-1704.

4.7 Procedure Qualification

None required. This procedure is self-qualifying due to its dependence on analytical standards.

5.0 REFERENCES

- Dohrmann DC80 Total Organic Carbon Analysis System Equipment Manual, XERTEX, Dohrmann, Santa Clara, CA.

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WORKING DOCUMENT IS IN THE LABORATORY

PNL TEST PROCEDURE

3.720 + 3.25
0.9.2

TITLE: HWVP-2; FLUORIDE ION IN AQUEOUS SAMPLES

1.0 APPLICABILITY

This procedure is applicable for the analyses of fluoride ion concentration in aqueous samples using the fluoride specific ion electrode.

2.0 DEFINITIONS

Total Ionic Strength Adjustor (TISAB) - Solution to provide a constant background ionic strength, decomplex fluoride and adjust solution pH.

3.0 RESPONSIBLE STAFF

Responsible Scientist
Cognizant Staff

4.0 PROCEDURE

4.1 Summary of method

An aliquot of the sample is mixed with TISAB and the fluoride ion determined using the specific fluoride ion electrode using the known addition method.

4.2 Specific Qualification

4.2.1 A RESPONSIBLE SCIENTIST shall supervise the individual performing the analyses.

4.2.2 The COGNIZANT STAFF shall follow this procedure in performing the analyses.

4.3 Reagent

4.3.1 Fluoride Standard Solution (1.0 ml = 1.0 mg F)

Dissolve 2.210 ± 0.005 g of sodium fluoride in water and dilute to 1 liter. Store in a polypropylene bottle. Or purchase a certified 1.00 g/L fluoride standard solution.

Concurrence <i>[Signature]</i>		Date 6/21/88	Approved <i>[Signature]</i> J. J. McCown		Date 6/21/88
Prepared by D. L. Widrig		Date 6/21/88	QAD Concurrence L. J. Ethridge		Date 6/21/88
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PNL TEST PROCEDURE

4.3.2 100 ppm Fluoride Standard With TISAB III

Pipet 25 ml of 1000 ppm fluoride standard solution into a 250 ml volumetric flask. Add 25 ml of TISAB III solution into the flask and dilute to volume with demineralized water. Store this solution in a polypropylene bottle.

4.3.3 10 ppm Fluoride Standard With TISAB III

Pipet 25 ml of 100 ppm fluoride standard from 4.3.2 into a 250 ml volumetric flask. Add 25 ml of TISAB III solution into the flask and dilute to volume with demineralized water. Store this solution in a polypropylene bottle.

4.3.4 TISAB III

A commercially available buffering mixture containing acetic acid, NaCl, and CDTA used to decomplex fluoride ion.

4.4 Sample Logging Procedure

4.4.1 COGNIZANT STAFF shall log the sample onto the sample log sheet. Series of similar liquid samples which require no special sample preparation except sample dilution can be logged under one laboratory serial number since the customer's sample identification maintains traceability. Samples which require a sample weighing or unique sample preparation (e.g. fusion) shall be logged with separate laboratory serial number.

4.4.2 For each laboratory serial number, prepare a "Report of Analysis" card (Exhibit 1) which uniquely identifies each customer's sample. Any analysis which requires weighing the sample or unique sample preparation (e.g. fusion) shall have the data written on the back of the analysis card. These entries shall be dated and signed by the COGNIZANT STAFF performing the analysis.

4.5 Calibration and Analyses of Sample

4.5.1 Turn the slope thumbwheel switches to read about -56.0. If the instrument had been used previously for fluoride analysis, do not change setting from previous values.

4.5.2 If the SET BLANK button is lit, press to turn it off.

4.5.3 Turn STD thumbwheel switches to read 10.0.

4.5.4 Set the mode switch KA10.

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PNL TEST PROCEDURE

- 4.5.5 For setting blank correction, place the electrode in 2.5 ml of distilled water. Add 250 microliter of TISAB. Allow the reading to stabilize. Press the CLEAR/READ MV button.
- 4.5.6 Press SET CONC button. The display may be unstable.
- 4.5.7 Pipet 250 microliter of 10 ppm standard fluoride into blank. Allow time for reading to stabilize.
- 4.5.8 Press SET BLANK button. The button light will turn on.
- 4.5.9 Rinse the electrode, blot dry and place 2.5 ml of 10 ppm standard into the disposable beaker. Add 250 microliter of TISAB to the beaker. Press CLEAR/READ MV button.
- 4.5.10 Allow time for reading to stabilize. Press SET CONC button.
- 4.5.11 Pipet 250 microliter of 10 ppm standard to the beaker. If reading is not $10.0 \pm .1$ ppm, adjust the thumbwheel switches so the display reads 10.00 ppm.
- 4.5.12 Run the .1, 1.0 and 10 ppm solution. Record these values in the notebook located at this station.
- 4.5.13 Fluoride concentration in the sample is measured by pipetting 2.5 ml sample into a disposable beaker. Add 250 microliter of TISAB. Place the electrode in the sample and press the CLEAR/READ MV button.
- 4.5.14 Allow time for reading to stabilize. Press SET CONC button. The display may be unstable if the fluoride concentration in the sample is very low.
- 4.5.15 Pipet 250 microliter of the 10 ppm standard into the sample cup.
- 4.5.16 Allow the reading to stabilize. Record the sample concentration from the display.

4.6 Calculation

The ORION RESEARCH microprocessor Ionalyzer/901 calculates the results automatically. The formula for calculating these results is given in the ORION operation manual.

4.7 Reporting Results

Upon completion of the analysis the COGNIZANT STAFF shall tabulate the values to be reported onto the front of the "Report of

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PNL TEST PROCEDURE

Analysis" card. These entries shall be signed and dated by the COGNIZANT STAFF. The RESPONSIBLE SCIENTIST shall review the results for acceptability and document this review by signing and dating the "Report of Analysis" card. The "Report of Analysis" card shall be xeroxed and the xeroxed copy submitted to the customer. The original "Report of Analysis" card shall be retained in the laboratory for at least one year.

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SECTION III

SAMPLE PREPARATION

A. Water Sample Preparation

1. Acid Digestion Procedure for Furnace Atomic Absorption Analysis

Shake sample and transfer 100 mL of well-mixed sample to a 250-mL beaker, add 1 mL of (1+1) HNO_3 and 2 mL 30% H_2O_2 to the sample. Cover with watch glass or similar cover and heat on a steam bath or hot plate for 2 hours at 95°C or until sample volume is reduced to between 25 and 50 mL, making certain sample does not boil. Cool sample and filter to remove insoluble material. (NOTE: In place of filtering, the sample, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.) Adjust sample volume to 100 mL with deionized distilled water. The sample is now ready for analysis.

Concentrations so determined shall be reported as "total".

If Sb is to be determined by furnace AA, use the digestate prepared for ICP/flame AA analysis.

2. Acid Digestion Procedure for ICP and Flame AA Analyses

Shake sample and transfer 100 mL of well-mixed sample to a 250-mL beaker, add 2 mL of (1+1) HNO_3 and 10 mL of (1+1) HCl to the sample. Cover with watch glass or similar cover and heat on a steam bath or hot plate for 2 hours at 95°C or until sample volume is reduced to between 25 and 50 mL, making certain sample does not boil. Cool sample and filter to remove insoluble material. (NOTE: In place of filtering, the sample, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.) Adjust sample volume to 100 mL with deionized distilled water. The sample is now ready for analysis.

Concentrations so determined shall be reported as "total".

B. Soil/Sediment Sample Preparation

1. Acid Digestion Procedure for ICP, Flame AA and Furnace AA Analyses

a. Scope and Application

This method is an acid digestion procedure used to prepare sediments, sludges, and soil samples for analysis by flame or furnace atomic absorption spectroscopy (AAS) or by inductively coupled plasma spectroscopy (ICP). Samples prepared by this method may be analyzed by AAS or ICP for the following metals:

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

b. Summary of Method

A representative 1 g (wet weight) sample is digested in nitric acid and hydrogen peroxide. The digestate is then refluxed with either nitric acid or hydrochloric acid. Hydrochloric acid is used as the final reflux acid for the furnace AA analysis of Sb, the flame AA or ICP analysis of Al, Sb, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, K, Ag, Na, Tl, V and Zn. Nitric acid is employed as the final reflux acid for the furnace AA analysis of As, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Se, Ag, Tl, V, and Zn. A separate sample shall be dried for a percent solids determination (Section IV, Part F).

c. Apparatus and Materials

- (1) 250 mL beaker or other appropriate vessel.
- (2) Watch glasses
- (3) Thermometer that covers range of 0° to 200°C
- (4) Whatman No. 42 filter paper or equivalent

d. Reagents

- (1) ASTM Type II water (ASTM D1193): Water must be monitored.
- (2) Concentrated Nitric Acid (sp. gr. 1.41)
- (3) Concentrated Hydrochloric Acid (sp. gr. 1.19)
- (4) Hydrogen Peroxide (30%)

e. Sample Preservation and Handling

Soil/sediment (nonaqueous) samples must be refrigerated at 4°C ($\pm 2^\circ$) from receipt until analysis.

f. Procedure

- (1) Mix the sample thoroughly to achieve homogeneity. For each digestion procedure, weigh (to the nearest 0.01gms) a 1.0 to 1.5 gm portion of sample and transfer to a beaker.
- (2) Add 10 mL of 1:1 nitric acid (HNO_3), mix the slurry, and cover with a watch glass. Heat the sample to 95°C and reflux for 10 minutes without boiling. Allow the sample to cool, add 5 mL of concentrated HNO_3 , replace the watch glass, and reflux for 30 minutes. Do not allow the volume to be reduced to less than 5 mL while maintaining a covering of solution over the bottom of the beaker.
- (3) After the second reflux step has been completed and the sample has cooled, add 2 mL of Type II water and 3 mL of 30% hydrogen peroxide (H_2O_2). Return the beaker to the hot plate for warming to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides, and cool the beaker.
- (4) Continue to add 30% H_2O_2 in 1 mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged. (NOTE: Do not add more than a total of 10 mL 30% H_2O_2 .)
- (5) If the sample is being prepared for the furnace AA analysis of Sb, the flame AA or ICP analysis of Al, Sb, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, K, Ag, Na, Tl, V, and Zn, add 5 mL of 1:1 HCl and 10 mL of Type II water, return the covered beaker to the hot plate, and heat for an additional 10 minutes. After cooling, filter through Whatman No. 42 filter paper (or equivalent) and dilute to 100 mL with Type II water. NOTE: In place of filtering, the sample (after dilution and mixing) may be centrifuged or allowed to settle by gravity overnight to remove insoluble material. The diluted sample has an approximate acid concentration of 2.5% (v/v) HCl and 5% (v/v) HNO_3 . Dilute the digestate 1:1 (200 mL final volume) with acidified water to maintain constant acid strength. The sample is now ready for analysis.
- (6) If the sample is being prepared for the furnace analysis of As, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Se, Ag, Tl, V, and Zn, continue heating the acid-peroxide digestate until the volume has been reduced to approximately 2 mL, add 10 mL of Type II water, and warm the mixture. After cooling, filter through Whatman No. 42 filter paper (or equivalent) and dilute to 100 mL with Type II water (or centrifuge the sample). NOTE: In place of filtering,

the sample (after dilution and mixing) may be centrifuged or allowed to settle by gravity overnight to remove insoluble material. The diluted digestate solution contains approximately 2% (v/v) HNO₃. Dilute the digestate 1:1 (200 mL final volume) with acidified water to maintain constant acid strength. For analysis, withdraw aliquots of appropriate volume, and add any required reagent or matrix modifier. The sample is now ready for analysis.

g. Calculations

- (1) A separate determination of percent solids must be performed (Section IV, Part F).
- (2) The concentrations determined in the digest are to be reported on the basis of the dry weight of the sample.

$$\text{Concentration (dry wt.) (mg/kg)} = \frac{C \times V}{W \times S}$$

Where,

- C = Concentration (mg/L)
- V = Final volume in liters after sample preparation
- W = Weight in kg of wet sample
- S = % Solids/100

h. Bibliography

Modification (by committee) of Method 3050, SW-846, 2nd ed., Test Methods for Evaluating Solid Waste, EPA Office of Solid Waste and Emergency Response, July 1982.

PART D - COLD VAPOR METHODS FOR MERCURY ANALYSIS⁺

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Mercury Analysis in Water by Automated Cold Vapor Technique Method 245.2 CLP-M	D-49
Mercury Analysis in Soil/Sediment by Manual Cold Vapor Technique Method 245.5 CLP-M	D-56

⁺A bibliography citing method references follows each method.

^{*}CLP-M modified for the Contract Laboratory Program.

MERCURY ANALYSIS IN WATER BY MANUAL COLD VAPOR TECHNIQUE

MERCURY

Method 245.1 CLP-M* (Manual Cold Vapor Technique)

1. Scope and Application

- 1.1 In addition to inorganic forms of mercury, organic mercurials may also be present. These organo-mercury compounds will not respond to the cold vapor atomic absorption technique unless they are first broken down and converted to mercuric ions. Potassium permanganate oxidizes many of these compounds, but recent studies have shown that a number of organic mercurials, including phenyl mercuric acetate and methyl mercuric chloride, are only partially oxidized by this reagent. Potassium persulfate has been found to give approximately 100% recovery when used as the oxidant with these compounds. Therefore, a persulfate oxidation step following the addition of the permanganate has been included to insure that organo-mercury compounds, if present, will be oxidized to the mercuric ion before measurement. A heat step is required for methyl mercuric chloride when present in or spiked to a natural system. For distilled water the heat step is not necessary.
- 1.2 The range of the method may be varied through instrument and/or recorder expansion. Using a 100 mL sample, a detection limit of 0.2 ug Hg/L can be achieved (See 10.2).

2. Summary of Method

- 2.1 The flameless AA procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. Organic mercury compounds are oxidized and the mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration and recorded in the usual manner.

3. Sample Handling and Preservation

- 3.1 Until more conclusive data are obtained, samples are preserved by acidification with nitric acid to a pH of 2 or lower immediately at the time of collection (Exhibit D, Section II).

*CLP-M modified for the Contract Laboratory Program.

4. Interference

- 4.1 Possible interference from sulfide is eliminated by the addition of potassium permanganate. Concentrations as high as 20 mg/l of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from distilled water (Exhibit D, Section II).
- 4.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on recovery of mercury from spiked samples.
- 4.3 Sea waters, brines and industrial effluents high in chlorides require additional permanganate (as much as 25 mL). During the oxidation step, chlorides are converted to free chlorine which will also absorb radiation of 253 nm. Care must be taken to assure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). Both inorganic and organic mercury spikes have been quantitatively recovered from the sea water using this technique.
- 4.4 While the possibility of absorption from certain organic substances actually being present in the sample does exist, EMSL has not encountered such samples. This is mentioned only to caution the analyst of the possibility.

5. Apparatus

- 5.1 Atomic Absorption Spectrophotometer: (See Note 1) Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed.

NOTE 1: Instruments designed specifically for the measurement of mercury using the cold vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

- 5.2 Mercury Hollow Cathode Lamp: Westinghouse WL-22847, argon filled, or equivalent.
- 5.3 Recorder: Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.
- 5.4 Absorption Cell: Standard spectrophotometer cells 10 cm long, having quartz end windows may be used. Suitable cells may be constructed from plexiglass tubing, 1" O.D. X 4-1/2". The ends are ground perpendicular to the longitudinal axis and quartz windows (1" diameter X 1/16" thickness) are cemented in place.

The cell is strapped to a burner for support and aligned in the light beam by use of two 2" by 2" cards. One inch diameter holes are cut in the middle of each card; the cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to find the maximum transmittance.

- 5.5 Air Pump: Any peristaltic pump capable of delivering 1 liter of air per minute may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.
- 5.6 Flowmeter: Capable of measuring an air flow of 1 liter per minute.
- 5.7 Aeration Tubing: A straight glass fit having a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.
- 5.8 Drying Tube: 6" X 3/4" diameter tube containing 20 g of magnesium perchlorate (see Note 2). The apparatus is assembled as shown in Figure 1.

NOTE 2: In place of the magnesium perchlorate drying tube, a small reading lamp with 60W bulb may be used to prevent condensation of moisture inside the cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10°C above ambient.

6. Reagents

- 6.1 Sulfuric Acid, Conc: Reagent grade.

6.1.1 Sulfuric acid, 0.5 N: Dilute 14.0 mL of conc. sulfuric acid to 1.0 liter.

- 6.2 Nitric Acid, Conc: Reagent grade of low mercury content (see Note 3).

NOTE 3: If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

- 6.3 Stannous Sulfate: Add 25 g stannous sulfate to 250 mL of 0.5 N sulfuric acid. This mixture is a suspension and should be stirred continuously during use. (Stannous chloride may be used in place of stannous sulfate.)
- 6.4 Sodium Chloride-Hydroxylamine Sulfate Solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in distilled water and dilute to 100 mL. (Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.)
- 6.5 Potassium Permanganate: 5% solution, w/v. Dissolve 5 g of potassium permanganate in 100 mL of distilled water.

6.6 Potassium Persulfate: 5% solution, w/v. Dissolve 5 g of potassium persulfate in 100 mL of distilled water.

6.7 Stock Mercury Solution: Dissolve 0.1354 g of mercuric chloride in 75 mL of distilled water. Add 10 mL of conc. nitric acid and adjust the volume to 100.0 mL. 1 mL = 1 mg Hg.

Figure 1. Apparatus for Flameless Mercury Determination

6.8 Working Mercury Solution: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 ug per mL. This working standard and the dilutions of the stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot.

7. Calibration

7.1 Transfer 0, 0.5, 1.0, 5.0 and 10.0 mL aliquots of the working mercury solution containing 0 to 1.0 ug of mercury to a series of 300 mL BOD bottles. Add enough distilled water to each bottle to make a total volume of 100 mL. Mix thoroughly and add 5 mL of conc. sulfuric acid (6.1) and 2.5 mL of conc. nitric acid (6.2) to each bottle. Add 15 mL of KMnO_4 (6.5) solution to each bottle and allow to stand at least 15 minutes. Add 8 mL of potassium persulfate (6.6) to each bottle and heat for 2 hours in a water bath maintained at 95°C. Alternatively, cover the BOD bottles with foil and heat in an autoclave for 15 minutes at 120°C and 15 lbs. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution (6.4) to reduce the excess permanganate. When the solution has been decolorized wait 30 seconds, add 5 mL of the stannous sulfate solution (6.3) and immediately attach the bottle to the aeration apparatus forming a closed system. At this point the sample is allowed to stand quietly without manual agitation.

The circulating pump, which has previously been adjusted to a rate of 1 liter per minute, is allowed to run continuously (see Note 4). The absorbance will increase and reach maximum within 30 seconds. As soon as the recorder pen levels off, approximately 1 minute, open the bypass valve and continue the aeration until the absorbance returns to its minimum value (see Note 5). Close the bypass valve, remove the stopper and frit from the BOD bottle and continue the aeration. Proceed with the standards and construct a standard curve by plotting peak height versus micrograms of mercury.

NOTE 4: An open system where the mercury vapor is passed through the absorption cell only once may be used instead of the closed system.

NOTE 5: Because of the toxic nature of mercury vapor precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system to either vent the mercury vapor into an exhaust hood or pass the vapor through some absorbing media, such as:

- equal volumes of 0.1 M KMnO_4 and 10% H_2SO_4 or
- 0.25% iodine in a 3% KI solution. A specially treated charcoal that will adsorb mercury vapor is available.

8. Procedure

- 8.1 Transfer 100 mL, or an aliquot diluted to 100 mL, containing not more than 1.0 ug of mercury, to a 300 mL BOD bottle. Add 5 mL of sulfuric acid (6.1) and 2.5 mL of conc. nitric acid (6.2) mixing after each addition. Add 15 mL of potassium permanganate solution (6.5) to each sample bottle (see Note 6). For sewage samples additional permanganate may be required. Shake and add additional portions of potassium permanganate solution, if necessary, until the purple color persists for at least 15 minutes. Add 8 mL of potassium persulfate (6.6) to each bottle and heat for 2 hours in a water bath at 95°C.

NOTE 6: The same amount of KMnO_4 added to the samples should be present in standards and blanks.

Cool and add 6 mL of sodium chloride-hydroxylamine sulfate (6.4) to reduce the excess permanganate (see Note 7). Purge the head space in the BOD bottle for at least 1 minute and add 5 mL of Stannous Sulfate (6.3) and immediately attach the bottle to the aeration apparatus. Continue as described under Calibration.

NOTE 7: Add reductant in 6 mL increments until KMnO_4 is completely reduced.

9. Calculation

9.1 Determine the peak height of the unknown from the chart and read the mercury value from the standard curve.

9.2 Calculate the mercury concentration in the sample by the formula:

$$\text{ug Hg/L} = \frac{\text{ug Hg in aliquot} \times 1,000}{\text{volume of aliquot in mL}}$$

9.3 Report mercury concentrations as follows: Below 0.20 ug/L, 0.20 u; between 0.20 and 10.0 ug/L, two significant figures; equal to or above 10.0 ug/L, three significant figures.

10. Appendix

10.1 If additional sensitivity is required, a 200 mL sample with recorder expansion may be used provided the instrument does not produce undue noise. Using a Coleman MAS-50 with a drying tube of magnesium perchlorate and a variable recorder, 2 mv was set to read full scale. With these conditions, and distilled water solutions of mercuric chloride at concentrations of 0.15, 0.10, 0.05 and 0.025 ug/L the standard deviations were ± 0.027 , ± 0.0006 , ± 0.01 and ± 0.004 . Percent recoveries at these levels were 107, 83, 84 and 96%, respectively.

10.2 Directions for the disposal of mercury-containing wastes are given in ASTM Standards, Part 31, "Water", p. 349, Method D3223 (1976).

Bibliography

1. Kopp, J.F., Longbottom, M.C. and Lobring, L.B. "Cold Vapor Method for Determining Mercury", AWWA, vol. 64, p. 20, Jan. 1972.
2. Annual Book of ASTM Standards, Part 31, "Water", Standard D3223-73, p. 343 (1976).
3. Standard Methods for the Examination of Water and Wastewater 14th Edition, p. 156 (1975).

MERCURY ANALYSIS IN WATER BY AUTOMATED COLD VAPOE TECHNIQUE

MERCURY

Method 245.2 CLP-M* (Automated Cold Vapor Technique)

1. Scope and Application

- 1.1 The working range is 0.2 to 20.0 ug Hg/L.

2. Summary of Method

- 2.1 The flameless AA procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration and recorded in the usual manner.
- 2.2 In addition to inorganic forms of mercury, organic mercurials may also be present. These organo-mercury compounds will not respond to the flameless atomic absorption technique unless they are first broken down and converted to mercuric ions. Potassium permanganate oxidizes many of these compounds, but recent studies have shown that a number of organic mercurials, including phenyl mercuric acetate and methyl mercuric chloride, are only partially oxidized by this reagent. Potassium persulfate has been found to give approximately 100% recovery when used as the oxidant with these compounds. Therefore, an automated persulfate oxidation step following the automated addition of the permanganate has been included to insure that organo-mercury compounds, if present, will be oxidized to the mercuric ion before measurement.

3. Sample Handling and Preservation

- 3.1 Until more conclusive data are obtained, samples are preserved by acidification with nitric acid to a pH of 2 or lower immediately at the time of collection (Exhibit D, Section II).

4. Interferences (see NOTE 1)

- 4.1 Some sea waters and waste-waters high in chlorides have shown a positive interference, probably due to the formation of free chlorine.

*CLP-M modified for the Contract Laboratory Program.

4.2 Formation of a heavy precipitate, in some wastewaters and effluents, has been reported upon addition of concentrated sulfuric acid. If this is encountered, the problem sample cannot be analyzed by this method.

4.3 Samples containing solids must be blended and then mixed while being sampled if total mercury values are to be reported.

NOTE 1: All of the above interferences can be overcome by use of the Manual Mercury method.

5. Apparatus

5.1 Technicon Auto Analyzer or equivalent instrumentation consisting of:

5.1.1 Sampler II with provision for sample mixing.

5.1.2 Manifold.

5.1.3 Proportioning Pump II or III.

5.1.4 High temperature heating bath with two distillation coils (Technicon Part #116-0163) in series.

5.2 Vapor-liquid separator (Figure 1).

5.3 Absorption cell, 100 mm long, 10 mm diameter with quartz windows.

5.4 Atomic Absorption Spectrophotometer (see Note 2): Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed.

NOTE 2: Instruments designed specifically for the measurement of mercury using the cold vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

5.5 Mercury Hollow Cathode Lamp: Westinghouse WL-22847, argon filled, or equivalent.

5.6 Recorder: Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.

6. Reagents
- 6.1 Sulfuric Acid, Conc: Reagent grade
- 6.1.1 Sulfuric acid, 2 N: Dilute 56 mL of conc. sulfuric acid to 1 liter with distilled water.
- 6.1.2 Sulfuric acid, 10%: Dilute 100 mL conc. sulfuric acid to 1 liter with distilled water.
- 6.2 Nitric acid, Conc: Reagent grade of low mercury content.
- 6.2.1. Nitric Acid, 0.5% Wash Solution: Dilute 5 mL of concentrated nitric acid to 1 liter with distilled water.
- 6.3 Stannous Sulfate (See Note 3): Add 50 g stannous sulfate to 500 mL of 2 N sulfuric acid (6.1.1). This mixture is a suspension and should be stirred continuously during use.
- NOTE 3: Stannous chloride may be used in place of stannous sulfate.
- 6.4 Sodium Chloride-Hydroxylamine Sulfate (See Note 4) Solution: Dissolve 30 g of sodium chloride and 30 g of hydroxylamine sulfate in distilled water to 1 liter.
- NOTE 4: Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.
- 6.5 Potassium Permanganate: 0.5% solution, w/v. Dissolve 5 g of potassium permanganate in 1 liter of distilled water.
- 6.6 Potassium Permanganate, 0.1 N: Dissolve 3.16 g of potassium permanganate in distilled water and dilute to 1 liter.
- 6.7 Potassium Persulfate: 0.5% solution, w/v. Dissolve 5 g potassium persulfate in 1 liter of distilled water.
- 6.8 Stock Mercury Solution: Dissolve 0.1354 g of mercuric chloride in 75 mL of distilled water. Add 10 mL of conc. nitric acid and adjust the volume to 100.0 mL. 1.0 mL = 1.0 mg Hg.
- 6.9 Working Mercury Solution: Make successive dilutions of the stock mercury solution (6.8) to obtain a working standard containing 0.1 ug per mL. This working standard and the dilutions of the stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot. From this solution prepare standards containing 0.2, 0.5, 1.0, 2.0, 5.0, 10.0, 15.0 and 20.0 ug Hg/L.
- 6.10 Air Scrubber Solution: Mix equal volumes of 0.1 N potassium permanganate (6.6) and 10% sulfuric acid (6.1.2).

7. Procedure (See Note 5)

- 7.1 Set up manifold as shown in Figure 2.
- 7.2 Feeding all the reagents through the system with acid wash solution (6.2.1) through the sample line, adjust heating bath to 105°C.
- 7.3 Turn on atomic absorption spectrophotometer, adjust instrument settings as recommended by the manufacturer, align absorption cell in light path for maximum transmittance and place heat lamp directly over absorption cell.
- 7.4 Arrange working mercury standards from 0.2 to 20.0 ug Hg/L in sampler and start sampling. Complete loading of sample tray with unknown samples.
- 7.5 Prepare standard curve by plotting peak height of processed standards against concentration values. Determine concentration of samples by comparing sample peak height with standard curve.
- 7.6 After the analysis is complete put all lines except the H₂SO₄ line in distilled water to wash out system. After flushing, wash out the H₂SO₄ line. Also flush the coils in the high temperature heating bath by pumping stannous sulfate (6.3) through the sample lines followed by distilled water. This will prevent build-up of oxides of manganese.

NOTE 5: Because of the toxic nature of mercury vapor, precaution must be taken to avoid its inhalation. Venting the mercury vapor into an exhaust hood or passing the vapor through some absorbing media such as: a) equal volumes of 0.1 N KMnO₄ (6.6) and 10% H₂SO₄ (6.1.2), or b) 0.25% iodine in a 3% KI solution, is recommended. A specially treated charcoal that will absorb mercury vapor is also available.

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Figure 1. Vapor liquid separator
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MERCURY ANALYSIS IN SOIL/SEDIMENT BY MANUAL COLD VAPOR TECHNIQUE

MERCURY (in Sediments) Method 245.5 CLP-M* (Manual Cold Vapor Technique)

1. Scope and Application
 - 1.1 This procedure measures total mercury (organic and inorganic) in soils, sediments, bottom deposits and sludge type materials
 - 1.2 The range of the method is 0.2 to 5 ug/g. The range may be extended above or below the normal range by increasing or decreasing sample size or through instrument and recorder control
2. Summary of Method
 - 2.1 A weighed portion of the sample is acid digested for 2 minutes at 95°C, followed by oxidation with potassium permanganate and potassium persulfate. Mercury in the digested sample is then measured by the conventional cold vapor technique
 - 2.2 An alternate digestion involving the use of an autoclave is described in (8.2)
3. Sample Handling and Preservation
 - 3.1 Because of the extreme sensitivity of the analytical procedure and the omnipresence of mercury, care must be taken to avoid extraneous contamination. Sampling devices and sample containers should be ascertained to be free of mercury; the sample should not be exposed to any condition in the laboratory that may result in contact or air-borne mercury contamination
 - 3.2 Refrigerate solid samples at 4°C ($\pm 2^\circ$) upon receipt until analysis (see Exhibit D, Section II).
 - 3.3 The sample should be analyzed without drying. A separate percent solids determination is required, (Part F).
4. Interferences
 - 4.1 The same types of interferences that may occur in water samples are also possible with sediments, i.e., sulfides, high copper, high chlorides, etc.
 - 4.2 Samples containing high concentrations of oxidizable organic materials, as evidenced by high chemical oxygen demand values, may not be completely oxidized by this procedure. When this

*CLP-M modified for the Contract Laboratory Program.

occurs, the recovery of organic mercury will be low. The problem can be eliminated by reducing the weight of the original sample or by increasing the amount of potassium persulfate (and consequently stannous chloride) used in the digestion.

5. Apparatus

- 5.1 Atomic Absorption Spectrophotometer (see Note 1): Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed

NOTE 1: Instruments designed specifically for the measurement of mercury using the cold vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer

- 5.2 Mercury Hollow Cathode Lamp: Westinghouse WL-22847, argon filled, or equivalent
- 5.3 Recorder: Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.
- 5.4 Absorption Cell: Standard spectrophotometer cells 10 cm long, having quartz end windows may be used. Suitable cells may be constructed from pexiglass tubing, 1" O.D. X 4-1/2". The ends are ground perpendicular to the longitudinal axis and quartz windows (1" diameter X 1/16" thickness) are cemented in place. Gas inlet and outlet ports (also of plexiglass but 1/4" O.D.) are attached approximately 1/2" from each end. The cell is strapped to a burner for support and aligned in the light beam to give the maximum transmittance. Two 2" X 2" cards with one inch diameter holes may be placed over each end of the cell to assist in positioning the cell for maximum transmittance.
- 5.5 Air Pump: Any peristaltic pump capable of delivering 1 liter of air per minute may be used. A Masterflex pump with electronic speed control has been found to be satisfactory. (Regulated compressed air can be used in an open one-pass system.)
- 5.6 Flowmeter: Capable of measuring an air flow of 1 liter per minute.
- 5.7 Aeration Tubing: Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return. Straight glass tubing terminating in a coarse porous frit is used for sparging air into the sample
- 5.8 Drying Tube: 6" X 3/4" diameter tube containing 20 g of magnesium perchlorate (see Note 2).

NOTE 2: In place of the magnesium perchlorate drying tube, a small reading lamp with 60W bulb may be used to prevent condensation of moisture inside the cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10°C above ambient.

6. Reagents

- 6.1 Sulfuric acid, conc.: Reagent grade of low mercury content
- 6.2 Nitric acid, conc.: Reagent grade of low mercury content
- 6.3 Stannous Sulfate: Add 25 g stannous sulfate to 250 mL of 0.5 N sulfuric acid (6.2). This mixture is a suspension and should be stirred continuously during use
- 6.4 Sodium Chloride-Hydroxylamine Sulfate (See Note 3) Solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in distilled water and dilute to 100 mL

NOTE 3: A 10% solution of stannous chloride may be substituted for (6.3) and hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate in (6.4)

- 6.5 Potassium Permanganate: 5% solution, w/v. Dissolve 5 g of potassium permanganate in 100 mL of distilled water
- 6.6 Potassium Persulfate: 5% solution, w/v. Dissolve 5 g of potassium persulfate in 100 mL of distilled water
- 6.7 Stock Mercury Solution: Dissolve 0.1354 g of mercuric chloride in 75 mL of distilled water. Add mL of conc. nitric acid and adjust the volume to 100.0 mL. 1.0 = 1.0 mg Hg
- 6.8 Working Mercury Solution: Make successive dilutions of the stock mercury solution (6.7) to obtain a working standard containing 0.1 ug/mL. This working standard and the dilution of the stock mercury solutions should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot

7. Calibration

- 7.1 Transfer 0, 0.5, 1.0, 5.0 and 10 mL aliquots of the working mercury solutions (6.8) containing 0 to 1.0 ug of mercury to a series of 300 mL BOD bottles. Add enough distilled water to each bottle to make a total volume of 10 mL. Add 5 mL of conc. H_2SO_4 (6.1) and 2.5 mL of conc. HNO_3 (6.2) and heat 2 minutes in a water bath at 95°C. Allow the sample to cool and add 50 mL distilled water, 15 mL of $KMnO_4$ solution (6.5) and 8 mL of potassium persulfate solution (6.6) to each bottle and return to the water bath for 30 minutes. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution (6.4) to reduce the excess permanganate. Add 50 mL of distilled water. Treating each bottle individually, add 5 mL of stannous sulfate

solution (6.3) and immediately attach the bottle to the aeration apparatus. At this point the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 liter per minute, is allowed to run continuously. The absorbance, as exhibited either on the spectrophotometer or the recorder, will increase and reach maximum within 30 seconds. As soon as the recorder pen levels off, approximately 1 minute, open the bypass valve and continue the aeration until the absorbance returns to its minimum value (see Note 4). Close the bypass valve, remove the fritted tubing from the BOD bottle and continue the aeration. Proceed with the standards and construct a standard curve by plotting peak height versus micrograms of mercury

NOTE 4: Because of the toxic nature of mercury vapor, precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system to either vent the mercury vapor into an exhaust hood or pass the vapor through some absorbing media, such as: a) equal volumes of 0.1 N KMnO_4 and 10% H_2SO_4 , or b) 0.25% iodine in a 3% KI solution. A specially treated charcoal that will absorb mercury vapor is also available.

8. Procedure

- 8.1 Weigh a representative 0.2 g portion of wet sample and place in the bottom of a BOD bottle. Add 5 mL of sulfuric acid (6.1) and 2.5 mL of concentrated nitric acid (6.2) mixing after each addition. Heat two minutes in a water bath at 95°C. Cool, add 50 mL distilled water, 15 mL potassium permanganate solution (6.5) and 8 mL of potassium persulfate solution (6.6) to each sample bottle. Mix thoroughly and place in the water bath for 30 minutes at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate (6.4) to reduce the excess permanganate. Add 55 mL of distilled water. Treating each bottle individually, purge the head space of the sample bottle for at least one minute and add 5 mL of stannous sulfate (6.3) and immediately attach the bottle to the aeration apparatus. Continue as described under (7.1)
- 8.2 An alternate digestion procedure employing an autoclave may also be used. In this method 5 mL of conc. H_2SO_4 and 2 mL of conc. HNO_3 are added to the 0.2 g of sample. 5 mL of saturated KMnO_4 solution and 8 mL of potassium persulfate solution are added and the bottle is covered with a piece of aluminum foil. The sample is autoclaved at 121°C and 15 lbs. for 15 minutes. Cool, make up to a volume of 100 mL with distilled water and add 6 mL of sodium chloride-hydroxylamine sulfate solution (6.4) to reduce the excess permanganate. Purge the head space of the sample bottle for at least one minute and continue as described under (7.1)

9. Calculations

- 9.1 Measure the peak height of the unknown from the chart and read the mercury value from the standard curve
- 9.2 Calculate the mercury concentration in the sample by the formula:

$$\text{ug Hg/g} = \frac{\text{ug Hg in the aliquot}}{\text{wt of the aliquot in gms}} \\ \text{(based upon dry wt of the sample)}$$

- 9.3 Report mercury concentrations as described for aqueous mercury samples converted to units of ug/kg. The sample result or the detection limit for each sample must be corrected for sample weight and % solids before reporting.

Note that the minimum reportable number that can be substituted in the formula in section 9.2 is 0.02 ug Hg in the aliquot. Therefore a sample with a weight of 0.2 grams and 100 % solids that has a reading from the curve of less than 0.02 ug would be reported as 0.10U ug/kg.

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4. Op. cit. (#3), Methods 245.1 or 245.2

PART F - PERCENT SOLIDS DETERMINATION PROCEDURE

1. Immediately following the weighing of the sample to be processed for analysis (see Section III, Part B- Soil/Sediment Sample Preparation), add 5-10 g of sample to a tared weighing dish. Weigh and record the weight to the nearest 0.01 g.
2. Place weighing dish plus sample, with the cover tipped to allow for moisture escape, in a drying oven maintained at 103-105°C. Sample handling and drying should be conducted in a well-ventilated area.
3. Dry the sample overnight (12-24 hours) but no longer than 24 hours. If dried less than 12 hours, it must be documented that constant weight was attained.* Remove the sample from the oven and cool in a dessicator with the weighing dish cover in place before weighing. Weigh and record weight to nearest 0.01 g. Do not analyze the dried sample.
4. Duplicate percent solids determinations are required at the same frequency as are other analytical determinations. Duplicate results are to be recorded on FORM VI-IN.
5. For the duplicate percent solids determination, designate one sample aliquot as the "original" sample and the other aliquot as the "duplicate" sample. Calculate dry weight using the results of the "original" sample aliquot.
6. Calculate percent solids by the formula below. The value thus obtained will be reported on the appropriate FORM I-IN and, where applicable, FORM VI-IN. This value will be used for calculating analytical concentration on a dry weight basis.

$$\% \text{ Solids} = \frac{\text{Sample Dry Weight}}{\text{Sample Wet Weight}} \times 100$$

*For the purpose of paragraph 3, drying time is defined as the elapsed time in the oven; thus raw data must record time in and out of the oven to document the 12 hour drying time minimum. In the event it is necessary to demonstrate the attainment of constant weight, data must be recorded for a minimum of two repetitive weigh/dry/dessicate/weigh cycles with a minimum of 1 hour drying time in each cycle. Constant weight would be defined as a loss in weight of no greater than 0.01 g between the start weight and final weight of the last cycle.

END

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