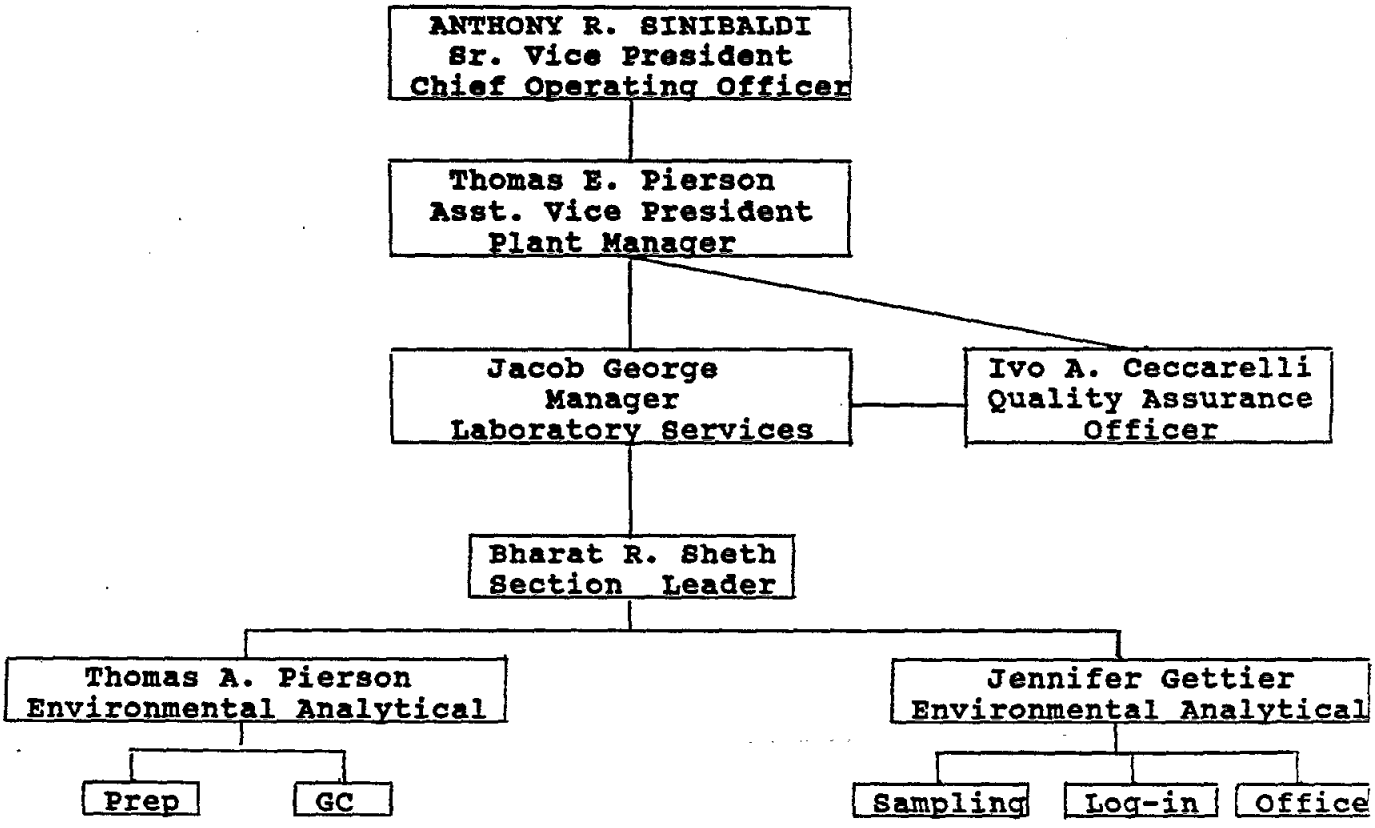
100205

APPENDIX

Contents

		Page No
(1)	Laboratory Organization	A-2
(2)	Resume: Jacob George	A-3
(3)	Resume: Bharat R. Sheth	A-5
(4)	Resume: Jennifer J. Gettier	A-7
(5)	Resume: Thomas A. Pierson	A-8
(6)	Labels: Chromatogram Identification	A-9
(7)	Labels: Sample Bottle	A-10
(8)	Sample Custody form (both sides)	A-11
(9)	Work Sheet: Extractables	A-12
(10)	Work sheet:Field Blank Analysis	A-13
(11)	Work Sheet: Method Blank Analysis	A-14
(12)	Work Sheet: Duplicate Analysis	A-15
(13)	Work Sheet: Spike Recovery	A-16 & 17
(14)	Critical Path For Corretive Action	A-18

LABORATORY ORGANIZATION STRUCTURE



PROJECT ORGANIZATION

Anthony R. Sinibaldi	CEO	(302) 366-8949
Thomas E. Pierson	Project Director	(302) 328-5259
Jacob George	Project Manager	(302) 368-2812
Ivo A. Ceccarelli	Project Quality Assurance Officer	(302) 239-4951
Bharat R. Sheth	Section Leader	(302) 731-1990
Thomas A. Pierson	Project Chemist	(302) 328-2246
Jennifer Gettier	Project Chemist	(302) 998-4479

Note: Monday to Friday, 8:30 to 5:00, all the above personnel can be reached at (302) 834-4536

Jacob George
104 Covered Bridge Lane
Newark, Delaware 19711

Career Summary:

* Organic industrial research and development experience
* Result oriented-recognized history of the new product development and existing product improvement
* Wide range of experience in analytical chemistry
* Expertise in gas chromatography and gas chromatography/mass spectrometry
* Extensive verbal and written communication skills
* Professional management abilities

Experience: Standard Chlorine of Delaware, Inc.
Delaware City, Delaware 19706

1986 to Present: Manager, Laboratory Services

Technical Responsibility: Plan and direct R & D projects; Plan and supervise pilot scale process development projects; Evaluate the data generated by the laboratory; Raw material and process chemistry support for the production plant; Develop new products based on chlorobenzene derivatives; Quality Control for the production plant; Technical services; SPC/SQC program; Develop, update and specify analytical methods; Coordinate and direct the environmental analysis for NPDES, RCRA and CERCLA; Coordinate the training program for the non-technical laboratory staff; Specify for purchasing analytical instrumentation, lab equipments and reagents; Supervise the water treatment for boilers and cooling towers; Initiate and execute cost saving process changes.

1978 to 1986: Senior Chemist and Laboratory Supervisor

Research and Process Development Area:

Conducted product, process and application research. Development work included catalysis in electrophilic aromatic substitution to control isomer ratio, isomerization, trans halogenation, and dehalogenation; development of vapor phase reactors to carry out halogenation, dehalogenation and animation; Identification of Zeolites and other molecular sieves to carry out selective halogenation and alkylation.

AR300272

Analytical Area:

Updated and developed analytical methods for quality control using gas chromatography, liquid chromatography and spectrophotometry. Developed and implemented QA/QC protocol. Supervised the SPC/SQC program. Developed methods for the analysis of trace incidental organics in the chlorinated aromatics using gas chromatography/mass spectrometry. Established an environmental analytical section in the lab to perform NPDES, RCRA, and CERCLA analysis for organics (GC, GC/MS), inorganics (spectrophotometry and other wet chemistry methods), limited chemistry and microbiology. Obtained certification from state of New Jersey to perform NPDES analysis. Developed QA/QC manual for the environmental analysis within the guidelines of CLP.

1975 to 1978: Quality Control Chemist

Performed quality control analysis for raw materials, in process materials and finished products using gas and liquid chromatography,spectrophotometry and wet chemistry methods. Analyzed plant waste effluent streams for priority pollutents by GC, AA and other wet chemistry methods to be used for NPDES purposes.

1973 to 1975: Research Fellow at University of Kanpur, India.

Conducted research as a graduate student under Dr. Thevari in analytical chemistry. Topics were the use of analytical instrumentation, mainly gas and liquid chromatography and mass spectrometry in the determination of organic pollutants in municipal waste and industrial discharge.

Summer months of 1972, 1973 and 1974: Part Time Teacher at Kings College, Kerala, India.

Chemistry instructor in undergraduate courses which also include Qualitative Organic Lab.

EDUCATION:

M. S. : Chemistry, West Chester State University, West Chester, PA. 1982. Emphasis was in Organic chemistry. Special topic of study: Synthesis of organometallic intermediates; Friedel-Crafts alkylation of Ferrocene.

Ph.D. Candidate: Department of Chemistry, University of Kanpur, India; 1973 - 1975.

M. S. : Chemistry, University of Kanpur, India, 1973. Emphasis was in Analytical Chemistry. Special Topic of Study: Use of analytical instrumentation (focused on gas chromatography) in the analysis of industrial discharge.

B. S. : Chemistry, University of Kerala, India, 1970.

Bharat R. Sheth
104 Fox Drive
Newark, DE 19713

Experience: Standard Chlorine of Delaware, Inc.
Delaware City, DE 19706

1987 to Present: Group Leader, Quality Assurance/Quality Control

Responsible for the QA/QC for the analytical services performed by Standard Chlorine of Delaware, Inc.'s laboratory. Results produced by the quality control and the environmental sections of the lab are assessed for acceptance before they are approved, using the guidelines established by the lab. Also responsible for statistical quality control for the process samples through control charts, establishment of upper and lower limits etc. Also supervise the quality control technicians in their day to day operations. Responsible for the maintenance of the analytical instrumentations and their calibration. Duties also include the preparation of standards, inventory control and reordering, scheduling of shift and sample collection etc.

1986-1987: Environmental Analytical Chemist

Performed the analysis of plant discharge for trace metals by atomic absorption, trace organics by purge-and-trap and gas chromatograph, trace organics by solvent extraction followed by concentration and electron capture gas chromatograph, BOD, solids, pH and other wet chemistry to be used for internal process control and NPDES purposes.

1978-1986: Laboratory Technician, Quality Control

Duties include routine Quality Control testing to support the production of chlorinated derivatives of benzene using gas chromatography and other wet chemistry methods. Different types of detectors and calibration procedures were utilized in the chromatography analyses. Performed trace analysis on plant waste effluent and process water for both organics using purge and trap GC and metals using atomic absorption. Performed trace analysis on boiler and cooling water to control the chemical treatment. Also helped in the lab preparation, preparation of standards, standardization and calibration of the analytical instruments etc.

Instruments Used: Different types and models of gas chromatographs, Atomic absorption spectrophotometer, automatic titration equipments, purge and trap equipments (Tekmar), pH meters, analytical balances etc.

1970-1977: Development Chemist; Sheth Phostroxide Manufacturing Co. Bombay, India.

Worked as a Development Chemist in the initial stages of the plant which manufacture tritolyl phosphate. Process was developed in the lab, then scaled up to the pilot and manufacturing stages. Later worked as a Process Chemist to help the smooth operation of the plant. Also performed quality control for the raw materials and the products.

EDUCATION:

B. S. : Chemistry; University of Bombay, India. (1970)

AR300275

Jennifer J. Gettier
2208 Alister Drive
Wilmington, DE 19808

Experience: Standard Chlorine of Delaware, Inc.
Delaware City, Delaware 19706

1988 to Present: Chemist, Environmental Analytical

Perform analysis on NPDES samples for trace metals by atomic absorption, and other routine analysis such as BOD, pH, solids and petrolium hydrocarbons. Also perform microbiological analysis and other wet chemistry on plant effluent and other sources of water related to NPDES. Other duties include collection of environmental samples, their preservation, and sample log-in. Analyze plant effluent samples and other process related samples for benzene and chlorinated derivatives of benzene by EPA methods 602 and 612.

1984 to 1988: Laboratory technician, Quality Control

Duties include routine Quality Control testing in the lab associated with the chlorobenzene production facility on finished products, process material, and the raw material using gas chromatography and other wet chemistry methods. Used different calibration methods such as internal standard, external standard and normalization in the day to day analysis of the process samples. Performed analysis on boiler and cooling water to control the water treatment. Helped the environmental chemist in the samples preparation of NPDES samples for metal analysis. Performed trace organic analysis on plant process water and waste treatment water samples by purge and trap methods. Helped the laboratory supervisor in the lab preparation, standardizing solutions and storage of lab supplies. Also trained new lab technicians in the daily operations.

Instruments Used: Gas Chromatographs: Hewlett Packard models 5830, 5840, 5880, 5890; Shimadzu: models mini-2, 9-A; Perkin Elmer sima 2 and 3; Varian 3400; Atomic absorption: Perkin Elmer 3030 B; pH meters; analytical balances, Tekmar Purge and Trap system, Karl Fischer titration equipments etc.

Education:

B. S. : Biology/Chemistry; Towson State University, Towson, MD 21204 (1984)

AR300276

Thomas A. Pierson
804 Christiana Meadows
Bear, Delaware 19701

Experience: Standard Chlorine of Delaware, Inc.
Delaware City, Delaware 19706

1987 to Present: Environmental Analytical Chemist

Responsible for the analysis of NPDES sample analysis for organics, metals, and other routine analysis such as BOD, pH, solids, petrolium and hydrocarbons etc. Familiar with EPA protocols for organic, metals, and limited chemistry analyses, samples collections, and preservation techniques. Perform microbiological analysis on plant effluent and other process samples. Schedule the collection of routine samples. Also responsible for the calibration of the analytical systems.

1983 to 1987: Laboratory Technician, Quality Control

Quality control testing on raw material, process samples, and the products to support the production of chlorobenzene. Performed the analysis mainly utilizing gas chromatography and other wet chemistry methods. Determined the electrical properties of chlorobenzenes. Helped in the analyses of environmental samples for trace organics using EPA methods. Performed analysis on water samples from boilers and cooling systems to control the chemical treatment. Helped in the preparation of standards and calibration of analytical instruments.

Instruments Used: Gas chromatographs (different types and models), Atomic Absorption Spectrophotometers (Perkin Elmer models 270 and 3030B), Automatic titrators, pH meters, analytical balances, etc.

Education:

B. S. : Currently in the senior level as a part time student at the University of Delaware, majoring in Chemistry. Expected graduation date: Fall of 1989.

AR300277

ANALYST:	METHOD : 601 / 602
SAMPLE NUMBER	:
LAB NUMBER	:
SAMPLE ID	:
SAMPLING DATE/TIME	:
ANALYSIS DATE/TIME	:
SAMPLE VOLUME USED (ml)	:
CONC. FACTOR	:
SURROGATE ADDED (ug / l)	:
% SURROGATE RECOVERY	:

1. Conc. Factor = $\frac{5 \text{ ml}}{\text{ml Used}}$

2. % Recovery = $\frac{(\text{Detected Conc.})}{(\text{Added Conc.})} \times 100$

ANALYST:	: METHOD :
SAMPLE NUMBER	:
LAB NUMBER	:
SAMPLE ID	:
SAMPLING DATE/TIME	:
EXTRACTION DATE/TIME	:
VOL. EXTRACTED (ml)	:
FINAL VOL. OF EXTRACT (ml)	:
EXTRACT INJECTED (ul)	:
GC ANALYSIS DATE	:
SURROGATE ADDED	:
SURROGATE RECOVERED	:
CONC. FACTOR	:

Note: 1. Conc. Factor = $\frac{\text{Vol. Extracted (ml)}}{\text{Final Vol. of Extract (ml)}}$

2. Actual Conc. = Detected Conc. x Conc. Factor

FIG A-1

CHROMATOGRAM IDENTIFICATION FOR
EPA METHODS

AR300278

Standard Chlorine of Delaware, Inc.

GOV. LEA RD. • DELAWARE CITY, DEL. 19706

SAMPLE DESCRIPTION: _____

_____

LOCATION: _____

DATE & TIME: _____

SAMPLE TYPE: _____

PRESERVATIVE: _____

SAMPLED BY: _____

SAMPLE
ID NO: _____ LAB NO: _____

REMARKS: _____

FIG. A-2

AR300279

STANDARD CHLORINE OF DELAWARE, INC.

Custody Transfer Record/Lab Work Request

Received By _____ Client _____ RFW Contact _____

Date _____ Client Contact _____ Date Due _____

Assigned to _____ Phone _____ Project Number _____

SAMPLE IDENTIFICATION						ANALYSES REQUESTED							
Sample No.	Client ID No.	Description	Matrix	Date Collected	Container/Preservative								

Matrix:
S- Soil DS- Drum Solids
W- Water DL- Drum Liquids
O- Oil X- Other

Special Instructions:

Items/Reason	Relinquished By	Received By	Date	Time	Items/Reason	Relinquished By	Received By	Date	Time

RFW 21-2[illegible]/A-3/86

FIG A-8
A-1

AR300280

STANDARD CHLORINE OF DELAWARE, INC.

WORKSHEET: EXTRACTABLES
EPA METHOD 612

PRIMARY STANDARD PREPARED: DATE:_____ TECH:_____

CALIBRATION STANDARD PREPARED: DATE:_____ TECH:_____

QC STANDARD PREPARED: DATE:_____ TECH:_____

CONCENTRATE FOR QC STANDARD: BATCH:_____ SOURCE:_____

MATRIX:_____

SAMPLE ID#	DATE REC'D	SAMPLE WT(g) or VOL.(ml)	CONCENTRATE VOL(ml)	SPIKE ADDED	SURR. ADDED	REM

COMMENTS;_____

SPIKE SOLUTION PREPARED: DATE:_____ TECH:_____

SURROGATE STANDARD PREPARED: DATE:_____ TECH:_____

AR300281

STANDARD CHLORINE OF DELAWARE, INC.

BLANK ANALYSIS SUMMARY

SAMPLE : FIELD BLANK

DATE COLLECTED :_____ DATE ANAYZED:_____

METHOD USED :_____ ANALYST :_____

COMPOUNDS	VOL. USED ml	PEAK AREA counts	RESPONSE factor	AMOUNT ug/l	XF	AMOUNT ACTUAL ug/l
BENZENE						
CHLOROBENZENE						
1,3-DCB						
1,4-DCB						
1,2-DCB						
NB						
1,2,4-TCB						
1,2,3-TCB						
1,2,4,5-TeCB						
1,2,3,4-TeCB						
MCNB						

COMMENTS:_____

_____

_____

_____

FIGURE . A-5

AR300282

STANDARD CHLORINE OF DELAWARE, INC.

BLANK ANALYSIS SUMMARY

SAMPLE : METHOD BLANK

DATE COLLECTED :_____ DATE ANAYZED:_____

METHOD USED :_____ ANALYST :_____

COMPOUNDS	VOL. USED ml	PEAK AREA counts	RESPONSE factor	AMOUNT ug/l	XF	AMOUNT ACTUAL ug/l
BENZENE						
CHLOROBENZENE						
1,3-DCB						
1,4-DCB						
1,2-DCB						
NB						
1,2,4-TCB						
1,2,3-TCB						
1,2,4,5-TeCB						
1,2,3,4-TeCB						
MCNB						

COMMENTS:_____

_____

_____

_____

FIGURE A-6

STANDARD CHLORINE OF DELAWARE, INC.

SUMMARY OF DUPLICATE ANALYSIS

DATE COLLECTED : _____ DATE ANAYZED: _____

METHOD USED : _____ ANALYST : _____

NOTE: For method 602; enter the volume of water used _____ ml

For method EPA 612; enter the volume of water used _____ ml and the final volume of the extract_____ ml

	SAMPLE 1					SAMPLE 2				
COMPOUND	AREA	Kf	AMOUNT	Xf	ACTUAL	AREA	Kf	AMOUNT	XF	ACTUAL
BENZENE										
MCB										
1,3-DCB										
1,4-DCB										
1,2-DCB										
NB										
MCNB										
1,2,4-TCB										
1,2,3-TCB										
1,2,4,5-TeCB										
1,2,3,4-TeCB										

COMMENTS: _____

_____

_____

FIGURE A-7

AR300284

STANDARD CHLORINE OF DELAWARE, INC.

SPIKE RECOVERY

SAMPLE :_____

DATE COLLECTED :_____ DATE ANAYZED:_____

METHOD USED :_____ ANALYST :_____

NOTE: For method 602; enter the volume of water used_____

For method EPA 612; 1 liter sample is concentrated to_____ml

COMPOUND	PEAK AREA counts	RESPONSE factor	AMOUNT ug/l	XF	AMOUNT DETECT ug/l	ACTUAL CONC ug/l
BENZENE						
CHLOROBENZENE						
1,3-DCB						
1,4-DCB						
1,2-DCB						
NB						
1,2,4-TCB						
1,2,3-TCB						
1,2,4,5-TeCB						
1,2,3,4-TeCB						

COMMENTS:_____

_____

_____

_____

FIGURE A-8

AR300285

SPIKE RECOVERY CONTINUED

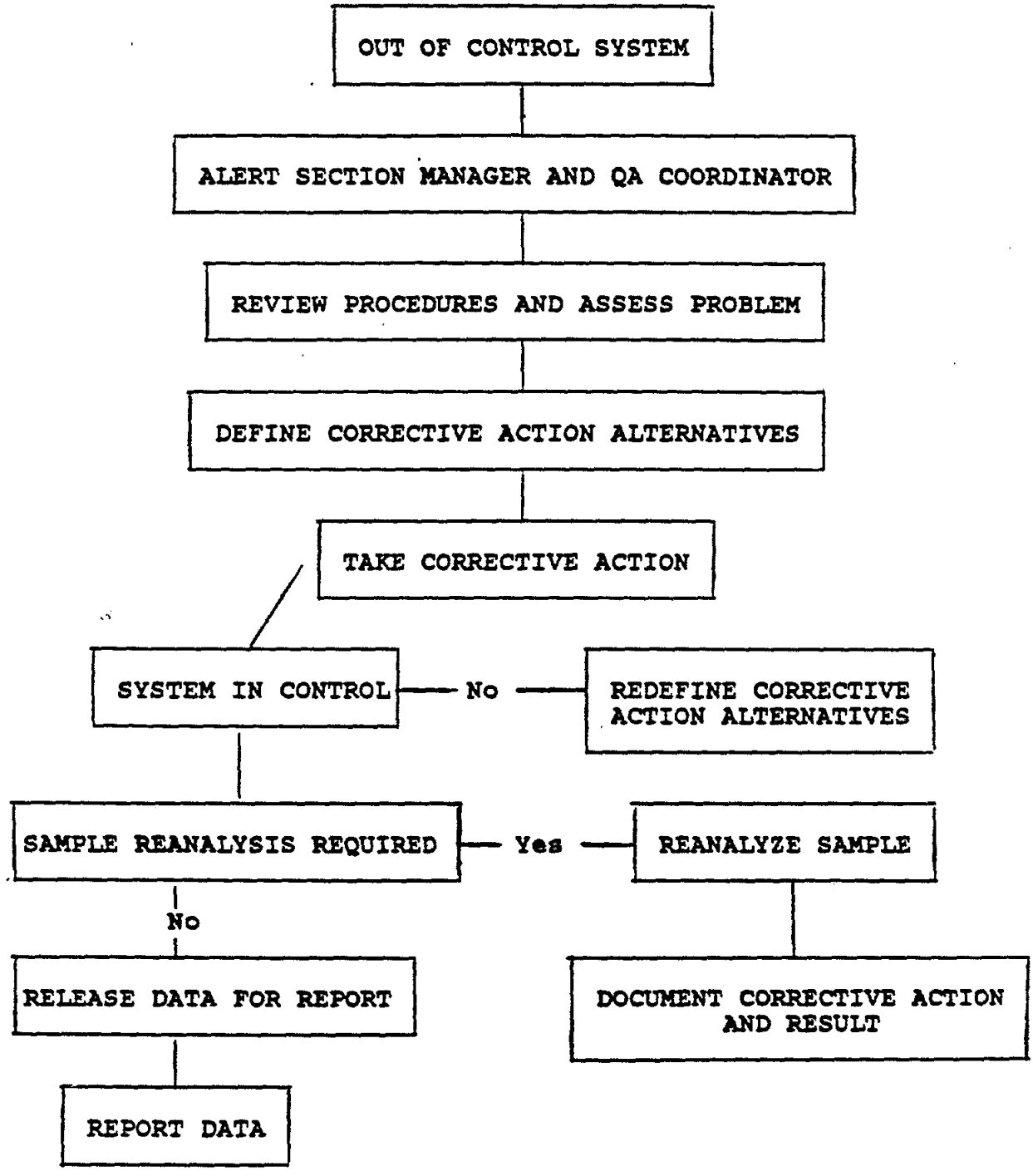
COMPOUND	AMOUNT DETE	AMOUNT ADDED	AMOUNT ORIGIN	AMOUNT RECOV	% RECOVERY	QC LIMITS
BENENE						
CHLOROBENZENE						
1,3-DCB						
1,4-DCB						
1,2-DCB						
NB						
1,2,4-TCB						
1,2,3-TCB						
1,2,4,5-TeCB						
1,2,3,4-TeCB						

COMMENTS: _____

FIGURE A-9

FIGURE A-10

CRITICAL PATH FOR CORRECTIVE ACTION



AR300287

WESTON

APPENDIX D

INTERIM METHODS FOR THE SAMPLING AND ANALYSIS OF PRIORITY POLLUTANTS IN SEDIMENT AND FISH TISSUE

1404E-1

AR300288

EPA 600/4-81-055

United States
Environmental Protection
Agency

EPA

RECEIVED
APR 21 1986
FISH & WILDLIFE SERVICE
ECOLOGICAL SERVICES

Research and Development

Interim Methods For The Sampling and Analysis of Priority Pollutants in Sediments and Fish Tissue

EAST LANSING FIELD OFFICE
RECEIVED
SEP 10 1984
ES
EAST LANSING, MICHIGAN
U.S. FISH & WILDLIFE SERVICE

Prepared for

Regional Guidance

Prepared by

Physical and Chemical Methods Branch
Environmental Monitoring and Support Laboratory
Cincinnati, Ohio 45268

AR300289

DRAFT

Interim Methods for the Sampling and Analysis of Priority Pollutants in Sediments and Fish Tissue

EAST LANSING FIELD OFFICE
RECEIVED
SEP 1 0 1984
ES
EAST LANSING, MICHIGAN
U.S. FISH & WILDLIFE SERVICE

U. S. Environmental Protection Agency
Environmental Monitoring and Support Laboratory
Cincinnati, Ohio 45268

August 1977

Revised October 1980

AR300290

SAMPLE HANDLING

1. Collection

1.1 Samples shall be collected according to recognized procedures. Preferably, all analyses should be performed on the same sample. A minimum of 250 grams are required for the total protocol.

1.2 The recommended container for the sediment sample is a standard one-quart, wide-mouth, screw-cap, glass bottle with a Teflon lid liner. It is particularly important that glassware used in organic residue analyses be scrupulously cleaned before initial use. At the time of collection, the bottle should be filled nearly to the top with the sediment sample. If the sample is collected below a water column, the threads and sealing surfaces should be washed off with sample water. "Top off" the collected sediment sample with sample water and seal with the Teflon-lined screw cap. Maximum effort must be made to seal the sample with a minimum of gaseous headspace. The sample must remain sealed until the aliquots for volatile organics are taken for analyses.

1.3 In the case of small fish, a sufficient number should be combined by sampling site location and species to obtain the minimum weight. The collected samples are wrapped in aluminum foil, labeled with freezer tape, and placed in the freezer chest with dry ice.

AR300291

2. Preservation

2.1 The sediment sample should be labeled with freezer tape and transferred to the laboratory in an ice chest maintained at or near 4°C. The samples should be processed as soon as possible.

2.2 Fish samples are to be frozen at the time of collection and must remain frozen until the subsamples are taken for purgeable organics.

3. Processing

3.1 Sediment

3.1.1 Decant the water from the top of the sediment. Transfer the sediment into a Pyrex tray and mix thoroughly with a Teflon spatula. Discard sticks, stones, and other foreign objects, if present. Weigh five 10.0-gram portions of the sample into separate 125-ml vials. Using a crimper, tightly secure a septum to each bottle with an aluminum seal. Store these sample aliquots in a freezer until ready for volatile organics analysis.

3.1.2 Determine the percent solids in the sediment by drying a 10-25g portion in a tared evaporating dish, overnight, at 103°C.

Calculate the % solids using the equation:

$$\% \text{ solids} = \frac{A}{B} \times 100$$

where: A = weight of dry residue in grams

B = weight of wet sample in grams

3.1.3 Transfer half of the remaining sediment sample back to the original sample bottle and store at 4°C. This portion will be used for those analyses requiring a wet sample.

Spread the other half of the sample uniformly in the tray and allow to dry at room temperature for four or five days in a contaminant-free environment. When dry - less than 10% water - grind the sample with a large mortar and pestle to a uniform particle size. Discard any foreign objects found during grinding and transfer the powdered sediment into a wide-mouthed glass jar and seal with a Teflon-lined lid. This air-dried sample will be used for those analyses requiring an air-dried sample.

3.2 Fish

3.2.1 To prepare the fish sample for analytical pretreatment, unwrap and weigh each fish. Combine small fish by site and species until a minimum combined weight of 250g is obtained. Chop the sample into 1-inch chunks using a sharp knife and mallet.

3.2.2 Grind the sample using a large commercial meat grinder that has been precooled by grinding dry ice. Thoroughly mix the ground material. Regrind and mix material two additional times. Clean out any material remaining in the grinder; add this to the sample and mix well.

3.2.3 Weigh five 10.0g portions of the sample into separate 125-ml vials. Using a crimper, tightly secure a septum to each bottle with a seal. Store these sample aliquots in a freezer until ready for volatile organics analysis.

3.2.4 Transfer the remaining fish sample to a glass container and store in a freezer for later subsampling and analysis.

AR300293

4. Special Equipment and Materials

4.1 Ice chest.

4.2 Wide-mouth quart bottles with Teflon lid liners.

4.3 Teflon-coated or porcelain spatula.

4.4 Pyrex glass tray, 8x12x2-inch.

4.5 Mortar and pestle (large).

4.6 Knife, heavy blade (or meat cleaver).

4.7 Mallet, plastic faces, 2 to 3 lb.

4.8 Electric meat grinder, 1/2 HP.

4.9 Dry ice.

4.10 Aluminum foil

4.11 Freezer tape, for labels.

4.12 Freezer.

4.13 Vials, 125-ml Hypo-Vials (Pierce Chemical Co., #12995), or equivalent.

4.14 Septa, Tuf-Bond (Pierce #12720), or equivalent.

4.15 Seals, aluminum (Pierce #13214), or equivalent.

4.16 Crimper, hand (Pierce #13212), or equivalent.

AR300294

Analysis of Sediments for Chlorinated Pesticides,

Polychlorinated Biphenyls and Non-polar Neutrals

1. Scope

1.1 The compounds listed in Table I are extracted from air-dried sediment by the Soxhlet extraction technique. The extract is subsequently analyzed for pesticides and PCBs using approved methods (1) as cited in the Federal Register (2). The remaining compounds are determined using the methods described in Appendix II of the Federal Register (3). While the above referenced methods have been proven for pesticides and PCBs, they have not been sufficiently tested through extensive experimentation for the non-polar neutral compounds in Table I.

2. Special Apparatus and Materials

2.1 Soxhlet extractor, 40-mm ID, with 500-ml round bottom flask.

2.2 Kuderna-Danish, 500-ml, with 10-ml graduated receiver and 3-ball Snyder column.

2.3 Chromatographic column - Pyrex, 20-mm ID x approximately 400-mm long, with coarse fritted plate on bottom.

3. Procedure

3.1 Extraction

3.1.1 Weigh 30.0 grams of the previously air-dried sample into a tared 200-ml beaker. Add 3 ml distilled water (10% of

AR300295

sample weight), mix well and allow to stand for 2 hours while mixing occasionally.

3.1.2 Place about 1/2" of preextracted glass wool in the bottom of the Soxhlet extractor chamber and quantitatively transfer the contents of the beaker into the chamber. Place a second glass wool plug on top of the sample. Wash the 200-ml beaker and all mixing tools several times with a 1:1 hexane/acetone mixture. Cycle the wash mixture through the extractor using a total of 300 ml of the mixed solvent.

3.1.3 Attach the extractor to a 500-ml round bottom flask containing a boiling stone and extract the solids for 16 hours.

3.1.4 After extraction is complete, dry and filter the extract by passing it through a 4" column of hexane-washed sodium sulfate. Wash the 500-ml flask and the sodium sulfate with liberal amounts of hexane. Collect the eluate in a 500-ml K-D evaporative flask with a 10-ml ampul. Concentrate the sample extract to 6-10 ml.

3.2 Cleanup and Separation

3.2.1 Adjust the sample extract volume to 10 ml and clean up the extraction by Florisil column chromatography according to the 304(g) methodology for PCBs (1), part 10.3. For sulfur removal, continue with part 10.5.3.4 of that method. NOTE: If sulfur crystals are present in the extract, separate the crystals from the sample by decantation.

AR300296

3.2.2 Analyze the Florisil eluates for the pesticides and PCBs appearing in Table I, according to the approved methods (1).

3.2.3 Analyze remaining compounds of Table I, Column C, using the methods described in Appendix II of the Federal Register (3).

3.3 Standard quality assurance protocols should be employed, including blanks, duplicates and dosed samples as described in the "Analytical Quality Control Handbook" (4). Dosing can be accomplished by injecting 1-20 µl of a standard into the homogenized sediment contained in the Soxhlet extractor chamber.

4. Reporting of Data

4.1 Report results in µg/kg on a dry weight basis using the percent moisture values determined earlier. Report all quality control data with the analytical results for the samples.

AR300297

Analysis of Fish for Chlorinated Pesticides and Polychlorinated Biphenyls

1. Scope

1.1 The chlorinated pesticides and polychlorinated biphenyls (PCBs) listed in Table I are extracted from fish using either method A or B as described below. Method A employs a blender, whereas a Tissumizer or the equivalent is required for Method B. Either procedure results in an extract that can be incorporated directly into the approved procedures (1) for pesticides or PCBs as cited in the Federal Register (2).

2. Special Apparatus and Materials

2.1 Method A Only

2.1.1 Blender, high-speed - Waring Blender, Courdos, Omni-Mixer, or equivalent. Explosion proof model recommended. Quart container is suitable size for routine use.

2.1.2 Buchner funnel - porcelain, 12-cm.

2.1.3 Filter paper - 110 mm sharkskin circles.

2.1.4 Flask, vacuum filtration - 500 ml.

2.2 Method B Only

2.2.1 Tissumizer SDT-182EN (available from Tekmar Company, P. O. Box 37207, Cincinnati, Ohio, 45222), or equivalent.

2.2.2 Centrifuge - capable of handling 100 ml centrifuge tubes.

2.3 Method A & B

2.3.1 Kuderna-Danish concentrator - 500 ml, with 10-ml graduated receiver and 3-ball Snyder column.

AR300298

2.3.2 Chromatographic column - pyrex, 20 mm ID x approximately 400 mm long, with coarse fritted plate on bottom.

3. Procedures

3.1 Method A

3.1.1 Weigh a 25 to 50g portion of frozen, ground fish and add to a high-speed blender. Add 100g anhydrous Na_2SO_4 to combine with the water present and to disintegrate the sample. Alternately, blend and mix with a spatula until the sample and sodium sulfate are well mixed. Scrape down the sides of the blender jar and break up the caked material with the spatula. Add 150 ml of hexane and blend at high speed for 2 min.

3.1.2 Decant the hexane supernatant through a 12-cm Buchner filter with two sharkskin papers into a 500-ml suction flask. Scrape down the sides of the blender jar and break up the caked material with the spatula. Reextract the residue in the blender jar with two 100 ml portions of hexane, blending 3 min. each time. (After one min. of blending, stop the blender, scrape the material from the sides of the blender jar, and break up the caked material between extractions.)

3.1.3 Decant the hexane supernatants through the Buchner and combine with the first extract. After the last blending, transfer the residue from the blender jar to the Buchner, rinsing the blender jar and material in the Buchner with three 25 to 50 ml portions of hexane. Immediately after the last rinse, press the residue in the Buchner with the bottom of a clean beaker to force out the remaining hexane.

AR300299

3.1.4 Pour the combined extracts and rinses through a column of anhydrous Na_2SO_4, 20 mm x 100 mm, and collect the eluate in a 500 ml Kuderna-Danish concentrator. Wash the flask and then the column with small portions of hexane and concentrate the extract below 10 ml.

3.2 Method B

3.2.1 Weigh 20.0g of frozen, ground fish and add to a 100-ml centrifuge tube. Add 20 ml of hexane and insert the Tissumizer into the sample. Turn on the Tissumizer and disperse the fish in the solvent for 1 min. Centrifuge and decant the solvent through a column of anhydrous Na_2SO_4, 20 mm x 100 mm, and collect the eluate in a 500-ml Kuderna-Danish concentrator.

3.2.2 Repeat the dispersion twice using a 20-ml aliquot each time, combining all dried portions of solvent in the concentrator. Rinse the Tissumizer and the column with small portions of hexane and concentrate the extract below 10 ml.

3.3 Cleanup and Analysis

3.3.1 Unless prior experience would indicate the fish species fat content is low (less than 3g per extract), the hexane/acetonitrile cleanup procedures described in the reference methods should be followed. In all cases, Florisil column chromatography should be used to clean up the extracts before gas chromatography (1). An electron capture detector is used for final measurement, and results

AR300300

are calculated in µg/kg. Identifications can be confirmed by GC/MS techniques as described in Appendix II of the Federal Register (3).

3.4 Quality Control

3.4.1 Standard quality assurance protocols should be employed, including blanks, duplicates, and dosed samples as described in the "Analytical Quality Control Handbook (4).

3.4.2 Dose fish sample aliquots by injecting minimum amounts (< 20 µl total) of concentrated pesticide or PCB solutions into the solid subsample 10 to 15 minutes before extraction.

4. Reporting of Data

4.1 Report results in µg/kg on a wet tissue basis. Report all quality control data with the analytical results for the samples.

AR300301

Analysis of Sediment for General Organics

by Mechanical Dispersion Extraction

1. Scope

1.1 This method is designed to determine solvent extractable organic compounds amenable to gas chromatography. Tables I, II, and III are a summary of compounds that should be extracted at an 80-100% efficiency. It is a GC/MS method intended for qualitative and semi-quantitative determination of these compounds. Although this approach has not been sufficiently tested through extensive experimentation, it is based on laboratory experience and is presently considered to be a reasonable analytical approach for these organic materials in sediment.

1.2 This method is not applicable to those very volatile pollutants listed in Table IV.

2. Special Apparatus and Materials

2.1 Mechanical dispersion device - Tissumizer

2.2 Centrifuge - capable of handling 100-ml centrifuge tubes.

2.3 Separatory funnels - 2 liter with Teflon stopcock.

2.4 Sieve, 20 mesh.

3. Procedure

3.1 Weigh 20.0g of wet, well-mixed sediment into a 100 ml centrifuge tube. If the sediment contains grit larger than 20 mesh, it is necessary to extrude the sample through a 20-mesh sieve in order to prevent damage to the mechanical dispersion device. Add 20 ml

AR300302

acetonitrile and insert the dispersion device into the sample. Disperse the sediment into the solvent for 1 min. Centrifuge and decant the solvent into a 2-liter separatory funnel containing 1300 ml of a 2 percent aqueous solution of sodium sulfate previously adjusted to pH 11 with 6N NaOH. Repeat the dispersion twice, using a 20-ml aliquot each time, and combine the acetonitrile washings in the separatory funnel. CAUTION: The dispersion should be carried out in a fume hood to avoid exposure to acetonitrile.

3.2 Extract the aqueous acetonitrile solution in the separatory funnel with 60 ml of hexane for 2 min. Drain the aqueous layer into a 2-liter Erlenmeyer flask and pour the hexane extract through a short column of anhydrous sodium sulfate prerinsed with hexane. Collect the dried extract in a 500-ml Kuderna-Danish (K-D) flask fitted with a 10 ml ampul. Repeat the extraction and drying steps twice, combining the extracts.

3.3 Evaporate the extract to 5 to 10 ml in a 500-ml K-D apparatus fitted with a 3-ball Snyder column and a 10-ml calibrated receiver tube. Allow the K-D to cool to room temperature. Remove the receiver and adjust the volume to 10 ml. Label this as the base neutral fraction. If additional sensitivity is required, add fresh boiling chips, attach a two-ball micro-Snyder column, and carefully evaporate to 1.0 ml or when active distillation ceases.

3.4 Return the aqueous acetonitrile solution to the separatory funnel and adjust the pH with 6N HCl to pH 2 or less. Extract three times with 60 ml of hexane each time. Combine the extracts, dry, and concentrate as described above. Label this as the acid fraction.

AR300303

3.5 Analyze both extracts according to the methods described in Appendix II of the Federal Register (3). Should the aceonitrile partition used in this procedure not sufficiently remove interferences, florisil (1), alumina (5), and silica gel (1), column chromatographic cleanup and separation techniques can be employed. Sulfur can be removed by treatment with mercury (1).

3.6 Standard quality control assurance protocols should be employed, including blanks, duplicates and dosed samples, as described in the "Analytical Quality Control Handbook" (4). Dosing can be accomplished by injecting 1-20 µl of a standard solution into the homogenized sediment contained in the centrifuge tube.

4. Reporting of Data

4.1 Report results in µg/kg on a dry weight basis using the percent moisture values determined earlier. Report all quality control data with the analytical results for the samples.

AR300304

Analysis of Fish for General Organics by Solvent Extraction

1. Scope

1.1 This method is designed to determine solvent extractable organic compounds amenable to gas chromatography. These compounds are listed in Tables II and III. It is a GC/MS method intended for qualitative and semi-quantitative determination of these compounds. Although this approach has not been sufficiently tested through extensive experimentation, it is based on laboratory experience and is presently the best analytical approach for these organic materials in fish.

2. Special Apparatus and Materials

2.1 Tissumizer SDT-182EN (available from Tekmar Company, P. O. Box 37202, Cincinnati, Ohio 45222), or equivalent.

2.2 Centrifuge - capable of handling 100-ml centrifuge tubes.

2.3 Separatory funnels - 2-liter with Teflon stopcock.

2.4 Organic-free water - prepared by passing distilled water through an activated carbon column.

3. Procedure

3.1 Weigh 20.0g of ground, homogeneous fish and add to a 100-ml centrifuge tube. Add 20 ml of acetonitrile and insert the Tissumizer into the sample. Turn on the Tissumizer and disperse the fish into the solvent for 1 min. Centrifuge and decant the solvent into a 2-liter separatory funnel containing 1300 ml of a 2 percent aqueous solution of sodium sulfate. Repeat the dispersion twice, using a 20-ml aliquot each time, and combine the acetonitrile in the separatory funnel.

AR300305

CAUTION: The dispersion should be carried out in a fume hood to avoid exposure to acetonitrile.

3.2 Adjust the pH of the sodium sulfate/acetonitrile solution with 6N NaOH to pH 11 or greater. Use multirange pH paper for the measurement. Extract the aqueous acetonitrile solution with 60 ml of hexane. Shake the separatory funnel for 2 min. Drain the aqueous layer into a 2-liter Erlenmeyer flask and pour the hexane extract through a short column of prerinsed anhydrous sodium sulfate. Collect the dried extract in a 500-ml Kuderna-Danish (K-D) flask fitted with a 10-ml ampul. Repeat the extraction and drying steps twice, combining the extracts. Evaporate the extract to 5 to 10 ml in a 500-ml K-D apparatus fitted with a 2-ball Snyder column and a 10 ml. Analyze by GC/MS. If additional sensitivity is required, add fresh boiling chips, attach a two-ball micro-Snyder column, and carefully evaporate to 1.0 ml or when active distillation ceases.

3.3 Return the aqueous acetonitrile solution to the separatory funnel and adjust the pH with 6N HCl to pH 2 or less. Extract three times with 60 ml of hexane each time. Combine the extracts, dry, and concentrate as described above. Analyze by GC/MS.

NOTE: Should the partition used in this procedure not sufficiently remove the lipid material, gel permeation can be employed. (However, special expensive equipment is necessary for this procedure (6)).

3.4 Standard quality assurance prptocols should be employed, including blanks, duplicates, and dosed samples, as described in the

AR300306

"Analytical Quality Control Handbook" (4). Dosing can be accomplished by injecting 1 to 20 µl of a standard solutuon into the homogenized tissue contained in a centrifuge tube.

4. Reporting of Data

4.1 Report results in µg/kg on a wet tissue basis. Report all quality control data with the analytical results for the samples.

AR300307

Determination of Purgeable Organics in Sediment

1. Scope

1.1 This procedure is intended for use in the analysis of volatile organic compounds found in sediment samples (Table IV). The procedure applies a modified purge/trap technique in the direct analysis of an undiluted sediment sample. The method relies on the use of a mass spectrometer detection system, although other selective detectors may be used for specific compound types.

1.2 Under ideal conditions, the minimum detectable limit has been determined to be 0.5 ppb. Actual detection limits will vary due to sediment surfaces, water content and nonvolatile organic loading factors which will influence the partition coefficients of the volatile organics.

2. Special Apparatus and Materials

2.1 Tekmar LSC-1 or equivalent purge/trap apparatus.

2.2 Septum - Teflon-faced silicone (Pierce 12722).

2.3 Vial with sealable cap - 20 ml (Pierce-Hypovial).

2.4 Heating tape with temperature control.

2.5 Hand crimper

2.6 Standard solutions of compounds of interest - two concentration levels (10 µg/l and 100 µg/l).

AR300308

3. Procedure

3.1 Allow samples to equilibrate to room temperature for weighing and analysis. Samples may be shipped and stored at wet ice temperatures; freezing is not necessary.

3.2 Drill two holes into the septum to allow for the snug insertion of two 1/8" glass tubes to be used as purge gas inlet and outlet.

3.3 The purge gas inlet should be extended to the bottom of the septum vial. The purge gas outlet should extend 1/2" below the septum.

3.4 Wrap the vial in heating tape and connect the glass tubes to the appropriate gas lines.

3.5 Heat the sample at 80°C for 5 minutes.

3.6 Withdraw the source of heat and purge the sample chamber with helium gas for 4 minutes at a rate of 60 ml/min.

3.7 Desorb the trapped organics from the trap tube onto the chromatographic column for analysis.

3.8 Standard quality assurance protocols should be employed, including blanks, duplicates and dosed samples as described in the "Analytical Quality Control Handbook" (4).

4. Calibration

4.1 For purposes of this procedure, five sample vials of each sediment type must be available.

4.2 Dose one sample vial through the septum with 10 µl of one standard solution. Dose a second vial with 10 µl of the other standard solution.

4.3 Proceed with the analysis of the two dosed samples and one non-dosed sample, using the procedure described in Section 3. Store the two remaining vials at 4°C for possible future analysis.

AR300309

4.4 After each sample has been analyzed, proceed with data analysis. Subtract the peak areas of compounds found in the undosed sample from the corresponding compounds contained in the dosed sample. Construct a calibration curve from the corrected dosed data; quantify the unknown.

NOTE: If the calculated sample concentration is greater than the concentration of the dosed standard used in the dosing step, it will be necessary to prepare additional standards to bracket the unknown.

4.5 Dry weight of the sediment is obtained after the analysis, by first removing the Teflon seal and drying the sample vial at 103-105°C overnight. The gross dry weight is obtained after reequilibrating the sample vial to room temperature. The tare weight of the vial is then determined after removal of the dried sediment.

5. Reporting of Data

5.1 Report all results in µg/kg on a dry weight basis. Report all quality control data with the analytical results for the sample.

AR300310

Analysis of Fish for Volatile Organics by Purge and Trap Analyses

1. Scope

1.1 This method is designed to determine volatile organic compounds amenable to purge and trap analyses. These compounds are listed in Table IV. It is a GC/MS method intended for qualitative and semi-quantitative determination of these compounds.

1.2 Although the above approach has not been sufficiently tested through extensive experimentation, it is based on laboratory experience and is presently considered to be the best analytical approach for volatile organic materials in fish.

2. Special Apparatus and Materials

2.1 Sonifier Cell Disrupter W-350 with microprobe (manufactured by Brawson Sonic Power Co., Danbury, Connecticut), or equivalent.

2.2 Gas-tight syringe - 5 cc.

2.3 Organic-free water - Prepared by passing distilled water through an activated carbon column.

2.4 Standard solutions - Prepare three standard methanol solutions of the compounds listed in Table IV at the 50 ng/µl, 150 ng/µl, and 300 ng/µl concentrations. The standard solutions should be stored at less than 0°C. Solutions should be allowed to warm to room temperature before dosing. Fresh standards should be prepared weekly.

NOTE: Specific GC detectors can be substituted for the MS.

2.5 Tekmar LSC-1 or equivalent purge/trap apparatus.

2.6 Septum - Teflon-faced silicone (Pierce 12722).

AR300311

2.7 Vial with sealable cap - 20 ml (Pierce-Hypovial).

2.8 Heating tape with temperature control unit.

3. Procedure

3.1 Remove four of the sample vials containing 10.0g of homogenized fish from the freezer. Open the vials and add 10 ml of organic-free water to each while the fish is still frozen. Sonify the fish for 30 sec. at maximum probe power. Immediately reseal the vials.

3.2 Dose one sample vial through the septum below the water level with 10 µl of the 50 ng/µl standard methanol solution. Dose a second vial with 10 µl of the 150 ng/µl standard and a third vial with 10 µl of the 300 ng/µl standard.

3.3 Allow samples to equilibrate to room temperature for weighing and analysis.

3.4 Drill two holes into the septum to allow for the snug insertion of two 1/8" glass tubes to be used as purge gas inlet and outlet. The purge gas inlet should be extended to the bottom of the system vial. The purge gas outlet should extend 1/2" below the septum cap.

3.5 Wrap each vial with heating tape and connect the glass tubes to the appropriate gas line.

3.6 Heat each sample at 80°C for 5 minutes.

3.7 Withdraw the source of heat and purge the sample chamber with helium gas for 4 minutes at a rate of 60 ml/min.

3.8 After purging is complete, desorb the trap tube into the gas chromatograph for analysis. The trap column should be rapidly heated to 180°C and backflush with an inert gas at 20 to 60 ml/min. for 4 minutes during this procedure.

AR300312

3.9 Analyze the undosed sample first, followed by the 50 ng/µl dosed sample. If no compounds of interest are found in the undosed sample and the dosed sample produces peaks to indicate recovery of the protocol compounds, do not analyze the remaining samples. Calculate lower limits of detection based on the response obtained from the dosed sample. If compounds are observed in the undosed sample, analyze the two remaining dosed samples in exactly the same manner. Subtract the peak areas of compounds found in the undosed sample from the corresponding compounds contained in the dosed data; quantify the unknown.

NOTE: If the calculated sample concentration is greater than the concentration of the dosed standard used in the dosing step, it is necessary to prepare additional standards in order to bracket the unknown. Utilize the remaining sample in the freezer for this purpose.

3.10 Standard quality assurance protocols should be employed, including blanks, duplicates, and dosed samples, as described in the "Analytical Quality Control Handbook" (4).

4. Reporting of Data

4.1 Report all results in µg/kg on a wet tissue basis. Report all quality control data with the analytical results for the samples.

AR300313

Analysis of Sediment for Cyanide

1. Scope and Application

   1.1 This method is used for the determination of cyanide in sediments. Insoluble cyanide complexes are dissolved in 10% sodium hydroxide. The cyanide, as hydrocyanic acid (HCN), is released from the sample by means of a reflux-distillation and absorbed in a scrubber containing sodium hydroxide solution. The cyanide in the absorbing solution is then determined colorimetrically or potentiometrically or by titration.

   1.2 For cyanide levels exceeding 0.2 mg per 200 ml of absorbing liquid, the silver nitrate titrimetric method is used. For cyanide levels below this value, the colorimetric procedure is used. The probe method may be used for concentrations of 0.001 to 200 mg per 200 ml absorbing liquid.

2. Sample Preparation

   2.1 Although a dry sample is preferred, a wet sample may also be taken for analysis. In either case, the sediment samples must be well mixed to ensure a representative aliquot.

3. Interferences

   3.1 Interferences are eliminated or lessened by using the distillation procedure.

   3.2 Fatty acids will distill and form soap under the alkaline titration conditions. Therefore, acidification and extraction with isooctane, hexane, or chloroform is recommended.

AR300314

3.3 Ammonia and thiosulfate interfere with the electrode method yielding higher measurements of cyanide ion activity than are actually present.

4. Preparation of Calibration Curve

4.1 The calibration curve is prepared as described in step 8.7, (Method 335.2), Reference 7.

4.2 The standards must contain the same concentration of NaOH (7.1) as the sample.

4.3 At least one standard should be treated as outlined below.

4.4 The calibration curve is prepared by plotting the absorbance or the mv reading versus the cyanide concentration.

5. Sample Procedure

5.1 Place a weighed portion of the well-mixed sediment (1 to 10g) in an 800 ml beaker with 500 ml of 10% NaOH solution and stir for 1 hour.

5.2 Transfer the mixture to a 1-liter boiling flask. Rinse the beaker with several portions of deionized distilled water and add to the boiling flask.

5.3 Add 50 ml of 5% NaOH solution to the absorbing tube and dilute if necessary with deionized, distilled water to obtain an adequate depth of liquid in the absorber. Connect the boiling flask, condenser, absorber, and trap in the distillation train as shown in Figure 1 (Method 335.2), Reference 7.

5.4 Add 50 ml of conc. H_2SO_4 slowly through the air inlet tube. Rinse with distilled water. Add 20 ml of $MgCl_2.6H_2O$ (510 g/l) solution through the air inlet tube and again rinse with distilled water. Continue with steps 8.4 through 8.6 (Method 335.2), Reference 7.

AR300315

5.5 Record the absorbance or my reading and determine the cyanide concentration from the calibration curve.

6. Quality Assurance

6.1 Initially demonstrate quantitative recovery with each distillation digestion apparatus by comparing distilled aqueous standards to non-distilled aqueous standards. Each day, distill at least one standard to confirm distillation efficiency and purity of reagents.

6.2 At least 15% of the cyanide analyses should consist of duplicate and spiked samples. Quality control limits should be established and confirmed as described in Chapter 6 of the "Analytical Quality Control Handbook," Reference 4.

7. Reporting of Data

7.1 Report cyanide concentrations on a dry weight basis as follows: less than 1.0 mg/kg, to the nearest 0.01 mg/kg; 1.0 mg/kg and above, to two significant figures.

7.2 Report all quality control data with the analytical results for the samples.

AR300316

Analysis of Fish for Cyanide

1. Scope and Application

1.1 This method is used for the determination of cyanide in fish. All samples must be distilled prior to the analytical determination. For cyanide levels exceeding 0.2 mg/200 ml of absorbing liquid, the silver nitrate titrimetric method is used. For cyanide levels below this value, the colorimetric procedure is used.

2. Sample Preparation

2.1 A 5g portion of the frozen, ground fish (see "Sample Handling") is used for the analysis. The sample should be thawed before the analysis begins.

3. Preparation of Calibration Curve

3.1 The calibration curve is prepared from values for portions of spiked fish tissue distilled in the manner used for the tissue sample being analyzed. For preparation of the calibration standards, choose and weigh a 50g portion of fish and blend in a Waring blender (or equivalent) with 10 ml of 10% NaOH and sufficient deionized, distilled water to bring the volume of the mixture to 500 ml.

3.2 Using a volumetric pipet which has had the tip removed, withdraw eight 50 ml portions and place in a series of 1 liter boiling flasks. Seven of the flasks should be spiked with progressively larger volumes of the cyanide standard as given in 8.7 (Method 335.2), Reference 7. Adjust the final volume of each flask to 500 ml with deionized, distilled water.

AR300317

3.3 Add 50 ml of 5% NaOH solution to the absorbing tube and dilute, if necessary, with deionized distilled water to obtain an adequate depth of liquid in the absorber. Connect the boiling flask, condenser, absorber, and trap in the train as shown in Figure 1 (Method 335.2), Reference 7.

3.4 Continue with step 8.2 through 8.6 (Method 335.2), Reference 7.

3.5 The calibration curve is prepared by plotting the absorbance versus the cyanide concentration. The blank absorbance value must be subtracted from each value before plotting the curve.

4. Sample Procedure

4.1 Place a weighed portion of the ground fish (approximately 5g) in a blender with 100 ml of deionzized, distilled water and 1 ml of 5% NaOH solution.

4.2 Blend until a homogeneous mixture is obtained and transfer to a 1-liter boiling flask. Rinse the blender with several portions of deionized, distilled water totaling 400 ml and add to the boiling flask.

4.3 Add 50 ml of 5% NaOH solutuion to the absorbing tube and dilute if necessary with deionized, distilled water to obtain an adequate depth of liquid in the absorber. Connect the boiling flask, condenser, absorber, and trap in the distillation train as shown in Figure 1 (Method 335.2) and continue with step 8.2 through 8.6, Reference 7.

4.4 Read the absorbance and determine the cyanide concentratjion from the calibration curve.

AR300318

5. Quality Assurance

5.1 Initially, demonstrate quantitative recovery with each distillation digestion apparatus by comparing distilled aqueous standards to non-distilled aqueous standards. Each day, distill at least one standard to confirm distillation efficiency and purity of reagents.

5.2 At least 15% of the cyanide analyses should consist of duplicate and spiked samples. Quality control limits should be established and confirmed as described in Chapter 6 of the "Analytical Quality Control Handbook," Reference 4.

6. Reporting of Data

6.1 Report cyanide concentrations as follows: less than 1.0 mg/kg, to the nearest 0.01 mg; 1.0 mg/kg and above, to two significant figures.

6.2 Report all quality control data with the analytical results for the samples.

AR300319

Analysis of Sediment for Phenols

1. Scope and Application

   1.1 This method is used for the determination of phenolics in sediments. All samples must be distilled prior to the determination of phenols, using the procedure given on page 576, Reference 8. Use Method 510B for samples that contain less than 1 mg phenol/kg and method 510C for samples that contain more than 1 mg phenol/kg.

2. Sample Preservation and Preparation

   2.1 Biological degradation is inhibited by cooling the sample to 4°C. If the sample cannot be analyzed within 24 hours, it should be frozen.

   2.2 A 5g portion of the wet, or air-dried sediment is used for the analysis. If the sample has been frozen, it should be thawed before the analysis begins.

3. Preparation of Calibration Curve

   3.1 The calibration curve is prepared as described on p. 579, 4.a.3 (Ref. 8) for samples containing less than 1 mg/kg and p. 581 for samples above 1 mg/kg.

   3.2 Record the absorbance of the standards and plot the values against micrograms of phenol.

4. Sample Procedure

   4.1 Place a 5g portion of the wet, or air-dried sediment into a 200 ml beaker with 100 ml of distilled water. Mix well and lower the pH to 4.0 with (1 + 0) H_3PO_4 using a pH meter.

AR300320

4.2 Add 5 ml of 10% $CuSO_4$ solution, mix and transfer to a 1-liter distilling flask.

4.3 Rinse the beaker with several portions of distilled water and add to the distilling flask. Adjust the volume in the flask to 500 ml.

4.4 Using a 500-ml graduated cylinder as a receiver, begin the distillation as described on p. 577, Method 510A; 4b, Reference 8.

4.5 Continue with the procedure using either the Chloroform Extraction Method 510B, p. 577, Reference 8, or the Direct Photometric Method 510C, p. 580, Reference 8.

4.6 Record the absorbance and determine the micrograms of phenol from the appropriate calibration curve.

5. Quality Assurance

5.1 Demonstrate quantitative recovery with each distillation apparatus by comparing aqueous distilled standards to non-distilled standards. Each day, distill at least one standard to confirm the distillation efficiency and purity of reagents.

5.2 At least 15% of the phenol analyses should consist of duplicate and spiked samples. Quality control limits should be established and confirmed as described in Reference 4.

6. Reporting of Data

6.1 Report phenol concentrations on a dry weight basis as follows:

Method 510B, to the nearest µg/kg

Method 510C, for less than 1.0 µg/kg to the nearest 0.01 µg and for 1.0 mg/kg and above to two significant figures.

6.2 Report all quality control data when reporting results of sample analysis.

AR300321

Analysis of Sediment for Mercury

1. Scope and Application

   1.1 This method is used for the determination of total mercury (organic and inorganic) in sediment. A weighed portion of the sample is digested with aqua regia for 2 minutes at 95°C followed by oxidation with potassium permanganate. Mercury is subsequently measured by the cold vapor technique.

   1.2 The range of the method is 0.2 to 5 µg/g but may be extended above or below the normal range by increasing or decreasing sample size or through instrument and recorder control.

   1.3 For a complete description of the method, the reader is referred to "Methods for Chemical Analysis of Water and Waste" (7), Method 245.5.

2. Sample Preparation

   2.1 Although a wet sample may be taken for analysis, a dry sample provides for ease of handling, better homogeniety, and better storage.

3. Preparation of Calibration Curve

   3.1 The calibration curve is prepared using distilled water standards, treated in the same manner as the sediment samples being analyzed. Plot peak height versus the mercury concentration. The peak height of the blank is subtracted from each of the other values.

4. Sample Procedure

   4.1 Weigh 0.2 to 0.3g portions of the dry sample and place in the bottom of a BOD bottle. (If a wet sample is to be analyzed, a

AR300322

proportionately larger sample must be taken.) Add 5 ml of distilled water and 5 ml of aqua regia and place the bottle in a water bath maintained at 95°C for 2 minutes.

4.2 Cool, add 50 ml distilled water, 15 ml of potassium permanganate solution and return the bottle to the water bath for an additional 30 minutes. Add additional $KMnO_4$, as necessary, to maintain oxidizing conditions.

4.3 Continue with the procedure as described.

5. Calibration

5.1 Measure the peak height of the unknown from the chart and read the mercury value from the standrd curve.

5.2 Calculate the mercury concentration in the sample by the formula:

$$\mu g\ Hg/gram = \frac{\mu g\ Hg\ in\ aliquot}{wt.\ of\ aliquot\ in\ gms}$$

5.3 Report mercury concentrations on a dry weight basis as follows: Below 0.1 µg/gm, < 0.1 µg; between 0.1 and 10 µg/gm, to nearest 0.01 µg; above 10 µg/gm, to nearest µg.

6. Quality Assurance

6.1 Standard quality assurance protocols should be employed, including blanks, duplicates, and spiked samples, as described in the "Analytical Quality Control Handbook" (4).

7. Precision and Accuracy

7.1 The following standard deviations on replicate sediment samples were recorded by a single operator at the indicated levels: 0.29 µg/gm±0.02 and 0.82 µg/gm±0.03. Recovery of mercury at these levels, added as methyl mercuric chloride, was 97% and 94%, respectively.

AR300323

Analysis of Fish for Mercury

1. Scope and Application

   1.1 This method is used for determination of total mercury (organic and inorganic) in fish. A weighed portion of the sample is digested with sulfuric and nitric acid at 58°C followed by overnight oxidation with potassium permanganate at room temperature. Mercury is subsequently measured by the conventional cold vapor technique.

   1.2 The range of the method is 0.2 to 5 µg/g but may be extended above or below the normal instrument and recorder control.

2. Sample Preparation

   2.1 The sample may be prepared as described under "Sample Handling" or the special metal procedure may be used. A 0.2 to 0.3g portion should be taken for each analysis. The sample should not be allowed to thaw before weighing.

3. Preparation of Calibration Curve

   3.1 The calibration curve is prepared from values for portions of spiked fish tissue treated in the manner used for the tissue samples being analyzed. For preparation of the calibration standards, choose a 5g portion of fish and blend in a Waring blender.

   3.2 Transfer accurately weighed portions to each of six dry BOD bottles. Each sample should weigh about 0.2 grams. Add 4 ml of conc. H_2SO_4 and 1 ml of conc. HNO_3 to each bottle and place in water bath at 58°C until the tissue is completely dissolved (30 to 60 min.).

AR300324

3.3 Cool and transfer 0-, 0.5- 1.0-, 2.0-, 5.0- and 10.0- ml aliquots of the working mercury solution containing 0 to 1.0 µg of mercury to the BOD bottles. Cool to 4°C in an ice bath and cautiously add 15 ml of potassium permanganate solution. Allow to stand overnight at room temperature under oxidizing conditions.

3.4 Add enough distilled water to bring the total volume to approximately 125 ml. Add 6 ml of sodium chloride-hydroxylamine sulfate solution to reduce the excess permangante.

3.5 Wait at least 30 sec. after the addition of hydroxylamine. Treating each bottle individually, add 5 ml of the stannous sulfate solution and immediately attach the bottle to the aeration apparatus.

3.6 Continue with the procedure as given in Method 245.1 for water (7). The calibration curve is prepared by plotting the peak height versus the mercury concentration. The peak height of the blank is subtracted from each of the other values.

4. Sample Procedure

4.1 Weigh 0.2 to 0.3g portions of the sample and place in the bottom of a dry BOD bottle. Care must be taken that none of the sample adheres to the side of the bottle. Add 4 ml of conc. H_2SO_4 and 1 ml of conc. HNO_3 to each bottle and place in a water bath maintained at 58°C until the tissue is completely dissolved (30 to 60 minutes).

4.2 Cool to 4°C in an ice bath and cautiously add 5 ml of potassium permanganate solution in 1 ml increments. Add an additional 10 ml of more of permangante, as necessary to maintain oxidizing

AR300325

conditions. Allow to stand overnight at room temperature (see NOTE). Continue as described under 3.4.

NOTE: As an alternate to the overnight digestion, the solubilization of the tissue may be carried out in a water bath at 80°C for 30 min. The sample is then cooled and 15 ml of potassium permanganate solution added cautiously. At this point, the sample is returned to the water bath and digested for an additional 90 min. at 30°C (9). If this method is followed, the calibration standards must also be treated in this manner. Continue as described under 3.4.

5. Calculation

5.1 Measure the peak height of the unknown from the chart and read the mercury value from the standard curve.

5.2 Calculate the mercury concentration in the sample by the formula:

$$\mu g\ Hg/gram = \frac{\mu g\ Hg\ in\ aliquot}{wt.\ of\ aliquot\ in\ gms}$$

5.3 Report mercury concentrations as follows:

Below 0.1 µg/gm, < 0.1 ug; between 0.1 and 1 µg/gm, to nearest 0.01 µg; between 1 and 10 µg/gm, to nearest 0.1 µg; above 10 µg/gm, to nearest µg.

6. Quality Assurance

6.1 Standard quality assurance protocols should be employed, including blanks, duplicates, and spiked samples as described in the "Analytical Quality Control Handbook" (4).

6.2 Report all quality control data when reporting resaults of sample analyses.

AR300326

7. Precision and Accuracy

7.1 The following standard deviations on replicate fish samples were recorded at the indicated levels: 0.19 µg/gm±0.02, 0.74 µg/gm±0.05, and 2.1 µg/gm±0.06. The coefficients of variation at these levels were 11.9%, 7.0%, and 3.6%, respectively. Recovery of mercury at these levels, added as methyl mercuric chloride, was 112%, 93%, and 86%, respectively.

AR300327

Analysis of Sediments for Metals

1. Scope and Application

1.1 This method is used for the determination of antimony, beryllium, cadmium, chromium, copper, lead, nickel, silver, thallium, and zinc in sediments.

2. Summary of Method

2.1 The sediment is prepared for analysis by drying and grinding the sample. A representative portion is subjected to wet oxidation-digestion prior to analysis by atomic absorption.

2.2 For a discussion of basic principles, general operating parameters, preparation of standards and calibration, and the method of standard addition, the reader is referred to "Methods for Chemical Analysis of Water and Wastes" (7) and the individual methods as follow:

AR300328

Page References to "Methods for Chemical Analysis of Water and Wastes, 1979"[7]

ELEMENT	Ag	Be	Cd	Cr	Cu	Ni	Pb	Sb	Tl	Zn
METHOD	272.1	210.1	213.1	218.1	220.1	249.1	239.1	204.1	279.1	289.1

3. Preservation and Handling

3.1 The sample should be stored at 4°C if the analysis can be carried out within 7 days of collection. For longer periods, the samples should be frozen. An alternative is to dry the sample as soon as possible, grind it with a mortar and pestle removing rocks, sticks, and other foreign objects and store the sediment in a vial or other suitable container.

3.2 Dust in the laboratory environment, impurities in reagents, and impurities on laboratory apparatus, which the sample contacts, are all sources of potential contamination. All glassware should be thoroughly washed with detergent and tap water, rinsed with 1:1 nitric acid, tap water, and finally deionized, distilled water in that order. NOTE: Chromic acid may be useful to remove organic deposits from glassware; however, the analyst should be cautioned that the glassware must be thoroughly rinsed with water to remove the last trace of chromium. This is especially important if chromium is to be included in the analytical scheme. A commercial product - NOCHROMIX - available from Godax Laboratories, 6 Varick, New York, NY 10013, can be used in place of chromic acid.

4. Sample Preparation

4.1 Dry a representative portion of the well-mixed sample (10 to 25g) at 60°C until all moisture has been removed.

AR300329

4.2 Grind the dry sample with a mortar and pestle, removing sticks, stones, and other foreign material. Store the sample in glass or plastic vials removing aliquots as needed.

5. Procedure

5.1 Weigh 1.00g of the well-mixed sediment into a 250 ml Erlenmeyer flask and add 50 ml deionized water, 0.5 ml HNO_3 (sp. gr. 1.42) and 5 ml of HCl (sp. gr. 1.10) to each flask.

5.2 Heat the samples, blanks and standards on a hotplate maintained at approximately 95°C until the volume has been reduced to 15 to 20 ml, making certain that the samples do not boil.

5.3 Cool and clarify the sample by centrifugation or by filtration through Whatman No. 42 filter paper or equivalent.

5.4 Dilute the sample to 100 ml or some appropriate volume based on the concentration present.

5.5 Proceed with the appropriate method for the atomic absorption analysis of the metals of interest.

6. Calibration

6.1 From the values read off the appropriate calibration curve, calculate the concentration of each metal pollutant in the sediment as follows:

$$\text{mg/kg} = \frac{\text{mg/l of constituent prepared sample} \times \text{volume of prepared sample in ml}}{\text{weight of dry sample in g}}$$

7. Quality Assurance

7.1 Standard quality assurance protocols should be employed, including blanks, duplicates, spiked and samples as described in the "Analytical Quality Control Handbook" (4).

AR300330

7.2 Report all quality control data when reporting results of sample analyses.

AR300331

Analysis of Fish for Metals

1. Scope

   1.1 This method is used for the determination of antimony, arsenic, beryllium, cadmium, chromium, copper, lead, nickel, selenium, silver, thallium, and zinc in fish tissue.

2. Summary of Method

   2.1 The fish is prepared for analysis by being chopped into small pieces, homogenized in a blender with dry ice, and solubilized by either dissolution after dry ashing or a wet oxidation digestion. After sample preparation, atomic absorption - either direct aspiration, gaseous hydride, or a flameless technique - is used to measure the concentration of the pollutant.

3. Preservation and Handling

   3.1 Although an aliquot of the ground fish as prepared under "Sample Handling" may be used for the metals determination, it may be more desirable to prepare an individual fish to avoid possible metal contamination from the grinder. Dust in the laboratory environment, impurities in reagents, and impurities on laboratory apparatus that the sample contacts are all sources of potential contamination. All glassware should be thoroughly washed with detergent and tap water, rinsed with 1:1 nitric acid, then tap water, and finally deionized, distilled water.

   NOTE: Chronic acid may be useful to remove organic deposits from glasware; however, the analyst should be cautiuoned that the glassware must be thoroughly rinsed with water to remove the last

AR300332

trace of chromium. This is especially important if chromium is to be included in the analytical scheme. A commercial product - NOCHROMIX - available from Godax Laboratories, 6 Varick Street, New York, NY, 10013, can be used in place of chromic acid.

4. Sample Homogenization

4.1 If a fish sample other than that prepared under "Sample Handling" is to be used for metals analyses, unwrap and weigh the frozen fish at the time of processing. Select a fish that weighs between 50 and 300g. If an analysis is required for a fish, < 300g, a 50g representative portion must be taken from the sample after it has been pretreated as described in "Sample Handling" on page 1 of this document.

4.2 After weighing, the fish should be chopped into approximately 1-in. or smaller chunks with a meat cleaver or a knife and mallet (2 to 3-lb). Smaller pieces ensure efficient grinding.

4.3 Place crushed or pelleted dry ice into the blender container. The weight of dry ice should be equal to, or greater than, the weight of the fish.

4.4 Turn on the blender for 10 sec. to pulverize the ice and chill the blender.

4.5 Add the pieces of fish and blend at high speed until the mixture is homogeneous. This usually requires 2 to 5 minutes. Add more dry ice if needed to keep the fish frozen.

4.6 Pour the homogenate into a plastic bag and close the bag with a rubber band. Do not seal the bag tightly to allow CO_2 to escape.

AR300333

4.7 Place the bag in the freezer (-12°C for at least 16 hr.) until ready to proceed with the digestion step.

NOTE: If desired, the blender blades can be modified in order to have the leading edge of the blades (the sharpened edge) turned down so that, as it rotates, the blade will throw the material upwards. Stainless steel blades may be a possible source of nickel and chromium contamination and should be noted if detected. If a tantalum blade is available, it should be substituted for the stainless steel.

The hole in the blender lid should be enlarged sufficiently to allow the evolved gas to escape. Hold a cloth or labwipe over this hole when blending to prevent loss of the sample material. A glove should be worn to prevent possible freezing of the skin by escaping gas.

5. Reagents

5.1 Deionized, distilled water: Prepare by passing distilled water through a mixed bed of cation and anion exchange resins. Use deionized, distilled water for the preparation of all reagents and calibration standards and as dilution water.

5.2 Nitric acid (conc.): If metal impurities are present, distill reagent grade nitric acid in a borosilicate glass distillation apparatus.

5.3 Sulfuric acid, ACS grade (95.5% to 96.5%).

5.4 Sulfuric acid - 20% V/V solution. Carefully add 200 ml of concentrated H_2SO_4 to 500 ml of water. Cool and dilute to 1 liter with water.

AR300334

5.5 Hydrochloric acid, ACS grade.

5.6 Hydrogen Peroxide, 50% stabilized ACS grade.

5.7 Dry ice (frozen carbon dioxide), pellet form preferred.

6. Apparatus

6.1 Blender, Waring, two-speed, stainless steel blade or tantalum blade, if available, glass container capacity 1000 ml, or equivalent equipment.

6.2 Drying oven - Controllable with the range of 100° to 150°C with less than ±5°C variation. Check calibration of oven temperature control to ensure accurate ashing temperatures. Furnace must be operated in suitable fume hood.

6.3 Hot plate, controllable within the range of 80°C to 400°C. Hot plate must be operated in fume hood.

7. Procedure

Except for mercury, which requires a cold vapor technique, the metals can be divided into two groups for continued processing.

Group I: Be, Cd, Cr, Cu, Pb, Ni, Ag, Tl, and Zn.

Group II: As and Se.

Group I is digested by a dry ashing process (11) with the use of an ashing aid; Group II is prepared utilizing a wet ashing process.

7.1 Group I - Metals

7.1.1 Remove the homogenized sample from the freezer and weigh approximately 10g into a tared, 100-ml tall form, Pyrex beaker. Subtract the beaker weight from the total and record the wet sample weight.

AR300335

7.1.2 Add 25 ml of 20% sulfuric acid. Mix each sample thoroughly with a glass stirring rod ensuring all sample material is wetted by the acid. Rinse the stirring rod with water into the ashing vessel and cover the sample with a ribbed watch glass.

7.1.3 Heat the samples in an oven or furnace at 110±5°C until a charred viscous sulfuric acid/sample residue remains. Usually 12 to 16 hrs. (overnight) is sufficient. Transfer the ashing vessels containing the samples to a cold, clean muffle furnace which is provided with good external ventilation (fume hood), ensuring that the sample remains covered during the transfer. Initially set the furnace at 125°C and increase the temperature approximately every hour in 50° increments up to 275°C. Hold the temperature at 275°C for 3 hrs. Finally, increase the temperature to 450°C (at 50° per hour) and hold for 12 to 16 hrs. (overnight). Remove the covered ashing vessels from the furnace and allow to cool to room temperature in a clean, draft-free area.

7.1.4 After initial overnight ashing, some residual carbon may remain in the samples. Treat each sample ash with 0.5 ml of water and 1 ml of concentrated nitric acid (whether or not they are already white). Evaporate carefully just to dryness on a warm hotplate (in a fume hood). Place the ashing vessels (covered with watch glasses) in a cool muffle furnace and raise the temperature to 300°C and hold for

AR300336

exactly 30 min. Remove each covered sample ash from the furnace and allow to cool as before. If residual carbon remains, repeat the nitric acid treatment until a carbon-free white ash is obtained. The covered ashing vessels containing the ash may be stored in a dessicator or in a laminar flow clean hood.

NOTE: Copious carbon residues (i.e., black ashes) after overnight ashing may indicate inefficient or uneven heating within the furnce. Routine calibration of the furnace is advised.

7.1.5 Add 0.5 ml of nitric acid and 10 ml of water to each cool ashing vessel, then warm gently on a hotplate at 80 to 90°C for 5 to 10 min. to effect dissolution of the ash. A small amount of insoluble white siliceous-like residue may remain undissolved; do not filter the residue because of the possibility of contamination. Quantitatively transfer the contents of each ashing vessel into a 100 ml volumetric flask, dilute to volume with water, and shake thoroughly. Allow any residue to settle to the bottom of the flask (about 2 hr). Do not shake the sample further before taking an aliquot. The sample is now ready for analysis.

NOTE: The presence of a precipitate other than the insoluble siliceous-like material may result in low or eratic results for Pb. Precipitate formation can result from heating the samples too long or at too high a temperature after nitric acid treatment of the ash.

AR300337

Precipitate formation must be avoided by maintenance of appropriate ashing temperatures.

7.1.6 The prepared sample should be analyzed by atomic absorption. For a discussion of basic principles, the method of standard addition, the chelation/solvent extraction procedures, general instrumental operating parameters, and preparation of standards and calibration see the section on "Atomic Absorption Methods" (7), and the individual analyses sheets as follow:

ELEMENT	Ag	Be	Cd	Cr	Cu	Ni	Pb	Sb	Tl	Zn
METHOD	272.1	210.1	213.1	218.1	220.1	249.1	239.1	204.1	279.1	289.1

7.1.7 Because of the adequate sensitivity by conventional flame AA and the expected concentration levels of cadmium, copper, and zinc in the sample, these three elements should be analyzed by direct aspiration. The furnace technique is preferred for the analysis of the other Group I metals because of their expected low concentrations. When using the furnace technique, the operating parameters and instructions as specified by the particular instrument manufacturer should be followed. If the concentration detected by the furnace procedure is beyond the working range of the standard curve, the sample should be either diluted and reanalyzed or analyzed by direct aspiration. The method of standard additions should be employed when needed. If the sample matrix is so complex that sample dilution followed by furnace analysis cannot be used, or if the use of the chelation/solvent extraction technique for

AR300338

concentration of Ag, Ni, Pb, and Tl is preferred, the procedure as described in Methods for Chemical Analysis of Water and Wastes, Reference 7, should be utilized.

7.2 Group II - Metals

7.2.1 Remove the homogenized sample from the freezer and weigh approximately 5g into a tared, 120-ml conical beaker. Subtract the beaker weight from the total and record the wet sample weight.

7.2.2 Add 5 ml of conc. HNO_3. Then slowly add 6 ml of conc. H_2SO_4 and cover with a watch glass.

7.2.3 Place beaker on hot plate and warm slightly. Continue heating until the mixture becomes dark or a possible reducing condition is evident. Do not allow the mixture to char. Remove beaker from hotplate and allow to cool.
NOTE: Remove beaker if foaming becomes excessive.

7.2.4 Add an additional 5 ml of conc. HNO_3, cover with a watch glass, and return beaker to hotplate. Repeat step 7.2.3.

7.2.5 When mixture again turns brown, cool, and slowly add 5 ml of 50% hydrogen peroxide. Cover with watch glass and heat gently until the initial reaction has ceased. If the solution becomes dark, repeat the peroxide addition, several times if necessary, and heat to SO_3 fumes. If charring occurs, add further 1 ml portions of hydrogen peroxide until the fuming sulfuric acid remains colorless or very light yellow. (If at any stage it appears that the sulfuric acid may apprpach dryness, cool, add 2 to 3 ml of sulfuric acid, and continue.)

AR300339

7.2.6 Cool, add 40 ml of conc. HCl and dilute to 100 ml with deionized, distilled water. The sample is now ready for analysis.

7.2.7 The Group II metals should be analyzed by atomic absorption using the gaseous hydride technique. The apparatus setup, standard preparation and calibration, and analysis procedure that is to be followed is given, starting on Page 159, Reference 8. From the prepared sample, a 25-ml aliquot should be withdrawn and the analysis continued as described in Section 3.d, Page 162, Reference 8.

8. Calculation

8.1 Using the values from the appropriate calibration curve, calculate the concentration of each metal pollutant in the fish as follows:

If the concentration of standards in the calibration curve is plotted as mg/l,

$$\text{ug/gram} = \frac{\text{mg/l of constituent in prepared sample} \times \text{volume of prepared sample in ml}}{\text{weight of wet sample in g}}$$

If the concentration of standards in the calibration curve is plotted as µg/l,

$$\text{µg/gram} = \frac{\text{µg/l of constituent in prepared sample} \times \text{volume of prepared sample in ml}}{\text{weight of wet sample in g}}$$

9. Quality Assurance

9.1 Standard quality assurance protocols should be employed, including blanks, duplicates, and spiked samples, as described in the "Analytical Quality Control Handbook (4).

AR300340

9.2 Report all quality control data when reporting results of sample analyses.

AR300341

Analysis of Sediment for Arsenic and Selenium

1. Scope and Application

1.1 This method is to be used for the determination of arsenic and selenium in sediment. A weighed portion of the wet, well-mixed sediment is digested with HNO_3 and H_2SO_4 followed by treatment with H_2O_2. Arsenic and selenium are subsequently determined by the gaseous hydride technique.

1.2 The range of the method is _____ to _____ µg/g but may be extended by varying the sample size.

2. Sample Preparation

2.1 The analysis should be performed on a wet, well-mixed sample.

3. Preparation of Calibration Curve

3.1 The calibration curve is prepared using distilled water standards, treated in the same manner as the samples being analyzed.

4. Procedures

4.1 Weigh approximately 5 grams of the wet, well-mixed, sediment into a tared 125-ml conical beaker.

4.2 Add 5 ml of conc. HNO_3. Then slowly add 6 ml conc. H_2SO_4 and cover with a watch glass.

4.3 Place the beaker on hot plate and warm slightly. (NOTE: Remove beaker if foaming becomes excessive.) Continue heating until the mixture becomes dark or a possible reducing condition is evident. Do not allow the mixture to char. Remove the beaker from the hotplate and allow to cool.

4.4 Add an additional 5 ml of conc. HNO_3, cover with a watch glass, and return beaker to hot plate. Repeat step 4.3.

AR300342

4.5 When mixture again turns brown, cool, and slowly add 5 ml of 50% hydrogen peroxide. Cover with watch glass and heat gently until the initial reaction has ceased. If the solution becomes dark, repeat the peroxide addition, several times if necessary, and heat to SO_3 fumes. If charring occurs, add additional 1 ml portions of hydrogen peroxide until the fuming sulfuric acid remains colorless or very light yellow. (If at any stage the sulfuric acid approaches dryness, cool, add 2 to 3 ml of additional sulfuric acid, and continue.)

4.6 Cool, add 40 ml of conc. HCl and dilute to 100 ml with deionized, distilled water. The sample is now ready for analysis by the gaseous hydride technique.

4.7 The apparatus setup, standard preparation and calibration, and analytical procedure to be followed is given beginning on page 159, Reference 8. A 25-ml aliquot should be withdrawn from the prepared sample and the analysis continued as described in Section 3.d, page 162, Reference 8.

5. Calibration

5.1 Calculate the concentration of arsenic and selenium present in mg/kg on a dry weight basis.

6. Quality Assurance

Standard quality assurance protocols should be employed, including blanks, duplicates, and spiked samples as described in the "Analytical Quality Control Handbook" (4).

AR300343

REFERENCES

1. "Methods for Benzidine, Chlorinated Organic Compounds, Pentachlorophenol and Pesticides in Water and Wastewater," U. S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, 45268, 1978.
2. Federal Register, Volume 41, No. 232, p. 52780, Wednesday, December 1976.
3. Federal Register, Volume 44, No. 233, p. 69464, Monday, December 3, 1979.
4. Handbook for Analytical Quality Control in Water and Wastewater Laboratories. U. S. Environmental Protection Agency, Technology Transfer, 1979.
5. Boyle, H. W., et al., Adv. Chem. Serv., 60, 207 (1966).
6. Stalling, D. L.; R. C. Tindle; J. L. Johnson; "Cleanup of Pesticide and Polychlorinated Biphenyl Residues in Fish Extracts by Gel Permeation Chromatography." JOAC, 55, 32-38 (1972).
7. "Methods for Chemical Analysis of Water and Wastes," U. S. Environmental Protection Agency, Technology Transfer. (1979).
8. "Standard Methods for the Examination of Water and Wastewater," 14th edition (1975).
9. Bishop, J. N., "Mercury in Fish," Ontario Water Resources Comm., Toronto, Ontario, Canada, 1971.
10. Jones, J. W.; R. J. Gajan; K. W. Boyer; J. A. Fiorino; "Dry Ash - Voltammetric Determination of Cadmium, Copper, Lead, and Zinc in Foods." JOAC, 60, 826. (1977).
11. Jones, J. W.; R. J. Gajan, K. W. Boyer; J. A. Fiorino; "Dry Ash - Voltammetric Determination of Cadmium, Copper, Lead, and Zinc in Foods." JOAC, 60, 826. (1977).

AR300344

TABLE I

Priority Pollutants Analyzed by Soxhlet Extraction

Pesticides

Aldrin	DDD	Endosulfan sulfate
a-BHC	DDE	Endrin
b-BHC	DDT	Endrin aldehyde
d-BHC	Dieldrin	Heptachlor
g-BHC	Endosulfan - I	Heptachlor epoxide
Chlordane	Endosulfan - II	Toxaphene

PCBs

Aroclor 1016	Aroclor 1242	Aroclor 1254
Aroclor 1221	Aroclor 1248	Aroclor 1260
Aroclor 1232		

Non-polar Neutrals

Acenaphthylene	1,3-dichlorobenzene	Bis (2-ethylhexyl) phthalate
Acenaphthene	1,4-dichlorobenzene	Benzo (a) anthracene
Isophorone	Hexachlorethane	Benzo (b) fluoranthene
Fluorene	1,2-dichlorobenzene	Benzo (k) fluoranthene
Phenanthrene	Hexachlorobutadiene	Benzo (a) pyrene
Anthracene	1,2,4-trichlorobenzene	Indeno (1,2,3-cd) pyrene
Dimethylphthalate	2,6-dinitrotoluene	Dibenzo (a,h) anthracene
Diethylphthalate	Hexachlorobenzene	Benzo (ghi) perylene
Fluoranthene	4-bromophenyl phenyl ether	4-chlorophenyl phenyl ether
Pyrene	Bis (2-chloroethoxy) methane	2,3,7,8-tetrachlorodibenzo-p-diox
Naphthalene	2-chloronaphthalene	Di-n-butylphthalate
Chrysene		Butyl benzylphthalate

AR300345

Table II Base-neutral Extractables

Compound Name	RRT[1] (hexachloro-benzene)	Limit of Detection (ng)	Characteristic EI ions (Rel. Int.)	CI ions (Methane)
1,3-dichlorobenzene	0.35	40	146(100), 148(64), 113(12)	146, 148, 150
1,4-dichlorobenzene	0.36	40	146(100), 148(64), 113(11)	146, 148, 150
hexachloroethane	0.38	40	117(100), 199(61), 201(99)	199, 201, 203
1,2-dichlorobenzene	0.39	40	146(100), 148(64), 113(11)	146, 148, 150
bis(2-chloroisopropyl) ether	0.47	40	45(100), 77(19), 79(12)	77, 135, 137
hexachlorobutadiene	0.55	40	225(100, 223(63), 227(65)	223, 225, 227
1,2,4-trichlorobenzene	0.55	40	74(100), 109(80), 145(52)	181, 183, 209
naphthalene	0.57	40	128(100), 127(10), 129(11)	129, 157, 169
bis(2-chloroethyl)ether	0.61	40	93(100), 63(99), 95(31)	63, 107, 109
hexachlorocyclopentadiene	0.64	40	237(100), 235(63), 272(12)	235, 237, 239
nitrobenzene	0.64	40	77(100), 123(50), 65(15)	124, 152, 164
bis(2-chloroethoxy)methane	0.68	40	93(100), 95(32), 123(21)	65, 107, 137
2-chloronaphthalene	0.76	40	162(100), 164(32), 127(31)	163, 191, 203
acenaphthylene	0.83	40	152(100), 153(16), 151(17)	152, 153, 181
acenaphthene	0.86	40	154(100), 153(95), 152(53)	154, 155, 183
isophorone	0.87	40	82(100), 95(14), 138(18)	139, 167, 178
fluorene	0.91	40	166(100), 165(80), 167(14)	166, 167, 195
2,6-dinitrotoluene	0.93	40	165(100), 63(72), 121(23)	183, 211, 223
1,2-diphenylhydrazine	0.96	40*	77(100), 93(58), 105(28)	185, 213, 225
2,4-dinitrotoluene	0.98	40	165(100), 63(72), 121(23)	183, 211, 223
N-nitrosodiphenylamine	0.99	40*	169(100), 168(71), 167(50)	169, 170, 198
hexachlorobenzene	1.00	40	284(100), 142(30), 249(24)	284, 286, 288
4-bromophenyl phenyl ether	1.01	40	248(100), 250(99), 141(45)	249, 251, 277
phenanthrene	1.09	40	178(100), 179(16), 176(15)	178, 179, 207
anthracene	1.09	40	178(100), 179(16), 176(15)	178, 179, 207
dimethylphthalate	1.10	40	163(100), 164(10), 194(11)	151, 163, 164
diethylphthalate	1.15	40	149(100), 178(25), 150(10)	177, 223, 251
fluoranthene	1.23	40	202(100), 101(23), 100(14)	203, 231, 243
pyrene	1.30	40	202(100), 101(26), 100(17)	203, 231, 243
di-n-butylphthalate	1.31	40	149(100), 150(27), 104(10)	149, 205, 279
benzidine	1.38	40*	184(100),92(24), 185(13)	185, 213, 225
butyl benzylphthalate	1.46	40	149(100), 91)50)	149, 299, 327

AR300346

Table II Base-neutral Extractables (Cont'd.)

Compound Name	RRT[1] (hexachloro-benzene)	Limit of Detection (ng)	Characteristic EI ions (Rel. Int.)	CI ions (Methane)
chrysene	1.46	40	228(100), 229(19), 226(23)	228, 229, 257
bis(2-ethylhexyl)phthalate	1.50	40	149(100), 167(31), 279(26)	149
benzo(a)anthracene	1.54	40	228(100), 229(19), 226(19)	228, 229, 257
benzo(b)fluoranthene	1.66	40	252(100), 253(23), 125(15)	252, 253, 281
benzo(k)fluoranthene	1.66	40	252(100), 253(23), 125(16)	252, 253, 281
benzo(a)pyrene	1.73	40	252(100), 253(23), 125(21)	252, 253, 281
indeno(1,2,3-cd)pyrene	2.07	100	276(100), 138(28), 277(27)	276, 277, 305
dibenzo(a,h)anthracene	2.12	100	278(100), 139(24), 279(24)	278, 279, 307
benzo(g h i)perylene	2.18	100	276(100), 138(37), 277(25)	276, 277, 305
N-nitrosodimethylamine			42(100), 74(88), 44(21)	
N-nitrosodi-n-propylamine			130(22), 42(64), 101(12)	
4-chloro-phenyl phenyl ether			204(100), 206(34), 141(29)	
endrin aldehyde				
3,3'-dichlorobenzidine			252(100), 254(66), 126(16)	
2,3,7,8-tetrachlorodibenzo-p-dioxin			322(100), 320(90), 59(95)	
bis(chloromethyl)ether			45(100), 49(14), 51(5)	
deuterated anthracene (d10)	1.09	40	188(100), 94(19), 80(18)	189, 217

1 1% SP-2250 on 100/120 mesh Supelcoport in a 6' x 2 mm id glass column; He @ 30 ml/min; Program: 50° for 4 min, then 8°/min to 260° and hold for 15 min.

* Conditioning of column with base is required.

AR 300347

Table III Acid Extractables

Compound Name	RRT[1] (2-nitrophenol)	Limit of Detection (ng)	Characteristic EI ions (Rel. Int.)	CI ions (Methane)
2-chlorophenol	0.63	100	128(100), 64(54), 130(31)	129, 131, 157
phenol	0.66	100	94(100), 65(17), 66(19)	95, 123, 135
2,4-dichlorophenol	0.96	100	162(100), 164(58), 98(61)	163, 165, 167
2-nitrophenol	1.00	100	139(100), 65(35), 109(8)	140, 168, 122
p-chloro-m-cresol	1.05	100	142(100), 107(80), 144(32)	143, 171, 183
2,4,6-trichlorophenol	1.14	100	196(100), 198(92), 200(26)	197, 199, 201
2,4-dimethylphenol	1.32	100	122(100), 107(90), 121(55)	123, 151, 163
2,4-dinitrophenol	1.34	2 µg	184(100), 63(59), 154(53)	185, 213, 225
4,6-dinitro-o-cresol	1.42	2 µg	198(100), 182(35), 77(28)	199, 227, 239
4-nitrophenol	1.43	100	65(100), 139(45), 109(72)	140, 168, 122
pentachlorophenol	1.64	100	266(100), 264(62), 268(63)	267, 265, 269
deuterated anthracene (d10)	1.68	40	188(100), 94(19), 80(18)	189, 217

[1] Column: 6' glass, 2 mm i.d.
Tenax GC - 60/80 mesh
180° - 300° @ 8°/min.
He @ 30 ml/min

AR300348

Table IV

Characteristic Ions of Volatile Organics

Compound	EI Ions (Relative intensity)	Ion used to quantify
chloromethane	50(100); 52(33)	50
dichlorodifluoromethane	85(100); 87(33); 101(13); 103(9)	101
bromomethane	94(100); 96(94)	94
vinyl chloride	62(100); 64(33)	62
chloroethane	64(100); 66(33)	64
methylene chloride	49(100);51(33); 84(86); 86(55)	84
trichlorofluoromethane	101(100); 103(66)	101
1,1-dichloroethylene	61(100); 96(80); 98(53)	96
bromochloromethane(IS)	49(100); 130(88); 128(70); 51(33)	128
1,1-dichloroethane	63(100); 65(33); 83(13); 85(8); 98(7); 100(4)	63
trans-1,2-dichloroethylene	61(100); 96(90); 98(57)	96
chloroform	83(100); 85(66)	83
1,2-dichloroethane	62(100); 64(33); 98(23); 100(15)	98
1,1,1-trichloroethane	98(100); 99(66); 117(17); 119(16)	97
carbon tetrachloride	117(100); 119(96); 121(30)	117
bromodichloromethane	83(100); 85(66); 127(13); 129(17)	127
bis-chloromethyl ether	79(100); 81(33)	79
1,2-dichloropropane	63(100); 65(33); 112(4); 114(3)	112
trans-1,3-dichloropropene	75(100): 77(33)	75
trichloroethylene	95(100); 97(66); 130(90); 132(85)	130
dibromochloromethane	129(100); 127(78); 208(13); 206(10)	127
cis-1,3-dichloropropene	75(100); 77(33)	75

AR300349

Table IV

Compound	EI Ions (Relative intensity)	Ion used to quantify
1,1,2-trichloroethane	83(95); 85(60); 97(100); 99(63); 132(9); 134(8)	97
benzene	78(100)	78
2-chloroethylvinyl ether	63(95); 65(32); 106(18)	106
2-bromo-1-chloropropane(IS)	77(100); 79(33);156(5)	77
bromoform	171(50);173(100); 175(50); 250(4); 252(11); 254(11); 256(4)	173
1,1,2,2-tetrachloroethene	129(64); 131(62); 164(78); 166(100)	164
1,1,2,2-tetrachloroethane	83(100); 85(66); 131(7); 133(7); 166(5); 168(6)	168
1,4-dichlorobutane(IS)	55(100); 90(30); 92(10)	55
toluene	91(100); 92(78)	92
chlorobenzene	112(100); 114(33)	112
ethylbenzene	91(100); 106(33)	106
acrolein	26(49); 27(100); 55(64); 56(83)	56
acrylonitrile	26(100); 51(32); 52(75); 53(99)	53

AR300350

WESTON

APPENDIX E

WESTON ANALYTICS DIVISION LABORATORY QUALITY ASSURANCE PLAN

1404E-1

AR300351

ANALYTICAL LABORATORY QUALITY ASSURANCE PLAN

Table of Contents

1.0 PURPOSE

2.0 DISCUSSION

3.0 ORGANIZATION

- 3.1 Laboratory Manager
- 3.2 Section Managers
- 3.3 Quality Assurance/Quality Control Coordinator
- 3.4 Laboratory Personnel

4.0 SAMPLE MANAGEMENT

- 4.1 Client File
- 4.2 Bottle Preparation and Sample Preservation
- 4.3 Chain-of-Custody
- 4.4 Sample Receipt
- 4.5 Sample Storage
- 4.6 Sample Retention and Disposal

5.0 ANALYTICAL SYSTEMS

- 5.1 Instrument Maintenance
- 5.2 Instrument Calibration
- 5.3 Personnel Training
- 5.4 Standard Analytical Methods:
  - 5.4.1 Gas Chromatography/Mass Spectroscopy
    - 5.4.1.1 GC/MS Instrument Performance
    - 5.4.1.2 GC/MS Method Performance
    - 5.4.1.3 GC/MS Detection Limits
  - 5.4.2 Gas Chromatography and High Performance Liquid Chromatography
    - 5.4.2.1 GC/HPLC Instrument Performance
    - 5.4.2.2 GC/HPLC Method Performance
    - 5.4.2.3 GC/HPLC Detection Limits

5.4.3 Atomic Absorption Spectrophotometry

5.4.3.1 AA Instrument Performance
5.4.3.2 AA Method Performance
5.4.3.3 AA Detection Limits

5.4.4 Inductively Coupled Plasma Spectroscopy

5.4.4.1 ICP Instrument Performance
5.4.4.2 ICP Method Performance
5.4.4.3 ICP Detection Limits

5.4.5 Total Organic Carbon

5.4.5.1 TDC Instrument Performance
5.4.5.2 TDC Method Performance
5.4.5.3 TDC Detection Limits

5.4.6 Ion Chromatography

5.4.6.1 IC Instrument Performance
5.4.6.2 IC Method Performance
5.4.6.3 IC Detection Limits

5.4.7 Spectrophotometric (Colorimetric) Methods

5.4.7.1 Instrument Performance
5.4.7.2 Method Performance
5.4.7.3 Detection Limits

5.4.8 Miscellaneous Analyses

5.5 Method Development
5.6 Reference Materials
5.7 Reagents
5.8 Corrective Actions

6.0 DATA MANAGEMENT

6.1 Data Collection
6.2 Data Reduction
6.3 Data Review
6.4 Data Reporting
6.5 Data Archiving

7.0 SUBCONTRACTED ANALYSES

1.0 PURPOSE

Establish routine operating practices to ensure that all data generation in the laboratory conform to specific requirements for accuracy, precision, and completeness. The purpose and goal of quality assurance/quality control (QA/QC) is to ensure that all data generated in the laboratory conform to specific requirements for accuracy, precision, and completeness. This quality assurance/quality control plan describes the organization and procedures routinely incorporated into all analyses performed by the WESTON laboratory for the purpose of producing reliable data.

2.0 DISCUSSION

Customized, client-specific quality control measures (to include project-specific quality assurance/quality control plans) can be added to these basic guidelines to satisfy the special needs of individual programs. Laboratory personnel are available to discuss the design, advantages, and disadvantages of other quality control options.

This plan has been prepared in accordance with "Guidelines and Specifications for Preparing Quality Assurance Program Plans," QAMS-004/80, 20 September 1985.

3.0 ORGANIZATION

3.1 Laboratory Manager

The ultimate responsibility for the generation of reliable laboratory data rests with the Laboratory Manager. The Laboratory Manager is vested with the authority to effect those policies and procedures to ensure that only data of the highest attainable caliber are produced.

3.2 Section Managers

To assist the Laboratory Manager in achieving his goals, the Organic Section Manager, Inorganic Section Manager, and Support Section Manager as well as the laboratory Quality Assurance/Quality Control Coordinator and analytical project managers are responsible for the implementation of the established policies and procedures. They possess the authorities commensurate with their responsibilities for the day-to-day enforcement and monitoring of laboratory activities.

Section Managers have the responsibility for ensuring that their personnel are adequately trained to perform analyses, that equipment and instrumentation under their control are calibrated

and functioning properly, and that system audits are performed on a periodic basis. These system audits will include the analysis of external check samples to determine the analyst/instrument capability to identify and quantify routine analytes.

3.3 Quality Assurance/Quality Control Coordinator

The Quality Assurance/Quality Control Coordinator has the responsibility for the conduct of and evaluation of results from system audits. In addition, the preparation of standard operating procedures and quality assurance documentation for the laboratory is a function of the Quality Assurance/Quality Control Coordinator. The Quality Assurance/Quality Control Coordinator will review program plans for consistency with organizational and contractual requirements and will advise appropriate personnel of inconsistencies.

3.4 Laboratory Personnel

Any effective quality assurance and quality control program depends not only on organization and management but also on the efforts of each and every individual on the laboratory staff. The initial review for acceptability of analytical results rests with the analysts conducting the various tests. Observations made during the performance of an analytical method may indicate that the analytical system is not in control. Analysts must be constantly aware for indications of perturbations from the norm and be ready to verify that the system is in control before continuing analyses or reporting results of analyses.

4.0 SAMPLE MANAGEMENT

An organized and efficient sample management system is a necessary and critical foundation on which actual analyses of samples are based. Sample management includes client file creation, bottle preparation, sample preservation, sample receipt, sample storage, chain-of-custody documentation, reporting and invoicing, and sample retention and disposal.

4.1 Client File

On notification of a sampling and analysis effort, the laboratory will create a client file to maintain records associated with the project. In addition to administrative information (work order and plan numbers, client contacts, etc.), requests for sample containers, preservatives, and required analyses will be included in the file. As the project progresses, chain-of-custody and analytical results as well as any other pertinent information will be added to the file.

4.2 Bottle Preparation and Sample Preservation

On request by the Project Manager, sample bottles will be prepared by the laboratory and made available to the sampling team. The bottles will be prepared according to WESTON standard operating procedures and will include sample preservatives appropriate to the analytes and matrices of concern. Addition of preservatives to samples shall be recorded in field notebooks and on chain-of-custody forms. WESTON adheres to the most recent recommendations from the U.S. Environmental Protection Agency (EPA) for proper sample containers and preservatives.

If sample bottles are not supplied by the laboratory, the client assumes responsibility for bottle selection and preparation.

4.3 Chain-of-Custody

Chain-of-custody procedures document the history of samples and constitute a crucial part of sampling and analysis programs. Chain-of-custody documentation assists and enables the identification and tracing of a sample from the time of collection through the time of analysis.

When sample bottles are supplied by the laboratory, chain-of-custody forms will accompany the containers to the field. As samples are collected, entries are made on the chain-of-custody forms. Data to be noted include:

- Date
- Samples
- Sample description
- Client/program
- Container and preservative
- Analyses required
- Special instructions/notes

Sample containers are also labelled with:

- Date
- Sample description
- Preservatives
- Analyses required
- Client/program

When samples are received at the laboratory, the sample custodian will verify each and every sample against the chain-of-custody forms, note any discrepancies or losses of samples, and then sign for receipt of the samples. Samples will remain under the control of the sample custodian until samples are transferred to

the analysts for processing. Analysts will acknowledge receipt of samples by signing the chain-of-custody forms.

A sample is considered to be in custody if it:

- Is in the physical possession of the responsible party.
- Is in view of the responsible party.
- Is secured by the responsible party to prevent tampering.
- Is secured by the responsible party in a restricted area.

4.4 Sample Receipt

Samples received at the laboratory are inspected for integrity, and any field documentation is reviewed for accuracy and completeness. If chain-of-custody forms do not accompany the samples, the sample custodian will initiate these forms. When samples are received with missing or deficient chain-of-custody forms, the legal traceability of these samples cannot extend to the time of collection but must begin at the time of laboratory receipt.

Chain-of-custody and sample integrity problems are noted and recorded during sample log-in. The Project Manager is informed of the deficiencies and will advise the laboratory on the desired disposition of the samples. Chain-of-custody forms and deficiency notices are maintained in the client file.

Each sample that is received by the laboratory is assigned a unique sequential WESTON sample number which will identify the sample in the laboratory's internal tracking system.

References to a sample in any communication will include the assigned sample number to specify which sample is of concern.

4.5 Sample Storage

Samples will be stored in a locked refrigerator at 4°C. The temperature of the storage refrigerators will be monitored and recorded daily by the sample custodian. Sample fractions and extracts will also be stored under these same conditions.

4.6 Sample Retention and Disposal

Samples will be retained in the refrigerator for thirty (30) calendar days after the date of the invoice accompanying the analytical results. Unless a written request is received for retaining the sample beyond the thirty (30) days, the samples will be disposed of in an appropriate manner.

5.0 ANALYTICAL SYSTEMS

5.1 Instrument Maintenance

Instruments will be maintained in accordance with manufacturers' specifications. More frequent maintenance may be dictated dependent on operational performance. Instrument logs will be maintained to document the date and type of maintenance performed.

Contracts on major instruments with manufacturers and service agencies are used to provide routine preventive maintenance and to ensure rapid response for emergency repair service. Minimal instrument down-time is experienced through the use of these contracts.

5.2 Instrument Calibration

Before any instrument can be used as a measurement device, the instrumental response to known reference materials must be determined. The manner in which the various instruments are calibrated will be dependent on the particular instrument and the intended use of the instrument. All sample measurements will be made within the calibrated range of the instrument. Preparation of all reference materials used for calibration will be documented in a standards preparation notebook.

Laboratory balances will be calibrated annually and will be checked before and after use on a daily basis. A record of calibrations and daily checks will be kept in the balance log.

Oven thermometers will be calibrated annually against a National Bureau of Standards certified thermometer in the range of interest. Annual calibrations will be recorded in a calibration notebook. Daily readings will be recorded with the respective analysis (e.g., the solids book).

5.3 Personnel Training

Prior to conducting analyses on an independent basis, analysts are trained by experienced personnel in the complete performance

of an analytical method. If instrumentation is particularly complicated, analysts may be trained at instrument manufacturers' training courses. The analyst is then required to independently generate data on several method and/or matrix spikes to demonstrate proficiency in that analytical method. The type of data to be generated will be dependent on the analytical method to be performed. Results of this "certification" are then reviewed by the appropriate supervisor for adequacy.

Since method blanks and method spikes are required routine samples in every lot, performance on a day-to-day basis can be monitored by comparison with the original and cumulative data on similar samples. Supervisors and the laboratory Quality Assurance/Quality Control Coordinator are responsible for ensuring that samples are analyzed by only competent analysts.

5.4 Standard Analytical Methods

General: Analytical methods are routinely conducted as outlined in published sources (EPA, Standard Methods, ASTM, AOAC, etc.). Modifications to these methods may be necessary in order to provide accurate analyses of particularly complex matrices. When modifications to standard analytical methods are performed, the specific alterations as well as the reason for the change will be reported with the results of analyses.

5.4.1 Gas Chromatography/Mass Spectroscopy (GC/MS)

5.4.1.1 GC/MS Instrument Performance Documentation

Mass spectrometers are tuned on a daily basis to manufacturer's specifications with FC-43. In addition, once per shift, these instruments are tuned with decafluorotriphenylphosphine (DFTPP) or 4-bromo-fluorobenzene (BFB) for semi-volatiles or volatiles, respectively. Ion abundances will be within the windows dictated by the specific program requirements. Once an instrument has been tuned, initial calibration curves for analytes (appropriate to the analyses to be performed) are generated for at least five (5) solutions containing known concentrations of authentic standards of compounds of concern. The calibration curve will bracket the anticipated working range of analyses.

Calibration data, to include linearity verification determined by response factor evaluation (RSD <30 percent for compounds named in ensuing section 5.4.1.2 of this operating practice) will be maintained in the laboratory's permanent records of instrument calibrations.

5.4.1.2 GC/MS Method Performance Documentation

During each operating shift, a midpoint calibration standard is analyzed to verify that the instrument responses are still within the initial calibration determinations. The calibration check compounds will be those analytes used in the EPA Contract Laboratory Program's multicomponent analyses (e.g., priority pollutants and hazardous substances list) with the exception that benzene is used in place of vinyl chloride (volatiles) and di-n-octyl phthalate is deleted from the semi-volatile list.

The response factor drift (% D, i.e., percent difference compared to the average response factor from the initial calibration) will be calculated and recorded. If significant (>30%) response factor drift is observed, appropriate corrective actions will be taken to restore confidence in the instrumental measurements.

All GC/MS analyses will include analysis of a method blank, a method blank spike (semi-volatiles and pesticides/PCB's), a matrix spike, and a laboratory duplicate in each lot of twenty (20) or fewer samples. The US EPA-CLP matrix spike solutions will be used for both matrix spikes and blank spikes. In addition, appropriate surrogate compounds specified in EPA methods will be spiked into each sample. Recoveries from method spikes and surrogate compounds are calculated and recorded on control charts to maintain a history of system performance.

A method blank spike duplicate sample may be analyzed in place of the matrix spike for analytical lots of less than ten (10) samples.

Audit samples will be analyzed periodically to compare and verify laboratory performance against standards prepared by outside sources.

5.4.1.3 GC/MS Detection Limits

The US EPA-CLP contract required quantitation limits (CRQL) are used for reporting GC/MS data. These detection limits are compared with laboratory-determined instrument detection limits to ensure that the reported values are attainable. Instrument detection limits are determined from triplicate analysis of target compounds measured at three to five times the CRQL. The calculated instrument detection limit is three times the standard deviation of the measured values.

5.4.2 Gas Chromatography and High Performance Liquid Chromatography (GC and HPLC)

5.4.2.1 GC and HPLC Calibration

Gas chromatographs and high performance liquid chromatographs will be calibrated prior to each day of use. Calibration standard mixtures will be prepared from appropriate reference materials and will contain analytes appropriate for the method of analysis.

Working calibration standards will be prepared fresh daily. The working standards will include a blank and a minimum of five (5) concentrations to cover the anticipated range of measurement. At least one of the calibration standards will be at or below the desired instrument detection limit. The correlation coefficient of the plot of known versus found concentrations (or response) must be at least 0.996 in order to consider the responses linear over a range. If a correlation coefficient of 0.996 cannot be obtained, additional standards must be analyzed to define the calibration curve. A midpoint calibration check standard will be analyzed each shift to confirm the validity of the initial calibration curve. The check standard must be within twenty (20) percent of the initial response curve to demonstrate that the initial calibration curve is still valid.

Calibration data, to include the correlation coefficient, will be entered into laboratory notebooks to maintain a permanent record of instrument calibrations.

5.4.2.2 GC and HPLC Quality Control

At least one method blank and two method spikes will be included in each laboratory lot of samples. Regardless of the matrix being processed, the method spikes and blanks will be in aqueous media. Method spikes will be at a concentration of approximately five (5) times the detection limits.

The method blanks will be examined to determine if contamination is being introduced in the laboratory.

The method spikes will be examined to determine both precision and accuracy. Accuracy will be measured by the percent recovery of the spikes. These recoveries will be plotted on control charts to monitor method accuracy. Precision will be measured by the reproducibility of both method spikes and will be calculated as relative percent difference (% RPD). These % RPD's will be plotted on control charts to monitor method precision.

5.4.2.3 GC and HPLC Detection Limits

The US EPA-CLP contract required quantitation limits (CRQL) are for reporting GC data. These detection limits are compared with laboratory determined instrument detection limits to ensure that the reported values are attainable. Instrument detection limits are determined from triplicate analysis of target compounds measured at three to five times the CRQL. The calculated instrument detection limit is three times the standard deviation of the measured values.

The detection limits for HPLC analyses are reported as equal to the concentration of the lowest calibration standard analyzed on a particular day. The only exception to this for HPLC analyses are analyses conducted according to USATHAMA analytical and Quality Assurance Protocols. In those cases, detection limits are reported in accordance with procedures described in "USATHAMA Quality Assurance Plan," December 1985, Revision 1 (U.S. Army Toxic and Hazardous Materials Agency, Aberdeen Proving Ground, MD 21010-5401).

5.4.3 Atomic Absorption Spectrophotometry (AA)

5.4.3.1 AA Calibration

Atomic absorption spectrophotometers will be calibrated prior to each day of use.

Calibration standards will be prepared from appropriate reference materials, and working calibration standards will be prepared fresh daily. The working standards will include a blank and a minimum of three (3) concentrations to cover the anticipated range of measurement.

Duplicate injections will be made for each concentration. At least one of the calibration standards will be at or below the desired instrument detection limit. The correlation coefficient of the plot of known versus found concentrations will be at least 0.996 in order to consider the responses linear over a range. If a correlation coefficient of 0.996 cannot be achieved, the instrument will be recalibrated prior to analysis of samples.

Calibration data, to include the correlation coefficient, will be entered into laboratory notebooks to maintain a permanent record of instrument calibrations.

5.4.3.2 AA Quality Control

At least one method blank and two method blank spikes (laboratory control samples: LCS) will be included in each laboratory lot of samples. Regardless of the matrix being processed, the LCS and blanks will be in aqueous media. The LCS will be at a concentration of approximately five (5) times the detection limit.

The method blanks will be examined to determine if contamination is being introduced in the laboratory and will be introduced at a frequency of one per analytical lot or five (5) percent of the samples, whichever is more. The LCS will be examined to determine both precision and accuracy. Accuracy will be measured by the percent recovery (% R) of the spikes. The recovery must be within the range 80-120 percent to be considered acceptable. Additionally, the LCS % R will be plotted on control charts to monitor method performance.

Precision will be measured by the reproducibility of both LCS and will be calculated as relative percent difference (% RPD). Results must agree within twenty (20) percent RPD in order to be considered acceptable.

5.4.3.3 AA Detection Limits

The laboratory routinely reports EPA-CLP Contract Required Quantitation Limits (CRQL's) for client reports. These limits are compared with laboratory-determined Instrument Detection Limits (IDL's) on a quarterly basis to ensure that the reported values are attainable. IDL's are determined from three nonconsecutive day's analysis of seven consecutive measurements of target compounds at three to five times the IDL. Each day's seven measured values are averaged and the respective standard deviation calculated. Three times the standard deviation of the average of the standard deviations obtained from the three days' analysis is defined as the IDL. The IDL's must be at or below the CRQL's.

5.4.4 Inductively Coupled Plasma Spectroscopy (ICP)

5.4.4.1 ICP Calibration

The inductively coupled plasma spectrometer will be calibrated prior to each day of use. Calibration standards will be prepared from reliable reference materials and will contain all metals for which analyses are being conducted. Working calibration standards will be prepared fresh daily. The working standards will include a blank and a minimum of five (5) concentrations to

cover the anticipated range of measurement. Duplicate readings will be made for each concentration. At least one of the calibration standards will be at or below the desired instrumental detection limit. The correlation coefficient of the plot of responses versus concentrations will be at least 0.996 in order to consider the responses linear. If a correlation coefficient of 0.996 cannot be obtained, the spectrometer will be recalibrated prior to analysis of samples. This calibration will be done quarterly to verify the linear range of the instrument.

Calibration data, to include the correlation coefficient, will be entered into laboratory notebooks to maintain a permanent record of instrument calibrations.

On a daily basis, the instrument will be calibrated using a standard at the high end of the calibration range. This standard must not deviate more than ±5 percent from the quarterly established value. The calibration is verified with a mid-range calibration check standard which is prepared from a different source than the instrument calibration standard. This standard must not deviate more than ±10 percent from the target value. In addition, a linear range check at approximately two times the detection limit will be analyzed to verify linearity near the detection limit.

5.4.4.2 ICP Quality Control

At least one method blank and two method blank spikes (laboratory control samples: LCS) will be included in each laboratory lot of samples. Regardless of the matrix being processed, the LCS's and blanks will be in aqueous media. The LCS will be at a concentration of approximately five (5) times the detection limit.

The method blanks will be examined to determine if contamination is being introduced in the laboratory.

The LCS results will be examined to determine both precision and accuracy. Accuracy will be measured by the percent recovery (% R) of the spikes. The recovery must be within the range 80-120 percent to be considered acceptable. Additionally, the LCS % R will be plotted on control charts to monitor method accuracy.

Precision will be measured by the reproducibility of both LCS and will be calculated as relative percent difference (% PRD). Results must agree within twenty (20) percent RPD in order to be considered acceptable.

5.4.4.3 ICP Detection Limits

The laboratory routinely reports EPA-CLP Contract Required Quantitation Limits (CRQL's) for client reports. These limits are compared with laboratory-determined Instrument Detection Limits (IDL's) on a quarterly basis to ensure that the reported values are attainable. IDL's are determined from three nonconsecutive day's analysis of seven consecutive measurements of target compounds at three to five times the IDL. Each day's seven measured values are averaged and the respective standard deviation calculated. Three times the standard deviation of the average of the standard deviations obtained from the three days' analysis is defined as the IDL. The IDL's must be at or below the CRQL's.

5.4.5 Total Organic Carbon (TOC)

5.4.5.1 TOC Calibration

The total organic carbon analyzer will be calibrated prior to each day of use.

Calibration standards will be prepared from potassium hydrogen phthalate, and working calibration standards will be prepared fresh daily. The working standards will include a blank and a minimum of five (5) concentrations to cover the anticipated range of measurement.

At least one of the calibration standards will be at or below the desired instrument detection limit. The correlation coefficient of the plot of known versus found concentrations will be at least 0.996 in order to consider the responses linear over a range. If a correlation coefficient of 0.996 cannot be achieved, the instrument will be recalibrated prior to analysis of samples. Calibration data, to include the correlation coefficient, will be entered into laboratory notebooks to maintain a permanent record of instrument calibrations.

5.4.5.2 TOC Quality Control

At least one method blank and two method spikes will be included in each laboratory lot of samples. Method spikes will be at a concentration of approximately five (5) times the detection limit.

The method blanks will be examined to determine if contamination is being introduced in the laboratory. The method spikes will be examined to determine both precision and accuracy. Accuracy will be measured by the percent recovery (% R) of the spikes. The recovery must be within the range 90-110 percent to be considered

acceptable. In addition, % R will be plotted on control charts to monitor method accuracy.

Precision will be measured by the reproducibility of both method spikes and will be calculated as relative percent difference (% RPD). Results must agree within twenty (20) percent RPD in order to be considered acceptable.

2.4.5.3 TOC Detection Limits

The detection limits are based on the concentration of the lowest standard analyzed. Results below the lowest standard are rpeorted as below the detection limit.

5.4.6 Ion Chromatography (IC)

5.4.6.1 IC Calibration

The ion chromatograph will be calibrated prior to each day of use. Calibration standards will be prepared from appropriate reference materials, and working calibration standards for the ions of interest will be prepared fresh daily. The working standards will include a blank and a minimum of five (5) concentrations to cover the anticipated range of measurements. At least one of the calibration standards will be at or below the desired instrument detection limit. The correlation coefficient of the plot of known versus found concentrations will be at least 0.996 in order to consider the responses linear over a range. If a correlation coefficient of 0.996 cannot be achieved, the instrument will be recalibrated prior to analysis of samples.

Calibration data, to include the correlation coefficient, will be entered into laboratory notebooks to maintain a permanent record of instrument calibrations.

5.4.6.2 IC Quality Control

At least one method blank and two method spikes will be included in each laboratory lot of samples. Regardless of the matrix being processed, the method spikes and blanks will be in aqueous media. Method spikes will be at a concentration of approximately five (5) times the detection limit.

The method blanks will be examined to determine if contamination is being introduced in the laboratory.

The method spikes will be examined to determine both precision and accuracy. Accuracy will be measured by the percent recovery (% R) of the spikes. The recovery must be within the range of

85-115 percent to be considered acceptable. Additionally, % R will be plotted on control charts to monitor method accuracy.

Precision will be measured by the reproducibility of both method spikes and will be calculated as relative percent difference (% RPD). Results must agree within twenty (20) percent RPD in order to be considered acceptable.

5.4.6.3 Ion Chromatography Detection Limits

The detection limits are based on the concentration of the lowest standard analyzed. Results below the lowest standard are reported as below the detection limit.

5.4.7 Spectrophotometric (Colorimetric) Methods

5.4.7.1 Spectrophotometer Calibration

Spectrophotometers will be calibrated prior to each day of use. Calibration standards will be prepared from reference materials appropriate to the analyses being performed, and working calibration standards will be prepared fresh daily. The working standards will include a blank and minimum of five (5) concentrations to cover the anticipated range of measurement. At least one of the calibration standards will be at or below the desired instrument detection limit. The correlation coefficient of the plot of known versus found concentrations will be at least 0.996 in order to consider the responses linear over a range. If a correlation coefficient of 0.996 cannot be achieved, the instrument will be recalibrated prior to the analysis of samples.

Calibration data, to include the correlation coefficient, will be entered into laboratory notebooks to maintain a permanent record of instrument calibrations.

5.4.7.2 Spectrophotometer Quality Control

At least one method blank and two method spikes will be included in each laboratory lot of samples. Regardless of the matrix being processed, the method spikes and blanks will be in aqueous media. Method spikes will be at a concentration of approximately five (5) times the detection limit.

The method blanks will be examined to determine if contamination is being introduced in the laboratory.

The method spikes will be examined to determine both precision and accuracy.

Accuracy will be measured by the percent recovery (% R) of the spikes. The recovery must be in the range (90-110 percent) in order to be considered acceptable. Additionally, % R will be plotted on control charts to monitor method accuracy.

Precision will be measured by the reproducibility of both method spikes and will be calculated as relative percent difference (% RPD). Results must agree within twenty (20) percent RPD in order to be considered acceptable.

5.4.7.3 Spectrophotometric Methods Detection Limits

The detection limits are based on the concentration of the lowest standard analyzed. Results below the lowest standard are reported as below the detection limit.

5.5 Methods Development

When standard (published) methods of analyses are not applicable to analyses to be performed, methods can be developed to provide the desired information. However, the lack of a historical data base does not obviate the necessity for documented quality control data to demonstrate the validity of the generated results. Reference material sources must be identified, and proof of compound identity and purity must be available. Instrumental operating parameters as well as calibration data must be documented, and specific procedures (to include sampling, if applicable) must be noted. Quality control samples (method blanks, method spikes, method spike duplicates, matrix spikes, and matrix duplicates) should be analyzed with greater frequency than with standard analytical methods to demonstrate the certainty and uncertainty of generated data. Exact requirements for demonstrating the reliability of developed methods are normally dictated by the specific program.

5.6 Reference Materials

Whenever possible, primary reference materials will be obtained from the National Bureau of Standards (NBS) or the U.S. Environmental Protection Agency (EPA). In the absence of available reference materials from these organizations, other reliable sources will be sought. These reference materials will be used for instrument calibration, quality control spikes, and/or performance evaluations. Secondary reference materials may be used for these functions provided that they are traceable to an NBS standard or have been compared to an NBS standard within the laboratory.

5.7 Reagents

Laboratory reagents will be of a quality to minimize or eliminate background concentrations of the analyte to be measured. Reagents must also not contain other contaminants that will interfere with the analyte of concern.

5.8 Corrective Actions

An analysis or analytical system is considered to be out-of-control when it does not conform to the conditions specified by the method or standard operating procedures which apply. To confirm that an analysis or analytical system is in control, the laboratory routinely performs instrument calibration checks, analysis of method blanks and method blank spikes and compares the results of quality control samples to laboratory control charts or analytical protocol criteria (e.g., U.S. EPA-CLP).

When an analysis or analytical system is determined to be out-of-control, the person who identifies that there is a problem is responsible for documenting the occurrence and notifying his or her supervisor and/or Section Manager.

A Corrective Action Documentation Form (Figure 1) is to be completed for each out-of-control situation. It will be distributed to the Section Manager, QA Coordinator and Project Manager. The analyst, working with his or her supervisor or Section Manager, will attempt to determine the cause of the problem and take appropriate corrective action. Analysis may not resume until the problem has been corrected and it is determined that the analysis is back in control. Demonstration of the restoration of analytical control will normally be accomplished by generating satisfactory calibration and/or quality control sample data. This documentation will be attached to the corrective action documentation form.

6.0 DATA MANAGEMENT

6.1 Data Collection

In addition to the data collected in the field and recorded on the chain-of-custody forms, data describing the processing of samples will be accumulated in the laboratory and recorded in laboratory notebooks. Laboratory notebooks will contain:

- Date of processing
- Sample numbers
- Client (optional)
- Analyses or operation performed

- Calibration data
- Quality control samples included
- Concentrations/dilutions required
- Instrument readings
- Special observations (optional)
- Analysts signature

6.2 Data Reduction

Data reduction is performed by the individual analysts and consists of calculating concentrations in samples from the raw data obtained from the measuring instruments. The complexity of the data reduction will be dependent on the specific analytical method and the number of discrete operations (extractions, dilutions, and concentrations) involved in obtaining a sample that can be measured.

For those methods utilizing a calibration curve, sample responses will be applied to the linear regression line to obtain an initial raw result which is then factored into equations to obtain the estimate of the concentration in the original sample. Rounding will not be performed until after the final result is obtained to minimize rounding errors, and results will not normally be expressed in more than two (2) significant figures.

Copies of all raw data and the calculations used to generate the final results will be retained on file to allow reconstruction of the data reduction process at a later date.

6.3 Data Review

System reviews are performed at all levels. The individual analyst constantly reviews the quality of data through calibration checks, quality control sample results, and performance evaluation samples. These reviews are performed prior to submission to the Section Managers or the Analytical Project Manager.

The Section Manager and/or the Analytical Project Manager review data for consistency and reasonableness with other generated data and determine if program requirements have been satisfied. Selected hard copy output of data (chromatograms, spectra, etc.) will be reviewed to ensure that results are interpreted correctly. Unusual or unexpected results will be reviewed, and a resolution will be made as to whether the analysis should be repeated. In addition, the Analytical Project Manager or Section Manager will recalculate selected results to verify the calculation procedure.

The Quality Assurance Officer independently conducts a complete review of selected projects to determine if laboratory and client quality assurance/quality control requirements have been met. Discrepancies will be reported to the appropriate Section Manager and/or Analytical Project Manager for resolution.

The final routine review is performed by the Laboratory Manager prior to reporting the results to the client. Non-routine audits are performed by regulatory agencies and client representatives. The level of detail and the areas of concern during these reviews are dependent on the specific program requirements.

6.4 Data Reporting

Reports will contain final results (uncorrected for blanks and recoveries), methods of analysis, levels of detection, surrogate recovery data, and method blanks data. In addition, special analytical problems, and/or any modifications of referenced methods will be noted. The number of significant figures reported will be consistent with the limits of uncertainty inherent in the analytical method. Consequently, most analytical results will be reported to no more than two (2) significant figures. Data are normally reported in units commonly used for the analyses performed. Concentrations in liquids are expressed in terms of weight per unit volume (e.g., milligrams per liter). Concentrations in solid or semi-solid matrices are expressed in terms of weight per unit weight of sample (e.g., micrograms per gram).

Reported detection limits will be the concentration in the original matrix corresponding to the low level instrument calibration standard after concentration, dilution, and/or extraction factors are accounted for.

6.5 Data Archiving

The laboratory will maintain on file all of the raw data, laboratory notebooks, and other documentation pertinent to the work on a given project. This file will be maintained for five (5) years from the date of invoice unless a written request is received for an extended retention time.

Data retrieval from archives will be handled in a similar fashion to a request for analysis. Specifically, a written work request to include a quotation must be submitted for retrieval of data.

Client confidentiality will be maintained with retrieved data. Consequently, the laboratory can honor only those requests for data authorized by the original client.

7.0 SUBCONTRACTED ANALYSES

The subcontracting of analytical services does not relieve the laboratory of requirements set forth in this plan. Adherence to the provisions of this plan will be part of the subcontracting agreement, and data generated by the subcontractor laboratory will be reviewed with the same rigor as those analyses performed at WESTON facilities.

Figure 1

Corrective Action Documentation Form

CORRECTIVE ACTION DOCUMENTATION

AUDIT REPORT # _____
PAGE ___ OF ___

DATE/ORIGINATOR: _____
PERSON RESPONSIBLE FOR RESPONSE: _____

DISTRIBUTION:
- EARL JANSEN
- DEB WHITE
- CARTER NULTON
- J. MICHAEL TAYLOR
- DIANNE CHERRY
- MONTHLY REPORT FILE

DESCRIPTION OF PROBLEM and when identified: _____

State cause of problem if known or suspected: _____

SEQUENCE OF CORRECTIVE ACTION: (If no responsible person is identified, bring this form directly to the QA Coordinator)

State date, person, and action planned: _____

CA Initially Approved By: _____ Date: _____

Follow-up dates: _____

Description of follow-up: _____

Final CA Approved By: _____ Date: _____