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ANALYTICAL METHODS FOR U.S. EPA PRIORITY POLLUTANTS AND 301(h) PESTICIDES IN ESTUARINE AND MARINE SEDIMENTS

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SECTION I

The primary authors were Mr. Robert C. Barrick and Mr. Harry R. Beller. The assistance of Mr. Raleigh C. Farlow is appreciated.

Existing U.S. EPA analytical methods were incorporated into Section I whenever possible. Specifically, many sections were adapted from the Contract Laboratory Program for Organics Analysis (Section I, reference 2) and U.S. EPA Method 1625 Revision B (Section I, reference 3), which was developed by the Industrial Technology Division of the Office of Water Regulation and Standards.

Validation data presented in Section I (Precision and Accuracy) were generated by California Analytical Laboratories and Weyerhaeuser Technology Center.

SECTION II

The primary authors were Mr. Robert C. Barrick and Mr. Harry R. Beller. The assistance of Mr. Raleigh C. Farlow is appreciated.

The procedure described in Section II is largely a compilation of methods developed by U.S. EPA. Specifically, the methods were developed by the Environmental Monitoring Systems Laboratory (EMSL) in Las Vegas (Section II, references 1 and 2) and the Industrial Technology Division of the Office of Water Regulation and Standards (Section II, reference 3). Dr. M. Hiatt (Analytical Technologies, Inc., National City, CA, previously at EMSL Las Vegas) was a valuable source of technical information presented in this document.

SECTION III

The primary authors were Mr. Robert C. Barrick, Mr. Harry R. Beller, and Mr. Robert W. Deverall. The assistance of Dr. Charles R. Lytle is appreciated.

Validation data presented in Section III (Precision and Accuracy) were generated by Analytical Service Laboratories, Ltd.

Mention of trade names or commercial products herein does not constitute endorsement for use by U.S. EPA or Tetra Tech, Inc.

INTRODUCTION

The three analytical methods in this document have been designed to be consistent with probable uses of 301(h) monitoring data. Comparison of sediment contaminant concentrations from contaminated and relatively uncontaminated areas often require sensitive analytical techniques for a wide range of chemically diverse pollutants. The recommended 301(h) procedures allow for sensitive analyses of the target compounds with a reasonable amount of laboratory effort. Organophosphate 301(h) pesticides have not yet been tested with the recommended techniques (i.e., Malathion, Parathion, Demeton, Guthion). Analyses for 2,3,7,8-TCDD with appropriate detection limits will require the dedicated U.S. EPA Contract Laboratory Program procedure for dioxin analysis (9/15/83), which involves selected ion monitoring (SIM) GC/MS analysis.

There are currently no formally approved U.S. EPA procedures for analyzing priority pollutants and 301(h) pesticides in sediments at trace levels (e.g., at the low part per billion level for organic pollutant analysis). However, various U.S. EPA procedures were reviewed during development of this report [e.g., Interim Methods for the Sampling and Analysis of Priority Pollutants in Sediments and Fish Tissue (1977, revised 1980); Contract Laboratory Program procedures for organics analysis and inorganics analysis]. Consequently, the recommended 301(h) procedures include portions of U.S. EPA analytical and quality assurance procedures that were considered appropriate for sensitive, full-scan analyses. The 301(h) methods have been assembled according to guidelines for EMSL (Environmental Monitoring and Support Laboratory, Cincinnati) analytical methods (as specified in EPA-600/8-83-020).

SECTION I

ANALYSIS OF EXTRACTABLE ORGANIC COMPOUNDS IN ESTUARINE AND MARINE SEDIMENTS

ANALYSIS OF EXTRACTABLE ORGANIC COMPOUNDS IN ESTUARINE AND MARINE SEDIMENTS

1.0 SCOPE AND APPLICATION

1.1 This method is designed to determine the semivolatile priority pollutants (Table I-1) associated with the Clean Water Act Section 301(h) regulation [40 CFR 125.58(k) and (v)]. Additional compounds amenable to extraction and analysis by capillary column gas chromatography-mass spectrometry (GC/MS) and/or gas chromatography-electron capture detection (GC/ECD) may be suitable for analysis, subject to testing.

These procedures are applicable when low part per billion analyses are required to monitor differences between sediments from relatively uncontaminated reference areas and those from contaminated estuarine and marine environments.

Two GC/MS options included in the method are analyses by isotope dilution GC/MS (strongly recommended) or by a GC/MS internal standard technique (minimum required). In both cases, the laboratory procedures for sample extraction and concentration of the resulting extract are identical. Compound-specific recovery corrections used in the isotope dilution technique are designed to increase the accuracy of the analysis and the comparability of results among laboratories. In addition, use of the multiple recovery standards in each analysis increases confidence in the validity of detection limits reported for undetected target compounds. By forcing a search for every recovery standard in the sample extract (more than 50 are available), the technique also increases the efficiency of detection and reporting frequency of target compounds that otherwise may be overlooked in complex extracts.

1.2 The compounds listed in Table I-1 include pesticides subject to regulation under Section 301(h) of the Clean Water Act. However, the applicability of this method to non-chlorinated organophosphorous pesticides (Malathion, Parathion, Demeton, and Guthion) has not been demonstrated. Chemists at the Food and Drug Administration recently published a technique for determining organophosphate pesticides of wide ranging polarity in matrices including fatty animal tissue (J.J. Blaha and P.J. Jackson, J. Assoc. Anal. Chem., Vol. 68, pp. 1095-1099, 1985). The technique involves liquid-liquid partitioning and gel permeation chromatography [both are included in this recommended 301(h) procedure] as well as N/P alkali thermionic or flame photometric detection. Further work is required to determine the suitability of the recommended 301(h) procedure for organophosphorous pesticides in sediments.

1.3 The detection limit of this method is usually dependent upon the level of interferences rather than instrumental limitations. The limits listed in Table I-1 represent the minimum quantity that can be detected with no interferences present.

Lower limits of detection (LLD) are established by analysts based on their experience with the instrumentation and with interferences in the sample matrix being analyzed. LLD are greater than the instrumental detection limits in Table I-1 because they take into account sample interferences. To estimate LLD, the noise level should be determined in the retention window for the quantitation mass of representative analytes. These determinations should be made for at least three field samples in the sample set under analysis. The signal required to attain a signal/noise ratio of at least two should then be estimated. This signal is the minimum response required to identify a potential signal for quantification. The LLD is the concentration corresponding to the level of this signal based on calibrated response factors. Based on best professional judgment, this LLD would then be applied to samples in the set with comparable or lower interference. Samples with much higher interferences (e.g., at least a factor of two higher) should be assigned LLD at a multiple of the original LLD.

These LLD values may be less than the rigorously defined method detection limits specified in the revised "Guidelines Establishing Test Procedures for the Analysis of Pollutants" (40 CFR Part 136, 10/26/84). This latter procedure requires the analysis of seven replicate samples and a statistical determination of the method detection limit with 99 percent confidence. Data quantified between the LLD and the rigorous method detection limit are valid and useful in environmental investigations of low-level contamination, but have a lower statistical confidence associated with them than data quantified above the method detection limit.

LLD for the described analytical method on a dry-weight basis are 10-25 ug/kg for aromatic hydrocarbons, phthalates, chlorinated hydrocarbons, and halogenated ethers (GC/MS analysis). LLD for GC/MS analyses of pesticides are 50 ug/kg (dry weight). The corresponding GC/ECD detection limits for pesticides are 0.1-5 ug/kg. An LLD of 10 ug/kg is attainable for GC/ECD analysis of total PCBs.

1.4 The GC/MS portions of this method are for use only by analysts experienced with GC/MS or under the close supervision of such qualified persons. Laboratories unfamiliar with the analyses of environmental samples by GC/MS should run the performance tests in reference 1 before beginning.

1.5 This procedure has been designed to analyze for a large number of organic compounds with wide-ranging chemical properties (e.g., polarity, molecular weight) while minimizing procedural complexity. The accuracy and sensitivity that can be attained in a dedicated analysis for only one of the compounds in Table I-1 cannot always be attained in such a comprehensive analysis.

1.6 Several analytes are particularly susceptible to decomposition during analysis. Benzidine can be subject to oxidative losses during solvent extraction. Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition. Some polycyclic aromatic hydrocarbons are also photosensitive, especially benzo(a)pyrene.

2.0 SUMMARY OF METHOD

2.1 A homogenized sediment sample is Soxhlet-extracted with methylene chloride/methanol (2/1, v/v). The resulting extract is subjected to liquid-liquid partitioning with water and is dried by elution through a sodium sulfate column. Elemental sulfur, a common interferent in estuarine and marine sediments, is removed from the extract with metallic mercury. Biological macromolecules are then removed from the extract by gel permeation chromatography (GPC) (reference 2). A portion of the extract (20%) is subjected to alumina chromatography to separate polar compounds from pesticides and PCBs prior to capillary GC/ECD analysis (reference 2). The remaining 80% of the extract is subjected to reverse phase column chromatography (bonded C_{18} solid phase) to reduce interferences from unresolved paraffinic hydrocarbons prior to capillary GC/MS analysis for acid, base, and neutral compounds. An isotope dilution technique (EPA Method 1625 Revision B, reference 3) is highly recommended but not required for all compounds analyzed by GC/MS. This technique involves spiking the homogenized sediment sample with the stable isotope-labeled analogs of most of the pollutants to be analyzed by GC/MS. The advantage of isotope dilution is that reliable recovery corrections can be made for each analyte with a labeled analog or a chemically similar analog.

2.1.1 Much of the text of EPA Method 1625 Revision B has been incorporated into this method in modified form. The modifications were necessary because, in relation to Method 1625 Revision B, the present method involves different sample matrices (sediments), different calibration requirements, and additional analytes (pesticides and PCBs, both requiring GC/ECD analysis).

2.2 Identification of compounds is performed by comparing the GC retention times and background-corrected characteristic spectral masses with those of authentic standards. Tentative identifications of low levels of pesticides and PCBs are made by comparing GC retention times to standards. The identities of pesticides and PCBs are confirmed by GC/ECD analysis on an alternative column phase or by GC/MS when sufficient concentrations occur.

`.3 Quantitative analysis is performed by GC/MS using extracted ion current profile (EICP) areas. Isotope dilution, with labeled analogs of pollutants acting as recovery standards, is the method of quantification when labeled compounds are available. When the isotope dilution technique is used but certain labeled compounds are unavailable [e.g., labeled indeno(1,2,3-c,d) pyrene], the nearest eluting, most chemically similar labeled compound is used as a recovery standard. Pesticides and PCBs are quantified by an internal standard method. Concentrations of compounds quantified by GC/MS are reported after correcting for method recoveries when the isotope dilution technique is used. Recoveries of isotope labeled standards are determined with the internal standard technique.

3.0 INTERFERENCES

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield contamination artifacts and/or elevated baselines, causing misinterpretation of chromatograms and spectra. All materials should be demonstrated to be free from interferences under the conditions of the analysis by running method blanks initially and with each sample lot (Sect. 9.4). Specific selection of reagents and purification of solvents by distillation in all-glass systems are required. High-purity, distilled-in-glass solvents are commercially available (e.g., Burdick and Jackson Laboratories, Muskegon, MI). An effective way of cleaning laboratory glassware is to cover it with aluminum foil, heat it at 450° C for several hours, and rinse it with polar and non-polar solvents before use. Note that heating without subsequent solvent rinsing may not eliminate laboratory residues of PCBs and other chlorinated hydrocarbons.

3.2 Phthalates are common laboratory contaminants that are used widely as plasticizers. Phthalates can derive from plastic labware, plastic tubing, plastic gloves, plastic coated glassware clamps, and have been found as a contaminant in Na_2SO_4. Polytetrafluoroethylene (PTFE) can be used instead of polypropylene or polyethylene to minimize this potential source of contamination. However, use of PTFE labware will not necessarily preclude

all phthalate contamination. Also PTFE has been shown to be capable of adsorbing certain priority pollutants, so careful rinsing must be employed.

3.3 Interferences coextracted from sediment samples affect the lower limits of detection (LLD) and quantitation limits. For this reason, sample extract cleanup is necessary to yield reproducible and reliable analyses of contaminants present at low concentrations in sediment samples.

3.3.1 Elemental sulfur, often prevalent in poorly oxygenated sediments, is coextracted with organic pollutants and can interfere significantly with both GC/ECD and GC/MS analyses. Sulfur removal is an integral step in this method to alleviate this interference (Sect. 10.1.11).

3.3.2 Paraffinic, chromatographically unresolvable hydrocarbons, derived from petroleum contamination, can interfere with GC/MS analyses of a broad range of compounds. Reverse phase column chromatography (Sect. 10.1.16) is included in the procedure to reduce this interference.

4.0 SAFETY

4.1 The toxicity or carcinogenicity of each compound or reagent used in this method has not been precisely determined. However, each chemical compound should be treated as a potential health hazard and exposure should be reduced as much as possible. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. These procedures for the safe handling of chemicals should be made available to and followed by all personnel involved in these analyses. Additional information on laboratory safety can be found in references 4-6.

4.2 The following compounds covered by this method have been tentatively classified as known or suspected human or mammalian carcinogens: benzene, benzo(a)anthracene, 3,3'-dichlorobenzidine, benzo(a)pyrene, dibenzo(a,h)anthracene, N-nitrosodimethylamine, 4,4'-DDT, alpha-, beta-, delta-, and gamma-hexachlorocyclohexane, and PCBs. Standards of these compounds should be

prepared in a hood and a NIOSH/MESA-approved toxic gas respirator should be orn when high concentrations are handled. All people working with toxic chemicals should receive adequate instruction and training on when and how to use respirators. See OSHA regulations for further guidance.

5.0 APPARATUS AND EQUIPMENT

5.1 Soxhlet Extractor - 50-mL extractor (Corning 3740-S or equivalent), or 85-mL extractor (Corning 3740-M or equivalent), with 250-mL flask (Corning 4320-250 or equivalent) and condenser with 34/45 joint. Cellulose thimbles of the appropriate size should be cleaned with the extraction solvent mixture for at least 30 cycles.

5.2 Drying Column - 30 cm x 2 cm borosilicate glass chromatography column with glass wool plug. Glass wool should be extracted with the appropriate solvents and allowed to dry before use.

5.3 Kuderna-Danish (K-D) Apparatus -

5.3.1 Concentrator Tube - 10 mL, graduated (Kontes K-570050-1025 or equivalent). A ground glass stopper (19/22 joint) is used to prevent evaporation of extracts.

5.3.2 Evaporation Flask - 500 mL (Kontes K-570050-0500 or equivalent), attached to concentrator tube with springs (Kontes K-662750-0012).

5.3.3 Snyder Column - three-ball macro (Kontes K-503000-0232 or equivalent).

5.3.4 Snyder Column - two-ball micro (Kontes K-469002-0219 or equivalent).

5.3.5 Silicon Carbide Boiling Chips - approximately 10/40 mesh, extracted with methylene chloride and heated at 450° C for 1 h minimum. Uncleaned boiling chips can be a significant source of contamination.

5.4 Separatory Funnel - 500 mL, borosilicate glass with PTFE stopcock.

5.5 Borosilicate Glass Beaker - 400 mL and 100 mL.

5.6 Water Bath - heated, with concentric ring cover, capable of temperature control ($\pm 2^{\circ}$ C), installed in a fume hood.

5.7 Sample Vials - amber glass, 2-5 mL with PTFE-lined screw cap.

5.8 Analytical Balance - capable of weighing 0.1 mg.

5.9 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 is suitable.

5.10 Balance - capable of 100 g to the nearest 0.01 g.

5.11 Disposable Pasteur Pipets - sealed with aluminum foil and annealed at 450° C for several h, and rinsed with solvents before use.

5.12 Drying Oven.

5.13 Annealing Oven - capable of reaching 450° C.

5.14 Dessicator.

5.15 Chromatography Column for Alumina - 5-mL, disposable, borosilicate glass serological pipet with borosilicate glass wool plug. (Glass wool must be extracted with the appropriate solvents and allowed to dry before use).

5.16 Reverse Phase Cleanup Columns - 3-mL, solid phase extraction (SPE) columns containing Octadecyl (Baker-10 SPE, #7020-3, or equivalent). Column cleaning/conditioning is discussed in Sect. 10.1.16.

5.17 Gel Permeation Chromatography Cleanup Device -

5.17.1 Automated system: gel permeation chromatograph (GPC), Analytical Biochemical Labs, Inc. GPC Autoprep 1002, including:

- 25 mm ID x 600 - 700 mm glass column packed with 70 g of Bio Beads S-X3
- Syringe - 10 mL with Luer Lok fitting
- Syringe Filter Holder and Fitters - stainless steel and PTFE, Gelman 4310 or equivalent.

5.17.2 Manual system assembled from parts (Wise, R.H., D.F. Bishop, R.I. Williams, and B.M. Austern. Gel permeation chromatography in the GC/MS analysis of organics in sludges. U.S. EPA, Municipal Environmental Research Laboratory, Cincinnati, OH. 45268). (See reference 2, p. D-35).

5.18 Gas Chromatograph - 1) one equipped with electron capture detector (ECD) and 2) one interfaced to the mass spectrometer (Sect. 5.19). Both should have splitless injection ports for capillary column, temperature programs with 30^{0} C hold, and should meet all the performance specifications in Sect. 9.9.

5.18.1 Column - 30±5 m x 0.25±0.02 mm I.D. 5% phenyl, 94% methyl, 1% vinyl silicone bonded phase (0.25 um film thickness) fused silica capillary column (J & W DB-5 or equivalent).

5.19 Mass Spectrometer - 70 eV electron impact ionization, should repeatedly scan from 35 to 450 amu in 0.95 to 1.00 second and should produce a unit resolution (valleys between m/z 441-442 less than 10% of the height of the 441 peak), background-corrected mass spectrum from 20 ng decafluorotriphenylphosphine (DFTPP) introduced through the GC inlet. The spectrum should meet the mass-intensity criteria in Table I-2 (reference 7). The use of a conversion dynode to enhance high mass sensitivity is recommended. The

mass spectrometer should be coupled with the GC such that the end of the capillary column terminates within 1 cm of the ion source but does not intercept the electron or ion beams. All portions of the column that connect the GC to the ion source should remain at or above the column temperature during analysis to preclude condensation of less volatile compounds.

5.20 Data System - should collect and record MS data, store mass intensity data in spectral libraries, process GC/MS data, generate reports, and compute and record response factors.

5.20.1 Data Acquisition - mass spectra should be collected continuously throughout the analysis and stored on a mass storage device.

5.20.2 Mass Spectral Libraries - user-created libraries containing mass spectra obtained from analysis of authentic standards should be employed to reverse search GC/MS runs for the compounds of interest (Sect. 8.2).

5.20.3 Data Processing - the data system should be used to search, locate, identify, and quantify the compounds of interest in each GC/MS analysis. Software routines should be employed to compute retention times and peak areas. Displays of spectra, mass chromatograms, and library comparisons are required to verify results.

5.20.4 Response Factors and Multipoint Calibrations - the data system should be used to record and maintain lists of response factors (response ratios for the isotope dilution technique) and multipoint calibration curves (Sect. 8). Computations of relative standard deviation (coefficient of variation) are useful for testing calibration linearity.

6.0 REAGENTS AND CONSUMABLE MATERIALS (partially adapted from references 2 and 3).

6.1 Reagents

6.1.1 Acetone, benzene, n-hexane, isooctane, methanol, and methylene chloride (CH_2Cl_2) (pesticide quality, distilled-in-glass).

6.1.2 Alumina - neutral, super Woelm or equivalent (Universal Scientific, Atlanta, GA). Extract alumina with methylene chloride for 30-40 cycles in a Soxhlet extractor to remove contamination. Allow solvent to evaporate. Prepare activity III alumina by adding 7 percent (v/w) reagent water to neutral alumina that has been activated at approximately 225° C for at least 2 h or preferably overnight. Store in tightly sealed, clean glass container.

6.1.3 Hydrochloric acid - concentrated, make 2N HCl with reagent water. Solvent clean in a separatory funnel with methylene chloride.

6.1.4 Metallic mercury - reagent mercury cleaned with pesticide quality CH_2Cl_2 or equivalent.

6.1.5 Potassium hydroxide - reagent grade, 6N in reagent water. Solvent clean in a separatory funnel with methylene chloride.

6.1.6 Sodium sulfate - reagent grade, granular anhydrous, rinsed with CH_2Cl_2 (20 mL/g) and conditioned at 450° C for 1 h minimum.

6.1.7 Reagent water - water in which the compounds of interest and interfering compounds are not detected by this method.

6.2 GPC Calibration Solutions:

6.2.1 Corn oil - 200 mg/mL in CH_2Cl_2.

6.2.2 Bis(2-ethylhexyl)phthalate and pentachlorophenol - 4 mg/mL in CH_2Cl_2.

6.3 Stock Standard Solutions - purchased as solutions or mixtures with certification to their purity, concentration, and authenticity, or prepared from materials of known purity and composition. If the compound purity is 96 percent or greater, the weight may be used without correction to compute the concentration of the standard. When not being used, standards are stored in the dark at -20 to -10° C in screwcapped vials with PTFE-lined lids. A mark is placed on the vial at the level of the solution so that solvent evaporation loss can be detected. The vials are brought to room temperature prior to use. Any precipitate is redissolved and solvent is added if solvent loss has occurred.

6.3.1 Preparation of stock solutions - prepare in methylene chloride, benzene, isooctane, or a mixture of these solvents according to the steps below. Observe the safety precautions given in Sect. 4. The large number of labeled and unlabeled acid and base/neutral compounds used for combined calibration (Sect. 8) and calibration verification (Sect. 9.9.1.3) require high concentrations (approximately 40 mg/mL) when individual stock solutions are prepared, so that dilutions of mixtures will permit calibration with all compounds in a single set of solutions. The working range for most compounds is 1-50 ug/mL. Compounds with a reduced MS response may be prepared at higher concentrations.

Standards for GC/ECD have lower working ranges (e.g., 0.04 to 2.0 ug/mL for single component pesticides) than GC/MS standards. However, GC/ECD stock solutions should be prepared with at least 10 mg of the pure material (e.g., in 10 mL of solvent) to reduce potential weighing error.

6.3.2 Dissolve an appropriate amount of assayed reference material in a suitable solvent. For example, weigh 400 mg naphthalene in a 10-mL ground glass stoppered volumetric flask and fill to the mark with benzene. After the naphthalene is completely dissolved, transfer the solution to a 15 mL vial with PTFE-lined cap.

6.3.3 Stock standard solutions should be checked for signs of degradation prior to the preparation of calibration or performance test standards. Quality control check samples that can be used to determine the accuracy of calibration standards are available from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

6.3.4 Stock standard solutions should be replaced after 6 mo, or sooner if comparison with quality control check samples indicates a change in concentration.

6.4 Injection Internal Standard Solutions

6.4.1 GC/MS internal standard solution - prepare 2,2'-difluorobiphenyl (DFB) at a concentration of 2 mg/mL in benzene.

6.4.2 GC/ECD internal standard solution - prepare decafluorobenzophenone (DFBP) at a concentration of 2.5 ug/mL in isooctane.

6.5 GC/MS Secondary Dilution Standards - using stock solutions (Sect. 6.3), prepare a secondary standard containing each of the unlabeled priority pollutants in Table I-1 at a concentration of 100 ug/mL, or at a higher concentration appropriate to the MS response of the compounds.

6.6 Labeled Compound Spiking Solution - prepare a spiking solution from stock standard solutions prepared as in Sect. 6.3, or from mixtures, at a concentration of 100 ug/mL or at a concentration appropriate to the MS response of each compound. The deuterium and ^{13}C-labeled compounds listed in Table I-1 are commercially available individually or as mixtures (e.g., Merck Sharp & Dohme/Isotopes, Montreal, Canada).

6.7 Solutions for obtaining authentic mass spectra (Sect. 8.2) - prepare mixtures of labeled and unlabeled compounds at concentrations that will assure that authentic spectra are obtained for storage in libraries.

6.8 Calibration Solutions - the concentrations of calibration solutions suggested in the following sections are intended to bracket concentrations that will be encountered during sample analysis without overloading GC columns or saturating detection systems.

6.8.1 GC/MS calibration solutions - combine 0.1 mL of the spiking solution (Sect. 6.6) with 10, 50, 100, 200, and 500 uL of the secondary dilution solution (Sect. 6.5) and bring to 1.00 mL total volume each. This will produce calibration solutions of nominal 1, 5, 10, 20, and 50 ug/mL of the pollutants and a constant nominal 10 ug/mL of the labeled compounds. Spike each solution with 10 uL of the GC/MS internal standard solution, yielding 20 ug/mL.

6.8.2 PCB calibration solutions -

6.8.2.1 Aroclor stock solution for GC/MS - prepare a solution in hexane with 250 ng/uL of each of three PCB mixtures, Aroclor 1016, Aroclor 1254, and Aroclor 1260.

6.8.2.2 Aroclor standard solution for GC/ECD - dilute the stock solution (Sect. 6.8.2.1) to one-tenth its original concentration. It is essential that this solution be prepared directly from the batch used for Sect. 6.8.2.1. Combine 20, 50, 250, 500, and 1,000 uL of the diluted standard with 100 uL of the GC/ECD internal standard solution (Sect. 6.4.2) and bring each solution to a final volume of 5.0 mL.

This will produce calibration solutions of nominal concentrations of 100, 250, 1,250, 2,500, and 5,000 ng/mL of the 1:1:1 Aroclor mixture and a constant nominal concentration of 50 ng/mL of internal standard.

6.8.3 Pesticide calibration solution - combine 20 uL of the GC/ECD internal standard solution with 2, 5, 10, 50, and 100 uL of a 20 ug/mL stock solution of all chlorinated pesticides listed in Table I-1 (except toxaphene) and bring to a 1.0 mL total volume. This will produce calibration solutions

of 40, 100, 200, 1,000, and 2,000 ng/mL of each pesticide and a constant nternal standard concentration of 50 ng/mL.

6.8.4 Toxaphene calibration solution - prepare toxaphene solutions of 100, 250, 1,250, 2,500, and 5,000 ng/mL with constant internal standard concentration of 50 ng/mL.

6.8.5 DFTPP solution - prepare at 20 ug/mL in acetone from a stock solution at 1 mg/mL. The dilute (20 ug/mL) solution is susceptible to adsorption to vial walls and reaction with solvent impurities and may require weekly replacement. The stock solution is likely to be stable for 6 mo to several years (reference 1).

6.9 Stability of Solutions - all standard solutions (Sect. 6.4-6.8.4) should be analyzed within 48 h of preparation and on a monthly basis thereafter for signs of degradation. Standards will remain acceptable if response factors relative to the internal standard correspond within ±15 percent to hose obtained in the initial analysis of the standard.

7.0 SAMPLE COLLECTION, PREPARATION, AND STORAGE

7.1 Minimize handling and avoid possible sources of contamination during collection (e.g., sampling gear, grease from ship winches or cables, ship engine exhaust, improper subsampling procedures).

7.2 Collection of a minimum of 100 g (wet weight) should be sufficient for analysis. Sediment samples are stored in 240-mL (8-oz) or larger, wide-mouth jars with PTFE-lined screw lids. The container, lid, and liner should be detergent washed, rinsed twice with tap water, once with distilled water, once with methanol or acetone, and once with high-purity methylene chloride. Firing of the glass jar at 450° C for 1 h may be substituted for the solvent rinses.

7.3 Samples should be stored in the dark and frozen at -20° C until extraction. Care should be taken to prevent container breakage during

freezing. Leave sufficient headspace for the water to expand and freeze the containers at an angle.

7.4 U.S. EPA gives no official guidance on sediment holding times but recommends that water samples stored at 4° C be extracted within 10 days of sample receipt (reference 2). Because sediments can be frozen at -20° C, longer holding times (e.g., up to 6 mo) are appropriate. Extracts should be analyzed within 40 days of extraction (reference 2). Effort should be made to analyze the samples as soon as possible after extraction because some of the more labile analytes may degrade in solution. Degradation may occur even in the dark under refrigeration, possibly as the result of free radical formation.

8.0 CALIBRATION AND STANDARDIZATION (adapted from reference 3)

8.1 Establish the GC/MS operating conditions in Table I-1. Analyze standards per the procedure in Sect. 10.2 to demonstrate that the analytical system meets the detection limits in Table I-1 and the mass-intensity criteria in Table I-2 for 20 ng DFTPP.

8.2 Mass Spectral Libraries - detection and identification of compounds of interest are dependent upon spectra stored in user-created libraries.

8.2.1 Obtain a mass spectrum of each pollutant, labeled compound, and the internal standard by analyzing an authentic standard either singly or as part of a mixture in which no interference exists between closely eluting components. Confirmation that only a single compound is present is attained by examination of the spectrum. Fragments not attributable to the compound under study indicate the presence of an interfering compound.

8.2.2 Adjust the analytical conditions and scan rate (for this test only) to produce an undistorted spectrum at GC peak maximum. An undistorted spectrum will be obtained if five complete spectra are collected across the upper half of the GC peak. Software algorithms designed to "enhance" the spectrum may eliminate distortion, but may also eliminate authentic masses or introduce other distortion.

8.2.3 The authentic reference spectrum is obtained under DFTPP tuning conditions (Sect. 8.1 and Table I-2) to normalize it to spectra from other instruments.

8.2.4 The spectrum is edited for entry in the library by saving the five most intense mass spectral peaks and all other mass spectral peaks greater than 10 percent of the base peak. This edited spectrum is stored for reverse search and for compound confirmation.

8.3 Polar Compound Detection - demonstrate that unlabeled pentachlorophenol and benzidine are detectable at the 10 ug/mL level (per all criteria in Sect. 10.4). The 10 ug/mL calibration standard (Sect. 6.8.1) can be used to demonstrate this performance.

8.4 Calibration with the isotope dilution technique - the isotope dilution technique is used when labeled compounds are available and interferences do not preclude its use. If either of these conditions precludes isotope dilution, the internal standard method (Sect. 8.5) is used and noted as such in the report.

8.4.1 A calibration curve encompassing the concentration range is prepared for each compound determined. The relative response (pollutant to labeled) versus concentration in standard solutions is plotted or computed using a linear regression. The example in Figure I-1 shows a calibration curve for an unlabeled compound and its labeled analog. Also shown are the ±10 percent error limits (dotted lines). Relative Response (RR) is determined according to the procedures described below. A minimum of five data points are employed for calibration.

8.4.2 The relative response of a pollutant to its labeled analog is determined from isotope ratio values computed from acquired data. Three isotope ratios are used in this process:

R_x = the isotope ratio measured for the pure pollutant

R_y = the isotope ratio measured for the labeled compound

R_m = the isotope ratio of an analytical mixture of pollutant and labeled compounds.

The m/zs are selected such that $R_x > R_y$. If R_m is not between 2 R_y and 0.5R_x, the method does not apply and the sample is analyzed by the internal standard method (Sect. 8.5).

8.4.3 Capillary columns usually separate the pollutant-labeled pair, with the labeled compound eluting first (Figure I-2). For this case,

$$R_x = (\text{area } m_1/z)/1$$

at the retention time of the pollutant (RT_2) and

$$R_y = 1/(\text{area } m_2/z)$$

at the retention time of the labeled compound (RT_1). Also,

$$R_m = [\text{area } m_1/z \text{ (at } RT_2)]/[\text{area } m_2/z \text{ (at } RT_1)]$$

as measured in the mixture of the pollutant and labeled compounds (Figure I-2), and $RR = R_m$.

8.4.4 Special precautions are taken when the pollutant and its labeled analog are not chromatographically separated and have overlapping spectra, or when another labeled compound with interfering spectral masses overlaps the pollutant (which can occur with isomeric compounds). In such cases, it is necessary to determine the respective contributions of the pollutant and labeled compounds to the respective EICP areas. If the peaks are separated well enough to permit the data system or operator to remove the contributions of the compounds to each other, the equations in Sect. 8.4.3 apply. This usually occurs when the height of the valley between the two GC peaks at the same m/z is less than 10 percent of the height of the shorter of the two

peaks. If significant chromatographic and spectral overlap occur, RR is omputed using the following equation:

$$RR = (R_y - R_m)(R_x + 1)/(R_m - R_x)(R_y + 1)$$

where R_x is measured as shown in Figure I-3A, R_y is measured as shown in Figure I-3B, and R_m is measured as shown in Figure I-3C. For the example,

$$R_x = 46100/4780 = 9.644$$

$$R_y = 2650/43600 = 0.0608$$

$$R_m = 49200/48300 = 1.019$$

8.4.5 To calibrate the analytical system by isotope dilution, analyze a 1.0 uL aliquot of each of the GC/MS calibration standards (Sect. 6.8.1) using the procedure in Sect. 10.2. Compute the RR at each concentration.

8.4.6 Linearity - if the ratio of relative response to concentration for any compound is constant (less than 20 percent coefficient of variation) over the five-point calibration range, an averaged relative response/concentration ratio may be used for that compound; otherwise, the complete calibration curve for that compound should be used over the five-point calibration range.

8.5 Calibration by Internal Standard - used when criteria for isotope dilution (Sect. 8.4) cannot be met. The internal standard used for both acid and base/neutral analyses is 2,2'-difluorobiphenyl. The internal standard for pesticide and PCB analysis by GC/ECD is decafluorobenzophenone. The internal standard method is used to measure labeled compounds for intralaboratory statistics (Sect. 9.5.1).

8.5.1 Response factors - calibration requires the determination of response factors (RF) which are defined by the following equation:

$$RF = (A_s \times C_{is})/(A_{is} \times C_s)$$

where:

A_s = the area of the target peak in the daily standard
A_{is} = the area of the internal standard peak
C_{is} = the concentration of the internal standard (ug/mL)
C_s = the concentration of the compound in the daily standard (ug/mL).

8.5.1.1 The response factor is determined over the range of concentrations described in Sect. 6.8.1, 6.8.2, 6.8.3, and 6.8.4. The amount of internal standard added to each extract is the same so that C_{is} remains constant. The RF is plotted versus concentration for each compound (or class of compounds in the case of toxaphene) in the standard (C_s) to produce a calibration curve.

8.5.1.2 Linearity - If the response factor (RF) for any compound is constant (less than 35 percent coefficient of variation) over the calibration range, an averaged response factor may be used for that compound; otherwise, the complete calibration curve for that compound should be used over the range.

8.6 Combined Calibration - By using calibration solutions (Sect. 6.8.1) containing the pollutants, labeled compounds, and the internal standard, a single set of analyses can be used to produce calibration curves for the isotope dilution and internal standard methods. These curves are verified each shift by analyzing the 10 ug/mL calibration standard (Sect. 9.9.1). Pesticide and PCB calibration standards must be analyzed separately by GC/ECD. Recalibration is required only if calibration verification (Sect. 9.9.1.3) criteria cannot be met.

8.7 Ongoing Calibration (see Sect. 9.9)

9.0 QUALITY ASSURANCE/QUALITY CONTROL [For further guidance, see Quality Assurance/Quality Control (QA/QC) for 301(h) Monitoring Programs: Guidance on Field and Laboratory Methods (Tetra Tech 1986).]

9.1 Laboratories that use this method are required to operate formal quality assurance programs. The requirements of the programs are an initial demonstration of laboratory capability, analyses of replicates and matrix spikes used to evaluate and document data quality, and analysis of standards and blanks used to test continued performance.

9.2 Initial Demonstration of GC/MS Capability - the analyst should make an initial demonstration of the ability to generate acceptable accuracy and precision with the GC/MS component of this method. This ability is established as described in reference 1.

9.3 The analyst is permitted to modify this method to improve separations or lower the costs of measurements, provided that the new method is demonstrated to perform comparably to the present method (i.e., with comparable spike recoveries and precision).

9.4 Blanks - method blanks should be analyzed by GC/MS and GC/ECD to demonstrate freedom from contamination.

9.4.1 At least one method blank must be included with each batch of samples; method blanks must constitute at least 5 percent of all samples analyzed.

9.4.2 Method blank concentrations of compounds of interest and of potentially interfering compounds should be less than 5 percent of the expected values for the corresponding analytes in samples and below the LLD, if possible. It is recommended that if blank concentrations of compounds of interest (except phthalates) are greater than 30 percent of the corresponding analyte concentrations in samples, sample analysis should be halted until the contamination source is eliminated.

9.5 Spiked samples are required to assess method performance on the sample matrix.

9.5.1 For samples analyzed by the isotope dilution technique, the percent recovery (P) of labeled compounds can be computed by the internal standard method (Sect. 8.5) and serves as an indication of analytical accuracy (but not necessarily of extraction efficiency). After the analysis of five samples, compute the average percent recovery (P) and the standard deviation of the percent recovery (s_p) for the labeled compounds only. Express the accuracy assessment as a percent recovery interval from $P - 2s_p$ to $P + 2s_p$. For example, if P = 90 percent and s_p = 10 percent, the accuracy interval is expressed as 70-110 percent. Update the accuracy assessment for each compound on a regular basis (e.g., after each 5-10 new accuracy measurements).

9.5.2 Laboratories unable to use isotope dilution must analyze matrix spikes of pollutants (other than pesticides and PCBs) at a frequency of 5 percent of all samples analyzed or once with each sample set, whichever is more frequent. Compounds should be added at concentrations 1 to 5 times those in the sample.

9.5.3 All laboratories are required to spike samples with PCBs or pesticides at a frequency of 5 percent of all samples analyzed or once per sample set, whichever is more frequent. The spike can be a standard pesticide mixture or an Aroclor mixture, whichever is considered to be more representative of the sample. The mixture should be added at one to five times the sample concentration of these compounds.

9.6 Replicates (i.e., analyses of at least two separate aliquots from a sediment homogenate) must be analyzed by GC/MS and GC/ECD to monitor the precision of laboratory analyses. At a minimum, 5 percent of the analyses should be laboratory replicates. A triplicate analysis should be performed with each sample batch of over 40 samples.

9.7 The laboratory should maintain records to define the quality of data that are generated. These records include documentation of blanks and reports of labeled compound recovery (Sect. 9.5.1), if the latter is applicable.

9.8 The laboratory should, on an ongoing basis, demonstrate through calibration verification that the analysis system is in control (Sect. 9.9.1.3).

9.9 System and Laboratory Performance

9.9.1 At the beginning and end of each 12-h shift during which analyses are performed, GC/MS system performance and calibration are verified for all pollutants and labeled compounds. For these tests, analysis of the 10 ug/mL calibration standards (Sect. 6.8.1) should be used to verify all performance criteria. The GC/ECD performance is checked at the beginning and end of each shift or at least every 6 h by analyses of 250 and 100 ug/mL solutions of the PCB and pesticide standards (Sect. 6.8.2.2 and 6.8.3).

9.9.1.1 Retention times - the absolute GC/MS retention time of 2,2'-difluorobiphenyl should be within the range of 1078 to 1248 sec. The absolute GC/ECD retention time of 4,4'-DDT should be within the range of 1050 and 1200 sec.

9.9.1.2 GC resolution for GC/MS analysis - the valley height between anthracene and phenanthrene at m/z 178 (or the analogs at m/z 188) should not exceed 10 percent of the taller of the two peaks.

GC resolution for GC/ECD analysis - the valley height between two peaks should not exceed 25 percent of the taller of the two peaks for the following pairs: beta- and delta-HCH, dieldrin and 4,4'-DDE, 4,4'-DDD and endrin aldehyde, and endosulfan sulfate and 4,4'-DDT.

9.9.1.3 Ongoing calibration verification - compute the concentration of each pollutant (Table I-1) by isotope dilution (Sect. 8.4) for those compounds that have labeled analogs. Compute the concentration of each pollutant that has no labeled analog with the nearest eluting labeled standard. Compute the concentration of the labeled compounds by the internal standard method. Also compute individual pesticide concentrations and total PCB and toxaphene concentrations by the internal standard method (GC/ECD). These

concentrations are computed based on the calibration data determined in Sect. 8. Preparations of new calibration standards or revisions of calibration curves are required if observed responses of analytes vary from predicted responses by more than ±20 percent. Samples and blanks may be run only after calibration performance meets this control limit.

9.9.1.4 Multiple peaks - each compound injected should give a single, distinct GC peak.

9.9.2 DFTPP spectrum validity - inject 1 uL of the DFTPP solution (Sect. 6.8.5) either separately or within a few seconds of injection of the standard (Sect. 9.9.1) analyzed at the beginning of each shift. The criteria in Table I-2 should be met.

10.0 PROCEDURE (see Figure I-4)

10.1 Sample Extraction and Concentration

10.1.1 Homogenize samples prior to analysis to ensure that representative aliquots are taken. Mix any water that has separated from the sediment back into the sample. Remove and make note of nonrepresentative material (e.g., twigs, leaves, shells, rocks, and any material larger than 1/4 in). It is recommended that any removal of material be performed in the field by the sampling personnel if sampling conditions permit (e.g., if contamination can be avoided on board ship).

10.1.2 Add a 100-g (wet wt) sediment aliquot (weighed to the nearest 0.1 g) to a precleaned Soxhlet thimble for extraction. Spike with 10 ug of each neutral stable isotope-labled compound and 15 ug of each acid stable isotope-labeled compound if using the isotope dilution technique. Use a separate aliquot for a dry-wt to wet-wt ratio determination.

10.1.2.1 To determine the sediment dry weight, transfer an aliquot of approximately 3 g (weighed to the nearest 0.1 g) to a preweighed dish. Allow the sample to dry in a 105° C oven overnight and determine the solid

residue weight (to the nearest 0.1 g). Calculate and report the percent solids (T_s) as:

$$T_s = [\text{dry residue wt (g)}]/[\text{wet sample wt (g)}] \times 100\%$$

10.1.3 Soxhlet-extract the sediment with CH_2Cl_2/MeOH (2/1) for 24 h (60-90 cycles). Before extraction, fill the thimble (containing sediment) with pure MeOH and stir the sediment-methanol mixture to enhance removal of water. Cover the sample with a thin layer of solvent-cleaned glass wool. Add CH_2Cl_2/MeOH to the 250-mL flask such that the combined total of solvent in the thimble and flask is at least 210 mL. Stir the sample in the thimble at least twice (after the second cycle and after approximately 12 h) to prevent solvent channeling. (The glass wool should be removed during stirring and then replaced.) The Soxhlet apparatus should be wrapped up to the condenser with aluminum foil to ensure even heating during cycling.

10.1.4 Re-extraction of sediments at a pH below the pK_as (i.e., the negative logarithm of an acid dissociation constant) of target acidic compounds may enhance extraction recoveries for these compounds. For example, an extraction pH of 2 would be well below the pK_as of the acidic analytes (e.g., the pK_a of pentachlorophenol is approximately 4.7). This additional extraction step is optional and has not been tested with this 301(h) protocol. It is not acceptable to acidify the extract before the initial Soxhlet extraction because acidification at the temperatures required for the Soxhlet extraction can degrade some potential analytes.

10.1.5 Alternative methods of sediment extraction may be used if evidence of acceptable performance (i.e., equivalent or better apparent extraction efficiency) is provided.

10.1.6 Liquid-Liquid Extraction

10.1.6.1 After Soxhlet extraction, transfer the extract to a 500-mL separatory funnel. Rinse the Soxhlet flask twice with clean extraction solvent and add this rinse to the extract in the separatory funnel. Wash

the solvent extract with approximately 100 mL of pH 2, 50% Na_2SO_4 saturated organic-free water. The pH of the water should be adjusted with solvent-cleaned HCl. Oxidizing acids (e.g., H_2SO_4) must not be used because they can cause losses of target compounds. Collect and store the CH_2Cl_2 layer. The purpose of washing the extract with an acidic aqueous solution is to remove water and methanol from the CH_2Cl_2 and to enhance the partitioning of acidic organic compounds into the CH_2Cl_2 layer. Re-extract the acidic aqueous phase twice with 60 mL of clean CH_2Cl_2 and add both extracts to the initial CH_2Cl_2 fraction.

10.1.6.2 Adjust the pH of the aqueous phase to $\geq$12 with solvent-cleaned, 6 N KOH. Back-extract the base compounds three times with 60 mL CH_2Cl_2. The pH adjustment to alkaline conditions enhances the partitioning of basic compounds into the CH_2Cl_2 layer. Combine all CH_2Cl_2 layers from Sect. 10.1.6.1 and 10.1.6.2.

10.1.6.3 Formations of emulsions or precipitates during liquid-liquid extraction should be noted and considered when reviewing results. The addition of Na_2SO_4 may reduce emulsions. However, 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 on the sample and may include stirring, filtration of the emulsion through pre-cleaned glass wool, centrifugation, or other physical methods (reference 2).

10.1.7 Dry the total combined solvent extract by pouring it through an anhydrous Na_2SO_4 drying column (approximately 30 cm x 2 cm). Use approximately 30 mL of CH_2Cl_2 to rinse the drying column and combine this with the dried extract. Collect the extract in a Kuderna-Danish (K-D) 500-mL evaporation flask containing 1 to 2 clean boiling chips.

10.1.8 Attach a 3-ball macro Snyder column to the K-D evaporation flask and concentrate the extract on an 80° C water bath. Pre-wet the Snyder column by adding about 1 mL of CH_2Cl_2 to the top of the column. Place the K-D apparatus on the hot water bath 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. 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 reaches 5 mL, remove the K-D apparatus from the water bath and rinse the flask with 3 mL CH_2Cl_2 draining into the concentrator tube. Reduce the contents of the concentrator tube to 3 mL using a stream of purified N_2 gas, never allowing the extract to go to dryness.

10.1.9 Alternative methods of extract concentration may be used if evidence of acceptable performance [i.e., retention of more volatile compounds (e.g., naphthalene) comparable to that of K-D concentration] is provided.

10.1.11 Elemental sulfur removal - Mercury cleanup is required to remove elemental sulfur, which interferes with GC/MS and GC/ECD analyses, from the extract. Some losses of benzidine and endrin aldehyde may occur in this step.

10.1.11.1 Transfer the extract to a clean, screw-capped test tube and shake vigorously with approximately 0.5 mL precleaned mercury for at least 4 h. Filter the desulfurized extract to remove metallic mercury and its salts. Shake the test tube and mercury with 1-2 mL of CH_2Cl_2, rinse the filter with this solvent, and combine the rinsing with the desulfurized extract. This process may have to be repeated for samples with high sulfur content.

Alternatively, mercury treatment could be performed more quickly by vigorous agitation for several minutes on a vortex mixer. A potential problem with this technique is that the mercury could become so finely dispersed that it would pass through the filter. Vortex mixers may be used only if appropriate method performance can be demonstrated (e.g., mercury should not pass through the filter).

10.1.11.2 Another commonly used method of sulfur removal, elution through an activated copper column, may not be a suitable substitute for mercury treatment because copper may strongly retain some polar analytes.

10.1.12 Extract cleanup - GPC cleanup is required to separate biological macromolecules from the analytes.

10.1.12.1 GPC setup and calibration (reference 2).

10.1.12.1.1 Place 70 g of Bio Beads S-X3 in a 400-mL beaker. Cover the beads with CH_2Cl_2. Allow the beads to swell overnight. Transfer the swelled beads to the column and start pumping solvent through the column, from bottom to top, at 5 mL/min. After 1 h, adjust the pressure on the column to 7-10 psi and pump for an additional 4 h to remove air from the column. Adjust the column pressure as required to maintain 7-10 psi.

10.1.12.1.2 Calibration of the column - Load 5 mL of the corn oil solution into sample loop No. 1 and 5 mL of the phthalate-PCP solution into loop No. 2. Inject the corn oil solution and collect 10 mL fractions for 36 min. Determine the corn oil elution pattern by evaporation of each fraction to dryness followed by a gravimetric determination of the residue. Analyze the phthalate-PCP fractions by GC/FID, a UV-spectrophotometer at 254 nm, or a GC/MS system. Plot the concentration of each component in each fraction versus total eluant volume. Choose a "dump time" that allows $\geq$85% removal of the corn oil and $\geq$85% recovery of the phthalate. Select the "collect time" to extend at least 10 min after the elution of pentachlorophenol. Wash the column for at least 15 min between samples. Typical parameters are: dump time, 30 min (150 mL); collect time, 36 min (180 mL); and wash time, 15 min (75 mL). The S-X3 Bio Beads column may be reused for several months, but should be checked by system recalibration for every 20 extracts loaded onto the GPC.

10.1.12.2 Extract cleanup - Prefilter or load all extracts via the filter holder to avoid particulates that might cause system blockage. Load the extract (approximately 3 mL) onto the GPC column. Do not apply

excessive pressure when loading the GPC. Purge the sample loading tubing horoughly with solvent between extracts. Process the extracts using the dump, collect, and wash parameters as selected from the calibration and collect the cleaned extracts in 400-mL beakers.

10.1.12.3 Rerun the phthalate-PCP calibration solution to check and recalibrate the system once for every 20 extracts loaded onto the GPC. The recoveries and elution profiles are reported as deliverables.

10.1.13 Transfer the extract to a Kuderna-Danish (K-D) concentrator consisting of a 10-mL concentrator tube, a 500-mL evaporation flask, boiling chips, and a Snyder column. Carefully concentrate the extract to 2.5 mL using methods previously described and the N_2 gas blowdown technique. Nitrogen blowdown should be performed at approximately 35^{o} C. A gentle stream of clean, dry N_2 (filtered through a column of activated carbon) should be used. The inside walls of the tube containing the extract should be rinsed down with the appropriate solvent several times during concentration. The extract must not be allowed to go to dryness.

10.1.14 Use a 20% aliquot (500 uL) of the extract for alumina column cleanup (Sect. 10.1.15) and subsequent GC/ECD analysis for pesticides and PCBs. Use the remaining 80% (2 mL) for GC/MS analysis. If the sediment sample appears contaminated with petroleum or was collected from an area of known or suspected petroleum contamination (e.g., most nearshore environments near urban or industrial centers) a further extract cleanup is required prior to GC/MS analysis. SPE column cleanup (Sect. 10.1.16) removes some of the paraffinic hydrocarbon constituents that contribute to the unresolved complex mixture (UCM) typically observed in gas chromatograms of petroleum extracts.

10.1.14.1 Solvent exchange of extract for alumina cleanup (reference 2) - transfer 0.5 mL of the extract to a separate concentrator tube. Add 5 mL of hexane and a boiling chip and mix using a 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 min. Concentrate the extract to an apparent volume of approximately 1 mL. Use N_2 blowdown to reduce the volume to 0.5 mL. Dilute to 1 mL by adding 0.5 mL of acetone. Proceed with alumina column cleanup.

10.1.15 Alumina column setup and use - The alumina column cleanup is required to remove polar interferences prior to GC/ECD analysis of pesticides and PCBs (reference 2).

10.1.15.1 Add 3 g of activity III neutral alumina to the clean, 5-mL disposable serological pipet (with glass wool plug). Tap the column to settle the alumina. Do not prewet the alumina with solvent.

10.1.15.2 Transfer the 1.0 mL hexane/acetone extract (Sect. 10.1.14.1) to the top of the alumina column with a disposable Pasteur pipet. Collect the eluate in a 10 mL K-D concentration tube. 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.

10.1.15.3 Note that batches of alumina may differ and storage may alter the water content of deactivated alumina. Thus, column performance must be checked regularly and for each batch of alumina. PCB and pesticide standards (e.g., from Sect. 6.8.2.2, 6.8.3) and a suitable model polar compound (e.g., tribromophenol) should be used to determine the appropriate elution volumes for these pollutants. Recovery of single PCB or pesticide components should be greater than 85% and the tribromophenol should not be detected.

10.1.15.4 Concentrate the eluate to a final volume of 500 uL using a micro-Snyder column and the N_2 gas blowdown technique.

10.1.15.5 Care must be taken to allow the N_2 gas to create only a small dimple on the surface of the solvent and prevent blowdown to dryness. Submit extract for GC/ECD analyses.

10.1.16 SPE or reverse phase column cleanup - used to reduce or eliminate the interferences caused by chromatographically unresolvable, nonpolar petroleum constituents. While this procedure enhances the sensitivity of GC/MS analyses for many pollutants, it can also result in only partial recovery of some potential analytes (e.g., dichlorobenzenes, chlorinated butadienes, certain PCB congeners) from the extract because the interferents removed in this step partially co-elute with these compounds. These partial recoveries should be assessed with standards prior to routine use of SPE columns. Elution volumes may be adjusted to optimize recoveries while reducing the UCM as much as possible. The use of the isotope dilution technique will enable correction for losses of compounds with labeled analogs.

10.1.16.1 Exchange the 2 mL extract into MeOH as follows: Use the N_2 blowdown technique to reduce the extract volume to approximately 0.5 mL. Add 3 mL of MeOH to the extract and carefully reduce the volume to 1 mL using the N_2 gas blowdown technique. Repeat this procedure to ensure that the extract is adequately exchanged from CH_2Cl_2 to MeOH. The presence of even a small amount of CH_2Cl_2 will reduce the polarity differences between liquid and solid phases that control the chromatographic process and will thus allow carryover of interferents into the final extract.

10.1.16.2 Condition the SPE column with three column volumes of methanol prior to applying the extract. It is also recommended that 10 mL of 0.5% HCl (pH 2-3) be eluted through the column after methanol elution. Although not discussed by the manufacturer, this cleanup step has been reported to be effective at reducing residual contamination (R.J. Ozretich and W.P. Schroeder. Submitted for publication. "Determination of Priority Organic Pollutants in Marine Sediment, Tissue, and Reference Materials Utilizing Bonded-phase Sorbents". Analytical Chemistry).

10.1.16.3 Place a K-D concentrator tube beneath the column prior to applying the extract. Apply and draw the 1-mL extract (in MeOH) to the top of the column, followed by a 0.5-mL rinse of MeOH from the concentrator tube. Elute additional MeOH until a total of 7 mL is collected in the K-D concentrator tube.

10.1.16.4 Exchange and concentrate the eluate to a final volume of 0.4 mL (in CH_2Cl_2). Care must be taken to avoid the loss of volatile pollutants during concentration. Use CH_2Cl_2 and the N_2 gas blowdown technique to adjust the final volume.

Methanol is not an ideal solvent for solvent exchange because of its low volatility relative to many organic analytes. It is possible that acetone (because of its polarity and relatively high volatility) would be a favorable substitute for methanol for the reverse phase column cleanup step. However, acetone has not been tested and no validation data are available.

10.1.16.5 Submit the extract for GC/MS analysis.

10.2 GC/MS Analysis

10.2.1 Establish the following operating conditions for the GC (Table I-1): 5 min at 30° C; 30-280° C at 8° C/min; isothermal at 280° C until benzo(g,h,i)perylene elutes. Make certain that the concentrated extract or standard is at room temperature and make note of any precipitate that does not redissolve.

10.2.2 Add 5 uL of the GC/MS internal standard solution to the 400 uL extract to yield a 10 ug spike. Add the solution immediately prior to injection to minimize the possibility of loss by evaporation, adsorption, or reaction. Mix thoroughly.

10.2.2.1 It is advised that a late eluting internal injection standard (e.g., 5-alpha-cholestane) be used in addition to DFB. The use of

early eluting (DFB) and late eluting injection standards will allow the analyst to detect and compensate for problems in the GC injection port related to differential loading of analytes onto the GC column.

10.2.3 Inject 1.0-1.5 uL and start the GC column initial isothermal hold. Start MS data collection after the solvent peak elutes. Stop data collection after the benzo(g,h,i)perylene elutes.

10.2.3.1 Dilution and re-injection are required for samples that exceed the upper concentration limit of the calibration standards. Data for compounds within the calibration range should be acquired in the initial run. Data for compounds exceeding the calibration range should be acquired after dilution. Respike the sample with labeled compounds and assume 100 percent recovery. This assumption is not unreasonable considering the high concentrations of native compounds involved when dilution is necessary.

10.3 GC/ECD Analysis

10.3.1 The recommended GC conditions are modified from those specified in reference 2:

Helium carrier gas: 4 mL/min at 280° C and 25 psi
Septum purge: 15 mL/min
Split vent: none
Initial temperature: 60° C, initial hold - 2 min
Program at 25° C/min to 160° C
Program at 5° C/min from 160° C
Final temperature: 270° C;
hold until decachlorobiphenyl elutes
Injection port temperature: 225° C

10.3.2 Add 10 uL of the GC/ECD internal standard solution to the 500 uL extract to yield a 25 ng spike. Add the solution immediately prior to injection to minimize the possibility of loss by evaporation, adsorption, or reaction. Mix thoroughly. Inject 1.0-1.5 uL.

10.3.3 Dilution and re-injection are required for samples that exceed the upper concentration limit of the calibration standards. Data for compounds within the calibration range should be retained from the initial run. Data for compounds exceeding the calibration range should be acquired after dilution.

Column overloading can result in abnormal peak shape, which can reduce the accuracy of quantification. It may also result in a marked increase in the retention time of the peak maximum, which can displace an analyte from the retention time window established with standards at lower concentrations.

10.4 Qualitative Determination

10.4.1 Qualitative determination is accomplished by comparison of data from analysis of a sample or blank with data from analysis of the shift standard (Sect. 9.9.1) and, for GC/MS analyses, with data stored in the spectral libraries (Sect. 8.2.4). Identification is confirmed when spectra and retention times agree per the criteria below.

10.4.2 Labeled compounds and pollutants having no labeled analog:

10.4.2.1 The signals for all characteristic masses stored in the spectral library (Sect. 8.2.4) should be present and should maximize within the same two consecutive scans.

10.4.2.2 Either 1) the background corrected extracted ion current profile (EICP) areas, or 2) the corrected relative intensities of the mass spectral peaks at the GC peak maximum should agree within a factor of two (0.5 to 2 times) for all masses stored in the spectral library.

10.4.2.3 The retention time difference between an analyte and the nearest eluting internal standard during sample analysis should be within ± 5 scans or ± 5 sec (whichever is greater) of this difference in the shift standard (Sect. 9.9.1).

10.5 Pollutants Having a Labeled Analog:

10.5.1 The signals for all characteristic masses stored in the spectral library (Sect. 8.2.4) should be present and should maximize within the same two consecutive scans.

10.5.2 Either 1) the background corrected EICP areas, or 2) the corrected relative intensities of the mass spectral peaks at the GC peak maximum should agree within a factor of two for all masses stored in the spectral library.

10.5.3 The retention time difference between the pollutant and its labeled analog should agree within $\pm$2 scans or $\pm$2 sec (whichever is greater) of this difference in the shift standard (Sect. 9.9.1).

10.6 If an experimental mass spectrum contains masses that are not present in the reference mass spectrum, an experienced spectrometrist is to determine the presence or absence of the compound.

10.7 Chlorinated Pesticides and PCBs

10.7.1 Single component chlorinated pesticides are tentatively identified by comparison of sample peak relative retention times to those of authentic standards (Sect. 6.8.3). Three times the standard deviation of relative retention times established from calibration standards (Sect. 6.8.3) can be used to calculate relative retention time window boundaries. Confirm the identities of pesticides by comparing the relative retention times of sample and standard peaks on another column phase (e.g., 86% dimethyl[14%]-cyanopropyl phenyl polysiloxane or J&W DB-1701). Confirmation by GC/MS is required when concentrations are sufficient.

10.7.2 Peaks of multi-component mixtures (PCBs and toxaphene) are tentatively identified in samples by comparison of relative retention times to those of authentic standards (Sect. 6.8.2.2 and 6.8.4). Three times the standard deviation of relative retention times established from standards

can be used to calculate relative retention time window boundaries. Choose as many peaks as possible while avoiding those with potential interferences (e.g., PCBs co-eluting with DDT and DDE isomers). Label on all sample chromatograms the peaks identified as PCB and toxaphene congeners. All GC/ECD chromatograms are part of the deliverables. Interpretation of chromatograms requires the attention of an experienced analyst. Chromatograms of individual Aroclors (e.g., 1242, 1254, 1260 in three separate standards) may facilitate interpretation. Confirm the identities of all selected congeners by injection on an alternative column phase (e.g., J&W DB-1701). Confirmation by GC/MS is required if concentrations are sufficient.

10.8 Tentatively Identified Compounds (GC/MS Analysis) - The ten non-target peaks of greatest area in the RIC (reconstructed ion chromatogram) should be identified and quantified, if possible.

10.8.1 Guidelines for making tentative identification (reference 2):

1) Tentative identifications should be based on a forward search of the EPA/NIH mass spectral library. Sample spectra should be visually compared with the most similar library match.

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

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

4) Molecular ions present in reference spectrum should be present in sample spectrum.

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.

10.8.1.1 If, in the opinion of the mass 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 (e.g., unknown phthalate, unknown hydrocarbon, unknown aromatic compound, unknown chlorinated compound). If probable molecular weights can be distinguished, include them.

10.8.2 Tentative quantification - quantification of TICs will be based on the internal standard technique and an assumed response factor of one (in the absence of data from authentic standards). The uncertain nature of this quantification should be clearly noted in the data report.

11.0 QUANTITATIVE DETERMINATION (CALCULATIONS)

11.1 Isotope Dilution Technique - by adding a known amount of a labeled compound to every sample prior to extraction, correction for losses of the pollutant during the analysis can be made because the pollutant and its labeled analog exhibit similar behavior during extraction, concentration, and gas chromatography. Note that pollutants and their labeled analogs are not always retained identically by complex matrices, so their behavior during the extraction step may differ. It is not the intention of this technique to account for matrix recovery efficiency, only for subsequent analytical recovery efficiency.

11.1.1 Relative response (RR) values for sample mixtures are used in conjunction with calibration curves described in Sect. 8.4 to determine concentrations directly, so long as labeled compound spiking levels are constant.

11.1.2 Specifically, the concentration, C(in ug/kg), can be determined as:

$$C(ug/kg) = \frac{C_A(ug/kg) \times RR \times n}{\sum_{i=1}^{n} \left(\frac{RR_i \times Z_{Ai}}{Z_i} \right)}$$

where:

C_A = the concentration of the stable isotope-labeled compound as spiked into the sample, dry weight

RR = relative response of unlabeled pollutant to isotope labeled surrogate in the sample

RR_i = relative response of i^{th} point in calibration

Z_i = absolute amount of unlabeled compound of i^{th} point in calibration

Z_{Ai} = absolute amount of labeled compound of i^{th} point in calibration

n = number of calibration points.

11.2 Internal Standard - all data reported as determined by this method are uncorrected for method recoveries.

11.2.1 GC/MS internal standards method - Compute the concentration in the sample, C (in ug/kg), using the response factor, RF (Sect. 8.5.1), determined from calibration data, and the following equation:

$$C(ug/kg) = (A_x \times Z_{is} \times 1.25 \times 10^3)/(S \times A_{is} \times RF)$$

where:

A_x = the area at the characteristic mass for the compound in the sample

A_{is} = the area of the characteristic mass for the internal standard

Z_{is} = the absolute amount, in ug, of the GC/MS internal standard added to the final extract prior to instrumental analysis

S = sample dry weight (g) that was extracted.

This technique is not preferred and is unnecessary if the nearest eluting, most chemically similar labeled compound is used as a recovery standard for pollutants without available labeled analogs.

11.2.1.1 The stable isotope labeled compound recovery, X, is determined and reported for each sample in the following manner:

$$X = [C(ug/kg)/C_A(ug/kg)] \times 100\%$$

where C and C_A are as defined in Sections 11.2.1 and 11.1.2, respectively.

11.2.2 GC/ECD internal standard method

11.2.2.1 Pesticides - compute the concentration in the sample, C (in ug/kg), using the response factor (RF, determined from calibration data) and the following equation:

$$C(ug/kg) = (A_x \times Z_{is} \times 5 \times 10^3)/(S \times A_{is} \times RF)$$

where:

A_x = the area of the integrated GC peak for the compound in the sample (A_x represents the summation of areas for a group of GC peaks if toxaphene is being quantified)

A_{is} = the area of the integrated GC peak for the internal standard

Z_{is} = the absolute amount, in ug, of the GC/ECD internal standard added to the final extract prior to instrumental analysis

S = the sample dry weight (g) that was extracted.

11.2.2.2 PCBs - accurate PCB quantification is difficult to achieve in routine full-scan analyses. It has been common practice to quantify PCBs with packed-column GC/ECD by comparing several selected peaks in samples to corresponding peaks in commercial Aroclor formulations that most closely resemble the sample. Shortcomings of this technique have been described elsewhere (e.g., references 8 and 9). The critical difficulties with this

procedure relate to two factors: (1) environmental PCB assemblages often differ considerably from commercial Aroclor mixtures because of the variable properties of PCB congeners (e.g., aqueous solubility, volatility, susceptibility to biodegradation) and (2) the ECD has a markedly variable response to the 209 PCB congeners depending on the number and position of chlorine atoms on the biphenyl nucleus (e.g., reference 10).

It has been suggested that "the least systematic error [in PCB quantification] will be given by the summation of all or at least nearly all areas of PCB peaks corrected by their individual ECD-response factor and their biphenyl content" (reference 11). Another alternative is to use GC/MS instead of GC/ECD. However, GC/MS analysis is relatively insensitive unless selected ion monitoring (SIM) is used, which can involve considerable effort and expense.

The quantification technique recommended in this 301(h) document relies on high resolution (capillary column) GC/ECD and a determination of response factors for resolvable PCB peaks (as suggested in the previous paragraph). The technique is modified from the Webb and McCall technique (reference 12), which has been widely used for packed-column PCB quantification. Briefly, the resolved peaks in a PCB standard (Sect. 6.8.2.1, 6.8.2.2) are quantified by GC/MS and GC/ECD. The GC/MS results are used to correct for the variability of ECD response. Samples are analyzed and quantified by GC/ECD. Total PCBs are calculated as the sum of all resolved, response factor-corrected PCB peaks.

11.2.2.2.1 GC/MS analysis of PCB standard - each resolvable peak in a PCB calibration standard (Sect. 6.8.2.1) is quantified by GC/MS, which can identify the chlorine content of biphenyls in each peak and can quantify PCBs based on their chlorine content. This quantification does not require that the analyst know the exact identity of the congeners constituting a peak, only the chlorine content must be determined.

Another GC/MS calibration standard is necessary to perform this quantification. An MS response factor standard consisting of representatives of all the congener groups (mono- through deca-chlorobiphenyl) is necessary to convert areas of peaks in ion plots to the appropriate masses of chloro-

biphenyls. A standard solution should be made with approximately 10 ng/uL of each of the following congeners (see reference 13 for an explanation of these choices):

2
2,3
2,4,5
2,2',4,6
2,2',3,4,5'
2,2',4,4',5,6'
2,2',3,4',5,6,6'
2,2',3,3',4,5',6,6'
2,2',3,3',4,4',5,5',6,6' - (used for nona- and deca-congeners).

These congeners are available from Ultra Scientific, Inc. (Hope, RI) except the heptachloro-congener, which is available from Wellington Environmental Consultants, Inc. (Guelph, Ontario, Canada). The primary quantification ions used for mono- through deca-chlorobiphenyl are: 188, 222, 256, 292, 326, 360, 394, 430, 464, and 498. The spectrum for each peak should be manually confirmed at least once for the Aroclor standard.

Relative amounts of co-eluting congeners of different chlorine content in a given peak in the standard can be determined during GC/MS analysis. Co-elution can be accounted for with appropriate response factors. For example, if a peak is composed of tetrachloro- and pentachloro-isomers as determined by ion plots of m/z 292 and 326, the 2,2',4,6 response factor is used for the m/z 292 area and the 2,2',3,4,5' response factor for the m/z 326 area. Care must be taken to ensure that M-70 ions are not interpreted as M+ ions if congeners differing by two chlorine atoms co-elute.

11.2.2.2.2 GC/ECD analysis of PCB standard (Sect. 6.8.2.2) - each resolvable peak in the PCB calibration standard is quantified by GC/ECD according to the internal standard technique (Sect. 8.5). The GC/ECD analysis is performed with the same GC column phase and temperature program used for GC/MS analysis of the standard. An ECD response factor is established for

GC/MS analysis of the standard. An ECD response factor (RF) is established for each peak based on the GC/MS analysis of the PCB standard using the equation defined in Section 8.5.1

where:

C_s = the mean concentration of the peak in the PCB standard as determined by GC/MS (determined with at least three replicate analyses).

11.2.2.2.3 GC/ECD PCB quantification in samples - total PCBs are calculated as the sum of all PCB peaks identified in a sample (Sect. 10.7.2):

$$C \text{ (ug/kg, dry wt)} = \sum_{i=1}^{n} [(A_x \times Z_{is} \times 5 \times 500)/(S \times A_{is} \times RF)]_i$$

where:

i = each identified PCB peak, with n total peaks
A_x = area of the integrated GC peak for the compound in the sample
A_{is} = area of the integrated GC peak for the internal standard
Z_{is} = the absolute amount, in ug, of the GC/ECD internal standard added to the final extract prior to instrumental analysis
S = the sample dry weight (g) extracted
RF = calibration response factor (Sect. 8.5.1).

11.2.2.2.4 This quantification method involves two noteworthy imitations:

(1) Interferences can be a significant problem in ECD analyses. PCB peaks co-eluting with interferents may be neglected or quantified, in either case resulting in a decrease in accuracy. It is essential that experienced analysts evaluate chromatograms to determine the presence of suspected interferents. Interferents suspected of overwhelming PCB peaks should be neglected. The mercury and alumina column cleanup steps are designed to preclude major interferences. High resolution capillary columns also reduce the potential for co-eluting interferences.

(2) When two or more congeners have identical retention times on a given column phase, it is impossible to determine their relative concentrations in a peak when using GC/ECD. Thus, it is not possible to determine whether sample peaks are composed of the same relative combination of congeners as corresponding standard peaks. Thus, the response factor for a peak may be different during calibration and sample analysis. The potential error in assigning appropriate reponse factors has been minimized in this technique by the use of high resolution capillary columns.

11.2.2.2.5 Alternative techniques of detection [e.g., Hall electrolytic conductivity detector (HECD) or MS (with selected ion monitoring)] can provide comparable or superior PCB identification and quantification relative to ECD (e.g., references 13 and 14) and are acceptable substitutes for ECD detection. Although ECD is widely available and is more sensitive for PCBs than HECD or MS, HECD has a linear response to chlorine content and is more specific to chlorinated compounds, and MS offers more definitive compound identification than ECD.

11.2.2.3 Quantify PCBs by summing the response factor-corrected areas of the characteristic PCB peaks identified in Sect. 10.7.2. Report the results as total PCBs.

11.3 Report results for all pollutants and labeled compounds found in all standards and samples, in ug/kg, to two significant figures. Note in the report all compounds that have not been recovery corrected. Report results for blanks as total ng/sample.

12.0 PRECISION AND ACCURACY

Laboratory intercomparison studies of the precision and accuracy attainable with this technique will be required. Available precision data for single laboratory analyses of a series of contaminated estuarine sediments are given in Table I-3 (data from reference 15). In these analyses, spiking levels for base/neutral compounds were lower than those recommended in this protocol (i.e., 5 ug spike instead of 10 ug), and methanol was not added directly to the extraction thimble as now recommended in Sect. 10. PCB results were generated by packed column analysis and comparison of sample chromatograms to Aroclor standards. The accuracy of these PCB analyses was not assessed. Validation data using the PCB quantification procedure in this 301(h) document has not yet been generated.

In a recent method test using the same procedure, replicate blanks were spiked with known amounts of labeled and unlabeled compounds. The blanks were then taken through the entire procedure and the amounts of the unlabeled compounds were calculated using the isotope dilution technique (i.e., the calculated amounts of the unlabeled compounds were adjusted for the recovery of the labeled compounds). The ratio of the calculated amount of the unlabeled compounds relative to their actual spiked amount (expressed as percent) is given in Table I-4. The precision and accuracy results for blanks (Table I-4) compare favorably with acceptance criteria in Method 1625 Revision B. Compounds outside acceptance criteria for either precision or accuracy include: benzidine, bis(2-chloroisopropyl) ether, bis(2-chloroethoxy) methane, hexachlorocyclopentadiene, N-nitrosodiphenylamine, N-nitrosodipropylamine,

N-nitrosodimethylamine, and butylbenzyl phthalate. The spike level used in hese preliminary tests was less than 0.1 that in Method 1625 and the analytical procedure requires several stages of sample cleanup (none is required in Method 1625 Revision B).

13.0 REFERENCES

1. "Performance Tests for the Evaluation of Computerized Gas Chromatography/-Mass Spectrometry Equipment and Laboratories," USEPA, EMSL/Cincinnati, OH 45268, EPA-600/4-80-025 (April 1980).

2. U.S. Environmental Protection Agency. 1984 (revised January, 1985). U.S. EPA Contract Laboratory Program - statement of work for organics analysis, multi-media, multi-concentration. IFB WA 85-J176, J177, J178.

3. Fed. Register, Vol. 49, No. 209, October 26, 1984, pp. 43416-43429.

4. "Carcinogens - Working with Carcinogens," DHEW, PHS, CDC, NIOSH, Publication 77-206 (Aug 1977).

5. "OSHA Safety and Health Standards, General Industry," OSHA 2206, 29 CFR 1910 (revised Jan 1976).

6. "Safety in Academic Chemistry Laboratories," ACS Publications, Committee on Chemical Safety, 3rd Edition (1979).

7. Eichelberger, J.W., L.E. Harris, and W.L. Budde, "Reference compound to calibrate ion abundance measurement in gas chromatography-mass spectrometry," Anal. Chem. Vol. 47, 1975, pp. 995-1000.

8. Duinker, J.C., M.T.J. Hillebrand, K.H. Palmork, and S. Wilhelmsen, "An evaluation of existing methods for quantitation of PCBs in environmental samples and suggestions for an improved method based on measurement of individual components," Bull. Environm. Contam. Toxicol. Vol. 25, 1980, pp. 956-964.

9. Alford-Stevens, A.L., W.L. Budde, and T.A. Bellar, "Interlaboratory study on determination of PCBs in environmentally contaminated sediments," Anal. Chem. Vol. 57, 1985, pp. 2452-2457.

10. Mullin, M.D., C.M. Pochini, S. McCrindle, M. Romkes, S.H. Safe, and L.M. Safe, "High-resolution PCB analysis: synthesis and chromatographic properties of all 209 PCB congeners," Environ. Sci. Technol. Vol. 18, 1984, pp. 468-476.

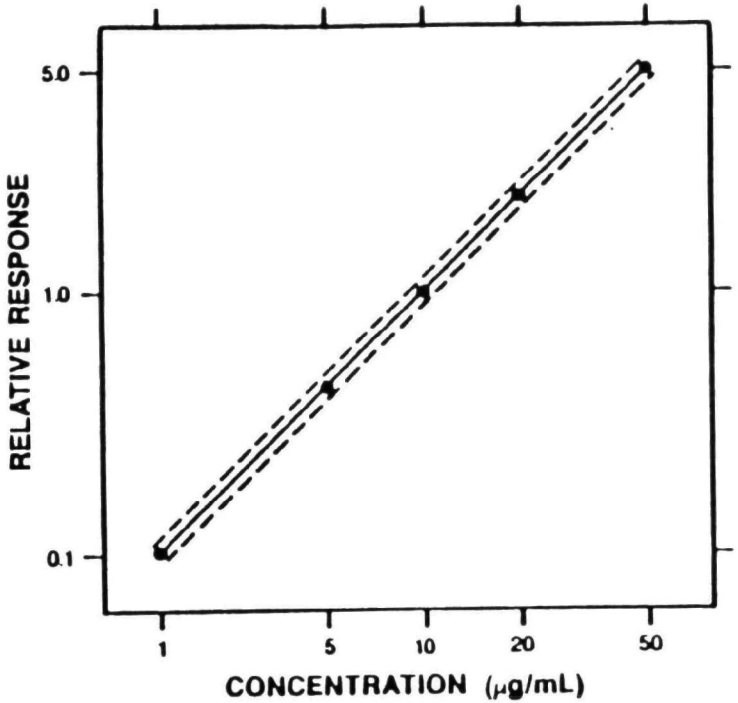
11. Ballschmiter, K., and M. Zell, "Analysis of PCB by glass capillary gas chromatography," Fresenius Z. Anal. Chem. Vol. 302, 1980, pp. 20-31.

12. Webb, R.G., and A.C. McCall, "Quantitative PCB standards for electron capture gas chromatography," J. Chromatographic Science, Vol. 11, 1973, pp. 366-373.

13. Gebhart, J.E., T.L. Hayes, A.L. Alford-Stevens, and W.L. Budde, "Mass spectrometric determination of polychlorinated biphenyls as isomer groups," Anal. Chem. Vol. 57, 1985, pp. 2458-2463.

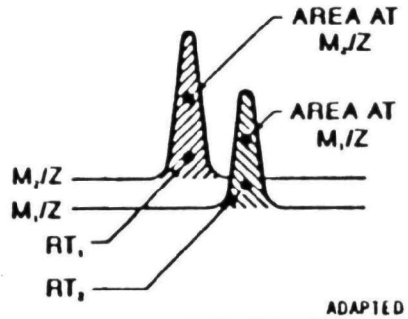
14. Sonchik, S., D. Madeleine, P. Macek, and J. Longbottom, "Evaluation of sample preparation techniques for the analysis of PCBs in oil," J. Chromatographic Science, Vol. 22, 1984, pp. 265-271.

15. Tetra Tech, Inc. Commencement Bay nearshore/tideflats remedial investigation. Vol. 1. Final report prepared for the Washington State Department of Ecology and U.S. Environmental Protection Agency. 1985.



ADAPTED FROM REFERENCE 3

1.



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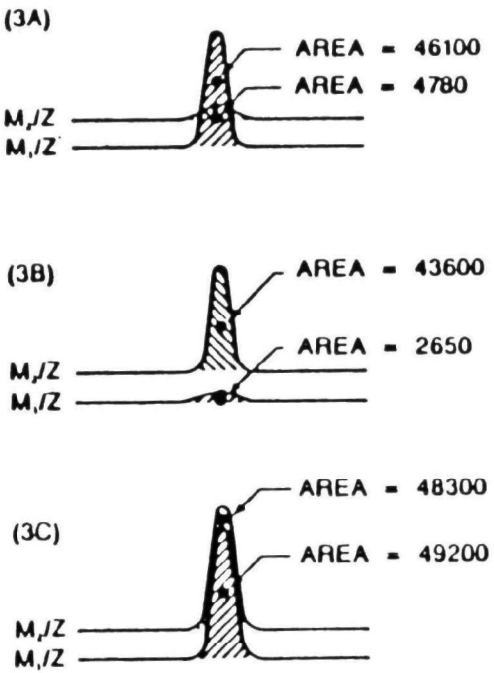
2.



ADAPTED FROM REFERENCE 3

3.

Figure I-1. Relative response calibration curve.
Figure I-2. Extracted ion current profiles for chromatographically resolved labeled (m_2/z) and unlabeled (m_1/z) pairs.
Figure I-3. Extracted ion current profiles for (3A) unlabeled compound, (3B) labeled compound, and (3C) equal mixture of unlabeled and labeled compounds.

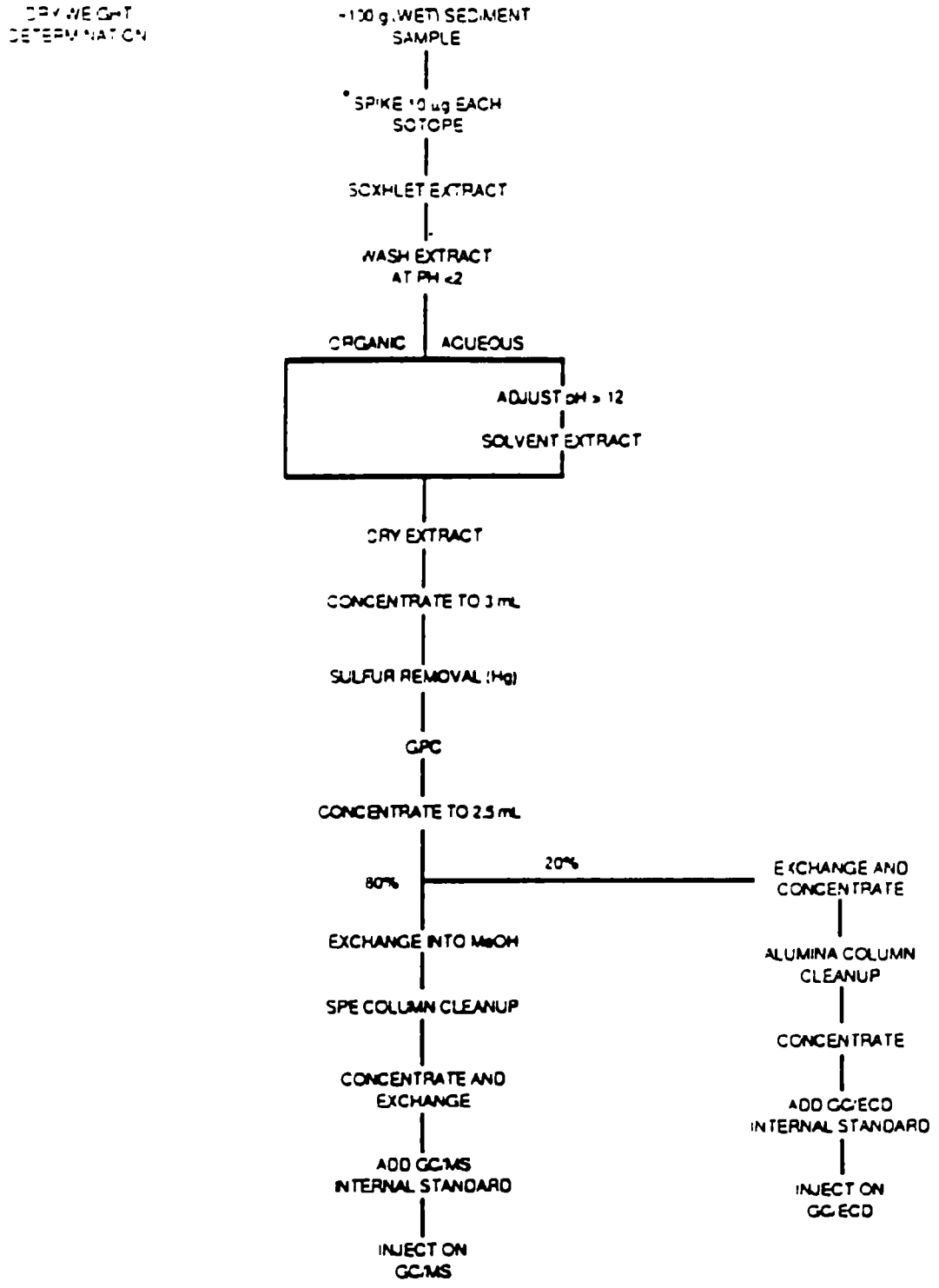


Figure I-4. Flow chart for sample preparation.

TABLE I-1. GAS CHROMATOGRAPHY OF EXTRACTABLE COMPOUNDS

Compound	Retention Time Sec	Relative[a]	Quantitation (Primary) m/z	Instrumental Sensitivity (ng) GC/MS	ODES	CASRN
2,2'-difluorobiphenyl (DFB)	1163	1.000	190	1		
N-nitrosodimethylamine	385	0.330	74	5	NNOMA	62-75-9
phenol-d_5[1]	696	0.600	71	1		
phenol	700	1.003	94	1	PHENOL	108-95-2
bis(2-chloroethyl)ether-d_8	696	0.596	101	1		
bis(2-chloroethyl)ether	704	1.012	93	1	BCEE	111-44-4
1,3-dichlorobenzene-d_4	722	0.621	152	1		
1,3-dichlorobenzene	724	1.003	146	1	13-2CLBNZ	541-73-1
1,4-dichlorobenzene-d_4	737	0.634	152	1		
1,4-dichlorobenzene	740	1.004	146	1	14-2CLBNZ	106-46-7
1,2-dichlorobenzene-d_4	758	0.652	152	1		
1,2-dichlorobenzene	760	1.003	146	1	12-2CLBNZ	95-50-1
bis(2-chloroisopropyl)ether-d_{12}	788	0.678	131	1		
bis(2-chloroisopropyl)ether	799	1.014	121	1	B2CIE	108-60-1
hexachloroethane-^{13}C[2]	819	0.704	204	1		
hexachloroethane	823	1.005	201	1	6CLETH	67-72-1
N-nitrosodi-n-propylamine	830	0.714	70	2	NNONPRA	621-64-7
nitrobenzene-d_5	845	0.726	128	1		
nitrobenzene	849	1.005	123	1	NBNZ	98-95-3
isophorone-d_8	881	0.757	88	1		
isophorone	889	1.009	82	1	ISOPHORONE	78-59-1
2,4-dimethylphenol-d_3	921	0.792	125	1		
2,4-dimethylphenol	924	1.003	122	1	24-2MPHN	105-67-9
bis(2-chloroethoxy)methane	939	0.807	93	1	BCEOM	111-91-1
1,2,4-trichlorobenzene-d_3	955	0.821	183	1		
1,2,4-trichlorobenzene	958	1.003	180	1	124-3CLBNZ	120-82-1
naphthalene-d_8	963	0.828	136	1		
naphthalene	967	1.004	128	1	NAPHTHALENE	91-20-3
hexachlorobutadiene-$^{13}C_4$	1005	0.864	231	1		
hexachlorobutadiene	1006	1.000	225	1	6CLBUTAD	87-68-3
hexachlorocyclopentadiene-$^{13}C_4$	1147	0.986	241	3		
hexachlorocyclopentadiene	1142	0.996	237	3	6CLCYCPEN	77-47-4
2-chloronaphthalene-d_7	1185	1.019	169	1		
2-chloronaphthalene	1200	1.013	162	1	2-CLNAP	91-58-7
biphenyl-d_{10}	1205	1.036	164	1		
biphenyl	1211	1.005	154	1	BIPHENYL	92-52-4
acenaphthylene-d_8	1245	1.071	160	1		
acenaphthylene	1247	1.002	152	1	ACENAPTYLE	208-96-8
dimethylphthalate-d_4	1269	1.091	167	1		
dimethylphthalate	1273	1.003	163	1	DMP	131-11-3
2,6-dinitrotoluene-d_3	1283	1.103	167	2		
2,6-dinitrotoluene	1300	1.013	165	2	26-2NTOL	606-20-2
acenaphthene-d_{10}	1298	1.116	164	1		
acenaphthene	1304	1.005	154	1	ACENAPE	83-32-9
dibenzofuran-d_8	1331	1.144	176	1		
dibenzofuran	1335	1.003	168	1	DIBNZFURAN	132-64-9
fluorene-d_{10}	1395	1.119	176	1		
fluorene	1401	1.004	166	1	FLUORENE	86-73-7
4-chlorophenylphenyl ether-d_5	1406	1.209	209	1		
4-chlorophenylphenyl ether	1409	1.002	204	1	4CPPE	7005-72-3
diethyl phthalate-d_4	1409	1.211	153	1		
diethyl phthalate	1414	1.004	149	1	DEP	84-66-2
2,4-dinitrotoluene-d_3	1344	1.156	168	2		
2,4-dinitrotoluene	1359	1.011	165	2	24-2NTOL	121-14-2
1,2-diphenylhydrazine-d_8	1433	1.232	82	1		
1,2-diphenylhydrazine[3]	1439	1.004	77	1	12-2PHHYZ	122-66-7

TABLE I-1. (Continued)

diphenylamine-d_{10}	1437	1.236	179	1		
diphenylamine	1439	1.001	169	1	DPA	122-39-4
N-nitrosodiphenylamine-d_6	1438	1.236	175	1		
N-nitrosodiphenylamine	1439	1.001	169	1	NNP	86-30-6
4-bromophenyl phenyl ether	1498	1.288	248	1	4-BPPE	101-55-3
hexachlorobenzene-$^{13}C_6$	1521	1.308	292	1		
hexachlorobenzene	1522	1.000	284	1	6CLBNZ	118-74-1
phenanthrene-d_{10}	1578	1.357	188	1		
phenanthrene	1583	1.003	178	1	PHENANTHRN	85-01-8
anthracene-d_{10}	1588	1.365	188	1		
anthracene	1592	1.003	178	1	ANTHRACENE	120-12-7
dibenzothiophene-d_8	1559	1.340	192	1		
dibenzothiophene	1564	1.003	184	1	DIBNZTHIO	132-75-0
carbazole	1650	1.419	167	3	CARBAZOLE	86-74-2
di-n-butyl phthalate-d_4	1719	1.478	153	1		
di-n-butyl phthalate	1723	1.002	149	1	DINBP	84-74-2
fluoranthene-d_{10}	1813	1.559	212	1		
fluoranthene	1817	1.002	202	1	FLUORANTHN	206-44-0
pyrene-d_{10}	1844	1.586	212	1		
pyrene	1852	1.004	202	1	PYRENE	129-00-0
benzidine-d_8	1854	1.594	192	5		
benzidine	1855	1.000	184	5	BZID	92-87-5
butylbenzyl phthalate	2060	1.771	149	1	BUTBNZPHT	85-68-7
chrysene-d_{12}	2081	1.789	240	1		
chrysene	2083	1.001	228	1	CHRYSENE	218-01-9
benzo(a)anthracene-d_{12}	2082	1.790	240	1		
benzo(a)anthracene	2090	1.004	228	1	BAA	56-55-3
3,3'-dichlorobenzidine-d_6	2086	1.794	258	5		
3,3'-dichlorobenzidine	2088	1.001	252	5	33-2CLBZID	91-94-1
bis(2-ethylhexyl)phthalate-d_4	2123	1.825	153	1		
bis(2-ethylhexyl)phthalate	2124	1.000	149	1	BZETHXPHTH	117-81-7
di-n-octyl phthalate-d_4	2239	1.925	153	1		
di-n-octyl phthalate	2240	1.000	149	1	2NOCTP	117-84-0
benzo(b)fluoranthene-d_{12}	2281	1.961	264	1		
benzo(b)fluoranthene	2286	1.002	252	1	BBF	205-99-2
benzo(k)fluoranthene-d_{12}	2287	1.966	264	1		
benzo(k)fluoranthene	2293	1.003	252	1	BKF	207-08-9
benzo(a)pyrene-d_{12}	2350	2.021	264	1		
benzo(a)pyrene	2352	1.001	252	1	BAP	50-32-8
benzo(g,h,i)perylene-d_{12}	2741	2.357	288	2		
benzo(g,h,i)perylene	2750	1.003	276	2	BGHIP	191-24-2
indeno(1,2,3-c,d)pyrene	2650	0.967	276	2	INDENO-PYR	193-39-5
dibenzo(a,h)anthracene	2660	0.970	278	2	DBAHA	53-70-3
2-chlorophenol-d_4	701	0.603	132	1		
2-chlorophenol	705	1.006	128	1	2-CLPHN	95-57-8
2-nitrophenol-d_4	898	0.772	143	2		
2-nitrophenol	900	1.002	139	2	2-NPHN	88-75-5
2,4-dichlorophenol-d_3	944	0.812	167	1		
2,4-dichlorophenol	947	1.003	162	1	24-2CLPHN	120-83-2
4-chloro-3-methylphenol-d_2	1086	0.934	109	2		
4-chloro-3-methylphenol	1091	1.005	107	2	4-CL2-MPHN	59-50-7
2,4,6-trichlorophenol-d_2	1162	0.999	200	2		
2,4,6-trichlorophenol	1165	1.003	196	2	246-3CLPHN	88-06-2
2,4,5-trichlorophenol	1170	1.007	196	2		
2,3,6-trichlorophenol	1195	1.028	196	2	236-3CLPHN	93-37-55
2,4-dinitrophenol-d_3	1323	1.138	187	20		
2,4-dinitrophenol	1325	1.002	184	20	24-2NPHN	51-28-5
4-nitrophenol-d_4	1349	1.160	143	6		
4-nitrophenol	1354	1.004	139	6	4-NPHN	100-02-7
2-methyl-4,6-dinitrophenol-d_2	1433	1.232	200	13		
2-methyl-4,6-dinitrophenol	1435	1.001	198	13	46-2NOCRES	534-52-1
pentachlorophenol-$^{13}C_6$	1559	1.340	272	5		
pentachlorophenol	1561	1.001	266	5	5CLPHN	87-86-5

a Relative retention times for labeled compounds are referenced to DFB. Relative retention times for unlabeled compounds are referenced to their labeled analogs or to the most chemically similar, most closely eluting labeled compounds if labeled analogs are not listed.

TABLE I-1. (Continued)

Compound	Relative Retention Time to DFB	Quantitation (Primary) m/z	GC/MS (ng)	GC/ECD (pg)	ODES	CASRN
decafluorobenzophenone (DFBP)	0.736		-	5		
toxaphene (mixture)	1.2-1.9	231, 233	10	100	TOXAPHENE	8001-35-2
Aroclor 1242 (PCB mixture)			10	100	PCBS	53469-21-9
Aroclor 1254 (PCB mixture)			10	100	PCBS	11097-69-1
Aroclor 1260 PCB mixture)			10	100	PCBS	11096-82-5
α-HCH	1.32	183, 181	2	20	6CL-CHX-A	319-84-6
β-HCH	1.36	183, 181	3	5	6CL-CHX-B	319-84-7
γ-HCH	1.41	183, 181	2	5	LINDANE	319-86-8
δ-HCH	1.43	183, 181	3	20	6CL-CHX-D	58-89-9
aldrin	1.64	263, 265	2	5	ALDRIN	309-00-2
heptachlor	1.70	100, 272	2	5	HEPTACHLOR	76-44-8
heptachlor epoxide	1.83	353, 355	2	15	HEPCL EPOX	1024-57-3
γ-chlordane	1.85	373, 375	2	10		
α-endosulfan	1.88	195, 207	2	5	ENDOSULFAN	115-29-7
α-chlordane	1.91	373, 375	2	5		
dieldrin	1.98	241, 263	2	5	DIELDRIN	60-57-1
4,4'-ODE	2.00	246, 248	2	30	ODE	72-55-9
β-endosulfan	2.02	207, 195	2	5		115-29-7
endrin	2.02	263, 277	2	5	ENDRIN	72-20-8
endrin aldehyde	2.07			30	ENDRIN-ALD	7421-93-4
4,4'-ODD	2.10	235, 165	2	30	ODD	72-54-8
endosulfan sulfate	2.13	272, 387	5	30	ENDOSLFN-S	1031-07-8
γ-chlordene	2.13	336, 338	2	10		
4,4'-DDT	2.17	235, 237	2	.(5)	DDT	50-29-3
2,3,7,8-TCDD(6)	2.01	320, 322	3	40	DIOXIN	1746-01-6
Additional 301(h) Pesticides:						
Demeton					SYSTOX	8065-48-3
Guthion					GUTHION	86-50-0
Malathion	1.19	127, 99, 174			MALATHION	121-75-5
Parathion	1.19	291, 109, 139			PARATHION	56-38-2
Methoxychlor	1.51	238, 227, 274		50	METHOXYCL	72-43-5
Mirex	1.52	272, 237, 274		100	MIREX	2385-85-5

[1] Deuterium labeled recovery (surrogate) standard; isotopically labeled surrogates do not have ODES codes.

[2] ^{13}C-labeled recovery (surrogate) standard; isotopically labeled surrogates do not have ODES codes.

[3] Detected as azobenzene.

[4] Detected as diphenylamine.

[5] Low level amounts (<2 ng) of DDT are dehydronalogenated and converted to DDE at variable rates on the GC system.

[6] Acceptable detection limits will be attainable with the U.S. EPA Contract Laboratory Program Dioxin Analysis procedure [Soil/Sediment Matrix, Multi-Concentration, Selected Ion Monitoring (SIM) GC/MS Analysis; 9/15/83].

Column: 30 m x 0.25 mm i.d., 94% methyl, 4% phenyl, 1% vinyl bonded phase fused silica capillary (J&W DB-5, or equivalent)

Temperature program (GC/MS): 5 min at 30° C; 30-280° C at 8° C per min; isothermal at 280° C until mzo(g, h,i)perylene elutes.

Carrier gas linear velocity: 30 cm/sec, helium.

TABLE I-2. DFTPP MASS-INTENSITY SPECIFICATION

Mass	Intensity Required
51	30-60% of mass 198
68	Less than 2% of mass 69
70	Less than 2% of mass 69
127	40-60% of mass 198
197	Less than 1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	1% of mass 198
441	Less than mass 443
442	Greater than 40% of mass 198
443	17-23% of mass 442

TABLE I-3. SUMMARY OF AVAILABLE PRECISION AND RECOVERY DATA[a]

	Surface Sediments	Subsurface Sediments	English Sole Muscle	English Sole Livers
	Precision[b] (Mean Coefficient of Variation)			
Phenols	± 52	± 42	-	-
Aromatic hydrocarbons	± 17	± 18	-	-
Chlorinated hydrocarbons	± 25	± 41	-	-
Total PCBs	± 42	± 15	± 11	± 15
Phthalates	± 61	± 44	± 100	-
Miscellaneous compounds				
Benzyl alcohol	± 54	± 42	-	± 34
Dibenzofuran	± 17	± 9	-	-
	Percent Recovery[c]			
Phenols	47 (59)	69 (67)	17 (67)	-
Aromatic hydrocarbons	80 (99)	60 (94)	33 (98)	-
Chlorinated hydrocarbons	31 (120)	17 (140)	11 (124)	-
Phthalates	71	59	44	-

[a] Source: Tetra Tech, Inc. 1985. Commencement Bay Nearshore/Tideflats Remedial Investigation. Vol. 1. Final report prepared for the Washington State Department of Ecology and U.S. Environmental Protection Agency.

[b] Precision determined by multiple sets of replicate analyses. Value shown is mean coefficient of variation in sets of replicates with detected values (recovery corrected).

[c] Values shown are mean percent recoveries of isotopically labeled compounds added in quantities within a factor of ten of the lower limit of detection. The values in parentheses are the mean percent recoveries obtained from multiple matrix spike samples. The matrix spike compounds were added at levels several times higher than the isotope recovery standards.

TABLE I-4. PRECISION AND ACCURACY OF METHOD BLANKS

EPA Priority Pollutants	Percent Recovery[a] Blank 1	Blank 2	Blank 3	Blank 4	Mean	Coeff. of Variation
Phenols						
phenol	96	102	91	96	96	4.7
2,4-dimethylphenol	92	120	110	97	105	5.0
2-chlorophenol	100	102	110	104	104	4.2
2,4-dichlorophenol	98	101	100	110	102	5.2
4-chloro-3-methylphenol	99	97	110	100	102	5.7
2,4,6-trichlorophenol	98	100	140	100	110	18.6
pentachlorophenol	110	110	120	110	113	4.4
2-nitrophenol	96	99	120	110	106	10.3
4-nitrophenol	110	110	110	110	110	0.0
2,4-dinitrophenol	99	100	98	110	102	5.5
4,6-dinitro-2-methylphenol	110	100	110	110	108	4.7
Aromatic Hydrocarbons						
naphthalene	110	110	120	120	115	5.0
acenaphthene	120	110	120	120	118	4.3
acenaphthylene	110	110	120	120	115	5.0
fluorene	120	120	130	120	123	4.1
phenanthrene	120	120	120	130	123	4.1
anthracene	120	120	110	130	120	6.8
fluoranthene	120	120	130	130	125	4.6
pyrene	120	110	150	130	129	13.4
benz(a)anthracene	120	110	95	110	109	9.5
chrysene	120	120	150	130	130	10.9
benzo(b)fluoranthene	100	102	110	110	106	5.0
benzo(k)fluoranthene	110	113	120	110	113	4.2
benzo(a)pyrene	130	125	130	130	129	1.9
indeno(1,2,3-cd)pyrene	160	161	170	160	163	3.0
dibenzo(a,h)anthracene	150	189	180	190	177	10.6
benzo(ghi)perylene	120	120	120	120	120	0.0
Chlorinated Hydrocarbons						
1,2-dichlorobenzene	100	110	110	110	108	4.7
1,3-dichlorobenzene	87	120	94	120	105	16.4
1,4-dichlorobenzene	110	120	120	130	120	6.8
1,2,4-trichlorobenzene	93	98	130	100	105	15.9
2-chloronaphthalene	110	110	120	120	115	5.0
hexachlorobenzene	160	110	120	110	125	19.0
hexachloroethane	73	104	69	77	81	19.6
hexachlorobutadiene	98	105	130	110	111	12.4
hexachlorocyclopentadiene	23	25	24	25	24	3.9

TABLE I-4. (Continued)

Phthalates						
bis(2-ethylhexyl)phthalate	120	130	120	130	125	4.6
benzylbutylphthalate[b]	270	298	120	310	250	35.2
di-n-butylphthalate	120	120	130	120	123	4.1
di-n-octylphthalate	120	120	120	120	120	0.0
diethylphthalate	120	120	130	120	123	4.1
dimethylphthalate	110	120	140	120	123	10.3
Halogenated Ethers						
bis(2-chloroethyl)ether	91	93	91	100	94	4.6
bis(2-chloroisopropyl)ether	c	c	c	61	---	---
bis(2-chloroethoxy)methane	200	110	190	140	160	26.5
4-chlorophenylphenylether	120	120	140	120	125	8.0
4-bromophenylphenylether	150	140	120	150	140	10.1
Organonitrogen Compounds						
nitrobenzene	37	21	19	c	19	38.4
N-nitrosodipropylamine	26	135	150	73	96	59.7
N-nitrosodimethylamine	110	120	110	120	115	5.0
N-nitrosodiphenylamine	76	89	173	77	104	44.9
2,4-dinitrotoluene	120	120	120	100	115	8.7
2,6-dinitrotoluene	130	74	130	100	109	24.9
benzidine	0	0	0	0		
3,3'-dichlorobenzidine	120	170	140	120	138	17.2
1,2-diphenylhydrazine	120	110	140	100	118	14.5
Miscellaneous						
isophorone	130	120	72	120	111	23.6

[a] Method blanks were processed after spiking with known amounts of unlabeled and labeled compounds. Recovery-corrected concentration of unlabeled priority pollutants was calculated using the recovery of labeled analogs for each compound. The final percent recovery for the unlabeled compounds was then computed as the ratio of the calculated concentration to the known spike level of each compound.

[b] Benzylbutylphthalate results are anomolously high because of laboratory contamination traced to mercury used in the sulfur-removal step of the procedure. The contamination was subsequently eliminated.

[c] Spectral interferences precluded quantification.

SECTION II

ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN ESTUARINE AND MARINE SEDIMENTS

CONTENTS

ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN ESTUARINE AND MARINE SEDIMENTS

1.0 SCOPE AND APPLICATION

1.1 This method is designed to determine the volatile priority pollutants (Table II-1) associated with Clean Water Act Section 301(h) regulation [40 CFR 125.58(k) and (v)]. Additional compounds amenable to purge-and-trap gas chromatography-mass spectrometry (GC/MS) may be suitable for analysis, subject to testing.

1.2 The chemical compounds listed in Table II-1 can be determined in sediment samples collected from estuarine and marine environments by this method.

1.3 The detection limit of this method is usually dependent upon the level of interferences rather than instrumental limitations.

Lower limits of detection (LLD) are established by analysts based on their experience with the instrumentation and with interferences in the sample matrix being analyzed. LLD are greater than instrumental detection limits because they take into account sample interferences. To estimate LLD, the noise level should be determined in the retention window for the quantitation mass of representative analytes. These determinations should be made for at least three field samples in the sample set under analysis. The signal required to exceed the average noise level by at least a factor of two should then be estimated. This signal is the minimum response required to identify a potential signal for quantification. The LLD is the concentration corresponding to the level of this signal based on calibrated response factors. Based on best professional judgment, this LLD would then be applied to samples in the set with comparable or lower interference. Samples with much higher interferences (e.g., at least a factor of two higher) should be assigned LLD at a multiple of the original LLD.

These LLD values may be less than the rigorously defined method detection limits specified in the revised "Guidelines Establishing Test Procedures for the Analysis of Pollutants" (40 CFR Part 136, 10/26/84). This latter procedure requires the analysis of seven replicate samples and a statistical determination of the method detection limit with 99 percent confidence. Data quantified between the LLD and the rigorous method detection limit are valid and useful in environmental investigations of low-level contamination, but have a lower statistical confidence associated with them than data quantified above the method detection limit.

The LLD are roughly 5-10 ppb (wet weight) with the exception of acrolein, which has not been thoroughly tested on sediment matrices with this method.

2.0 SUMMARY OF METHOD

2.1 Volatile organic compounds are vacuum extracted from a 5-g (wet wt) sediment sample and concentrated in a cryogenic trap cooled with liquid nitrogen (references 1 and 2). The cryogenic trap is then transferred to a conventional purge-and-trap device. The extract is diluted to 5 mL with water and treated as an aqueous sample. In the purge-and-trap device, the volatile organic compounds are purged from the aqueous phase into a gaseous phase with an inert carrier gas. The volatile compounds are passed into a sorbent column and trapped. After purging is completed, the trap is backflushed and heated rapidly to desorb the compounds into a gas chromatograph (GC). The compounds are separated by GC and detected with a mass spectrometer (MS).

Analysis is carried out by GC/MS either according to the isotope dilution technique (U.S. EPA Method 1624 Revision B; reference 3) or U.S. EPA Method 624 (reference 4). Both of these methods were developed for water/wastewater sample matrices. The isotope dilution technique, which requires spiking the sample with a mixture of stable isotope labeled analogs of the analytes, is preferred because it provides reliable recovery data for each analyte. Method 624 requires spiking samples with only three surrogate compounds and does not allow for recovery corrections. If uniformly high recoveries can

be attained with Method 624, then addition of numerous labeled compounds (Method 1624 Revision B) and recovery corrections are unnecessary. However, until such performance can be demonstrated, Method 1624 Revision B provides a detailed and valuable assessment of analytical performance.

Hiatt (reference 5) proposed another vacuum distillation procedure (for tissue matrices) that did not include a purge-and-trap device. In this technique, volatile organic compounds are transferred directly from a cryogenically cooled trap to a fused-silica capillary column for GC/MS analysis. This capillary column technique allows for optimum resolution and rapid conditioning between samples. However, the performance of the technique has not been thoroughly tested (reference 6). A potential problem is that water can enter the capillary column and cause chromatographic problems or it can freeze, effectively plugging the column. Thus, Hiatt's original procedure (references 1 and 2), which has been tested more thoroughly, is recommended here.

Vacuum distillation is recommended rather than direct or heated purge-and-trap extraction (i.e., without vacuum distillation) because the former technique has been demonstrated to allow for better recoveries of spiked compounds than the latter techniques (reference 1).

2.2 Laboratories may use alternative analytical procedures if evidence of performance comparable to the recommended procedure is provided.

3.0 INTERFERENCES

3.1 Impurities in the purge gas, organic compounds out-gassing from the plumbing upstream of the trap, and solvent vapors in the laboratory account for the majority of contamination problems. The analytical system is demonstrated to be free from interferences under conditions of the analysis by analyzing blanks initially and with each sample lot (samples analyzed on the same 8-h shift), as described in Sect. 9.3. Common laboratory solvents (e.g., methylene chloride) are often contaminants in volatiles analyses.

3.1.1 Newly packed traps should be conditioned overnight at 170°-180° C by backflushing with an inert gas at a flow rate of 20-30 mL/min. Traps must be conditioned daily for a minimum of 10 min before use.

3.2 There is potential for ambient contamination of samples and extracts when using vacuum and cryogenic concentration techniques. Care must be taken to eliminate any leaks in the vacuum extraction and concentration device: A critical source of potential contamination is pump oil vapor and exhaust from the vacuum pump; this should not be a problem if the system is properly sealed. A cold trap is placed between the vacuum pump and concentration trap to prevent condensation of pump oil vapors in the concentration trap (Figure II-1). All materials in the vacuum extraction and concentration device that contact the sample and its vapors must be made of stainless steel and/or borosilicate glass. All connections and seals must be free of elastomers or grease that either outgas or allow penetration of ambient contaminant vapors.

3.3 Samples can be contaminated by diffusion of volatile organic compounds (particularly methylene chloride) through the bottle seal during shipment and storage. A field blank prepared from reagent water and carried through the sampling and handling protocol serves as a check on such contamination.

3.4 Contamination by carry-over can occur when high level and low level samples are analyzed sequentially. When an unusually contaminated sample is analyzed, it should be followed by analysis of a reagent water blank to check for carry-over. Because the transfer lines, trap, and other parts of the system can retain contaminants and interferences, frequent bakeout and purging of the entire system may be required.

4.0 SAFETY

4.1 The toxicity or carcinogenicity of each compound or reagent used in this method has not been precisely determined. However, each chemical compound should be treated as a potential health hazard and exposure should be reduced as much as possible. The laboratory is responsible for maintaining

a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets should also be made available to all personnel involved in these analyses. Additional information on laboratory safety can be found in references 7-9.

4.2 The following compounds covered by this method have been tentatively classified as known or suspected human or mammalian carcinogens: benzene, carbon tetrachloride, chloroform, and vinyl chloride. Primary standards of these toxic compounds should be prepared in a hood, and a NIOSH/MESA-approved toxic gas respirator should be worn when high concentrations are handled.

4.3 The following safety measures must be employed when handling cryogenic and vacuum systems:

4.3.1 Liquid nitrogen (LN_2) must not be allowed to contact flesh since it will cause extreme frostbite and deaden (kill) tissues.

4.3.2 The concentrator and cold traps must never be closed off or sealed after allowing any concentration of liquid air. The liquid air will vaporize, resulting in tremendous pressure buildup and explosive damage to the vacuum system. Always vent any vessel <u>immediately</u> after removing the cryogenic or LN_2 bath. Wear safety goggles when working with cryogenic and vacuum systems.

5.0 APPARATUS AND EQUIPMENT

5.1 Sample Handling Equipment

5.1.1 Stainless steel spatula.

5.1.2 Sample vessel - Pyrex flask with 15 mm O-ring connector, washed with detergent and rinsed with distilled water and oven-dried at 450° C.

5.1.3 O-ring, Buna N - sonicated with 50 percent methanol/water then dried by vacuum at 60° C. O-rings made of TFE (tetrafluorothylene) are not recommended because they do not produce adequate seals under vacuum.

5.2 Apparatus for Vacuum Distillation and Cryogenic Concentration (Figure II-1).

5.2.1 Vacuum pump - capable of achieving 10^{-3} Torr and 25 L/min.

5.2.2 Vaccum/pressure gauge - with a range of subatmospheric pressure to 10 psi.

5.2.3 Concentrator trap or purge flask - 25 mL capacity (Tekmar Part No. 14-0957-024 or equivalent) modified with 9-mm O-ring connectors.

5.2.4 Cold trap - glass trap (easily produced by glassblowing, Figure II-1) with O-ring fittings (e.g., Kontes 671750-009).

5.2.5 Transfer line - 1/4 in o.d. glass-lined stainless steel tubing. Lines should be kept as short as possible to minimize sample carryover.

5.2.6 Vacuum valves - Nupro B-4BKT or equivalent.

5.2.7 Dewar flasks - 665 mL or 1,000 mL, for liquid nitrogen bath.

5.2.8 Assorted compression fittings and graphite ferrules (Figure II-1).

5.2.9 Ultrasonic bath - Branisonic 12 or equivalent.

5.2.10 Heater tape - to wrap around stainless steel lines and valve bodies to maintain a temperature of 60° C.

5.2.11 Pinch clamps, Thomas - to secure O-ring connections.

5.3 Purge-and-Trap Device - capable of meeting specifications listed in U.S. EPA Method 1624 Revision B (see below). Complete devices consisting of a purging device (the concentrator trap, Sect. 5.2.3), a Tenax/silica trap, and a desorber are commercially available (e.g., Tekmar Model LSC-2, Tekmar Co., Cincinnati, OH).

5.3.1 Trap - 25 to 30 cm x 2.5 mm i.d. minimum, containing the following:

5.3.1.1 Methyl silicone packing - one ±0.2 cm, 3 percent OV-1 on 60/80 mesh Chromosorb W, or equivalent.

5.3.1.2 Porous polymer - 15 ±1.0 cm, Tenax GC (2,6-diphenylene oxide polymer), 60/80 mesh, chromatographic grade, or equivalent.

5.3.1.3 Silica gel - 8 ±1.0 cm, Davison Chemical, 35/60 mesh, grade 15, or equivalent.

5.3.2 Desorber - should heat the trap to 175 ±5° C in 45 sec or less. The polymer section of the trap should not exceed 180° C, and the remaining sections should not exceed 220° C.

5.3.3 Commercial purge and trap devices are easily coupled to GC systems.

5.4 GC/MS (Gas Chromatograph-Mass Spectrometer) System.

5.4.1 GC - should be linearly temperature programmable with initial and final temperature holds.

5.4.2 GC column - 6 ft long x 0.1 in i.d. (stainless steel or glass) packed with 1 percent SP-1000 on Carbopak B, 60/80 mesh or equivalent.

5.4.3 MS - 70 eV electron impact ionization; capable of repeatedly scanning from 20 to 250 amu every 2 to 3 sec.

5.4.4 GC/MS interface - GC to MS interfaces constructed of all-glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichloro-dimethyl silane.

5.5 Data System - should collect and record MS data, store mass intensity data in spectral libraries, process GC/MS data and generate reports, and calculate and record response factors.

5.5.1 Data acquisition - mass spectra should be collected continuously throughout the analysis and stored on a mass storage device.

5.5.2 Mass spectral libraries - user-created libraries containing mass spectra obtained from analysis of authentic standards should be employed to reverse search GC/MS runs for the compounds of interest.

5.5.3 Data processing - the data system should be used to search, locate, identify, and quantify the compounds of interest in each GC/MS analysis. Software routines should be employed to compute retention times and extracted ion current profile (EICP) areas. Displays of spectra, mass chromatograms, and library comparisons are required to verify results.

5.5.4 Response factors and multipoint calibrations - the data system should be used to record and maintain lists of response factors (response ratios for isotope dilution) and generate multi-point calibration curves. Computations of relative standard deviation (coefficient of variation) are useful for testing calibration linearity.

5.6 Other Materials

5.6.1 Syringe, 10 uL $\pm$ 1 percent of volume.

5.6.2 Syringe, 50 uL $\pm$ 1 percent of volume.

5.6.3 Syringe, 5 mL ± 1 percent of volume, gas-tight with shut-off.

5.6.4 Bubble flowmeter.

6.0 REAGENTS AND CONSUMABLE MATERIALS

6.1 Reagent Water

6.1.1 Reagent water is defined as water free of interferences (i.e., interferents are not observed at the detection limits of the compounds of interest).

6.1.2 Prepare water by boiling 1 L of freshly distilled water down to 900 mL and transferring the water to a 1-L volumetric flask that has been modified by replacing the ground glass joint with a 15-mm i.d., Buna-N O-ring connector.

6.1.3 Connect the flask to the distillation apparatus at the sample chamber site and evacuate for 15 min while continuously agitating the flask in an ultrasonic cleaner.

6.1.4 After evacuation, release an inert gas (N_2 or He can be used) into the flask until equilibrium is obtained, then seal with a cap made from a Buna-N O-ring connector.

6.2 Methanol - pesticide quality or equivalent.

6.3 Standard Solutions - purchased as solutions or mixtures with certification of their purity, concentration, and authenticity, or prepared from materials of known purity and composition. If compound purity is 96 percent or greater, the weight may be used without correction to calculate the concentration of the standard.

6.4 Preparation of Stock Solutions - prepare in methanol using liquid or gaseous standards per the steps below. Observe the safety precautions given in Sect. 4.

6.4.1 Place approximately 9.8 mL of methanol in a 10-mL ground glass stoppered volumetric flask. Allow the flask to stand unstoppered for approximately 10 min or until all methanol-wetted surfaces have dried. In each case, weigh the flask, immediately add the compound, then immediately reweigh to prevent evaporation losses from affecting the measurement.

6.4.1.1 Liquids - using a 100 uL syringe, permit two drops of liquid to fall into the methanol without contacting the neck of the flask. Alternatively, inject a known volume of the compound into the methanol in the flask using a micro-syringe. With the exception of 2-chloroethylvinyl ether, stock standards of compounds that boil above room temperature are generally stable for at least 4 wk when stored at 4^{o} C.

6.4.1.2 Gases (chloromethane, bromomethane, chloroethane, vinyl chloride) - fill a valved 5-mL gas-tight syringe with the compound. Lower the needle to approximately 5 mm above the methanol meniscus. Slowly introduce the compound above the surface of the meniscus. The gas will dissolve rapidly in the methanol.

6.4.2 Fill the flask to volume, stopper, then mix by inverting several times. Calculate the concentration in mg/mL (ug/uL) from the weight gain (or density if a known volume was injected).

6.4.3 Transfer the stock solution to a Teflon sealed screw-cap bottle. Store, with minimal headspace, in the dark at -10 to -20^{o} C.

6.4.4 Prepare fresh standards weekly for the gases and 2-chloroethylvinyl ether. All other standards are replaced after 1 mo, or sooner if comparison with check standards indicates a change in concentration of over 10 percent. Quality control check standards that can be used to determine the accuracy

of calibration standards are available from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio.

6.5 Labeled Compound Spiking Solution - from stock standard solutions prepared as above, or from mixtures, prepare the spiking solution to contain a concentration such that a 5-10 uL spike into each 5-mL sample "extract", blank, or aqueous standard analyzed will result in a concentration of 10 ng/mL of each labeled compound. For the gases and for the water soluble compounds (acrolein, acrylonitrile), a concentration of 50 ng/mL may be used. Include the internal standards (Sect. 8.1.2) in this solution so that a concentration of 10 ng/mL in each sample, blank, or aqueous standard will be produced.

6.6 Secondary Standards - using stock solutions, prepare a secondary standard in methanol to contain each pollutant at a concentration of 250 ug/mL. For the gases and water soluble compounds (Sect. 6.5), a concentration of 1.25 mg/mL may be used.

6.7 Aqueous Calibration Standards - the concentrations of calibration solutions suggested in this section are intended to bracket concentrations that will be encountered during sample analysis that will not overload the analytical system. Use sufficient amounts of the secondary standard (Sect. 6.6) and reagent water to produce concentrations of 5, 10, 20, 50, and 100 ug/L in the aqueous calibration standards. The concentrations of gases and water soluble compounds will be higher (i.e., 25, 50, 100, 250, and 500 ug/L). Analysts may use a wider range of standard concentrations if linearity can be demonstrated.

6.8 Aqueous Performance Standard - an aqueous standard containing all pollutants, internal standards, labeled compounds, and BFB (4-bromofluorobenzene) is prepared daily and is analyzed each shift to demonstrate performance (Sect. 8.2). This standard should contain either 10 or 50 ug/L of the labeled and pollutant gases and water soluble compounds, 5 ug/L of BFB, and 10 ug/L of all other pollutants, labeled compounds, and internal standards. It may be the nominal 10 ug/L aqueous calibration standard (Sect. 6.7).

6.9 A methanolic standard containing all pollutants and internal standards is prepared to demonstrate recovery of these compounds when syringe injection and purge-and-trap analyses are compared. This standard should contain either 10 ug/mL or 50 ug/mL of the gases and water soluble compounds, and 10 ug/mL of the remaining pollutants and internal standards (consistent with the amounts in the aqueous performance standard in Sect. 6.8).

6.10 Other standards that may be needed are those for testing of BFB performance (Sect. 8.2.1) and for collecting mass spectra for storage in spectral libraries (Sect. 8.1.4).

6.11 High Purity Helium - 99.999 percent.

6.12 Liquid Nitrogen (LN_2).

7.0 SAMPLE COLLECTION, PREPARATION, AND STORAGE

7.1 In the field, sources of contamination include sampling gear, grease from ship winches or cables, ship engine exhaust, dust, and ice used for cooling. Efforts should be made to minimize handling and to avoid sources of contamination.

7.2 Fill two separate 40-ml, screw cap glass vials with sediment, leaving no headspace. The vials and tetrafluoroethylene (TFE)-backed silicon septa used for sealing them should be cleaned with detergent, rinsed once with tap water, rinsed with distilled water, and dried at >105^{o} C. Solvent cannot be used as it will interfere with the analysis. To obtain a sample with no headspace, fill the vial to overflowing so that a convex (upward) meniscus forms at the top (if there is adquate water in the sediment). Place the cap (TFE side down) carefully on the opening of the vial, displacing excess water. Screw on the vial cap and verify the seal by inverting the vial. If the vial is properly sealed, air bubbles will not appear when it is inverted. Samples should be taken from single grab samples, as volatile compounds can be lost during compositing of grab samples.

7.3 To avoid cross-contamination, equipment used in sample handling (e.g., spatulas) should be thoroughly cleaned before each sample is processed. Instruments must be of a material that can be easily cleaned (e.g., stainless steel, anodized aluminum, or borosilicate glass). Before the next sample is processed, instruments should be washed with a detergent solution, rinsed with tap water, soaked in high-purity acetone and methylene chloride, and finally rinsed with reagent water.

7.4 U.S. EPA recommends that sediment samples be stored in the dark at 4^{o} C and analyzed within ten days of sample receipt (reference 10). Freezing is not recommended because no headspace will be left to compensate for the expansion of water during freezing.

8.0 CALIBRATION AND STANDARDIZATION

8.1 Initial Calibration

8.1.1 Calibration by the isotope dilution technique -- the isotope dilution technique is used for the purgeable organic compounds when appropriate labeled compounds are available and when interferences do not preclude the analysis. If labeled compounds are not available or interferences are present, the internal standard technique (Sect. 8.1.2) is used. A calibration curve encompassing the concentration range of interest is prepared for each compound determined. The relative response (RR) versus concentration (ug/L) is plotted or computed using a linear regression. An example of a calibration curve for a pollutant and its labeled analog is given in Figure II-2. Also shown are the $\pm$10 percent error limits (dotted lines). Relative response is determined according to the procedures described below. A minimum of five data points is required for calibration (Sect. 6.7).

8.1.1.1 The relative response (RR) of pollutant to labeled compound is determined from isotope ratio values calculated from acquired data. Three isotope ratios are used in this process:

R_x = the isotope ratio measured in the pure pollutant (Figure II-3A)
R_y = the isotope ratio of pure labeled compound (Figure II-3B)
R_m = the isotope ratio measured in the analytical mixture of the pollutant and labeled compounds (Figure II-3C).

The correct way to calculate RR is:

$$RR = (R_y - R_m)(R_x + 1)/(R_m - R_x)(R_y + 1).$$

If R_m is not between $2R_y$ and $0.5R_x$, the method does not apply and the sample is analyzed by the internal standard technique (Sect. 8.1.2).

8.1.1.2 In most cases, the retention times of the pollutant and labeled compound are the same and isotope ratios (R's) can be calculated from the EICP areas, where:

$$R = (\text{area at } m_1/z)/(\text{area at } m_2/z)$$

If either of the areas is zero, it is assigned a value of one in the calculations; that is, if: area of m_1/z=50721, and area of m_2/z=0, then R=50721/1= 50721. The m/z's are always selected such that $R_x > R_y$. When there is a difference in retention times (RT) between the pollutant and labeled compounds, special precautions are required to determine the isotope ratios.

R_x, R_y, and R_m are defined as follows:

R_x = [area m_1/z (at RT_2)]/1
R_y = 1/[area m_2/z (at RT_1)]
R_m = [area m_1/z (at RT_2)]/[area m_2/z (at RT_1)].

8.1.1.3 An example of the above calculations can be taken from the data plotted in Figure II-3 for a pollutant and its labeled analog. For these data, R_x = 168920/1 = 168920, R_y = 1/60960 = 0.00001640, and R_m = 96868/82508 = 1.174. The RR for the above data is then calculated using the

equation given in Sect. 8.1.1.1. For the example, RR=1.174. Note: Not all labeled compounds elute before their pollutant analogs.

8.1.1.4 To calibrate the analytical system by isotope dilution, analyze a 5-mL aliquot of each of the aqueous calibration standards (Sect. 6.7) spiked with an appropriate constant amount of the labeled compound spiking solution (Sect. 6.5), using the purge-and-trap procedure in Sect. 10. Compute the RR at each concentration.

8.1.1.5 Linearity - if the ratio of relative response to concentration for any compound is constant (less than 20 percent coefficient of variation) over the five-point calibration range, an averaged relative response/concentration ratio may be used for that compound; otherwise, the complete calibration curve for that compound should be used over the five-point calibration range.

8.1.2 Calibration by internal standard - used when criteria for isotope dilution (Sect. 8.1.1) cannot be met. The method is applied to pollutants having no labeled analog and to the labeled compounds themselves. The internal standards used for volatiles analyses are bromochloromethane, 2-bromo-1-chloropropane, and 1,4-dichlorobutane. Concentrations of the labeled compounds and pollutants without labeled analogs are computed relative to the nearest eluted internal standard.

8.1.2.1 Response factors - calibration requires the determination of response factors (RF), which are defined by the following equation:

$$RF = (A_s \times C_{is})/(A_{is} \times C_s)$$

where:

A_s = the EICP area at the characteristic m/z for the compound in the daily standard

A_{is} = the EICP area at the characteristic m/z for the internal standard

C_{is} = the concentration (ug/L) of the internal standard
C_s = the concentration of the pollutant in the daily standard.

8.1.2.2 The response factor is determined at 5, 10, 20, 50, and 100 ug/L for the pollutants (optionally at five times these concentrations for gases and water soluble pollutants - see Sect. 6.6 and 6.7), in a way analogous to that for calibration by isotope dilution (Sect. 8.1.1.4). The RF is plotted against concentration for each compound in the standard (C_s) to produce a calibration curve.

8.1.2.3 Linearity - if the response factor (RF) for any compound is constant (less than 35 percent coefficient of variation) over the five-point calibration range, an averaged response factor may be used for that compound; otherwise, the complete calibration curve for that compound should be used over the five point range.

8.1.3 Combined calibration - by adding the isotopically labeled compounds and internal standards (Sect. 6.5) to the aqueous calibration standards (Sect. 6.7), a single set of analyses can be used to produce calibration curves for the isotope dilution and internal standard methods.

8.1.4 Mass spectral libraries - detection and identification of the compound of interest during calibration and sample analysis are dependent upon the spectra stored in user-created libraries.

8.1.4.1 Obtain a mass spectrum of each pollutant and labeled compound and each internal standard by analyzing an authentic standard either singly or as part of a mixture in which there is no interference between closely eluted components. That only a single compound is present is determined by examination of the spectrum. Fragments not attributable to the compound under study indicate the presence of an interfering compound. Adjust the analytical conditions and scan rate (for this test only) to produce an undistorted spectrum at the GC peak maximum. An undistorted spectrum will usually be obtained if five complete spectra are collected across the upper half of the GC peak. Software algorithms designed to

"enhance" the spectrum may eliminate distortion, but may also eliminate authentic ions or introduce other distortion.

8.1.4.2 Obtain the authentic reference spectrum under BFB tuning conditions (Table II-2) to normalize it to spectra from other instruments.

8.1.4.3 The spectrum is edited by saving the five most intense mass spectral peaks and all other mass spectral peaks greater than 10 percent of the base peak. This spectrum is stored for reverse search and for compound confirmation.

8.2 Ongoing Calibration

8.2.1 The BFB standard must be analyzed at the beginning of each 8-h shift. The tuning criteria in Table II-2 must be met before blanks and samples may be analyzed.

8.2.2 At the beginning and end of each 8-h shift, system calibration should be verified by purging the aqueous performance standard (Sect. 6.8).

8.2.2.1 Calibration is tested by computing the concentration of unlabeled compounds by the isotope dilution technique (Sect. 8.1.1) for compounds with labeled analogs. Concentrations of unlabeled compounds without labeled analogs are calculated according to the internal standard technique (Sect. 8.1.2).

A complete (five-point) recalibration should be performed when results vary from predicted concentrations by more than $\pm$25 percent. The last sample analyzed before failing criteria should then be reanalyzed. If the results differ by more than $\pm$20 percent (i.e., at least twice the mean reproducibility for replicate analysis of sediment samples, Table II-3), it is assumed that the instrument was out of control during the original analysis and the earlier data should be rejected. Reanalysis of samples should progress in reverse order until it is determined that there is $\leq$20 percent difference between initial and reanalysis results.

9.0 QUALITY CONTROL [For further guidance, see Quality Assurance/Quality Control (QA/QC) for 301(h) Monitoring Programs: Guidance on Field and Laboratory Methods (Tetra Tech 1986).]

9.1 Each laboratory that uses this method is required to operate a formal quality assurance program. The minimum requirements of this program consist of an initial demonstration of laboratory capability, analysis of samples spiked with labeled compounds to evaluate and document data quality, and analysis of standards and blanks as tests of continued performance.

9.2 Initial Demonstration of Laboratory Capability

9.2.1 Analyze the aqueous performance standard (Sect. 6.8) according to the purge-and-trap procedure in Sect. 10. Compute the area at the primary m/z (Table II-1) for each compound. Compare these areas to those obtained by injecting one uL of the methanolic standard (Sect. 6.9) to determine compound recovery. The recovery should be greater than 20 percent for the water soluble compounds (acrolein and acrylonitrile), and 60-110 percent for all other compounds. This recovery should be demonstrated initially for each purge-and-trap GC/MS system. The test should be repeated only if the purge and trap or GC/MS systems are modified in any way that might result in a change in recovery.

9.3 Blanks

9.3.1 Reagent water blanks must be analyzed to demonstrate freedom from carry-over (Sect. 3) and contamination.

9.3.1.1 The level at which the purge-and-trap system will carry greater than 5 ug/L of a pollutant of interest into a succeeding blank should be determined by analyzing successively larger concentrations of these compounds. When a sample contains this concentration or more, a blank should be analyzed immediately following this sample to demonstrate no carry-over at the 5 ug/L level.

9.3.1.2 With each sample lot (samples analyzed on the same 8-h shift), a blank should be analyzed immediately after analysis of the aqueous performance standard (Sect. 8.2.2) to demonstrate freedom from contamination. If any of the compounds of interest, except common laboratory contaminants (e.g., methylene chloride and toluene), or any potentially interfering compound is found in a blank at greater than 10 ug/L (assuming a response factor of 1 relative to the nearest eluted internal standard for compounds not listed in Table II-1), analysis of samples is halted until the source of contamination is eliminated and a blank shows no evidence of contamination at this level. This control action also applies if methylene chloride or toluene is detected in a blank at greater than 50 ug/L.

9.4 Sample Spiking

9.4.1 The laboratory should spike all samples with labeled compounds to assess method performance on the sample matrix.

9.4.2 Spike and analyze each sample according to the method beginning in Sect. 10.

9.4.3 Compute the percent recovery (P) of the labeled compounds using the internal standard technique (Sect. 8.1.2).

9.5 Replicates

9.5.1 Replicate analyses (i.e., analyses of two subsamples from the same sediment homogenate) must be performed to monitor laboratory precision.

9.5.2 At a minimum, 5 percent of the analyses should be laboratory replicates. A triplicate analysis should be performed with each sample batch of over 40 samples.

10.0 PROCEDURE

10.1 Sample Processing

10.1.1 Homogenize (stir) samples with a spatula prior to analysis to ensure that representative aliquots are taken. Mix any water that has separated from the sediment back into the sample. Remove and make note of nonrepresentative material (e.g., twigs, leaves, shells, rocks, and any material larger than 1/4 in). It is recommended that removal of material be performed in the field by sampling personnel.

10.1.2 Dry weight determination - dry weight determinations may be performed as follows: transfer an aliquot of approximately 3 g (weighed to the nearest 0.1 g) to a preweighed dish. Allow the sample to dry in an oven at 105° C overnight and determine the solid residue weight to the nearest 0.1 g. The percent total solids is calculated as:

$$T_s = [\text{dry residue wt (g)}]/[\text{wet sample wt (g)}]$$

10.1.3 Immediately after homogenization, use a stainless steel spatula to transfer a 5-g aliquot to a preweighed sample vessel (Sect. 5.1.2). Weigh the transferred portion to the nearest 0.1 g.

10.1.4 Spike 50 ng of each labeled compound (or 250 ng of gaseous and water soluble compounds) into 2 mL of reagent water and add to the sample matrix. Seal the sample vessel with an O-ring connector and clamp and sonicate for 10 min. After sonication, store the sample contained in the sample vessel overnight in a refrigerator/freezer and analyze the next day.

10.2 Vacuum Distillation and Concentration (Reference 2)

10.2.1 The vacuum extractor must be airtight and free of moisture before extraction can be started.

10.2.2 A clean 100-mL pyrex flask is connected to the vacuum distillation apparatus at the sample vessel site (see Figure II-1), the vacuum pump started, and V_2-V_4 opened to evacuate the apparatus. Line condensation is prevented by warming the transfer lines while evacuating the system. Heating tape is effective in creating even transfer line temperatures and can be used continuously during the procedure.

10.2.3 The vacuum apparatus is pressurized with helium by closing V_3 and opening V_1. The apparatus is tested for leaks with a helium leak detector or a liquid leak detector (e.g., Snoop), and appropriate adjustments are made as necessary. When the apparatus has been found to be airtight, close V_1, open V_3 and then heat the transfer lines and concentrator trap to 100° C for 5 min to eliminate any residual contamination.

10.2.4 The flask containing the sample should be immersed in liquid nitrogen before the flask is uncapped. To begin the distillation, close V_2 (with V_3 and V_4 remaining open), cool the concentrator trap with a liquid nitrogen bath, and replace the empty sample vessel with the cooled sample flask. Disconnect the vacuum source by closing V_3. Open V_2 to permit vapors from the sample vessel to reach the concentrator trap. Immerse the sample vessel in a 50° C water bath and sonicate for 5 min.

10.2.5 Connect the vacuum source to the sample vessel by opening V_3. The lower pressure hastens the transfer of volatile compounds from the sample to the cooled concentrator trap. After 15 min of vacuum, close V_3 and open V_1 to fill the system with helium to atmospheric pressure. Close V_1 and V_2 to isolate the condensate. The distillation is now completed and the condensate is ready for transfer to a purge-and-trap device. The condensate can be held in the liquid nitrogen bath for up to 1 h prior to analysis. Care should be taken to ensure that moisture does not freeze in the narrow glass tubing in the concentrator trap. Careful drying of the system prior to analysis and maintenance of an airtight system will preclude this problem.

10.2.6 Disconnect the sample concentrator trap from the vacuum apparatus and connect it to the purge-and-trap device. Some outgassing is observed when the sample condensate is melted; therefore, the condensate should be kept frozen until the concentrator trap is attached to the purge-and-trap device. After attachment, warm the concentrator trap walls to loosen the condensate and allow the ring of ice formed during condensation to drop to the bottom of the trap. To this partially melted extract, add 3 mL of reagent water containing 50 ng of each of the internal standards (bromochloromethane, 2-bromo-1-chloropropane, and 1,4-dichlorobutane). The internal standards are added after vacuum extraction to allow the analyst to assess analytical losses of labeled compounds during the extraction/concentration procedure.

10.3 Purge-and-Trap Procedure

10.3.1 Because commercial purge flasks must be slightly modified (with O-ring fittings) to be attached to the vacuum distillation apparatus, a simple O-ring adapter is necessary to connect the purge flask to the commercial device for which it was designed. The modified purge flask (Sect. 5.2.3) used in this procedure can be fitted to a commercial purgeand-trap device (e.g., a Tekmar ALS interfaced with a Tekmar LSC-2) with 9-mm O-ring fittings fused to short sections of glass tubing. Commercial purge-and-trap devices are almost entirely automated and are easy to operate with manufacturer's instructions.

10.3.2 Purge the extract solution with the concentrator trap immersed in an ice-water bath for 5 min followed by immersion in a 55^{o} C-water bath for an additional 7 min. This provides conditions for reproducibly melting the frozen extracts in order to obtain reproducible purging efficiencies.

10.3.3 The GC conditions for analysis are as follows:

Injector zone temp.	225° C
Initial GC oven temp.	60° C
Final GC temp.	175° C
Initial hold time	3 min
Ramp rate	8° C/min
Final hold time	24 min
Jet separator oven temp.	225° C

10.4 Qualitative Determination - accomplished by comparison of data from analysis of a sample or blank with data from analysis of the shift standard (Sect. 8.2.2). Identification is confirmed when spectra and retention times agree according to the criteria below.

10.4.1 Labeled compounds and pollutants having no labeled analog:

10.4.1.1 The signals for all characteristic masses stored in the spectral library (Sect. 8.1.4.3) should be present and should maximize within the same two consecutive scans.

10.4.1.2 Either 1) the background-corrected EICP areas or 2) the corrected relative intensities of the mass spectral peaks at the GC peak maximum should agree within a factor of two (0.5 to 2 times) for all masses stored in the library.

10.4.1.3 The retention time relative to the nearest eluted internal standard should be within $\pm$7 scans or $\pm$20 sec, whichever is greater, of this difference in the shift standard.

10.4.2 Pollutants with a labeled analog:

10.4.2.1 The signals for all characteristic masses stored in the spectral library should be present and should maximize within the same two consecutive scans.

10.4.2.2 Either 1) the background corrected EICP areas or 2) the corrected relative intensities of the mass spectral peaks at the GC peak maximum should agree within a factor of two for all masses stored in the spectral library.

10.4.2.3 The retention time difference between the pollutant and its labeled analog should agree within ±2 scans or ±6 sec, whichever is greater, of this difference in the shift standard.

10.4.2.4 If the experimental mass spectrum contains masses that are not present in the reference spectrum, an experienced spectrometrist must determine the presence or absence of the compound.

10.5 Tentatively Identified Compounds (GC/MS Analysis) - The ten non-target peaks of greatest area in the RIC (reconstructed ion chromatogram) should be identified and quantified, if possible.

10.5.1 Guidelines for making tentative identification (reference 10):

(1) Tentative identifications should be based on a forward search of the EPA/NIH mass spectral library. Sample spectra should be visually compared with the most similar library match.

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

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

(4) Molecular ions present in reference spectrum should be present in sample spectrum.

(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.

10.5.1.1 If, in the opinion of the mass 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 (e.g., unknown hydrocarbon, unknown aromatic compound, unknown chlorinated compound). If probable molecular weights can be distinguished, include them.

10.5.2 Tentative quantification - quantification of TICs will be based on the internal standard technique and an assumed response factor of one (in the absence of data from authentic standards). The uncertain nature of this quantification should be clearly noted in the data report.

11.0 QUANTITATIVE DETERMINATION (CALCULATIONS)

11.1 Isotope Dilution - by adding a known amount of a labeled compound to every sample prior to vacuum distillation, correction for recovery of the pollutant can be made because the pollutant and its labeled analog exhibit similar behavior during purging, desorption, and gas chromatography. Note that pollutants and their labeled analogs are not always retained identically by complex matrices, so their behavior during the extraction step may differ. Use of this technique is to enable correction for analytical losses after extraction, not for matrix recovery.

11.1.1 Relative response (RR) values for sample mixtures are used in conjunction with calibration curves described in Sect. 8.1.1 to determine concentrations directly, so long as labeled compound spiking levels are constant.

11.1.2 For the isotope dilution technique, concentration is calculated as follows:

C (ug/kg, dry wt sediment) =

$$\frac{C_A \text{ (ug/kg)} \times RR \times n}{\sum_{i=1}^{n} \left(\frac{RR_i \times Z_{Ai}}{Z_i} \right)}$$

where

C_A = the concentration of the stable isotope labeled compound as spiked into the sample

RR = relative response of unlabeled pollutant to isotope labeled surrogate in the sample

RR_i = relative response at i^{th} point in calibration

Z_i = absolute amount of unlabeled compound at i^{th} point of calibration

Z_{Ai} = absolute amount of labeled compound at i^{th} point in calibration

n = number of calibration points.

11.2 Internal Standard - calculate the concentration using the response factor determined from calibration data (Sect. 8.1.2) and the following equation:

Concentration = $(A_s \times C_{is})/(A_{is} \times RF)$ where the terms are as defined in Sect. 8.1.2.1, except that C_{is} is in ug/kg (dry sediment) and A_s is the EICP area at the characteristic m/z for the analyte in the sample.

11.3 If the EICP area at the quantitation mass for any compound exceeds the calibration range of the system, a smaller sample aliquot should be analyzed if possible. However, sample sizes of less than 0.5 g are not recommended because such small samples may not be representative.

11.4 Report results for all pollutants and labeled compounds found in samples, in ug/kg (dry weight) to three significant figures. Pollutants and labeled compounds in blanks should be reported in ng/sample.

12.0 PRECISION AND ACCURACY

12.1 Recoveries from replicate spiked water and sediment analyses are presented in Table II-3 (references 1 and 2). These analyses were not performed with the isotope dilution technique and recovery results are uncorrected.

13.0 REFERENCES

1. Hiatt, M.H., "Analysis of Fish and Sediment for Volatile Priority Pollutants," Anal. Chem. Vol. 53, 1981, pp. 1541-1543.

2. Hiatt, M.H., and T.L. Jones. Isolation of Purgeable Organics from Solid Matrices by Vacuum Distillation. U.S. Environmental Protection Agency, Region IX, Las Vegas Laboratory, 1984.

3. Fed. Register, Volume 49, No. 209, October 26, 1984, pp. 43407-43415.
4. Fed. Register, Volume 49, No. 209, October 26, 1984, pp. 43373-43384.

5. Hiatt, M.H., "Determination of Volatile Organic Compounds in Fish Samples by Vacuum Distillation and Fused Silica Capillary Gas Chromatography/Mass Spectrometry," Anal. Chem. Vol. 55, 1983, pp. 506-516.

6. Hiatt, M.H. 4 November 1985. Personal Communication (phone by Mr. Harry Beller). Analytical Technologies, Incorporated, National City, CA.

7. "Working with Carcinogens," DHEW, PHS, NIOSH, Publication 77-206 (1977).

8. "OSHA Safety and Health Standards, General Industry," 29 CFR 1910, OSHA 2206, (1976).

9. "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety (1979).

10. U.S. Environmental Protection Agency. 1984 (revised January, 1985). U.S. EPA Contract Laboratory Program - statement of work for organics analysis, multi-media, multi-concentration. IFB WA 85-J176, J177, J178.

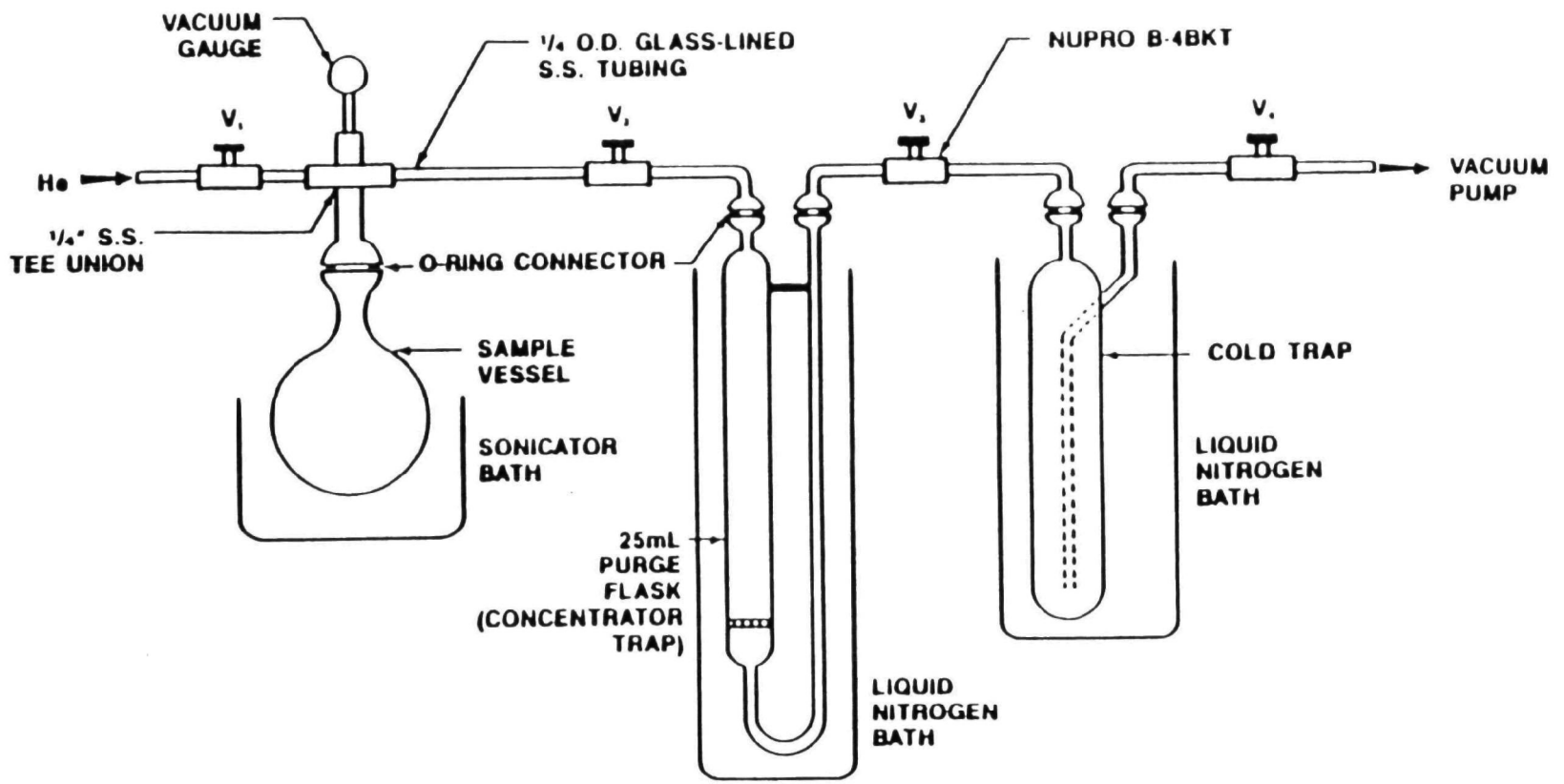
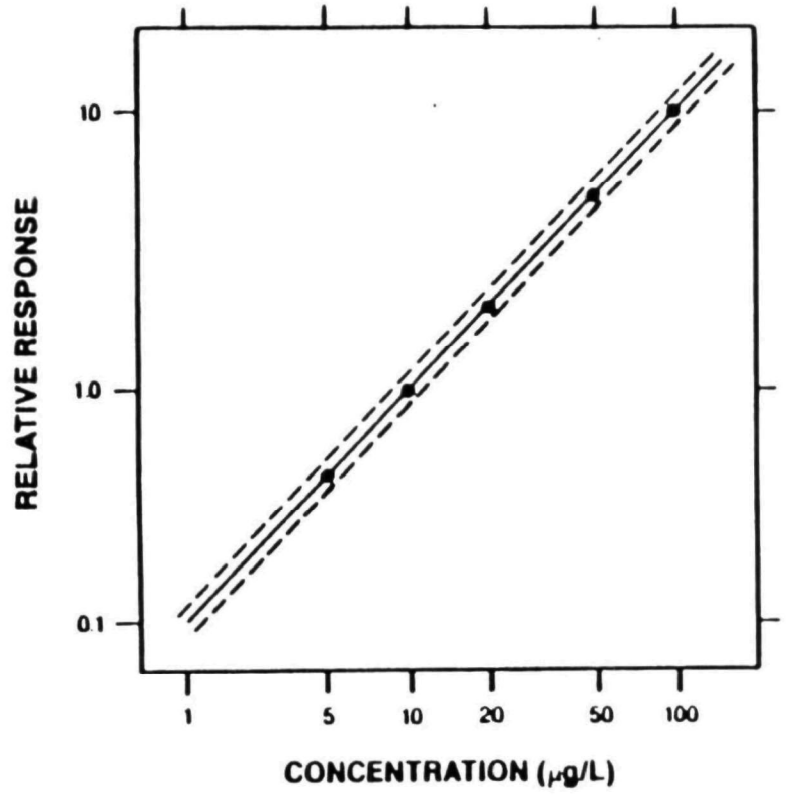
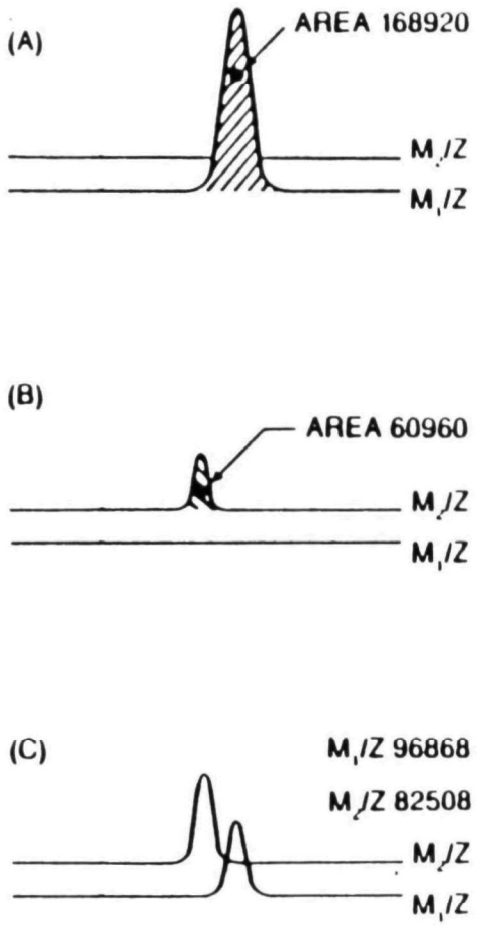


Figure II-1. Apparatus for vacuum distillation and cryogenic concentration.



ADAPTED FROM REFERENCE 3

2.



ADAPTED FROM REFERENCE 3

3.

Figure II-2. Relative response calibration curve.
Figure II-3. Extracted ion current profiles for (A) the unlabeled pollutant, (B) the labeled analog, and (C) a mixture of the labeled and the unlabeled compounds.

TABLE II-1. VOLATILE ORGANIC ANALYTES

Analyte	CASRN	ODES	Quantitation Ion (m/z)	Secondary Ion(s)
Acrolein	107-02-8	ACROLEIN	56	55
Acrylonitrile	107-13-1	ACRYLNTRLE	53	51, 52
Benzene	71-43-2	BENZENE	78	--
Bromodichloromethane	75-27-4	2CLBRMETHA	83	85, 129
Bromoform	75-25-2	BROMOFORM	173	171, 175
Bromomethane	74-83-9	METHYLBR	94	96
Carbon tetrachloride	56-23-5	CARBON TET	117	119, 121
Chlorobenzene	108-90-7	CLBNZ	112	114
Chloroethane	75-00-3	ETHYL CL	64	66
2-chloroethylvinyl ether	110-75-8	2-CLEVE	63	65, 106
Chloroform	67-66-1	CHLOROFORM	83	85
Chloromethane	74-87-3	METHYL CL	50	52
Dibromochloromethane	124-48-1	2BRCLMETH	129	206, 208, 127
1,1-dichloroethane	75-34-3	11-2CLETH	63	65, 83
1,2-dichloroethane	107-06-2	12-2CLETH	62	64, 98
1,1-dichloroethene	75-35-4	11-2CLETHE	96	61, 98
trans-1,2-dichloroethene	156-60-5	12-2CLETHE	96	61, 98
1,2-dichloropropane	78-87-5	12-2CLPRP	63	65, 114
cis-1,3-dichloropropene	10061-01-5	C13-2CLPRE	75	77
trans-1,3-dichloropropene	10061-02-6	T13-2CLPRP	75	77
Ethylbenzene	100-41-4	ETHYLBENZ	106	91
Methylene chloride	75-09-2	METHYLE CL	84	86
1,1,2,2-tetrachloroethane	79-34-5	4CLETHAN	83	85, 168
Tetrachloroethene	127-18-4	4CLETHE	164	129, 131, 166
Toluene	108-88-3	TOLUENE	92	91
1,1,1-trichloroethane	71-55-6	111-3CLETH	97	99, 117, 119
1,1,2-trichloroethane	79-00-5	112-3CLETH	97	83, 85, 99
Trichloroethene	79-01-6	3CLETHE	130	95, 97, 132
Vinyl chloride	75-01-4	VINYL CL	62	64

TABLE II-2. BFB MASS-INTENSITY SPECIFICATION

Mass	Intensity Required
50	15-40% of mass 95
75	30-60% of mass 95
95	Base peak, 100% relative abundance
96	5-9% of mass 95
173	<2% of mass 174
174	>50% of mass 95
175	5-9% of mass 174
176	>95% but <101% of mass 174
177	5-9% of mass 176.

TABLE II-3. PERCENT SPIKE RECOVERIES FOR VOLATILE PRIORITY POLLUTANTS USING VACUUM DISTILLATIONa

Spiking Compound	Average Percent Recovery (Water)b	Average Percent Recovery (Sediment)c
Chloromethane	105 ± 22	98 ± 22
Bromomethane	110 ± 23	86 ± 24
Vinyl chloride	83 ± 12	108 ± 35
Chloroethane	103 ± 16	106 ± 27
Methylene chloride	126 ± 22	LCd
1,1-dichloroethene	98 ± 5	82 ± 9
1,1-dichloroethane	96 ± 5	101 ± 7
trans-1,2-dichloroethene	98 ± 5	92 ± 10
Chloroform	93 ± 8	102 ± 11
1,2-dichloroethane	98 ± 10	96 ± 17
1,1,1-trichloroethane	104 ± 9	106 ± 11
Carbon tetrachloride	102 ± 10	100 ± 13
Acrylonitrile	85 ± 13	89 ± 8
Bromodichloromethane	108 ± 10	96 ± 8
1,2-dichloropropane	104 ± 7	96 ± 4
trans-1,3-dichloropropene	109 ± 9	91 ± 6
Trichloroethene	105 ± 9	98 ± 6
Benzene	106 ± 7	94 ± 4
Dibromochloromethane	102 ± 11	98 ± 10
1,1,2-trichloroethane	95 ± 8	98 ± 5
cis-1,3-dichloropropene	109 ± 9	92 ± 7
Bromoform	104 ± 14	90 ± 9
Tetrachloroethene	105 ± 9	104 ± 13
1,1,2,2-tetrachloroethane	90 ± 9	98 ± 8
Toluene	106 ± 7	102 ± 4
Chlorobenzene	101 ± 7	101 ± 5
Ethylbenzene	103 ± 5	97 ± 5
2-chloroethyl vinyl ether	94 ± 50	--
Acrolein	113 ± 76	NAe
Average compound recovery	102 ± 8	96 ± 7

a From references 1 and 2.
b Reagent water was spiked with 25 ug/L of each compound except acrolein and acrylonitrile, which were added at 100 ug/L. The recoveries are averaged from 9 analyses and were calculated by comparing vacuum extracted determinations to determinations for which spikes were added directly to a purge-and-trap device.
c Ten-gram sediment samples were spiked at 25 ppb. The recoveries were averaged from 9 analyses with three matrix types.
d Laboratory contamination prevented the generation of valid data.
e Compound was not added to this matrix.

SECTION III

ANALYSIS OF METALS AND METALLOIDS IN ESTUARINE AND MARINE SEDIMENTS

CONTENTS

ANALYSIS OF METALS AND METALLOIDS IN ESTUARINE AND MARINE SEDIMENTS

1.0 SCOPE AND APPLICATION

1.1 This method is designed to determine antimony, arsenic, beryllium, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, thallium, and zinc in sediments and dredged materials. These procedures are applicable when sensitive analyses are required to monitor concentration differences between relatively uncontaminated reference areas and contaminated estuarine and marine environments.

1.2 A universal wet oxidation procedure (acid digestion) is recommended that is capable of providing a clean extract suitable for analysis by atomic absorption spectrophotometry (AAS). This digestion has proven effective when determining most of the priority pollutant metals listed above (with the possible exception of beryllium and thallium) (e.g., Table III-2). Because of a lack of reference materials certified for beryllium and thallium, little is known regarding method suitability for these elements.

1.3 The proposed method involves a rigorous acid digestion that most probably extracts metal phases not available to biota (in addition to biologically available phases). However, the silicate matrix of the sediment will not be decomposed. Because of this, any element tightly bound as a naturally occurring silicate may not be fully recovered (a total metals digestion would include hydrofluoric acid).

1.4 Typical limits of detection (LOD) are presented in Table III-1. These vary depending upon the element measured, method of detection, and instrument sensitivity.

2.0 SUMMARY OF METHOD

2.1 A representative sample of sediment is homogenized wet, subsampled, and digested using a wet oxidation method. The resulting extract is analyzed for the metals of interest using various atomic absorption (AA) techniques such as:

- direct aspiration (DFAA) = for higher concentration metals
- graphite furnace (GFAA) = for lower concentration metals
- hydride generation (HYDAA) = for hydride forming elements (antimony, arsenic, selenium)
- cold vapor (CVAA) = for mercury.

Descriptions of these techniques may be found in references 1 through 5.

2.2 Alternative methods of detection may be used providing their performance, limitations, and applicability have been established and approved by U.S. EPA. Inductively coupled plasma (ICP) emission spectrometry may be used for routine metal analyses not requiring the generally lower detection limits attainable by graphite furnace atomic absorption.

3.0 DEFINITIONS

Certified Reference Materials (CRM): A homogeneous sample that has been analyzed a sufficient number of times by numerous qualified laboratories. The data are compiled and certified values are determined through statistical analysis. A number of CRM are commercially available in a wide range of matrices for metals analyses. For sediments, representative examples include National Bureau of Standards river sediment (SRM #1645) and estuarine sediment (SRM #1646) (references 6 and 7) and National Research Council of Canada marine sediments MESS-1 and BCSS-1 (reference 8).

Control Standard: A solution, independent of the calibration standards, whose analyte concentration is known. These are often analyzed as an external check after calibration.

Limit of Detection (LOD): The LOD is the lowest concentration level that can be determined to be statistically different from a blank. The recommended value for LOD is 3σ, where σ is the standard deviation of the blank in replicate analyses (reference 9).

Matrix Modifier: A reagent added to a sample that alters some aspect of its composition (references 10-12).

4.0 INTERFERENCES

4.1 Interferences should be considered to be any chemical or physical phenomenon that can influence the accuracy of the data during an analytical operation. These can have either a positive or a negative effect on the result depending on their nature.

4.2 Contamination of the sample can occur during any stage of collection, handling, storage, or analysis. Potential contaminant sources must be known and steps should be taken to minimize or eliminate them. Some of the most common sources of contamination include prolonged exposure of the sediment to fumes and dust containing metals; insufficiently clean sample containers, storage facilities, and testing apparatus; as well as the use of contaminated reagents during analysis (reference 13).

4.3 Most instrumental methods are prone to matrix interferences, which can either suppress or enhance the analyte signal. If a matrix interference is suspected, its effect should be determined and corrective action taken. A common first course of corrective action is the method of standard addition (MSA). Details of the technique are provided in Sect. 10.4.2 (adapted from reference 14). Some common matrix interferences are listed below, along with suggested corrective measures (references 15, 16).

4.3.1 Matrix products - spectral interferences can occur due to light scattering by products of the atomization process (e.g., refractory oxides). Flame temperature or fuel-to-oxidant ratio can be varied to minimize the

effect. Alternately, if the source of the interference is known, an excess of the interferent (radiation buffer) can be added to the sample and standards (reference 15).

4.3.2 Non-specific absorption (light scatter) - usually due to dissolved solids or suspended particulates present in the sample prior to atomization, which absorb analyte radiation. Background correction (e.g., continuous source deuterium lamp, Zeeman effect) should be used whenever this occurs.

4.3.3 Interelement interference - sediments contain elements in widely varying concentration ranges. In some cases, a trace component being sought may have its primary absorption line close to the absorption or emission line of a major component. If this occurs, an interference is observed proportional to the concentration of the interfering element. A secondary absorption line that is not affected may be used to overcome this problem.

4.4 Chemical interferences - some of which are poorly understood, can occur during instrumental analysis of the sample extracts and are a particular problem for GFAA. A great many of these interferences have been addressed in the literature and in most cases a sample pretreatment or instrumental modification has been proposed as a remedy. A review of the recent literature is provided by reference 17.

5.0 SAFETY

Laboratory personnel should be well versed in standard laboratory safety practices. It is the responsibility of all staff and management to ensure that safety training is mandatory. The laboratory is resonsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data on handling chemicals safely should also be made available to all personnel involved in these analyses. Additional information on laboratory safety can be found in references 18-20.

5.1 Chemicals and reagents should be properly labeled and stored in an area appropriate to their properties. Any reagents whose composition or properties may change with time must be dated and properly disposed of on or before the expiration date.

5.2 Areas where strong oxidizing agents and flammable or explosive materials are used should be well labeled and the necessary restrictions should be imposed.

5.3 Where laboratory apparatus and instrumentation are used, the manufacturer's safety precautions should be strictly followed.

5.4 Wearing of safety clothing such as lab coats, gloves, and eye protection should be mandatory when working with or around potentially dangerous equipment.

5.5 Contaminated sediments (including dredged materials) can contain levels of substances that may be hazardous. Anyone handling these samples should be aware of this and take the necessary precautions.

6.0 APPARATUS AND EQUIPMENT

6.1 Sample Containers - wide-mouth, screw-cap jars made of either borosilicate glass or noncontaminating plastic (linear or high-density polyethylene, or equivalent). Quartz or tetrafluoroethylene (TFE) containers are preferred but may be prohibitively expensive. All containers should be prerinsed with dilute acid and distilled deionized water (DDW) as described in Sect. 10.7.

6.2 Homogenizing Vessel - a plastic or glass container large enough to mix the entire sample. A plastic spatula or glass stirring rod will be used to homogenize the sediment. All sampling and subsampling tools should be rinsed with dilute acid and DDW, as described in Sect. 10.7, between each sample and subsample.

6.3 Digestion Vessels - 125-mL borosilicate glass Erlenmeyer flasks equipped with all glass reflux caps (Tuttle covers). Tuttle covers or equivalent

reflux caps are essential for preventing evaporative loss of volatile compounds or elements during high-temperature digestion. They are commercially available (e.g., Fisher Scientific) and are easily produced from borosilicate test tubes.

6.4 Hot Plate - a thermostatically controlled plate with a range of 75 to 400° C.

6.5 Fumehood - a properly constructed hood capable of withstanding acid fumes. It must be equipped with an exhaust fan having sufficient capacity to remove all fumes and should be constructed of noncontaminating materials (e.g., PVC), if possible.

6.6 Atomic Absorption Spectrophotometer (AAS).

6.6.1 The AAS must have sufficient sensitivity and stability to perform within the specifications required by the method (Sect. 11). The instrument should have automatic background correction, direct aspiration flame, as well as flameless capabilities. The instrument must have a routine maintenance program to ensure proper performance and trouble-free operation. All source lamps should be handled with care and the exit windows kept free of dust and fingerprints. Periodic intensity and stability checks of the lamps should be made. Any lamp showing signs of deterioration should be replaced (reference 4).

6.6.2 A graphite furnace (also called carbon rod) attachment for the AAS is recommended when determining most elements in the low concentration ranges. Most, if not all, AAS manufacturers offer this equipment as an accessory. The stability and sensitivity afforded by the furnace is typically one to two orders of magnitude better than direct aspiration (reference 21).

6.6.3 In addition to the graphite furnace, another flameless attachment can be used in conjunction with the AAS to determine the hydride-forming elements (arsenic, antimony, and selenium). Most such attachments may also be used to analyze for mercury using the cold vapor technique. These methods

are preferable to the graphite furnace since they vaporize the analyte from the sample matrix prior to detection.

6.6.4 If available, a dedicated mercury monitor may be used for the determination of mercury using the cold vapor technique. These units are typically designed to give maximum sensitivity required for low-level determinations.

6.7 ICP Emission Spectrometer (optional) - ICP emission spectroscopy enables one to make simultaneous multielement analyses. The ICP instrument must have sufficient sensitivity and stability to perform within the specifications required by the method. Certain elements of interest are not amenable to ICP analysis of sediments due to volatility or spectral interferences (i.e., As, Hg, Pb, Se, and Tl).

7.0 REAGENTS AND CONSUMABLE MATERIALS

The purity of all reagents used for trace metal determinations is extremely important. Reagents should be checked for purity prior to use to confirm the absence of contamination (reference 13). American Chemical Society (ACS) reagent grade acids are suitable for routine analyses. Low level analyses may require Instra-analyzed grade acids (J.T. Baker Chemical Company) or equivalent.

7.1 Distilled Deionized Water (DDW) - a water purified by distillation (or equivalent) followed by conditioning with a mixed bed ion exchanger. Such units are commercially available and yield a water with a typical resistivity of 18 megohms/cm.

7.2 Hydrochloric Acid - concentrated (35%).

7.3 Hydroxylamine Hydrochloride [20% (w/v)]: - dissolve 20 g of American Chemical Society (ACS) grade $NH_2OH \cdot HCl$ in 100 mL of DDW. Store in a precleaned glass or plastic bottle. Prepare weekly.

7.4 Nitric Acid - concentrated (70%).

7.5 Sodium Borohydride, ACS Grade - granular or powder.

7.6 Sodium Hydroxide, ACS Grade - pellets or flakes.

7.7 Stannous Chloride [20% (w/v)] - dissolve 20 g of ACS grade $SnCl_2$ in 20 mL of concentrated hydrochloric acid. Warm gently until solution clears, cool, and add DDW until the solution reaches a 100 mL volume. Store in a precleaned glass or plastic bottle. Prepare fresh daily.

7.8 Stock Standard Solutions - These standards (typically 1,000 ppm) can be purchased as certified solutions or prepared from ACS-grade metal salts and pure compounds. Suitable procedures for preparing stock solutions are well documented (e.g., reference 22) and include the steps below.

7.8.1 Accurately weigh 1,000 mg of pure metal or metal equivalent of the salt and dissolve in a minimum amount (usually about 20 mL) of an appropriate acid. Once the reagent is dissolved, dilute the solution to 1,000 mL with DDW and store in a precleaned plastic bottle. The solution is usually stable for at least a year but must be checked periodically against an in-house control standard (Sect. 10).

8.0 SAMPLE COLLECTION, PREPARATION, AND STORAGE

8.1 Possible problems during sample collection include contamination from the sampling device, airborne dust, engine exhaust, winches or steel cables, cross-contamination from previous samples, or improper subsampling procedures. Avoid using metal during sample collection, if possible. If metal must be used, high-grade stainless steel is preferred.

8.2 A minimum sample size of 5 g (wet wt) is required for the analysis of all priority pollutant metals. To allow for duplicates, spikes, and required reanalysis, a minimum sample size of 50 g (wet wt) is recommended. To allow

for mixing of the sample and possible nonrepresentative material, a 240 mL (8 oz) jar is recommended for collection.

8.3 Store samples in clean containers after collection and, if possible, pack them in ice. Samples should be stored at -20° C. Although freezing is not required for all U.S. EPA procedures (e.g., reference 23), it is recommended to minimize potential alteration of analytes by microbes. Care should be taken to prevent container breakage during freezing. Leave sufficient headspace for water to expand and freeze the containers at an angle.

8.4 No recommended holding time for sediments has been established by U.S. EPA. A holding time of 6 months (except for mercury samples, which should be held a maximum of 30 days) is consistent with the holding time required by U.S. EPA for water samples (reference 14).

9.0 CALIBRATION AND STANDARDIZATION

9.1 Calibration standards are prepared by serial dilutions of the stock solutions. The acid matrix of the standards should be as closely matched to the samples as possible. Mixed standards of more than one element may be prepared only after their compatibility has been determined. Some common mixed standards include, but may not be limited to, the following:

- Cd, Cu, Pb, Ni, and Zn
- As, Se, and Sb

9.1.1 Do not add an incompatible anion to a mixed or single element standard. For example, adding chloride to a silver standard could form a precipitate of silver chloride (AgCl).

9.1.2 Do not mix metals that are incompatible in solution. For example, lead and chromium may form a precipitate of lead chromate ($PbCrO_4$).

9.2 Concentration ranges of the standards should bracket those for the samples to be analyzed. At least four analyses (one blank and three standards

of increasing concentration) should be used to calibrate the instrument at the beginning of each shift.

9.3 Stability of a calibration standard varies with element, acid matrix, concentration, and presence of other elements. As a general rule, standards should be continuously monitored and replaced when necessary. As a matter of protocol, the following can be used as a guideline:

less than 0.1 ppm	-	prepare daily
0.1 to 1 ppm	-	prepare weekly
1.0 to 10 ppm	-	prepare monthly
10 to 100 ppm	-	prepare quarterly
100+ ppm	-	prepare yearly (at a minimum)

9.4 Initial Standardization - follow manufacturer's suggestions for standardizing instrument and check sensitivity performance with specifications. If performance is acceptable, proceed with analysis; if not, refer to manufacturer's troubleshooting guide.

9.5 After standardizing the instrument, analyze an independent control standard as a check. If the result is acceptable, proceed; otherwise, troubleshoot calibration standards, control standard, or instrument.

9.6 Ongoing Calibration (reference 14) - the instrument should be tested with a single point calibration every 2 h during an analysis run or at a frequeny of 10 percent of the analyses, whichever is more frequent. A calibration check must also be run after the last sample in a laboratory shift. A standard concentration in the middle of the initial calibration range should be used.

If the difference between the ongoing calibration result and the known standard concentration is greater than $\pm$10 percent (or $\pm$20 percent for mercury analysis), the instrument must be recalibrated and the preceding 10 samples reanalyzed for the analytes affected.

9.7 In the event that a sample is outside of the linear response of the instrument, it must be diluted to within range or reanalyzed using a less sensitive setup. This is commonly accomplished by calibrating the instrument with higher concentration standards using a secondary or tertiary wavelength with less sensitivity.

10.0 QUALITY CONTROL [see reference 14 and Quality Assurance/Quality Control (QA/QC) for 301(h) Monitoring Programs: Guidance on Field and Laboratory Methods (Tetra Tech 1986).]

A quality control program enables the assessment of the precision and accuracy of data. Precision is estimated by analysis of replicates. Accuracy is estimated by the analysis of blanks, spiked samples, and laboratory control samples (reference 24).

10.1 Replicates can be chosen to reflect the precision of most stages of the overall analytical method. Replicates can consist of different subsamples of a sediment homogenate or replicate instrumental analyses of the same digestion extract.

10.1.1 Replicate analyses of sediment subsamples are important because "the greatest potential for sample deterioration and/or contamination occurs during preanalysis steps of sample collection, handling, preservation, and storage" (reference 23).

10.1.2 Replicate analyses of a digestate focus only on the bench chemistry and instrumental variability of the method. Together with replicate analysis of sediment subsamples, they can be used to assess the impact of each stage on the overall precision of the analytical result.

10.1.3 At least one replicate (a subsample of a sediment homogenate) must be analyzed from each group of samples of a similar matrix type and concentration for each batch of samples or for each 20 samples, whichever is more frequent. If two analytical methods are used for the same element in a batch of samples, duplicates must be run by each method used.

The relative percent differences (RPD) for each component are calculated as follows:

$$RPD = \frac{D_1 - D_2}{(D_1 + D_2)/2} \times 100$$

where

D_1 = first sample value.

D_2 = second sample value.

10.2 As in the case of replicates, blanks can be chosen to address most stages of the overall analytical method. They include transportation, cross-contamination, reagent, and calibration blanks.

10.2.1 Transportation blanks are derived from empty containers that have been stored with samples in the field and carried with them to the laboratory. A small amount of 5 percent (v/v) HNO_3 is used to rinse the inside of the container. The acid rinse is then retained for analysis. Transportation blanks serve as estimates of contamination during preanalysis steps (Sect. 10.1.1).

10.2.2 Cross-contamination blanks are used to estimate concentration from sampling and homogenizing utensils that may carry over from one sample to the next. They are prepared by collecting a final rinse after cleaning utensils. The final rinse should be performed with a known volume of 5 percent (v/v) HNO_3. One cross-contamination blank should be analyzed for each batch of samples.

10.2.3 Reagent (preparation) blanks are aliquots of 5 percent (v/v) HNO_3 that are processed through each sample preparation step (e.g., reagent addition, digestion, dilution). At least one reagent blank must be prepared for each batch of samples or for every 20 samples, whichever is more frequent. Reagent blanks serve as estimators of contamination resulting from the chemical analysis steps.

All samples with at least one analyte concentration that is less than 10 times the corresponding concentration in the associated reagent blank must be redigested and reanalyzed.

10.2.4 Calibration blanks consist of 5 percent (v/v) HNO_3 and are analyzed each time the instrument is calibrated, at the beginning of each analysis run, and at a frequency of 10 percent during a run. Calibration blanks are used to ensure that the analytical instrument is not introducing false positive results during analysis. (Ongoing calibration quality assurance is discussed in Sect. 9.6.)

10.3 The results obtained from the reagent blanks can be used to calculate the LOD (Sect. 3) for the method. This is the assigned minimum value above which reliable data can be reported. Results for at least the reagent blank should be reported with the final data set.

10.4 Spiked samples are samples to which small volumes of standard solutions of the elements of interest have been added. Spiked samples provide a means of assessing losses during digestion, distillation, or other pretreatment steps. The spike is added before the pretreatment steps and should be 0.5 to 2.0 times the concentrations of the elements in the sample. At least one spiked sample must be analyzed for each batch of samples of a similar matrix type and concentration or for each 20 samples, whichever is more frequent.

10.4.1 The percent recovery for each element is calculated as follows:

$$\% \text{ Recovery} = \frac{(\text{spike + sample result}) - (\text{sample result})}{(\text{spike added})} \times 100$$

Spike percent recoveries should not be used to determine a correction factor to compensate for losses.

10.4.2 If graphite furnace AA is used, a single analytical spike is required <u>after</u> any digestion steps to determine if the method of standard additions (MSA) is required (reference 14 was used to develop this section).

The spike should be added at a concentration (in the sample) that is twice the LOD. The unspiked sample aliquot must be compensated for any volume change in the spiked samples by addition of DDW to the unspiked sample aliquot. The percent recovery of the spike should be calculated as in Sect. 10.4.1

10.4.2.1 If the sample absorbance or concentration is >50 percent of the spike[1] and the spike recovery is between 85 and 115 percent, the sample should be quantified directly from the calibration curve.

10.4.2.2 If the spike recovery is less than 40 percent, the sample must be diluted and rerun with another spike. Dilute the sample by a factor of 5 to 10 and rerun. This step must only be performed once. If after dilution the spike recovery is still <40 percent, there are interferences associated with the instrumental technique that prevent GFAA analysis of the sample.

10.4.2.3 If the spike recovery is >40 percent and the sample absorbance or concentration is <50 percent of the spike[1], report the analyte as less than the LOD or less than the LOD times the dilution factor if the sample was diluted.

10.4.2.4 If the sample absorbance or concentration is >50 percent of the spike[1] and the spike recovery is <85 or >115 percent, the sample must be quantified by MSA.

10.4.2.5 The following procedures should be incorporated into MSA analyses.

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[1][Note that spike[1] is defined throughout Sect. 10.4.2 as (absorbance or concentration of spike sample) minus (absorbance or concentration of the sample.]

a) Data from MSA calculations must be within the linear range as determined by the calibration curve generated at the beginning of the analytical run.

b) The sample and three spikes must be analyzed consecutively for MSA quantitation (the "initial" spike run data is specifically excluded from use in the MSA quantitation).

c) Spikes (post-digestion, as for the "initial" spike in Sect. 10.4.2) should be prepared such that:

- Spike 1 is approximately 50 percent of the sample absorbance.

- Spike 2 is approximately 100 percent of the sample absorbance.

- Spike 3 is approximately 150 percent of the sample absorbance.

d) The data for each MSA analysis should be clearly identified in the raw data documentation along with the slope, intercept and correlation coefficient (r) for the least squares fit of the data.

10.5 Laboratory control samples are certified reference materials (CRM) submitted blind to the laboratory. CRM provide an estimate of the accuracy of the overall method. A CRM must be chosen that has a similar matrix to samples and contains all the analytes. CRM can be purchased from a number of agencies and are available for a variety of sediments (see Sect. 3.0). A catalog of CRM (reference 7) is available from the National Bureau of Standards, Office of Standard Reference Materials, Room B311, Chemistry Building, National Bureau of Standards, Washington, DC 20234 (301/921-2045). Information on the National Research Council Canada CRMs (reference 8) is available from

Marine Analytical Chemistry Standards Program, Division of Chemistry, National Research Council, Montreal Road, Ottawa, Canada, K1A-0R9 (613/993-9101).

10.5.1 Unlike an analyte spike (Sect. 10.4), a CRM tests the dissolution technique as well as instrument calibration and matrix interferences.

10.5.2 A minimum of one CRM should be analyzed for each survey or 2 percent of the total number of samples (i.e., 1 per 50 samples), whichever is more frequent).

10.5.3 The percent recovery for each element for the overall method is calculated as follows:

$$\% \text{ Recovery} = \frac{x}{REF} \times 100$$

where

x = the analytical result for the element
REF = the certified result for the element.

The data obtained for each reference material should be used to troubleshoot the method if results fall outside the acceptable range (i.e., the 95 percent confidence interval). Percent recovery values should not be used to determine a correction factor to compensate for apparent procedural losses.

10.6 Maintenance of Records - the data obtained from any QC work should be recorded in an organized manner to allow for easy retrieval and reviewing. If sufficient data have been collected, it is recommended that these be plotted on a control chart for a quick visual assessment. A typical control chart for CRM results is presented in Figure III-1.

10.6.1 The quality control chart can be used to determine if the following recommended guidelines are met:

10.6.1.1 Not more than 5 percent of the results lie outside two standard deviations (warning limit). A result outside three standard deviations requires action.

10.6.1.2 There are no regular periodic variations.

10.7 Cleaning and preparation of labware is an integral part of a quality assurance/quality control (QA/QC) program. Many cleaning procedures have been proposed in the literature that are suitable for decontaminating equipment. The main concerns with cleaning are removing elements of interest from labware while maintaining an inactive surface. Some cleaning procedures tend to be too harsh, producing an surface with an ion exchange capacity. In this case a solution could partially or completely "lose" an analyte to the container walls (references 25, 26).

10.7.1 When analyte concentrations vary by orders of magnitude, it is best to use dedicated labware; i.e., relatively high-concentration samples should have their own labware that is never used for low-concentration samples. This helps avoid cross-contamination (carryover).

10.7.2 A good universal cleaning procedure for glass and plasticware is outlined below.

10.7.2.1 Wash labware with a metal-free detergent and warm water.

10.7.2.2 Rinse at least three times with tap water followed by distilled deionized water (DDW).

10.7.2.3 Soak equipment or labware in a dilute acid (25 percent HNO_3) bath for 24 h. If possible, the bath should be maintained at an elevated temperature (70^{o} C).

10.7.2.4 Rinse labware with large volumes of DDW and use immediately. If a time lapse must exist, the apparatus should be stored under dust-free conditions and rinsed further with DDW prior to use.

NOTES:
- Change the acid batch periodically such that no significant buildup of metals occurs.
- At no time should a metal-containing reagent such as chromic acid be used.

10.8 Round Robin or Interlaboratory Check Programs - In addition to the quality control measures discussed above, all laboratories should participate in interlaboratory check programs (see Part II of Exhibit E in reference 14).

11.0 PROCEDURE

11.1 Homogenize samples prior to analysis to ensure that representative aliquots are taken. Place the entire sample into the homogenizing vessel and blend with a plastic spatula or glass rod. Mix any water that has separated from the sediment back into the sample. Remove and make note of nonrepresentative material (e.g., twigs, leaves, shells, rocks, and any material larger than 0.25 in).

11.2 Analyze a separate aliquot of sediment for moisture content.

11.2.1 Weigh a small aluminum drying dish to the nearest 0.1 mg (D).

11.2.2 Add approximately 2-3 g of homogenized sediment to the dish and reweigh (A).

11.2.3 Dry sediment at 103° C overnight, cool in a dessicator, and reweigh (B).

11.2.4 Calculate percent moisture as follows:

$$\% H_2O = \frac{A-B}{A-D} \times 100$$

11.3 Accurately weigh a 5-g (wet) aliquot of homogenized sediment to the nearest 0.1 mg. Transfer the weighed sediment to a precleaned 125-mL Erlenmeyer

flask equipped with an all-glass reflux cap. Analyze a sufficient number of reagent blanks, sample duplicates, analyte spikes, and certified reference materials concurrently (Sect. 10).

11.4 Slowly add 5 mL of concentrated nitric acid followed by 10 mL of concentrated hydrochloric acid. If foaming occurs during acid addition, swirl the flasks while adding 2- to 3-mL increments. Allow flasks to stand at room temperature for approximately 15 hours in a dust-free ventilated environment. Periodically swirl the flasks to ensure adequate mixing of the sediment and acid.

11.5 After 15 hours, gently heat the flask to approximately 100° C and hold at this temperature for one hour. Gradually increase the temperature in 50° C increments to a maximum of 250° C. Continue heating until all reddish brown fumes have disappeared and organic matter has been digested. This usually takes about 4 hours. If large amounts of organic matter remain, additional nitric acid should be added in 2- to 3-mL increments and heating should be continued until the organic matter has been consumed. Do not rush the initial digestion as losses of volatile elements will likely occur. Once digestion is complete, cool flasks to room temperature.

NOTE: Most hotplates do not have a uniform temperature over the entire surface. Rotate flasks as required to ensure that all samples digest in approximately the same time.

11.6 When the digestion is complete, rinse the reflux caps with DDW and combine the rinse with the extract in the flask. Transfer the extract to a precleaned 100-mL volumetric flask. Rinse the Erlenmeyer flask three times with DDW and combine with the extract in the volumetric flask. Adjust the volume to 100 mL with DDW and transfer to a precleaned plastic bottle.

NOTE: Some elements are not as stable as others in solution and therefore should be analyzed first. Stability can be determined by daily analysis of the extracts. However, the following can be used as a guideline:

Sb, Pb, Hg, Se and Ag - analyze within 1 day
As and Cd - analyze within 2 days
Cr, Cu, Ni and Zn - analyze within 1 week
Be and Tl - to be determined.

11.7 Instrumental analysis - The extracts will be analyzed using various techniques of atomic absorption spectrophotometry (AAS) or atomic emission spectrophotometry. The method of choice depends on instrument availability, analyte concentration, and sample matrix. In some instances it may be useful to use more than one method to confirm a result.

11.7.1 Follow the manufacturer's instructions for initial setup and calibrate as outlined in Sect. 9 of this method. As every instrument responds uniquely to a given set of conditions, it is the analyst's responsibility to develop the optimum set of parameters. Use calibration standards and CRM to ensure that optimum conditions exist.

11.7.2 Table III-1 lists some general information for each of the priority pollutant metals.

11.7.3 It is possible to use alternate methods of detection providing they have been validated using a sufficient number of previously analyzed samples or CRM.

11.8 All data generated must be clearly recorded on a strip chart or printer, or manually logged in prepared tables. The order in which the extracts are analyzed should be the same as it appears in the records. The data, when assembled, should be reported in consistent units (i.e., mg/L) to avoid errors when calculating the final results (ug/g). The final report should contain all necessary methods, results, quality control data (e.g., reagent blank values), and limits of detection for each element. The report must clearly state if any data were blank-corrected.

12.0 CALCULATIONS

12.1 All results are reported as micrograms of element per dry gram of sediment:

$$\text{ug/g ELEMENT (dry weight basis)} = \frac{C \times V}{W\,(1-M)}$$

where:

C = concentration (may be blank corrected) of element in final extract (ug/mL)
V = volume of final extract (mL)
W = weight of wet sediment (g)
M = sediment moisture expressed as a decimal.

Reagent blank corrections may be made and blank values must always be reported.

13.0 PRECISION AND ACCURACY

In order to estimate precision and accuracy (single lab, multi-operator), a number of CRM and analyte spikes were analyzed using this method. Table III-2 summarizes typical data obtained. No data are currently available for either beryllium or thallium.

14.0 REFERENCES

1. Ebdon, L. 1982. An introduction to atomic absorption spectroscopy: a self-teaching approach. Heyden, London.

2. Dittrich, K. 1982. Atomic absorption spectrometry. Scientific Pocket-books, Vol. 276: Chemistry series. Akad-Verlag, Berlin.

3. Cresser, M.S. and B.L. Sharp (eds). 1981. Annual reports on analytical spectroscopy. The Royal Society of Chemistry, London.

4. Cantle, J.E. (ed). Techniques and instrumentation in analytical chemistry, Volume 5: Atomic absorption spectrometry. Elsevier, Amsterdam.

5. Slavin, W. 1984. Graphite furnce AAS - a source book. Perkin-Elmer Corp, Ridgefield, CT.

6. Taylor, J.K. 1985. Standard reference materials: handbook for SRM users. National Bureau of Standards Special Publication 260-100. National Bureau of Standards, Washington, DC.

7. Hudson, C.H. (ed). 1984. NBS standard reference materials catalog. 1984-1985. National Bureau of Standards Special Publication 260. National Bureau of Standards, Washington, DC.

8. National Research Council Canada. 1981. Marine sediment reference materials. National Research Council Canada, Division of Chemistry, Marine Analytical Chemistry Standards Program, Ottawa, Canada.

9. Keith, L.J., W. Crummet, J. Deegan, Jr., R.A. Libby, J.K. Taylor, and G. Wentler. 1983. Principles of environmental analysis. Anal. Chem. 55:2210-2218.

10. Manning, D.C., and W. Slavin. 1983. The determination of trace elements in natural waters using the stabilized temperature platform furnace. Applied Spectroscopy 37:1-11.

11. Hinderberger, E.J., M.L. Kaiser, and S.R. Koirtyohann. 1981. Furnace atomic absorption analysis of biological samples using the L'vov platform and matrix modification. Atomic Spectroscopy 2:1-7.

12. Sturgeon, R.E., S.N. Willie, and S.S. Berman. 1985. Preconcentration of selenium and antimony from seawater for determination by graphite furance atomic absorption spectrometry. Anal. Chem. 57:6-9.

13. Murphy, T.J. 1976. The role of the analytical blank in accurate trace analysis. pp. 509-539. In: Accuracy in Trace Analysis: Sampling, Sample Handling, and Analysis. National Bureau of Standards Special Publication 422. National Bureau of Standards, Washington, DC.

14. U.S. Environmental Protection Agency. 1985. U.S. EPA Contract Laboratory Program - statement of work for inorganic analyses, multi-media multi-concentration.

15. Skoog, D.A. 1985. Principles of Instrumental Analysis. Saunders, Philadelphia, PA. pp. 270-279.

16. Veillon, C. 1976. Optical atomic spectroscopic methods. pp. 123-181. In: Trace Analysis: Spectroscopic Methods for Elements. D. Winefordner (ed). Wiley, New York.

17. Slavin, W., and D.C. Manning. 1982. Graphite furnace interferences, a guide to the literature. Prog. Anal. Atomic Spectroscopy 5:243-340.

18. Carcinogens - working with carcinogens. DHEW, PHS, CDC, NIOSH. Publication 77-206 (Aug. 1977).

19. OSHA safety and health standards, general industry. OSHA 2206, 29 CFR 1910 (revised Jan. 1976).

20. Safety in academic chemistry laboratories. ACS Publications, Committee on Chemical Safety, 3rd Edition (1979).

21. Fuller, C.W. 1978. Electrothermal atomization for atomic absorption spectroscopy. The Chemical Society, London.

22. U.S. Environmental Protection Agency. 1979. Methods for chemical analysis of water and wastes. pp. 202.1-289.2. U.S. Environmental Protection Agency Environmental Monitoring and Support Laboratory. Cincinnati, OH.

23. Plumb, R.H., Jr. 1981. Procedures for handling and chemical analysis of sediment and water samples. Technical Report EPA/CE-81-1. Environmental Protection Agency/Corps of Engineers Technical Committee on Criteria for Dredged and Fill Material, U.S. Army Waterways Experiment Station, Vicksburg, MS. 471 pp.

24. U.S. Environmental Protection Agency. 1983. Guidance for preparation of combined work/quality assurance project plans for water monitoring. Office of Water Regulations and Standards, U.S. EPA, Washington, DC. 33 pp.

25. Batley, G.E., and D. Gardner. 1977. Sampling and storage of natural waters for trace metal analysis. Water Res. 44:745-756.

26. Laxen, D.P.H., and R.M. Harrison. 1981. Cleaning methods for polythene containers prior to the determination of trace metals in freshwater samples. Anal. Chem. 53:345-350.

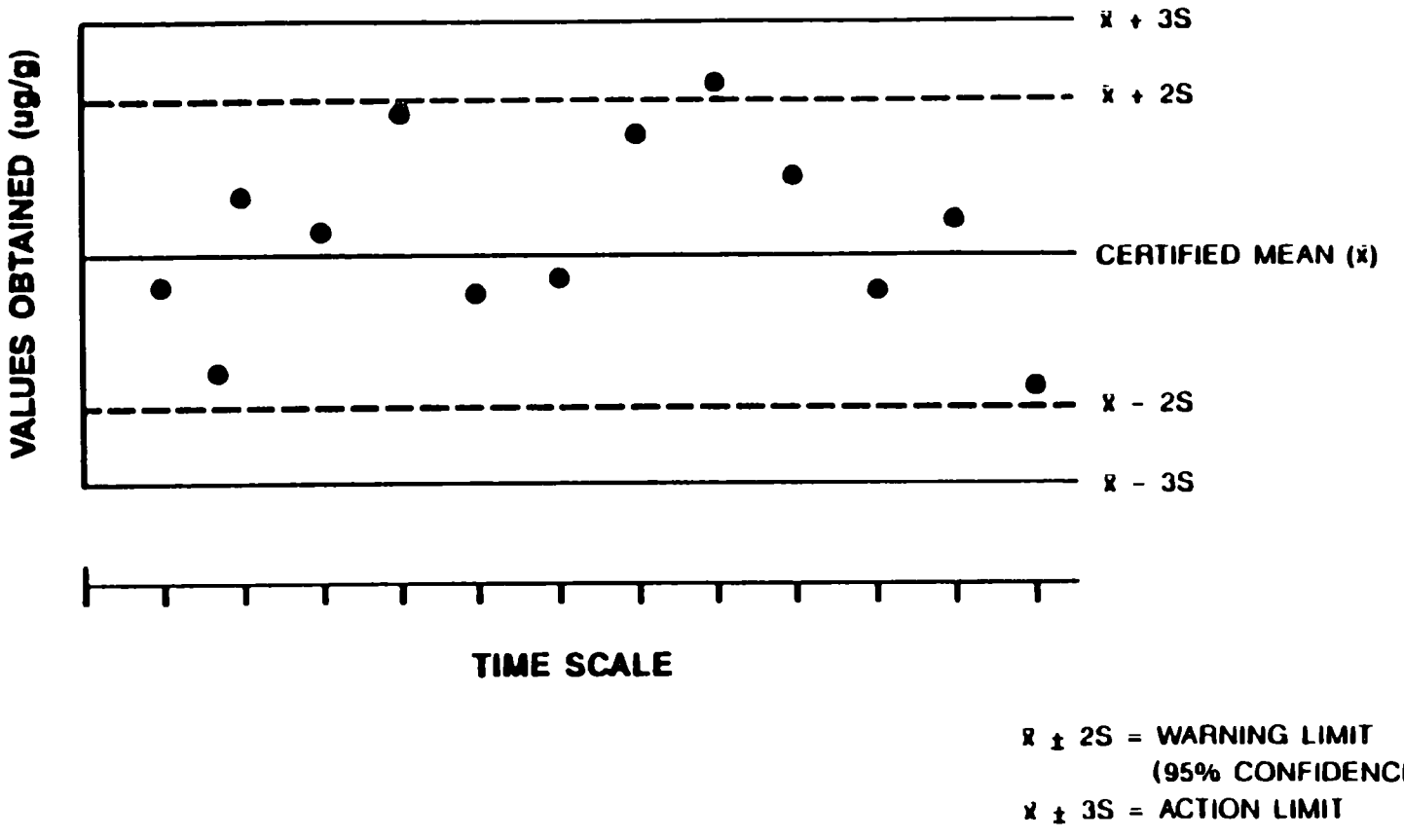

Figure III-1. Quality control chart.

TABLE III-1. GENERAL INFORMATION FOR EACH PRIORITY POLLUTANT METAL

Element	Method[1]	Wavelength (nm)	L.O.D.[2]	Signal	Notes[3]
Antimony	HYDAA	217.6	0.1	Peak Area	
	GFAA	217.6	0.1	Peak Height	
	ICP		3.0		
Arsenic	HYDAA	193.7	0.1	Peak Area	Requires a Matrix Modifier
	GFAA	193.7	0.1	Peak Height	[e.g., $Ni(NO_3)_2$]
Beryllium	GFAA	234.9	0.05	Peak Height	
Cadmium	DFAA	228.8	0.1	Direct	
	GFAA	228.8	0.1	Peak Height	
Chromium	DFAA	357.9	0.2	Direct	
	GFAA	357.9	0.02	Peak Height	
	ICP		6.0		
Copper	DFAA	324.7	0.1	Direct	
	GFAA	324.7	0.01	Peak Height	
	ICP		0.6		
Lead	DFAA	383.3	1.0	Direct	Requires a Matrix Modifier
	GFAA	383.3	0.1	Peak Height	(e.g., $NH_4H_2PO_4$)
Mercury	CVAA	253.6	0.01	Peak Height	
Nickel	DFAA	232.0	0.5	Direct	
	GFAA	232.0	0.02	Peak Height	
	ICP		1.5		
Selenium	HYDAA	197.3	0.01	Peak Area	Requires a Matrix Modifier
	GFAA	197.3	0.1	Peak Height	[e.g., $Ni(NO_3)_2$]
Silver	DFAA	328.1	0.1	Direct	
	GFAA	328.1	0.1	Peak Height	
	ICP		0.7		
Thallium	GFAA	276.8	0.1	Peak Height	
Zinc	DFAA	213.9	1.0	Direct	
	ICP		0.2		

1 HYDAA = Hydride generation atomic absorption.
GFAA = Graphite furnace atomic absorption.
DFAA = Direct flame atomic absorption.
CVAA = Cold vapor atomic absorption.
ICP = Inductively coupled plasma.

2 L.O.D. = limit of detection - micrograms of element per dry gram of sediment (ppm) based on 5 g (wet) to 100 mL. The limit was determined as twice the standard deviation of a repeated series of blanks (n=5 to 10; 95% confidence level).

3 For example, see reference 10 for discussion of these matrix modifiers.

ODES codes for all elements are the element names.

TABLE III-2. TYPICAL DATA OBTAINED ON A CERTIFIED REFERENCE MATERIAL [NATIONAL RESEARCH COUNCIL OF CANADA MARINE SEDIMENT (MESS - 1)]

Element		Certified/Spiked ($\bar{x} \pm$ S.D.)	n	Found ($\bar{x} \pm$ S.D.)	Detection Method2
Antimony	Sb	0.73 ± 0.08	5	0.61 ± 0.09	HYDAA
Arsenic	As	10.6 ± 1.2	20	9.43 ± 0.32	HYDAA
Beryllium	Be	1.9 ± 0.2	--	No Data	--
Cadmium	Cd	0.59 ± 0.10	20	0.58 ± 0.07	GFAA
Chromium	Cr	71. ± 11.	10	30. ± 2.0	DFAA
Copper	Cu	25.1 ± 3.8	20	22.5 ± 0.71	DFAA
Lead	Pb	34.0 ± 6.1	20	29.7 ± 1.8	DFAA/GFAA4
Mercury	Hg	0.171 ± 0.014	20	0.185 ± 0.015	CVAA
Nickel	Ni	29.5 ± 2.7	10	25.5 ± 2.1	DFAA
Selenium	Se	(0.4)	5	0.33 ± 0.02	HYDAA
Silver	Ag	50.0 (spike)	5	55.0 ± 6.0	DFAA
Thallium	Tl	N.C.3	--	No Data	--
Zinc	Zn	191. ± 17.	20	176. ± 4.5	DFAA

1 All results expressed as micrograms of element per gram of sediment.

2 HYDAA = Hydride generation atomic absorption.
GFAA = Graphite furnace atomic absorption.
DFAA = Direct flame atomic absorption.
CVAA = Cold vapor atomic absorption.

3 N.C. = Not Certified.

4 GFAA may require dilution.