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for Marine Environmental Quality

Sampling and Analytical Methods of the National Status and Trends Program National Benthic Surveillance and Mussel Watch Projects 1984-1992

Volume III

Comprehensive Descriptions of Elemental Analytical Methods

Silver Spring, Maryland
July, 1993

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Coastal Monitoring and Bioeffects Assessment Division
Office of Ocean Resources Conservation and Assessment
National Ocean Service

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Volume III

Comprehensive Descriptions of Elemental Analytical Methods

G. G. Lauenstein and A. Y. Cantillo
(Editors)

Silver Spring, Maryland
July, 1993

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C. Peven, A. Uhler and D. West

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PREFACE

The quantification of environmental contaminants and their effects by the National Oceanic and Atmospheric Administration's National Status and Trends Program began in 1984. Polycyclic aromatic hydrocarbons, butyltins, polychlorinated biphenyls, DDTs and other chlorinated pesticides, trace and major elements, and a number of measures of contaminant effects are quantified in estuarine and coastal samples. There are two major monitoring components in this program, the National Benthic Surveillance Project which is responsible for quantification of contamination in fish tissue and sediments, and developing and implementing new methods to define the biological significance of environmental contamination, and the Mussel Watch Project which monitors pollutant concentrations by quantifying contaminants in mollusk bivalves and sediments. Methods are described for sample collection, preparation, and quantification. The evolution of methods, method detection limits, and the Quality Assurance Project are also discussed.

This document is Volume III of the document entitled "National Benthic Surveillance and Mussel Watch Projects Analytical Protocols 1984-1992," and contains detailed descriptions of analytical methods used for the determination of major and trace elements in sediments and tissues by participating laboratories participating in the NS&T Program (Tables P.1 and P.2).

Table P.1. Laboratories analyzing National Status and Trends Program National Benthic Surveillance Project samples for major and trace elements and pertinent chapters in this document.

National Benthic Surveillance Project

Year	1984-1986	1987	1988-present
Northeast Coast	NEFSC (Sediments) Zdanowicz, Finneran and Kothe NEFSC (Tissues) Zdanowicz, Finneran and Kothe	NWFSC (Sediments) Robisch and Clark NWFSC (Tissues) Robisch and Clark	SEFSC (Sediments) (Evans and Hanson) SEFSC (Tissues) Evans and Hanson
Southeast and Gulf Coasts	SEFSC (Tissues) Evans and Hanson SEFSC (Sediments) Evans and Hanson	SEFSC (Tissues) (same) SEFSC (Sediments) (same)	SEFSC (Tissues) (same) SEFSC (Sediments) (same)
West Coast	NWFSC (Sediments) Robisch and Clark NWFSC (Tissues) Robisch and Clark	NWFSC (Sediments) (same) NWFSC (Tissues) (same)	NWFSC (Sediments) (same) NWFSC (Tissues) (same)

NEFSC - NOAA/NMFS/Northeast Fisheries Science Center, Sandy Hook, NJ.
SEFSC - NOAA/NMFS/Southeast Fisheries Science Center, Beaufort, NC.
NWFSC - NOAA/NMFS/Northwest Fisheries Science Center, Seattle, WA.

Table P.2. Laboratories analyzing National Status and Trends Program Mussel Watch Project samples for major and trace elements and pertinent chapters in this document.

Mussel Watch Project

Year	1986-1987	1988	1989	1990-1993
East Coast	Battelle	Battelle	Battelle	Battelle
	Crecelius *et al.*	(same)	(same)	(same)
Gulf Coast	TAMU	TAMU	TAMU	TAMU
	Taylor and Presley	(same)	(same)	(same)
West Coast				
California	SAIC	SAIC$^{\Delta}$	SAIC$^{\Diamond}$	Battelle
	Peven *et al.*	(same)	(same)	Crecelius *et al.*
Oregon	Battelle	Battelle	Battelle	Battelle
	Crecelius *et al.*	(same)	(same)	(same)
Washington	Battelle	Battelle	Battelle	Battelle
	Crecelius *et al.*	(same)	(same)	(same)
Alaska	Battelle	Battelle	NS	Battelle
	Crecelius *et al.*	(same)	-	(same)
Hawaii	SAIC	SAIC	NS	Battelle
	Peven *et al.*	(same)	-	Crecelius *et al.*

$^{\Delta}$ Sn analyzed by Battelle. $^{\Diamond}$ Se and Sn analyzed by Battelle. NS - Not sampled.
Battelle - Battelle Ocean Sciences, Duxbury, MA, and Sequim, WA.
TAMU - Geochemical and Environmental Research Group of Texas A&M University, College Station, TX.
SAIC - Science Applications International Corporation, Inc.

G. G. Lauenstein and A. Y. Cantillo
Editors

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National Ocean Service

Total Dissolution of Marine Sediment and Atomic Absorption Analysis of Major and Trace Elements

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ABSTRACT

Methods are described for the total dissolution of marine sediment and the instrumental analysis of 17 major and trace elements, at the Sandy Hook Laboratory as part of the National Benthic Surveillance Project of the National Status and Trends (NS&T) Program.

1. INTRODUCTION

These methods, for analysis of 17 metals in estuarine sediments, were developed as part of the National Benthic Surveillance Project of the National Status and Trends (NS&T) Program. The digestion procedure is a combination of those described by Bernas (1968), Buckley, and Cranston (1971), and Rantala and Loring (1975), adapted for use with Parr digestion bombs, and provides for total dissolution of sediments without loss of volatile elements. Seven of the 17 elements can be determined by flame atomization methods, which are relatively rapid, leaving 9 elements for graphite furnace determination; Hg is determined using the cold vapor technique. Although the primary objective in developing each instrumental method was that it should be as simple and straightforward as possible while producing acceptable accuracy and precision, most furnace methods contain multiple char steps and require matrix modification.

Users of the instrumental methods described below will probably have to modify certain parameter values to suit their particular instrumentation and equipment, due to variations in performance between instruments. Such variations are caused by differences in furnace calibrations, nebulizer characteristics, and other factors.

These methods were used at the NOAA National Marine Fisheries Service Northeast Fisheries Science Center Sandy Hook Laboratory to analyze NS&T samples collected from 1984 to 1986. Analytical results can be found in Zdanowicz and Gadbois (1990).

2. EQUIPMENT AND SUPPLIES

2.1. Instrumentation

Perkin-Elmer model Z/5000 spectrophotometer. Perkin-Elmer Corp., Norwalk, CT.

Burner (0040-0146) with flow spoiler and standard nebulizer (0303-0352)
Dual lamp EDL power supply
Furnace cooling unit
Model 056 dual pen recorder
Model 500 graphite furnace atomizer with Zeeman background correction system
Model 3600 data terminal with model PRS 100 printer
Model AS40 autosampler (for furnace analyses)

Model AS50 autosampler (for flame analyses)
Model PRS 10 printer

Perkin-Elmer model Z/5100 spectrophotometer

Dual lamp EDL power supply
Furnace cooling unit
Model 600 graphite furnace atomizer with Zeeman background correction system
Model 7700 data terminal with model PRS 210 printer
Model AS60 autosampler (for furnace analysis)

Mercury Analyzer, Gold Film, 511. Arizona Instruments, Clarksdale, AZ.

2.2. Supplies

Acetylene, pre-purified
Argon, 99.999% purity
Electrodeless discharge lamps (EDL)
Graphite tubes; pyrolytically coated, grooved, Perkin-Elmer B0109-322
Hollow cathode lamps (HCL)
Nitrous oxide, USP grade
Platforms, pyrolytically coated L'vov, Perkin-Elmer B0109-324

2.3. Labware

Balance, Mettler model PK300 with printer
Bottles, 125-mL, polyethylene
Cups, 2-mL, polyethylene
Filter paper, Whatman 41
Flasks, volumetric, 100-mL, polypropylene
Funnels, polypropylene
Glass mortars and pestles
Ovens, stainless steel, gravity convection, OV-18SA. Blue M, Blue Island, IL.
Parr bomb, 125-mL, Teflon tetrafluoroethylene (TFE) lined stainless steel, model 4748. Parr, Moline, IL.
Pipets, macro and micro
Spatulas or transfer tubes
Vials, 15-mL, Teflon polyfluoroalkoxy (PFA), threaded with screw caps, model 02.5. Savillex, Minnetonka, MN.

PFA vials were cleaned using Micro detergent and rinsed in tap water. They were then soaked for three days in hot (70-80°C) 10% HNO_3 / 5% HCl solution, rinsed with deionized water, soaked for 3 days in room-temperature 0.1 M ethylenediamine tetraacetic acid (EDTA), tetrasodium salt, rinsed with deionized water, soaked for 3 days in hot deionized water, and dried in Class 100 laminar flow hoods. All other plasticware was soaked for three days in 10% HNO_3 at room temperature, rinsed with deionized water, and dried as above.

2.4. Reagents

All reagents are ultrapure grades, except where so indicated.

Ammonium nitrate (NH_4NO_3) [6484-52-2], solid, 99.99%. Aesar, Ward Hill, MA.
Ascorbic acid ($C_6H_8O_6$) [50-81-7], solid, reagent grade. J. T. Baker, Phillipsburg, NJ.
Atomic absorption standards, 1000 µg/mL. Aesar, Ward Hill, MA.
Boric acid (H_3BO_3) [10043-35-3], solid, J. T. Baker 5168 or E. M. Science 765. J. T. Baker, Phillipsburg, NJ. or E. M. Science, Gibbstown, NJ.
Copper nitrate [$Cu(NO_3)_2 \cdot 2.5H_2O$] [19004-19-4], solid, reagent grade

Hydrochloric acid (HCl) [7647-01-0], concentrated (37%), 4800. J. T. Baker, Phillipsburg, NJ.

Hydrofluoric acid (HF) [7664-39-3], concentrated (48%), 4804. J. T. Baker, Phillipsburg, NJ.

Magnesium nitrate [$Mg(NO_3)_2 \cdot 6H_2O$] [13446-18-9], solid, 99.99%. Aesar, Ward Hill, MA.

Nitric acid (HNO_3) [7697-37-2], concentrated (70%), Baker 4801 or G. F. Smith 621. J. T. Baker, Phillipsburg, NJ, or G. Frederick Smith Chemicals, Columbus, OH.

Palladium nitrate [$Pd(NO_3)_2$], 9.984% Pd^{+2} solution, 12621. Aesar, Ward Hill, MA.

Water, deionized, 18 megohm-cm resistivity

2.5. Solvents and matrix modifiers

2.5.1. M19 Diluent

This solvent is used for making blank and sample dilutions and for most instrumental calibration standards (see Calibration section). It is prepared in deionized water and contains 40 g H_3BO_3, 60 mL concentrated HF, 7.5 mL concentrated HCl, and 2.5 mL concentrated HNO_3 per liter of solution.

2.5.2. 1646 Modifier

This solution contains approximately the concentrations of Si, Fe, and Al that would be found if 0.5 g NIST SRM 1646 were digested and brought to 100 mL volume. SRM 1646 was a standard reference material composed of estuarine sediment collected in Chesapeake Bay.

Dissolve 50.593 g $Na_2SiO_4 \cdot 6H_2O$ per 100 mL of solution in deionized water to obtain approximately 50,000 ppm Si.

Dissolve 10.851 g $Fe(NO_3)_2 \cdot 9H_2O$ per 100 mL of solution in deionized water to obtain approximately 15,000 ppm Fe.

Dissolve 4.172 g $Al(NO_3)_3 \cdot 9H_2O$ per 100 mL of solution in deionized water to obtain approximately 3,000 ppm Al.

Add 3 mL of the Si solution, 1 mL of the Fe solution, and 10 mL of the Al solution to approximately 50 mL of M19 diluent. Make up to 100 mL volume in a polypropylene volumetric flask using the M19 diluent.

This solution should be prepared 24-48 hr before use. It is used for calibration of Ag, Sn, As, Tl, and Sb analyses.

2.5.3. Matrix modifiers for graphite furnace analyses

Copper nitrate solution: 0.366 g $Cu(NO_3)_2 \cdot 2.5H_2O$ per 100 mL of solution in deionized water

Magnesium nitrate solution: 1.731 g $Mg(NO_3)_2 \cdot 6H_2O$ per 100 mL of solution in deionized water

Ammonium nitrate solution: 5.000 g NH_4NO_3 per 100 mL of solution in deionized water

Palladium nitrate solution: 500-fold dilution of a 9.984% Pd^{+2} solution in deionized water

Ascorbic acid solution: 5.000 g ascorbic acid per 100 mL of solution in deionized water

3. SAMPLE TREATMENT

3.1. Drying

The top 3 cm of each core sample were dried overnight in polyethylene weighing boats in a stainless steel gravity convection oven at 60-65°C, and subsequently cooled in a dessicator. They were then homogenized using glass mortars and pestles. The samples were stored in polyethylene vials at room temperature until composited and analyzed.

3.2. Compositing

Composites used for analysis were comprised of equal weight portions of each of the three sediment samples collected at each station and dried as described above.

3.3. Digestion

Sandy Hook Laboratory Method 19: Total Digestion of Sediments

Three reagent blanks and three standard reference material (SRM) samples were included in each analytical string of 36 samples. Reagent blanks contain no sample and were processed identically to the samples.

Weigh 450 ± 15 mg homogenized, dried sample into a 15-mL PFA vial. Add 750 µL concentrated HCl to each vial and begin wet-out of sample. Add 250 µL concentrated HNO_3 to each vial and continue wet-out of sample. Add 2 mL concentrated HF, swirling to complete sample wet-out. Add 4 mL concentrated HF, rinsing the walls of the vial to insure that all solids are washed down into the acid mixture.

Seal each vial tightly by hand. Place two vials in each bomb. Add 5 mL deionized water to each bomb liner and seal the bombs according to manufacturer's recommendations. Place bombs in oven and heat to 120°C overnight.

When cool, vent internal pressure carefully in a fume hood, and remove vials. Allow vials to cool to room temperature.

Quantitatively transfer the contents of each vial to a 125-mL polyethylene screw cap bottle, containing 50 mL of 4.0% (0.647 M) boric acid in deionized water using a wash bottle containing boric acid solution. The volume of each polyethylene bottle should be no more than 80 mL after transfer of the digest. Let stand 2-4 hours to allow dissolution of the fluorides.

Pretreat Whatman 41 filter paper by washing 3-4 times with M19 diluent, discarding the wash. Filter the sample solutions into 100-mL polypropylene volumetric flasks, removing any residue. Wash the filter paper 3-4 times with the boric acid solution and take to 100 mL with the boric acid solution.

4. CALIBRATION

Calibration standards were prepared by serial dilution of commercially available atomic absorption standards using class-A glass pipets and volumetric flasks, and 10% HNO_3. Final working standards, except for Ag, were prepared in M19 diluent using micropipets and plastic volumetric flasks. Concentrations of commercial standards were verified by comparison with National Institute of Standards and Technology (NIST) spectrophotometric standards.

Standards of four different concentrations including zero were used and at least three replicate determinations were made for each concentration. This was accomplished by analyzing a standard at the start of each analytical string and after every three samples. For a set of 36 samples, this resulted in at least 13 determinations of standards.

After each analytical string, the concentrations of the standards, together with the instrument readings obtained during the analysis of the standards, were used to calculate the slope, intercept, and correlation coefficient of the calibration curve using linear, least-squares regression. The correlation coefficient, r, was typically ≥0.98 for a well-behaved analysis.

4.1. Sn, Sb, Tl and As calibration

The instrumental sensitivity of these elements was affected by the concentrations of Si, Fe, and Al in the sample solutions, so calibration standards were prepared using the 1646 modifier.

For samples requiring dilution, the calibration standards were made-up using 1646 modifier diluted in the same proportions. For example, if in an analytical string of 36 samples, 12 were diluted twofold, 12 fivefold, and 12 tenfold, then separate sets of calibration standards were used for each set of 12 samples. The first set of standards was prepared in twofold-diluted 1646 modifier, the second in fivefold-diluted 1646 modifier, and the third in tenfold-diluted 1646 modifier. Samples and 1646 modifier were diluted with M19 diluent.

4.2. Ag calibration

The Ag standards were prepared in 10% HNO_3 to insure that no losses occurred due to the presence of halides. However, the sensitivity of the Ag analysis was also affected by the concentrations of Si, Fe, and Al in the sample solutions. To compensate for these effects, the following procedure was used. When analyzing a standard, 10 µL of standard and 10 µL of appropriately diluted 1646 Modifier (see above) were used, and when analyzing a sample, 10 µL of sample and 10 µL of 10% HNO_3 were used.

As with Sn, Sb, Tl, and As, when samples were diluted, appropriately diluted (see above) 1646 modifier was used for the standards.

4.3. Cd, Se, Sb, and Sn dilutions

Due to matrix effects, after digesting samples using SHL Method 19 described earlier, solutions were further diluted for the determination of Cd, Se, Sb, and Sn, even if these elements were present in very low concentrations. The signal from a diluted sample may fall below the limit of detection, while the signal from the undiluted sample may be above the limit of detection. However, the latter (undiluted) signal was usually erroneous and was biased low due to matrix interferences that were reduced by dilution with M19 diluent.

5. CALCULATIONS

Using the value of the slope, m, of the calibration curve obtained by linear regression analysis of the calibration standards data, the concentration of analyte in sample and reagent blank solutions was calculated using

$$C = \frac{Y}{m}$$

where C is the concentration (µg/mL or ng/mL) of analyte in solution, Y is the absorbance of the sample and m is the slope of the calibration curve.

For Hg determinations, the formula used was

$$C = \frac{Y}{m\ V_{Hg}}$$

where V_{Hg} is the volume of sample used for Hg analysis.

B, the average of the reagent blanks, and s_B, the standard deviation of B were then calculated.

The solution detection limit, DL_S, was then calculated using

$$DL_S = B + 3s_B$$

Since all the samples theoretically contain B, DL_S was used as a working detection limit to determine which samples required a "less than" calculation. The actual detection limit, DL, defined as the minimum solution concentration that is reliably different from the average reagent blank concentration, was calculated using

$$DL = DL_S - B = 3s_B$$

Typical method detection limits are listed in Table III.1.

The dry weight concentration of the analyte in the samples was calculated using the relation,

$$X = \frac{(C - B)\ (DF)\ (Vol)}{Wt}$$

where X is the concentration of analyte in the dry sample, C is the concentration of the analyte in solution, B is the average reagent blank, DF is the amount of any additional dilution of the sample solution, Vol is the volume of the original sample solution (e.g. 100 mL), and Wt is the dry weight of the sample (e.g. 0.465 g). When C is in µg/mL, X is in µg/g, and when C is in ng/mL, X is in ng/g.

For any sample with a solution concentration lower than the working detection limit, DL_S, of an element, a "less than" value was calculated using

$$X < \frac{(DL_S - B)\ (DF)\ (Vol)}{Wt}\ .$$

Table III.1. Typical detection limits for Sandy Hook Laboratory Method 19 [0.45 g sediment sample brought to 100 mL final volume (µg/g unless noted)].

Al	0.2 %	Se	0.1
Si	2 %	Ag	0.01
Cr	6	Cd	0.01
Mn	3	Sn	0.2
Fe	0.2 %	Sb	0.2
Ni	0.3	Hg	0.01
Cu	4	Tl	0.2
Zn	4	Pb	0.1
As	0.1		

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7. INSTRUMENTAL ANALYSIS

7.1. Aluminum

METHOD: Flame Atomic Absorption

DIGEST MATRIX: M19 diluent. Diluted ten-fold using M19 diluent.

INSTRUMENT SETTINGS:

Wavelength:	309.3 nm
Lamp:	HCL, 7 ma (Perkin-Elmer 0303-6009)
Fuel:	Acetylene
Oxidant:	Nitrous oxide
Mixture:	Rich (red)
Burner head:	Single-slot, 5 cm, 0° rotation
Slit width setting:	0.2H
Background correction:	None
Signal mode:	Peak height/hold
Scale expansion:	None
Read delay:	4 sec
Number of readings:	3 sec/reading, average of 3 reads
Output:	To data terminal and printer

STANDARDS: 0, 10, 30, and 50 µg Al/mL prepared in M19 diluent using Aesar Al spectral standard (13856). Auto-zero using deionized water.

TYPICAL SENSITIVITY: Absorbance is approximately 0.220 for a 50.0 µg/mL standard.

CALIBRATION: Peak height of standard versus concentration of standard. Compute the slope, intercept, and correlation coefficient using linear, least-squares regression.

MATRIX MODIFICATION: None

NOTES: Aspirate 10% HNO_3 between samples.
Scrape ash build-up off burner slot every 4-6 readings.

7.2. Silicon

METHOD: Flame Atomic Absorption

DIGEST MATRIX: M19 diluent. Diluted fifty-fold using M19 diluent.

INSTRUMENT SETTINGS:

Wavelength:	251.6 nm
Lamp:	HCL, 10 ma (Perkin-Elmer 0303-6061)
Fuel:	Acetylene
Oxidant:	Nitrous oxide
Mixture:	Lean (pale pink)
Burner head:	Single-slot, 5 cm, 0° rotation
Slit width setting:	0.2H
Background correction:	None
Signal mode:	Peak height/hold
Scale expansion:	None
Read time:	3 sec/reading, average of 3 reads
Output:	To data terminal and printer
Read delay:	4 sec

STANDARDS: 0, 10, 30, and 50 µg Si/mL prepared in M19 diluent using Aesar Si spectral standard (13814). Auto-zero using deionized water.

TYPICAL SENSITIVITY: Absorbance is approximately 0.130 for a 50.0 µg/mL standard.

CALIBRATION: Peak height of standard versus concentration of standard. Compute the slope, intercept, and correlation coefficient using linear, least-squares regression.

MATRIX MODIFICATION: None

NOTES: Aspirate 10% HNO_3 between samples.
Scrape ash build-up off burner slot every 4-6 readings.
Losses of Si as a precipitate observed in samples of high mass (>500 mg) and/or high sand content.

7.3. Chromium

METHOD: Flame Atomic Absorption

DIGEST MATRIX: M19 diluent. For additional dilutions use M19 diluent.

INSTRUMENT SETTINGS:

Wavelength:	357.9 nm
Lamp:	HCL, 25 ma (Perkin-Elmer 0303-6021)
Fuel:	Acetylene
Oxidant:	Air
Mixture:	Rich (pale yellow)
Burner head:	Three-slot, 10 cm, 0° rotation
Slit width setting:	0.7H
Background correction:	None
Signal mode:	Peak height/hold
Scale expansion:	None
Read time:	3 sec/reading, average of 3 reads
Output:	To data terminal and printer
Read delay:	4 sec

STANDARDS: 0, 1, 2, and 4 µg Cr/mL prepared in M19 diluent using Aesar Cr spectral standard (13864). Auto-zero using deionized water.

TYPICAL SENSITIVITY: Absorbance is approximately 0.240 for a 4.00 µg/mL standard.

CALIBRATION: Peak height of standard versus concentration of standard. Compute the slope, intercept, and correlation coefficient using linear, least-squares regression.

MATRIX MODIFICATION: None

NOTES: Aspirate 10% HNO_3 between samples.

7.4. Manganese

METHOD: Flame Atomic Absorption

DIGEST MATRIX: M19 diluent. For additional dilutions use M19 diluent.

INSTRUMENT SETTINGS:

Wavelength:	279.5 nm
Lamp:	HCL, 7 ma (Perkin-Elmer 0303-6043)
Fuel:	Acetylene
Oxidant:	Air
Mixture:	Lean (pale blue)
Burner head:	Three-slot, 10 cm, 0° rotation
Slit width setting:	0.2H
Background correction:	None
Signal mode:	Peak height/hold
Scale expansion:	None
Read time:	3 sec/reading, average of 3 reads
Output:	To data terminal and printer
Read delay:	4 sec

STANDARDS: 0, 0.5, 1, and 2 µg Mn/mL prepared in M19 diluent using Aesar Mn spectral standard (13826). Auto-zero using deionized water.

TYPICAL SENSITIVITY: Absorbance is approximately 0.250 for a 2 µg/mL standard.

CALIBRATION: Peak height of standard versus concentration of standard. Compute the slope, intercept, and correlation coefficient using linear, least-squares regression.

MATRIX MODIFICATION: None

NOTES: Aspirate 10% HNO_3 between samples.
Losses observed in sample solutions containing precipitated Si.

7.5. Iron

METHOD: Flame Atomic Absorption

DIGEST MATRIX: M19 diluent. Diluted fifty-fold using M19 diluent.

INSTRUMENT SETTINGS:

Wavelength:	248.3 nm
Lamp:	HCL, 30 ma (Perkin-Elmer 0303-6037)
Fuel:	Acetylene
Oxidant:	Air
Mixture:	Lean (pale blue)
Burner head:	Three-slot, 10 cm, 0° rotation
Slit width setting:	0.2H
Background correction:	None
Signal mode:	Peak height/hold
Scale expansion:	None
Read time:	3 sec/reading, average of 3 reads
Output:	To data terminal and printer
Read delay:	4 sec

STANDARDS: 0, 1, 2, and 4 µg Fe/mL prepared in M19 diluent using Aesar Fe spectral standard (13830). Auto-zero using deionized water.

TYPICAL SENSITIVITY: Absorbance is approximately 0.180 for a 4.00 µg/mL standard.

CALIBRATION: Peak height of standard versus concentration of standard. Compute the slope, intercept, and correlation coefficient using linear, least-squares regression.

MATRIX MODIFICATION: None

NOTES: Aspirate 10% HNO_3 between samples.
Alternate wavelength, 248.8 nm, may be used.

7.6. Nickel

METHOD: Graphite Furnace Atomic Absorption

DIGEST MATRIX: M19 diluent. For additional dilutions use M19 diluent.

INSTRUMENT SETTINGS:

Wavelength:	232.2 nm
Lamp:	HCL, 25 ma (Perkin-Elmer 0303-6047)
Platform:	L'vov, coated
Carrier gas:	Argon
Slit width setting:	0.2L
Background correction:	Zeeman
Signal mode:	Peak area
Scale expansion:	None
Read time:	5 sec
Output:	To data terminal, printer and recorder

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
Dry	120	10	25	300
Char l	450	10	10	300
Char 2	1450	10	10	300
Atomize	2900	0	5	0
Cool l	20	1	10	300
Cleanout	3000	1	5	300
Cool 2	20	1	10	300

STANDARDS: 0, 10, 20, and 40 µg Ni/mL prepared in M19 diluent using Aesar Ni spectral standard (13839). Auto-zero using air.

TYPICAL SENSITIVITY: Peak area is approximately 0.240 for a 40.0 ng/mL standard.

CALIBRATION: Peak area of standard versus concentration of standard. Compute the slope, intercept, and correlation coefficient using linear, least-squares regression.

INJECTION VOLUME: 20 µL

MATRIX MODIFICATION: None

7.7. Copper

METHOD: Flame Atomic Absorption

DIGEST MATRIX: M19 diluent. For additional dilutions use M19 diluent.

INSTRUMENT SETTINGS:

Wavelength:	324.8 nm
Lamp:	HCL, 15 ma (Perkin-Elmer 0303-6024)
Fuel:	Acetylene
Oxidant:	Air
Mixture:	Lean (pale blue)
Burner head:	Three-slot, 10 cm, 0° rotation
Slit width setting:	0.7H
Background correction:	None
Signal mode:	Peak height/hold
Scale expansion:	None
Read time:	3 sec/reading, average of 3 reads
Output:	To data terminal and printer
Read delay:	4 sec

STANDARDS: 0, 1, 3, and 5 µg Cu/mL prepared in M19 diluent using Aesar Cu spectral standard (13867). Auto-zero using deionized water.

TYPICAL SENSITIVITY: Absorbance is approximately 0.230 for a 5.00 µg/mL standard.

CALIBRATION: Peak height of standard versus concentration of standard. Compute the slope, intercept, and correlation coefficient using linear, least-squares regression.

MATRIX MODIFICATION: None

NOTES: Aspirate 10% HNO_3 between samples.

7.8. Zinc

METHOD: Flame Atomic Absorption

DIGEST MATRIX: M19 diluent. For additional dilutions, use M19 diluent.

INSTRUMENT SETTINGS:

Wavelength:	213.9 nm
Lamp:	HCL, 15 ma (Perkin-Elmer 0303-6081)
Fuel:	Acetylene
Oxidant:	Air
Mixture:	Lean (pale blue)
Burner head:	Three-slot, 10 cm, 0° rotation
Slit width setting:	0.7H
Background correction:	None
Signal mode:	Peak height/hold
Scale expansion:	None
Read time:	3 sec/reading, average of 3 reads
Output:	To data terminal and printer
Read delay:	4 sec

STANDARDS: 0, 0.25, 0.5, and 1 µg Zn/mL prepared in M19 diluent using Aesar Zn spectral standard (13835). Auto-zero using deionized water.

TYPICAL SENSITIVITY: Absorbance is approximately 0.255 for a 1.00 µg/mL standard.

CALIBRATION: Peak height of standard versus concentration of standard. Compute the slope, intercept, and correlation coefficient using linear, least-squares regression.

MATRIX MODIFICATION: None

NOTES: Aspirate 10% HNO_3 between samples.

7.9. Arsenic

METHOD: Graphic Furnace Atomic Absorption

DIGEST MATRIX: M19 diluent. For additional dilutions use M19 diluent.

INSTRUMENT SETTINGS:

Wavelength:	193.7 nm
Lamp:	EDL, 6 w (Perkin-Elmer 0303-6211)
Platform:	L'vov, coated
Carrier gas:	Argon
Slit width setting:	0.7L
Background correction:	Zeeman
Signal mode:	Peak area
Scale expansion:	None
Read time:	5 sec
Output:	To data terminal, printer, and recorder

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
Dry	120	10	30	300
Char l	450	10	10	300
Char 2	1000	10	10	300
Atomize	2550	0	5	0
Cool l	20	1	10	300
Cleanout	2900	1	5	300
Cool 2	20	1	10	300

STANDARDS: 0, 5, 15, and 30 µg As/mL prepared in appropriately diluted 1646 modifier using Aesar As spectral standard (13839). Auto-zero using air without modifier.

TYPICAL SENSITIVITY: Peak area is approximately 0.175 for a 30.0 ng/mL standard.

CALIBRATION: Peak area of standard versus concentration of standard. Compute the slope, intercept, and correlation coefficient using linear, least-squares regression.

INJECTION VOLUME: 20 µL

MATRIX MODIFICATION: 5 µL 1:1 mixture of palladium nitrate and magnesium nitrate solutions (see matrix modifiers section for preparation instructions).

NOTES: See Calibration section.

7.10. Selenium

METHOD: Graphic Furnace Atomic Absorption

DIGEST MATRIX: M19 diluent. Samples must be diluted at least two-fold.

INSTRUMENT SETTINGS:

Wavelength:	196.0 nm
Lamp:	EDL, 4.5 watts (Perkin-Elmer 0303-6262)
Platform:	L'vov, coated
Carrier gas:	Argon
Slit width setting:	2.0L
Background correction:	Zeeman
Signal mode:	Peak height
Scale expansion:	None
Read time:	5 sec
Output:	To data terminal, printer and recorder

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
Dry	120	10	20	300
Char1	350	10	10	300
Char2	600	10	10	300
Atomize	2600	0	5	0
Cool1	20	1	10	300
Cleanout	2900	1	5	300
Cool2	20	1	10	300

STANDARDS: 0, 5, 10, and 20 ng Se/mL prepared in M19 diluent using Aesar Se spectral standard (13845). Auto-zero using air without modifier.

TYPICAL SENSITIVITY: Absorbance is approximately 0.080 for a 20.0 ng/mL standard.

CALIBRATION: Peak height of standard versus concentration of standard. Compute the slope, intercept, and correlation coefficient using linear, least-squares regression.

INJECTION VOLUME: 20 µL

MATRIX MODIFICATION: 5 µL 1:1 mixture of copper nitrate and magnesium nitrate solutions (see matrix modifiers section for preparation instructions).

7.11. Silver

METHOD: Graphite Furnace Atomic Absorption

DIGEST MATRIX: M19 diluent. For additional dilutions, use M19 diluent.

INSTRUMENT SETTINGS:

Wavelength:	328.1 nm
Lamp:	HCL, 10 ma (Perkin-Elmer 0303-6064)
Platform:	L'vov, coated
Carrier gas:	Argon
Slit width setting:	0.7L
Background correction:	Zeeman
Signal mode:	Peak height
Scale expansion:	None
Read time:	5 sec
Output:	To data terminal, printer, and recorder

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
Dry	120	10	25	300
Char1	450	10	10	300
Char2	700	10	10	300
Atomize	2100	0	5	0
Cool1	20	1	10	300
Cleanout	2900	1	5	300
Cool2	20	1	10	300

STANDARDS: 0, 0.5, 1.5, and 3.0 ng Ag/mL prepared in 10% HNO_3 using Aesar Ag spectral standard (13849). Auto-zero using air without modifier.

TYPICAL SENSITIVITY: Absorbance is approximately 0.120 for a 3.0 ng/mL standard.

CALIBRATION: Peak height of standard versus concentration of standard. Compute the slope, intercept, and correlation coefficient using linear, least-squares regression.

INJECTION VOLUME: 10 µL

MATRIX MODIFICATION: 10 µL 10% HNO_3 for sample digests, and 10 µL appropriately diluted 1646 modifier solution for standards.

NOTES: See Calibration section.

7.12. Cadmium

METHOD: Graphite Furnace Atomic Absorption

DIGEST MATRIX: M19 diluent. Samples must be diluted at least two-fold.

INSTRUMENT SETTINGS:

Wavelength:	228.8 nm
Lamp:	HCL, 4 ma (Perkin-Elmer 0303-6016)
Platform:	L'vov, coated
Carrier gas:	Argon
Slit width setting:	0.7L
Background correction:	Zeeman
Signal mode:	Peak area
Scale expansion:	None
Read time:	5 sec
Output:	To data terminal, printer, and recorder

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
Dry	120	10	30	300
Char1	450	10	25	300
Atomize	1500	0	5	0
Cool1	20	1	10	300
Cleanout	2700	1	5	300
Cool2	20	1	10	300

STANDARDS: 0, 0.2, 0.5, and 1 ng Cd/mL prepared in M19 diluent using Aesar Cd spectral standard (13813). Auto-zero using air.

TYPICAL SENSITIVITY: Peak area is approximately 0.140 for a 1.00 ng/mL standard.

CALIBRATION: Peak area of standard versus concentration of standard. Compute the slope, intercept, and correlation coefficient using linear, least-squares regression.

INJECTION VOLUME: 20 µL

MATRIX MODIFICATION: None

7.13. Tin

METHOD: Graphite Furnace Atomic Absorption

DIGEST MATRIX: M19 diluent. Samples must be diluted at least two-fold.

INSTRUMENT SETTINGS:

Wavelength:	286.3 nm
Lamp:	EDL, 6 watts (Perkin-Elmer 0303-6274)
Platform:	L'vov, coated
Carrier gas:	Argon
Slit width setting:	0.7L
Background correction:	Zeeman
Signal mode:	Peak height
Scale expansion:	None
Read time:	5 sec
Output:	To data terminal, printer, and recorder

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
Dry	120	10	30	300
Char1	450	10	10	300
Char2	800	10	10	300
Atomize	2600	0	5	0
Cool1	20	1	10	300
Cleanout	2900	1	5	300
Cool2	20	1	10	300

STANDARDS: 0, 5, 15, and 30 ng Sn/mL prepared in appropriately diluted 1646 modifier solution using Aesar Sn spectral standard (13863). Auto-zero using air without modifier.

TYPICAL SENSITIVITY: Absorbance is approximately 0.270 for a 30.0 ng/mL standard.

CALIBRATION: Peak height of standard versus concentration of standard. Compute the slope, intercept, and correlation coefficient using linear, least-squares regression.

INJECTION VOLUME: 20 µL

MATRIX MODIFICATION: 5 µL 1:1 mixture of palladium nitrate and ammonium nitrate solutions (see matrix modifiers section for preparation instructions).

NOTES: See Calibration section.

7.14. Antimony

METHOD: Graphite Furnace Atomic Absorption

DIGEST MATRIX: M19 diluent. Samples must be diluted at least two-fold.

INSTRUMENT SETTINGS:

Wavelength:	217.6 nm
Lamp:	EDL, 6 watts (Perkin-Elmer 0303-6210)
Platform:	L'vov, coated
Carrier gas:	Argon
Slit width setting:	0.7L
Background correction:	Zeeman
Signal mode:	Peak height
Scale expansion:	None
Read time:	5 sec
Output:	To data terminal, printer, and recorder

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
Dry	120	10	30	300
Char1	450	10	10	300
Char2	1100	10	10	300
Atomize	2500	0	5	0
Cool1	20	1	10	300
Cleanout	2900	1	5	300
Cool2	20	1	10	300

STANDARDS: 0, 5, 15, and 30 ng Sb/mL prepared in appropriately diluted 1646 modifier solution using Aesar Sn spectral standard (13818). Auto-zero using air without modifier.

TYPICAL SENSITIVITY: Absorbance is approximately 0.200 for 30.0 ng/mL standard.

CALIBRATION: Peak height of standard versus concentration of standard. Compute the slope, intercept, and correlation coefficient using linear, least-squares regression.

INJECTION VOLUME: 20 µL

MATRIX MODIFICATION: 5 µL 1:1 mixture of palladium nitrate and ammonium nitrate solutions (see matrix modifiers section for preparation instructions).

NOTES: See Calibration section.

7.15. Mercury

METHOD: Cold Vapor/Gold Foil Detector

DIGEST MATRIX: M19 diluent.

INSTRUMENT SETTINGS:

Reaction volume:	30 mL
Diluent:	M19 diluent.
Carrier gas:	Air
Flow rate:	850 mL/min
Scale expansion:	None
Integration time:	2 min
Output:	To LC Display

REDUCTANT: 10% $SnCl_2$ in deionized water.

STANDARDS: 0, 10, 30, and 50 ng Hg from a 50 ng/mL standard in M19 diluent using Aesar Hg spectral standard (13865). Use aliquots of 0, 200, 600, and 1000 µL. Auto zero using air.

TYPICAL SENSITIVITY: 90% recovery of input standard.

CALIBRATION: Instrument read-out is in ng Hg. Calibration curve is based on Hg detected versus ng Hg in the standards. The slope, intercept, and correlation coefficient are calculated using linear, least-squares regression.

INJECTION VOLUME: Up to 30 mL.

REDUCTANT VOLUME: 1 mL

MATRIX MODIFICATION: None

7.16. Thallium

METHOD: Graphite Furnace Atomic Absorption

DIGEST MATRIX: M19 diluent. For additional dilutions, use M19 diluent.

INSTRUMENT SETTINGS:

Wavelength:	276.8 nm
Lamp:	EDL, 5 watts (Perkin-Elmer 0303-6271)
Platform:	L'vov, coated
Carrier gas:	Argon
Slit width setting:	0.7L
Background correction:	Zeeman
Signal mode:	Peak height
Scale expansion:	None
Read time:	5 sec
Output:	To data terminal, printer, and recorder

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
Dry	120	10	25	300
Char1	450	10	20	300
Char2	700	10	20	300
Atomize	1900	0	5	0
Cool1	20	1	10	300
Cleanout	2900	1	5	300
Cool2	20	1	10	300

STANDARDS: 0, 2, 5, and 10 ng Tl/mL prepared in appropriately diluted 1646 modifier solution using Aesar Tl spectral standard (13851). Auto-zero using air without modifier.

TYPICAL SENSITIVITY: Absorbance is approximately 0.070 for a 10.0 ng/mL standard.

CALIBRATION: Peak height of standard versus concentration of standard. Compute the slope, intercept, and correlation coefficient using linear, least-squares regression.

INJECTION VOLUME: 20 µL

MATRIX MODIFICATION: 5 µL 5% ascorbic acid solution in deionized water.

NOTES: See Calibration section.

7.17. Lead

METHOD: Graphite Furnace Atomic Absorption

DIGEST MATRIX: M19 diluent. For additional dilutions, use M19 diluent.

INSTRUMENT SETTINGS:

Wavelength:	283.3 nm
Lamp:	10 ma (Perkin-Elmer 0303-6039)
Platform:	L'vov, coated
Carrier gas:	Argon
Slit width setting:	0.7L
Background correction:	Zeeman
Signal mode:	Peak height
Scale expansion:	None
Read time:	5 sec
Output:	To data terminal, printer, and recorder

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
Dry	120	10	15	300
Char1	450	10	10	300
Char2	1000	10	10	300
Atomize	1900	0	5	0
Cool1	20	1	10	300
Cleanout	2900	1	5	300
Cool2	20	1	10	300

STANDARDS: 0, 5, 15, and 30 ng Pb/mL prepared in M19 diluent using Aesar Pb spectral standard (13853). Auto-zero using air.

TYPICAL SENSITIVITY: Absorbance is approximately 0.240 for a 30.0 ng/mL standard.

CALIBRATION: Peak height of standard versus concentration of standard. Compute the slope, intercept, and correlation coefficient using linear, least-squares regression.

INJECTION VOLUME: 20 µL

MATRIX MODIFICATION: None

Digestion of Fish Tissue and Atomic Absorption Analysis of Trace Elements

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ABSTRACT

Methods are described for the total dissolution of fish liver and the instrumental analyses of sixteen trace elements, developed at the Sandy Hook Laboratory as part of the National Benthic Surveillance Project of the National Status and Trends (NS&T) Program.

1. INTRODUCTION

The methods for the analyzing of 16 metals in marine fish livers were developed as part of the National Benthic Surveillance Project of the National Status and Trends (NS&T) Program. The procedures are based largely on those of Evans and Hanson (this document), and customized for our use and equipment. The digestion results in a total dissolution of tissue without loss of volatile elements. Four of the 16 elements can be determined by flame atomization methods, which are relatively rapid, leaving eleven elements for graphite furnace atomization. Mercury is determined using the cold vapor technique. Although the primary objective in developing each instrumental method was that it be simple and straightforward while producing acceptable accuracy and precision, most furnace methods contain multiple char steps and require matrix modification.

Due to variations in performance between instruments, users of the instrumental methods described below will probably have to modify certain parameters values to suit their particular instrumentation and equipment. Such variations are caused by differences in furnace calibrations, nebulizer characteristics, lamp intensities, and other factors.

These methods were used at the NOAA National Marine Fisheries Service Northeast Fisheries Science Center Sandy Hook Laboratory to analyze NS&T samples collected from 1984 to 1986. Analytical results can be found in Zdanowicz and Gadbois (1990).

2. EQUIPMENT AND SUPPLIES

2.1. Instrumentation

Perkin-Elmer model Z/5000 spectrophotometer. Perkin-Elmer Corp., Norwalk, CT.

Burner (0040-0146) with flow spoiler and standard nebulizer (0303-0352)
Dual lamp EDL power supply
Furnace cooling unit
Model 056 dual pen recorder
Model 500 graphite furnace atomizer with Zeeman background correction system
Model 3600 data terminal with model PRS 100 printer
Model AS40 autosampler (for furnace analyses)
Model AS50 autosampler (for flame analyses)
Model PRS 10 printer

Perkin-Elmer model Z/5100 spectrophotometer

Dual lamp EDL power supply
Furnace cooling unit
Model 600 graphite furnace atomizer with Zeeman background correction system
Model 7700 data terminal with model PRS 210 printer
Model AS60 autosampler (for furnace analyses)

Mercury Analyzer, Gold Film, model 511. Arizona Instruments, Clarksdale, AZ.

2.2. Supplies

Acetylene (C_2H_2) [74-86-2], pre-purified
Argon (Ar), 99.999% purity
Electrodeless discharge lamps (EDL)
Hollow cathode lamps (HCL)
Platforms, pyrolytically coated L'vov, Perkin-Elmer B0109-324
Graphite tubes, pyrolytically coated, grooved, Perkin-Elmer B0109-322

2.3. Labware

Balance, Mettler, model PK300 with printer
Cups, 2-mL, polyethylene
Graduated cylinders, 25-mL, glass
Ovens, stainless steel, gravity convection, model OV-18SA. Blue M Blue Island, IL.
Parr bomb, 125-mL, Teflon tetrafluoroethylene (TFE) lined stainless steel, 4748. Parr, Moline, IL.
Pipets, macro and micro
Spatulas or transfer tubes
Tubes, centrifuge, 15-mL, polystyrene
Vials, 2-mL, glass
Vials, 15-mL, Teflon polyfluoroalkoxy (PFA), threaded with screw caps, 02.5. Savillex, Minnetonka, MN.

PFA vials are cleaned using Micro detergent and rinsed in tap water. They are then soaked for three days in a hot solution (70-80°C) of mixed acids (10% HNO_3 and 5% HCl solution, by volume), rinsed with deionized water, soaked for 3 days in room-temperature 0.1 M ethylenediamine tetraacetic acid (EDTA) tetrasodium salt, rinsed with deionized water, soaked for 3 days in hot deionized water, and dried in Class 100 laminar flow hoods. All other plastic and glassware are soaked for three days in 10% HNO_3 at room temperature, rinsed with deionized water, and dried as above. All containers used for aluminum analysis also receive the EDTA soak.

Before use, PFA vials are brought to constant weight by heating at 120°C for 24-48 hours.

2.4. Reagents

All reagents are ultrapure grades, except where indicated.

Ammonium nitrate (NH_4NO_3) [6484-52-2], solid, 99.99%. Aesar, Ward Hill, MA.
Atomic absorption standards, 1000 µg/mL. Aesar, Ward Hill, MA.
Magnesium nitrate [$Mg(NO_3)_2 \cdot 6H_2O$] [13446-18-9], solid, 99.99%. Aesar, Ward Hill, MA.
Nitric acid (HNO_3) [7697-37-2], concentrated (70%), Baker 4801 or G. F. Smith 621. J. T. Baker, Phillipsburg, NJ, or G. Frederick Smith Chemicals, Columbus, OH.
Palladium nitrate, [$Pd(NO_3)_2$]; 9.984% Pd^{+2} solution, 12621. Aesar, Ward Hill, MA.
Water, deionized, 18 megohm-cm resistivity

2.5. Solvents and matrix modifiers

2.5.1. 10% HNO_3

This solvent is used for making blank and sample dilutions and for instrumental calibration standards (see Calibration section). It is prepared in deionized water and contains 142 mL concentrated HNO_3 per liter of solution.

2.5.2. Matrix modifiers for graphite furnace analyses

Magnesium nitrate solution: 1.731 g $Mg(NO_3)_2 \cdot 6H_2O$ per 100 mL of solution in deionized water

Ammonium nitrate solution: 5.000 g NH_4NO_3 per 100 mL of solution in deionized water

Palladium nitrate solution: 500-fold dilution of a 9.984% Pd^{+2} solution in deionized water

3. SAMPLE PREPARATION

Sandy Hook Laboratory Method 20: Total Digestion of Fish Liver

Three reagent blanks and three standard reference material (SRM) samples were included in each analytical string of 36 samples. Reagent blanks contained no sample and were processed identically to the samples. The steps marked with an asterisk (*) are included if Al is to be determined.

Record the tare weight of a 15-mL PFA vial. Weigh no more than 3 grams (wet weight) of liver tissue into the tared vial, re-weigh and record the weight.

Dry the samples overnight at 60-65°C. After cooling, re-weigh and record the weight.

Add 5 mL concentrated HNO_3 to each vial and let the vials stand in a fume hood for 1-2 hr. Seal each vial tightly by hand and place two vials in each bomb. Add 5 mL of deionized water to each bomb liner and seal the bombs according to manufacturer's instructions. Place bombs in oven and heat at 120°C overnight.

When cool, carefully vent the bombs in a fume hood. Disassemble bombs and remove vials. After vials cool, loosen caps and let stand overnight in fume hood to allow digests to de-gas.

* Weigh the vials and record the weight. Using a micropipette with a plastic pipet tip, remove a 500 µL aliquot of the digest from the vial and add this aliquot to a 15-mL centrifuge tube containing 6-8 mL 10% HNO_3. Flush the pipet tip using the liquid in the centrifuge tube. This solution is for aluminum analysis.

* Re-weigh the vial and record the weight. This remaining portion of the digest is used for analyses of the remaining elements.

Quantitatively transfer the contents of the vial to a 25-mL glass graduated cylinder containing 10-12 mL deionized water using distilled water and a small glass funnel. Rinse the

vial 2-3 times with 2-3 mL deionized water and add each rinse to the cylinder. Rinse and discard the funnel. Bring to 25.0 mL using deionized water.

* Bring the Al samples to 10.0 mL using 10% HNO_3.

4. CALIBRATION

Calibration standards were prepared by serial dilution of commercially available atomic absorption standards using class-A glass pipets and volumetric flasks, and 10% HNO_3. Final working standards were prepared in 10% HNO_3. Concentrations of commercial standards were verified by comparison with National institute of Standards and Technology (NIST) spectrophotometric standards.

Standards of four different concentrations including zero were used, and at least three replicate determinations are made for each concentration. This was accomplished by analyzing a standard at the start of each sample string analysis and after every three samples. For a set of 36 samples, this resulted in at least 13 determinations of standards.

After each analytical sample string was analyzed, the concentrations of the standards and the instrument readings obtained during the analysis of the standards were used to calculate the slope, intercept, and correlation coefficient of the calibration curve using linear, least-squares regression. The correlation coefficient, r, is typically >0.98 for a well-behaved analysis.

5. CALCULATIONS

Using the value of the slope, m, of the calibration curve obtained by linear regression analysis of the calibration standards data, the concentration of analyte in sample and reagent blank solutions is calculated using

$$C = \frac{Y}{m}$$

where C is the concentration (µg/mL or ng/mL) of analyte in solution, Y is the absorbance of the sample, and m is the slope of the calibration curve.

For Hg determinations, the formula used was

$$C = \frac{Y}{m\ V_{Hg}}$$

where V_{Hg} is the volume of sample solution used for Hg analysis.

B, the average of the reagent blanks, and s_B, the standard deviation of B were then calculated.

The solution detection limit, DL_S, was calculated using

$$DL_S = B + 3s_B .$$

Table III.2. Typical detection limits for Sandy Hook Laboratory Method 20 [1.0 g liver sample brought to 25 mL final volume (µg/g)].

Al	0.1	Se	0.2
Cr	0.04	Ag	0.01
Mn	1	Cd	0.02
Fe	5	Sn	0.2
Ni	0.1	Sb	0.2
Cu	2	Hg	0.01
Zn	1	Tl	0.2
As	0.1	Pb	0.05

Since all the samples theoretically contain B, DL_s was used as a working detection limit to determine which samples required a "less than" calculation. The actual detection limit, DL, defined as the minimum solution concentration that is reliably different from the average reagent blank concentration, was calculated using

$$DL = DL_s - B = 3s_B .$$

Typical method detection limits are listed in Table III.2.

The dry weight concentration of the analyte in the samples was calculated using the relation,

$$X = \frac{(C - B)\ (DF)\ (Vol)}{Wt}$$

where X is the concentration of analyte in the dry sample, C is the concentration of the analyte in solution, B is the average reagent blank, DF is the amount of any additional dilution of the original sample solution, Vol is the volume of the original sample solution (e.g. 25.0 mL), and Wt is the dry weight of the sample (e.g. 1.000 g). When C is in µg/mL, X is in µg/g; when C is in ng/mL, X is in ng/g.

For any sample with a solution concentration lower than the working detection limit (DL_s) for an element, a "less than" value was calculated using

$$X < \frac{(DL_s - B)\ (DF)\ (Vol)}{Wt} .$$

6. REFERENCES

Evans, D. W., and P. J. Hanson (1993) Analytical methods for trace elements in fish liver by atomic absorption spectrophotometry, this volume.

Zdanowicz, V. S., and D. F. Gadbois (1990) Contaminants in sediment and fish tissues from estuarine and coastal sites of the northeast United States: Data summary of the baseline phase of the National Status and Trends Program Benthic Surveillance Project, 1984 - 1986. NOAA Tech. Memo. NMFS-F/NEC-79. NOAA/National Marine Fisheries Service, Woods Hole, MA.

7. INSTRUMENTAL ANALYSIS

7.1. Aluminum

METHOD: Graphite Furnace Atomic Absorption

DIGEST MATRIX: 10% HNO_3. For additional dilutions, use 10% HNO_3.

INSTRUMENT SETTINGS:

Wavelength:	309.3 nm
Lamp:	HCL, 25 ma (Perkin-Elmer 0303-6009)
Platform:	L'vov, coated
Carrier gas:	Argon
Slit width setting:	0.7L
Background correction:	Zeeman
Signal mode:	Peak area
Scale expansion:	None
Read time:	5 sec
Output:	To data terminal, printer, and recorder

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
Dry	120	10	25	300
Char1	450	10	10	300
Char2	1400	10	10	300
Atomize	2600	0	5	0
Cool1	20	1	10	300
Cleanout	2900	1	5	300
Cool2	20	1	10	300

STANDARDS: 0, 5, 10, and 20 ng Al/mL prepared in 10% HNO_3 using Aesar Al spectral standard (13856). Auto-zero using air.

TYPICAL SENSITIVITY: Peak area is approximately 0.180 for a 20 ng/mL standard.

CALIBRATION: Peak area of standard versus concentration of standard. Compute the slope, intercept, and correlation coefficient using linear, least-squares regression.

INJECTION VOLUME: 20 µL

MATRIX MODIFICATION: None

7.2. Chromium

METHOD: Graphite Furnace Atomic Absorption

DIGEST MATRIX: 10% HNO_3. For additional dilutions, use 10% HNO_3.

INSTRUMENT SETTINGS:

Wavelength:	357.9 nm
Lamp:	HCL, 25 ma (Perkin-Elmer 0303-6021)
Platform:	L'vov, coated
Carrier gas:	Argon
Slit width setting:	0.7L
Background correction:	Zeeman
Signal mode:	Peak area
Scale expansion:	None
Read time:	7 sec
Output:	To data terminal, printer, and recorder

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
Dry	120	10	25	300
Char1	450	10	10	300
Char2	1500	10	10	300
Atomize	2600	0	7	0
Cool1	20	1	10	300
Cleanout	2900	1	5	300
Cool2	20	1	10	300

STANDARDS: 0, 2, 5, and 10 ng Cr/mL prepared in 10% HNO_3 using Aesar Cr spectral standard (13864). Auto-zero using air.

TYPICAL SENSITIVITY: Peak area is approximately 0.240 for a 10 ng/mL standard.

CALIBRATION: Peak area of standard versus concentration of standard. Compute the slope, intercept, and correlation coefficient using linear, least-squares regression.

INJECTION VOLUME: 20 µL

MATRIX MODIFICATION: None

7.3. Manganese

METHOD: Flame Atomic Absorption

DIGEST MATRIX: 10% HNO_3. For additional dilutions, use 10% HNO_3.

INSTRUMENT SETTINGS:

Wavelength:	279.5 nm
Lamp:	HCL, 7 ma (Perkin-Elmer 0303-6043)
Fuel:	Acetylene
Oxidant:	Air
Mixture:	Lean (pale blue)
Burner head:	Three-slot, 10 cm, 0° rotation
Slit width setting:	0.2H
Background correction:	None
Signal mode:	Peak height/hold
Scale expansion:	None
Read time:	3 sec/reading, average of 3 reads
Output:	To data terminal and printer
Read delay:	4 sec

STANDARDS: 0, 0.5, 1, and 2 µg Mn/mL prepared in 10% HNO_3 using Aesar Mn spectral standard (13826). Auto-zero using deionized water.

TYPICAL SENSITIVITY: Absorbance is approximately 0.250 for a 2 µg/mL standard.

CALIBRATION: Peak height of standard versus concentration of standard. Compute the slope, intercept, and correlation coefficient using linear, least-squares regression.

MATRIX MODIFICATION: None

7.4. Iron

METHOD: Flame Atomic Absorption

DIGEST MATRIX: 10% HNO_3. For additional dilutions use 10% HNO_3.

INSTRUMENT SETTINGS:

Wavelength:	248.3 nm
Lamp:	HCL, 30 ma (Perkin-Elmer 0303-6037)
Fuel:	Acetylene
Oxidant:	Air
Mixture:	Lean (pale blue)
Burner head:	Three-slot, 10 cm, 0° rotation
Slit width setting:	0.2H
Background correction:	None
Signal mode:	Peak height/hold
Scale expansion:	None
Read time:	3 sec/reading, average of 3 reads
Output:	To data terminal and printer
Read delay:	4 sec

STANDARDS: 0, 1, 2, and 4 µg Fe/mL prepared in 10% HNO_3 using Aesar Fe spectral standard (13830). Auto-zero using deionized water.

TYPICAL SENSITIVITY: Absorbance is approximately 0.180 for a 4 µg/mL standard.

CALIBRATION: Peak height of standard versus concentration of standard. Compute the slope, intercept, and correlation coefficient using linear, least-squares regression.

MATRIX MODIFICATION: None

NOTES: Alternate wavelength, 248.8 nm, may be used.

7.5. Nickel

METHOD: Graphite Furnace Atomic Absorption

DIGEST MATRIX: 10% HNO_3. For additional dilutions, use 10% HNO_3.

INSTRUMENT SETTINGS:

Wavelength:	232.2 nm
Lamp:	HCL, 25 ma (Perkin-Elmer 0303-6047)
Platform:	L'vov, coated
Carrier gas:	Argon
Slit width setting:	0.2L
Background correction:	Zeeman
Signal mode:	Peak area
Scale expansion:	None
Read time:	7 sec
Output:	To data terminal, printer, and recorder

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
Dry	120	10	25	300
Char l	450	10	15	300
Char 2	1500	10	10	300
Atomize	2800	0	7	0
Cool l	20	1	10	300
Cleanout	3000	1	5	300
Cool 2	20	1	10	300

STANDARDS: 0, 10, 20, and 30 ng Ni/mL prepared in 10% HNO_3 using Aesar Ni spectral standard (13839). Auto-zero using air.

TYPICAL SENSITIVITY: Peak area is approximately 0.180 for a 30 ng/mL standard.

CALIBRATION: Peak area of standard versus concentration of standard. Compute the slope, intercept, and correlation coefficient using linear, least-squares regression.

INJECTION VOLUME: 20 µL

MATRIX MODIFICATION: None

7.6. Copper

METHOD: Flame Atomic Absorption

DIGEST MATRIX: 10% HNO_3. For additional dilutions use 10% HNO_3.

INSTRUMENT SETTINGS:

Wavelength:	324.8 nm
Lamp:	HCL, 15 ma (Perkin-Elmer 0303-6024)
Fuel:	Acetylene
Oxidant:	Air
Mixture:	Lean (pale blue)
Burner head:	Three-slot, 10 cm, 0° rotation
Slit width setting:	0.7H
Background correction:	None
Signal mode:	Peak height/hold
Scale expansion:	None
Read time:	3 sec/reading, average of 3 reads
Output:	To data terminal and printer
Read delay:	4 sec

STANDARDS: 0, 1, 3, and 5 µg Cu/mL prepared in 10% HNO_3 using Aesar Cu spectral standard (13867). Auto-zero using deionized water.

TYPICAL SENSITIVITY: Absorbance is approximately 0.230 for a 5 µg/mL standard.

CALIBRATION: Peak height of standard versus concentration of standard. Compute the slope, intercept, and correlation coefficient using linear, least-squares regression.

MATRIX MODIFICATION: None

7.7. Zinc

METHOD: Flame Atomic Absorption

DIGEST MATRIX: 10% HNO_3. For additional dilutions, use 10% HNO_3.

INSTRUMENT SETTINGS:

Wavelength:	213.9 nm
Lamp:	HCL, 15 ma (Perkin-Elmer 0303-6081)
Fuel:	Acetylene
Oxidant:	Air
Mixture:	Lean (pale blue)
Burner head:	Three-slot, 10 cm, 0° rotation
Slit width setting:	0.7H
Background correction:	None
Signal mode:	Peak height/hold
Scale expansion:	None
Read time:	3 sec/reading, average of 3 reads
Output:	To data terminal and printer
Read delay:	4 sec

STANDARDS: 0, 0.25, 0.5, and 1 µg Zn/mL prepared in 10% HNO_3 using Aesar Zn spectral standard (13835). Auto-zero using deionized water.

TYPICAL SENSITIVITY: Absorbance is approximately 0.250 for a 1 µg/mL standard.

CALIBRATION: Peak height of standard versus concentration of standard. Compute the slope, intercept, and correlation coefficient using linear, least-squares regression.

MATRIX MODIFICATION: None

7.8. Arsenic

METHOD: Graphite Furnace Atomic Absorption

DIGEST MATRIX: 10% HNO_3. For additional dilutions, use 10% HNO_3.

INSTRUMENT SETTINGS:

Wavelength:	193.7 nm
Lamp:	EDL, 6 w (Perkin-Elmer 0303-6211)
Platform:	L'vov, coated
Carrier gas:	Argon
Slit width setting:	0.7L
Background correction:	Zeeman
Signal mode:	Peak area
Scale expansion:	None
Read time:	5 sec
Output:	To data terminal, printer, and recorder

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
Dry	120	10	25	300
Char l	450	10	15	300
Char 2	700	10	10	300
Atomize	2400	0	5	0
Cool l	20	1	10	300
Cleanout	2900	1	5	300
Cool 2	20	1	10	300

STANDARDS: 0, 5, 15, and 30 µg As/mL prepared in appropriately diluted 1646 modifier using Aesar As spectral standard (13839). Auto-zero using air without modifier.

TYPICAL SENSITIVITY: Peak area is approximately 0.180 for a 30 ng/mL standard.

CALIBRATION: Peak area of standard versus concentration of standard. Compute the slope, intercept, and correlation coefficient using linear, least-squares regression.

INJECTION VOLUME: 20 µL

MATRIX MODIFICATION: 5 µL 1:1 mixture of palladium nitrate and magnesium nitrate solutions (see matrix modifiers section).

7.9. Selenium

METHOD: Graphite Furnace Atomic Absorption

DIGEST MATRIX: 10% HNO_3

INSTRUMENT SETTINGS:

Wavelength:	196.0 nm
Lamp:	EDL, 4.5 watts (Perkin-Elmer 0303-6262)
Platform:	L'vov, coated
Carrier gas:	Argon
Slit width setting:	2.0L
Background correction:	Zeeman
Signal mode:	Peak area
Scale expansion:	None
Read time:	5 sec
Output:	To data terminal, printer, and recorder

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
Dry	120	10	25	300
Char1	450	10	15	300
Char2	600	10	15	300
Atomize	2600	0	5	0
Cool1	20	1	10	300
Cleanout	2900	1	5	300
Cool2	20	1	10	300

STANDARDS: 0, 5, 10, and 20 ng Se/mL prepared in 10% HNO_3 using Aesar Se spectral standard (13845). Auto-zero using air without modifier.

TYPICAL SENSITIVITY: Peak area is approximately 0.060 for a 20 ng/mL standard.

CALIBRATION: Peak area of standard versus concentration of standard. Compute the slope, intercept, and correlation coefficient using linear, least-squares regression.

INJECTION VOLUME: 20 µL

MATRIX MODIFICATION: 5 µL 1:1 mixture of palladium nitrate and magnesium nitrate solutions (see matrix modifiers section).

7.10. Silver

METHOD: Graphite Furnace Atomic Absorption

DIGEST MATRIX: 10% HNO_3. For additional dilutions, use 10% HNO_3.

INSTRUMENT SETTINGS:

Wavelength:	328.1 nm
Lamp:	HCL, 10 ma (Perkin-Elmer 0303-6064)
Platform:	L'vov, coated
Carrier gas:	Argon
Slit width setting:	0.7L
Background correction:	Zeeman
Signal mode:	Peak area
Scale expansion:	None
Read time:	5 sec
Output:	To data terminal, printer, and recorder

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
Dry	120	10	25	300
Char1	500	10	15	300
Atomize	1700	0	5	0
Cool1	20	1	10	300
Cleanout	2900	1	5	300
Cool2	20	1	10	300

STANDARDS: 0, 0.5, 1.5, and 3.0 ng Ag/mL prepared in 10% HNO_3 using Aesar Ag spectral standard (13849). Auto-zero using air.

TYPICAL SENSITIVITY: Peak area is approximately 0.180 for a 3 ng/mL standard.

CALIBRATION: Peak area of standard versus concentration of standard. Compute the slope, intercept, and correlation coefficient using linear, least-squares regression.

INJECTION VOLUME: 20 µL

MATRIX MODIFICATION: None

7.11. Cadmium

METHOD: Graphite Furnace Atomic Absorption

DIGEST MATRIX: 10% HNO_3. For additional dilutions, use 10% HNO_3.

INSTRUMENT SETTINGS:

Wavelength:	228.8 nm
Lamp:	HCL, 4 ma (Perkin-Elmer 0303-6016)
Platform:	L'vov, coated
Carrier gas:	Argon
Slit width setting:	0.7L
Background correction:	Zeeman
Signal mode:	Peak area
Scale expansion:	None
Read time:	5 sec
Output:	To data terminal, printer, and recorder

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
Dry	120	10	25	300
Char1	450	10	15	300
Atomize	1600	0	5	0
Cool1	20	1	10	300
Cleanout	2900	1	5	300
Cool2	20	1	10	300

STANDARDS: 0, 0.2, 0.5, and 1 ng Cd/mL prepared in 10% HNO_3 using Aesar Cd spectral standard (13813). Auto-zero using air.

TYPICAL SENSITIVITY: Peak area is approximately 0.180 for a 1 ng/mL standard.

CALIBRATION: Peak area of standard versus concentration of standard. Compute the slope, intercept, and correlation coefficient using linear, least-squares regression.

INJECTION VOLUME: 20 µL

MATRIX MODIFICATION: None

7.12. Tin

METHOD: Graphite Furnace Atomic Absorption

DIGEST MATRIX: 10% HNO_3. For additional dilutions, use 10% HNO_3.

INSTRUMENT SETTINGS:

Wavelength:	286.3 nm
Lamp:	EDL, 6 watts (Perkin-Elmer 0303-6274)
Platform:	L'vov, coated
Carrier gas:	Argon
Slit width setting:	0.7L
Background correction:	Zeeman
Signal mode:	Peak height
Scale expansion:	None
Read time:	5 sec
Output:	To data terminal, printer, and recorder

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
Dry	120	10	25	300
Char1	450	10	20	300
Char2	800	10	20	300
Atomize	2600	0	5	0
Cool1	20	1	10	300
Cleanout	2900	1	5	300
Cool2	20	1	10	300

STANDARDS: 0, 5, 15, and 30 ng Sn/mL prepared in 10% HNO_3 using Aesar Sn spectral standard (13863). Auto-zero using air without modifier.

TYPICAL SENSITIVITY: Absorbance is approximately 0.210 for a 30 ng/mL standard.

CALIBRATION: Peak height of standard versus concentration of standard. Compute the slope, intercept, and correlation coefficient using linear, least-squares regression.

INJECTION VOLUME: 20 µL

MATRIX MODIFICATION: 5 µL 1:1 mixture of palladium nitrate and ammonium nitrate solutions (see matrix modifiers section).

7.13. Antimony

METHOD: Graphite Furnace Atomic Absorption

DIGEST MATRIX: 10% HNO_3. For additional dilutions, use 10% HNO_3.

INSTRUMENT SETTINGS:

Wavelength:	217.6 nm
Lamp:	EDL, 6 watts (Perkin-Elmer 0303-6210)
Platform:	L'vov, coated
Carrier gas:	Argon
Slit width setting:	0.7L
Background correction:	Zeeman
Signal mode:	Peak height
Scale expansion:	None
Read time:	4 sec
Output:	To data terminal, printer, and recorder

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
Dry	120	10	25	300
Char1	450	10	15	300
Char2	1200	10	15	300
Atomize	2500	0	4	0
Cool1	20	1	10	300
Cleanout	2900	1	5	300
Cool2	20	1	10	300

STANDARDS: 0, 5, 10, and 20 ng Sb/mL prepared in 10% HNO_3 using Aesar Sn spectral standard (13818). Auto-zero using air without modifier.

TYPICAL SENSITIVITY: Absorbance is approximately 0.110 for 20 ng/mL standard.

CALIBRATION: Peak height of standard versus concentration of standard. Compute the slope, intercept, and correlation coefficient using linear, least-squares regression.

INJECTION VOLUME: 20 µL

MATRIX MODIFICATION: 5 µL 1:1 mixture of palladium nitrate and ammonium nitrate solutions (see matrix modifiers section).

7.14. Mercury

METHOD: Cold Vapor/Gold Foil Detector

DIGEST MATRIX: 10% HNO_3

INSTRUMENT SETTINGS:

Reaction volume:	30 mL
Diluent:	10% HNO_3
Carrier gas:	Air
Flow rate:	850 mL/min
Scale expansion:	None
Integration time:	2 min
Output:	To LC Display

REDUCTANT: 10% $SnCl_2$ in deionized water

STANDARDS: 0, 10, 30, and 50 ng Hg from a 50 ng/mL standard in 10% HNO_3 using Aesar Hg spectral standard (13865). Use aliquots of 0, 200, 600, and 1000µL. Auto zero using air.

TYPICAL SENSITIVITY: 90% recovery of input standard concentration.

CALIBRATION: Instrument read-out is in ng Hg. Calibration curve is based on ng Hg detected versus ng Hg in the standards. The slope, intercept, and correlation coefficient are calculated using linear, least-squares regression.

SAMPLE VOLUME: Up to 10 mL

REDUCTANT VOLUME: 1 mL

MATRIX MODIFICATION: None

7.15. Thallium

METHOD: Graphite Furnace Atomic Absorption

DIGEST MATRIX: 10% HNO_3. For additional dilutions, use 10% HNO_3.

INSTRUMENT SETTINGS:

Wavelength:	276.8 nm
Lamp:	EDL, 5 watts (Perkin-Elmer 0303-6271)
Platform:	L'vov, coated
Carrier gas:	Argon
Slit width setting:	0.7L
Background correction:	Zeeman
Signal mode:	Peak height
Scale expansion:	None
Read time:	4 sec
Output:	To data terminal, printer, and recorder

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
Dry	120	10	25	300
Char1	450	10	20	300
Char2	750	10	20	300
Atomize	2000	0	4	0
Cool1	20	1	10	300
Cleanout	2900	1	5	300
Cool2	20	1	10	300

STANDARDS: 0, 2, 5, and 10 ng Tl/mL prepared in 10% HNO_3 using Aesar Tl spectral standard (13851). Auto-zero using air without modifier.

TYPICAL SENSITIVITY: Absorbance is approximately 0.060 for a 10 ng/mL standard.

CALIBRATION: Peak height of standard versus concentration of standard. Compute the slope, intercept, and correlation coefficient using linear, least-squares regression.

INJECTION VOLUME: 20 µL

MATRIX MODIFICATION: 5 µL 1:1 mixture of palladium nitrate and ammonium nitrate solutions (see matrix modifiers section).

7.16. Lead

METHOD: Graphite Furnace Atomic Absorption

DIGEST MATRIX: 10% HNO_3. For additional dilutions, use 10% HNO_3.

INSTRUMENT SETTINGS:

Wavelength:	283.3 nm
Lamp:	HCL, 10 ma (Perkin-Elmer 0303-6039)
Platform:	L'vov, coated
Carrier gas:	Argon
Slit width setting:	0.7L
Background correction:	Zeeman
Signal mode:	Peak height
Scale expansion:	None
Read time:	5 sec
Output:	To data terminal, printer, and recorder

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
Dry	120	10	25	300
Char1	450	10	20	300
Atomize	1600	0	5	0
Cool1	20	1	10	300
Cleanout	2900	1	5	300
Cool2	20	1	10	300

STANDARDS: 0, 5, 15, and 30 ng Pb/mL prepared in 10% HNO_3 using Aesar Pb spectral standard (13853). Auto-zero using air.

TYPICAL SENSITIVITY: Absorbance is approximately 0.260 for a 30 ng/mL standard.

CALIBRATION: Peak height of standard versus concentration of standard. Compute the slope, intercept, and correlation coefficient using linear, least-squares regression.

INJECTION VOLUME: 20 µL

MATRIX MODIFICATION: None

Analytical Methods for Trace Elements in Sediments by Atomic Absorption Spectrophotometry

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Southeast Fisheries Science Center
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ABSTRACT

Methods are described for analysis of 17 major and trace elements in estuarine sediments as used by NOAA/NMFS/Beaufort Laboratory of the Southeast Fisheries Science Center as part of the Benthic Surveillance Project of the National Status and Trends Program.

1. INTRODUCTION

When the National Status and Trends (NS&T) Program Benthic Surveillance Project began in 1984, methods were needed for the analysis of 17 elements (Ag, Al, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, Se, Si, Sn, Tl, and Zn) in estuarine sediments. The Sandy Hook Laboratory of the NOAA National Marine Fisheries Service (NMFS) took the lead in developing a general approach based on total dissolution of sediments and analysis by atomic absorption spectrophotometry. The other participating NMFS laboratories developed, in parallel, specific methods suited to their analytical needs. We describe here the methods used at Beaufort Laboratory as they have evolved from this shared effort.

2. EQUIPMENT AND SUPPLIES

2.1. Equipment

2.1.1. Atomic absorption spectrophotometers

Perkin Elmer model Z/5100 Spectrophotometer. Perkin-Elmer, Norwalk, CT.
- Perkin Elmer model HGA-600 graphite furnace
- Perkin Elmer model AS-60 autosampler
- IBM AT computer
- Epson LQ-850 printer

Perkin Elmer model Z/3030 spectrophotometer
- Perkin Elmer model HGA-600 graphite furnace
- Perkin Elmer model AS-60 autosampler
- Printer, Printronix model S7024. Anadex, Irvine, CA.

Perkin Elmer model 603 spectrophotometer with manual burner control and deuterium lamp background correction
- Perkin Elmer model R100A strip chart recorder

2.1.2. Flow injection system

Connectors and tees, Teflon, variable bore. Omnifit, Atlantic Beach, NY.
Fittings, flangeless. Upchurch Scientific, Oak Harbor, WA.
Flow meters, panel-mounted flow-meters with aluminum fittings, 65 mm flow tubes and adjustable valves. Maximum air flow rates of 145 mL/min and 333 mL/min. Cole Palmer, Niles, IL.
Hg cold vapor absorption cell, custom, PFA Teflon, 0.6 mm I.D. by 13.5 mm long
Rainin Rabbit Plus 4 channel peristaltic pump with 0.89 mm and 2.29 mm I.D. PVC pump tubing. Rainin Rabbit, Woburn, MA.
Separator, custom, Teflon and acrylic gas/liquid
Tubing, Teflon, for reaction and separation coils and intercomponent connections, 1.5-mm O.D., 0.8-mm I.D., 3.0-mm O.D., and 1.5 mm I.D.
Valve, rotary injection Teflon, manual 6-way with 0.5 and 1.0 mL sample loops. Rheodyne, Cotati, CA.

2.1.3. Lamps and power supplies

Perkin-Elmer single lamp Electrodeless Discharge (EDL) power supply
Perkin-Elmer (EDL) lamps for As, Cd, Hg, Pb, Se, Sn, and Zn
Perkin-Elmer Hollow Cathode Lamps (HCL) for Al, Cr, Cu, Fe, Mn, Sb, Si, Tl, and Ag
VWR Scientific Hollow Cathode (HCL) for Ni. VWR, Atlanta, GA.

2.1.4. Sample digestion equipment

CEM Model MDS 81D microwave digestion oven. CEM Corp., Mathews, NC.
CEM pressure vessel capping station
CEM 120-mL perfluoroalkoxy (PFA) Teflon pressure vessels
CEM turntable
Vials, 30-mL PFA Teflon vials. Savillex, Minnetonka, MN.

2.1.5. General laboratory equipment

Balance, Model GT2100. Ohaus, Florham Park, NJ.
Balance, Model GT4800. Ohaus, Florham Park, NJ.
Balance, Model RP160. Sartorius, McGaw Park, IL.
Deionized water system, Milli-Q deionized water system. Millipore Corp., Bedford, MA.
Hood, benchtop, laminar flow. Environmental Air, Albuquerque, NM.
Hotplate. Thermolyne Cimarec, Dubuque, IA.
Ionizing unit, Staticmaster. Nuclear Products, Grand Island, NY.
Oven, air flow, model OV-510A-2 horizontal. Blue M, Blue Island, MN.
Oven, air flow, model OV-510A-3 horizontal. Blue M, Blue Island, MN.
Pipets, Pipetman, continuously adjustable, 2-20 µL, 10-100 µL, 20-200 µL, 100-1000 µL, and 500-5000 µL. Gilson, Worthington, OH.

2.2 Supplies

2.2.1. Atomic absorption spectrophotometry

L'vov Platforms, solid pyrolytic, Perkin-Elmer B010-9324
Pyrolytic graphite tubes with forked platforms, Perkin-Elmer B050-5057
Pyrolytic graphite tubes, grooved, Perkin-Elmer B010-9322

2.2.2. Compressed gases

Acetylene (C_2H_2) [74-86-2], pre-purified
Argon, 99.998% purity
Compressed air
Nitrogen, prepurified 99.998% purity

2.2.3. Plasticware

Bottles, 60-, 125-, 250-, 500-, and 1000-mL, FEP Teflon
Bottles, 125-, 250-, 500-, and 1000-mL, linear polyethylene bottles
Cups, autosampler with external snap caps, 2-mL conical bottom, polyethylene
Pipet tips, polypropylene, for Gilson pipets, clear natural trace metal free
Tubes, culture, with external snap caps, 12 x 75 mm (5-mL), and 17 x 100 mm (15-mL), polystyrene

2.2.4. Labware preparation

The PFA vials used for the digestions were rinsed and scrubbed inside with a brush after each use. They were washed in an automatic laboratory dishwasher using detergent and rinsed in distilled water. The vials were then placed upright in 1-L PFA jars fitted with lids containing ports that can be opened or closed. The jars were filled with a 3:1 mixture of concentrated HNO_3 and concentrated HCl, and the lids screwed tightly in place. The ports were left open to accommodate expansion and acid evaporation. The jars were heated on a hot plate in an exhaust hood at about 90°C for at least 24 hr. After cooling, the acid was poured off and the jars filled with Milli-Q water, shaken to rinse the vials, and the waste water poured off. This was repeated three times. The vials were removed from the jar and dried at room temperature in a laminar flow clean hood. The vial caps were cleaned similarly but separately. Vials used for tissue digestion and homogenization were cleaned separately and isolated from those used for sediment digestion or standards preparation.

Autosampler(AS 60) cups were placed in 1-L FEP Teflon bottles which were filled with 10% v/v HNO_3 in Milli-Q water. They were double sealed in polyethylene Ziploc bags and heated at 60°C for at least 24 hr. After cooling, they were rinsed at least three times with Milli-Q water as described above.

2.3. Chemicals and reagents

2.3.1. Atomic absorption standards

Al: 1000 ppm, Baker 6917-1 and 10,000 ppm NIST SRM 2127. J. T. Baker, Phillipsburg, NJ, and NIST, Gaithersburg, MD.
Sb: 1000 ppm, Baker 6918-1 and 10,000 ppm NIST SRM 2126
As: 1000 ppm, Baker 6919-1 and 10,000 ppm NIST SRM 2126
Cd: 1000 ppm, Baker 6924-1 and 10,000 ppm NIST SRM 2121
Cr: 1000 ppm, Baker 6926-1 and 10,000 ppm NIST SRM 2128
Cu: 1000 ppm, Baker 6928-1 and 10,000 ppm NIST SRM 2124
Fe: 1000 ppm, Baker 6929-1 and 10,000 ppm NIST SRM 2124
Pb: 1000 ppm, Baker 6930-1 and 10,000 ppm NIST SRM 2121
Mn: 1000 ppm, Baker 6933-1 and 10,000 ppm NIST SRM 2128
Hg: 1000 ppm, VWR VW0737-3 and 1000 ppm Fisher SO-M-114. VWR, Atlanta, GA, and Fisher Scientific, Pittsburg, PA.
Ni: 1000 ppm, Baker 6930-1 and 10,000 ppm NIST SRM 2124

Se: 1000 ppm, Baker 6938-1 and 10,000 ppm NIST SRM 2126
Si: 1000 ppm, VWR VW0756-3
Ag: 1000 ppm, Baker 6940-1 and 10,000 ppm NIST SRM 2121
Tl: 1000 ppm, Ricca 3890. Ricca, Arlington, TX.
Sn: 1000 ppm, Baker 1-6943 and 10,000 ppm NIST SRM 2126
Zn: 1000 ppm, Baker 6946-1 and 10,000 ppm NIST SRM 2121

2.3.2. Reagents

Ammonium phosphate, monobasic ($NH_4H_2PO_4$) [7722-76-1], Ultrex 4-4931. J. T. Baker, Phillipsburg, NJ.

Ascorbic acid ($C_6H_8O_6$) [50-81-7], reagent grade. Fisher Scientific, Pittsburg, PA.

Boric acid (H_3BO_3) [10043-35-3], analyzed reagent 0084-01. J. T. Baker, Phillipsburg, NJ.

Boric acid (H_3BO_3) [10043-35-3], Merck Suprapur Art. 765. Merck, Darmstadt, Germany.

Cobalt metal [7440-48-4], powder reagent grade, C-363. Fisher Scientific, Pittsburg, PA.

Hydrochloric acid (HCl) [7647-01-0], concentrated (38%), Instra-analyzed for trace metal analysis. J. T. Baker, Phillipsburg, NJ.

Hydrochloric acid (HCl) [7647-01-0], concentrated (38%), Seastar Ultra-high purity sub-boiling distilled in Teflon. Seastar Chemicals, Sidney, BC, Canada.

Hydrofluoric acid (HF) [7664-39-3], concentrated (48%), Instra-analyzed for trace metal analysis. J. T. Baker, Phillipsburg, NJ.

Hydrofluoric acid (HF) [7664-39-3], concentrated (48%), Seastar Ultra-high purity sub-boiling distilled in Teflon. Seastar Chemicals, Sidney, BC, Canada.

Nitric acid (HNO_3) [7697-37-2], concentrated (70%), Seastar Ultra-high purity sub-boiling distilled in Teflon. Seastar Chemicals, Sidney, BC, Canada.

Nitric acid (HNO_3) [7697-37-2], concentrated (70%), Instra-analyzed for trace metal analysis. J. T. Baker, Phillipsburg, NJ.

Palladium metal [7440-05-3], powder, grade 1 puratomic. Johnson Matthey, West Chester, PA.

Sodium borohydride ($NaBH_4$) [16940-66-2], 99% purity. Aldrich Chemical Co., Milwaukee, WI.

Sodium hydroxide (NaOH) [1310-73-2], analyzed reagent 3722-01. J. T. Baker, Phillipsburg, NJ.

Stannous chloride ($SnCl_2 \cdot 2H_2O$) [10025-69-1], suitable for mercury analysis, 3980-01. J. T. Baker, Phillipsburg, NJ.

3. SAMPLE TREATMENT

3.1. Sample matrix modification

Chemical modification of the sample matrix is often necessary to achieve unbiased analysis of samples using simple standard solutions in graphite furnace AAS. The development of matrix modifiers has evolved to take advantage of newer approaches or to adapt to specific analytical problems. The current matrix modifiers are described below.

250 µg Pd/mL in 4N HNO_3. This was used in the analysis of Ag, Cd, and Pb and was prepared by diluting 10,000 µg Pd/mL solution 40 fold with 4N HNO_3. The 10,000 µg Pd/mL solution was prepared using Johnson-Matthey Grade 1 Puratomic Pd metal dissolved in concentrated Seastar HNO_3 to which a few drops of Seastar HCl were added to aid dissolution. Heating to 90°C dissolved the Pd metal. The resulting solution was diluted with Milli-Q water to make 10,000 µg Pd/mL in 4N HNO_3.

1000 µg Pd/mL in 4N HNO_3. This was used in the analysis of Sn. It was prepared as above but with a 10-fold dilution of the 10,000 µg Pd/mL stock solution.

(2000 µg Pd + 2000 µg Co)/mL in 4N HNO_3. This solution was used in the analysis of As and Sb and was prepared by diluting 10,000 µg Pd/mL and 10,000 µg Co/mL solutions with 4N Seastar HNO_3. The 10,000 µg Co/mL solution was prepared by dissolving l g Co metal in 100 mL 4N HNO_3.

5% ascorbic acid. This solution was used in conjunction with the 250 µg Pd/mL modifier in the analysis of Tl. It was prepared by dissolving 5 g ascorbic acid (Fisher reagent grade) in 100 mL Milli-Q water.

3.2. Sample drying and compositing

All concentrations of trace elements in sediments are reported on the basis of sediment dry weight. Sediments were oven dried at 60° C for 16 hr in a forced air convection oven to constant dry weight. Standard reference materials were similarly dried. Samples were dried before compositing equal weight aliquots from the three cores representing each station at a sampling site. Samples are ground to a fine texture in an agate mortar before compositing.

3.3. Microwave digestion

3.3.1. Acid additions

Dissolution of sediment was accomplished with a mixture of HF, HCl, and HNO_3 using a method modified from Rantala and Loring (1975) employing microwave heating. Approximately 0.1200 ± 0.0100 g of sample or CRM were weighed into cleaned, tared, 30-mL PFA vials, and 0.9 mL HF, 0.12 mL HCl, and 0.04 mL HNO_3 were added.

Pipetting of acids was done using Gilson pipets with pre-rinsed polyethylene tips to minimize contamination. Pipets are disassembled after use and rinsed with Milli-Q water and dried to prevent corrosion of internal parts.

3.3.2. Digestion

The 30-mL PFA vials containing samples, CRMs, or blanks and added acids were capped and sealed tightly. The vials were then placed singly in CEM microwave pressure vessels. Five mL of Milli-Q water were added to each pressure vessel to generate a back pressure during heating. The Teflon vial within Teflon digestion vessel provides a double contamination barrier also used in tissue digestions. The pressure vessels were then capped and sealed tightly. Vessels were placed in alternating positions in the 12-position microwave carousel, and the vent tubes attached from the central chamber. Six samples were digested together using the following program sequence.

1. Close microwave door. Turn on exhaust fan to maximum. Start turntable.

2. Time = 60 min; Power = 20%.
   Cool vials for 20 min; vent each vessel by pressing on exhaust tube.

3. Uncap pressure vessels in an exhaust hood using the capping station. Remove the 30-mL PFA vials from the pressure vessels by floating them out with Milli-Q water. Allow the

PFA vials to dry in a laminar flow hood before opening. Dilute sample digests with 4.5% boric acid as described below.

3.3.3. Initial sample dilution and volume determination

Samples were diluted with 25 mL of a 4.5% boric acid in Milli-Q water to complex fluoride ions and prevent precipitation of fluorides of Al and Ca. Digests with added boric acid should be resealed and warmed to 60°C to aid dissolution of any possible precipitates. Slow precipitation of silica will occur over a period of days: samples intended for analysis of Si or Al should have aliquots removed and diluted immediately to obtain a representative aliquot. The acid digest with the added boric acid solution diluent is termed "diluted HF/Aqua Regia" in subsequent element specific sections (9.1 through 9.17).

The vials and contents were weighed to 0.01 g before any sample solution was removed, and the net solution weight was determined by subtracting the tare weight of the vial. Solution volume was calculated by dividing by an assumed solution density of 1.015 g/mL.

3.3.4. Alternate digestion

The microwave digestion procedure was developed from an earlier digestion procedure that used large Teflon-lined Parr bombs as pressure vessels with heating in a conventional laboratory oven. This method was modeled on one described by Okamoto and Fuwa (1984) for tissues. The Teflon pressure vessel provides an additional inert barrier to possible metal contamination while allowing use of relatively inexpensive PFA vials as primary digestion containers which can be cleaned and weighed in large numbers. The vials were used for direct weighing of samples and CRMs, initial dilutions, and sample storage. Contamination risks were reduced since digest transfers to other containers for volume determination and storage were unnecessary. Efficiency was increased by eliminating such procedures. For these reasons, we retained the configuration of a digestion vial within an inert pressure vessel when switching to microwave digestion.

Sample preparation and acid additions for the alternate Parr bomb digestion were the same as for the microwave digestion. The 30-mL PFA vials were placed singly in the Teflon liner of the 125-mL Parr bomb with 5 mL of Milli-Q water. After capping, the liner was placed in its stainless steel bomb jacket which was then assembled according to the manufacturer's instructions. The bombs were heated for 16 hr at 120°C and then cooled. After venting in a fume hood, the PFA vials were removed and treated as in the microwave digestion procedure. In both procedures, there was some venting of vapors from the PFA vials into the pressure vessel, but we observed no apparent loss of potentially volatile elements, such as mercury, from the PFA vials.

3.4. Dilution

Any sample or CRM digest whose concentration exceeded that of the highest standard was diluted. Extrapolation of the calibration curve beyond the range of the highest standard was not done. Diluents were selected to mimic the acid matrix of the samples, CRMs, and blanks.

The diluent used in graphite furnace analysis is "furnace sediment matrix solution." This is prepared using 964 mL of 4.5% boric acid solution, 31 mL 48% Seastar HF, 4.1 mL 38% Seastar HCl, and 1.4 mL 70% Seastar HNO_3.

In graphite furnace AAS, the diluent for analysis of Ag, As, Cd, Pb, and Sn is "furnace sediment matrix solution," which mimics the blank digest composition. The diluent used in

graphite furnace AAS analysis of Cu, Cr, and Ni is 4N $HN0_3$ 1:3 dilution of 70% Seastar $HN0_3$ (with Milli-Q water), which was substituted for furnace sediment matrix solution in order to reduce interferences and the graphite tube deterioration observed at the high atomization temperatures used in analysis of these elements.

For flame AAS analysis of Mn, Fe, and Zn, “flame sediment matrix solution” was used. This was prepared with the same composition as furnace sediment matrix solution but Baker acids were substituted for Seastar acids since reagent blanks need not be as low in flame level analyses. Flame AAS analysis of Al and Si use as a diluent "flame sediment matrix solution" to which 1 part in 10 (v/v) of 15,000 ppm K^+ (as KCl) is added as an ionization suppressant.

For hydride generation AAS analysis of Se, 1N HCl was used as a diluent after the automatic two-fold dilution with concentrated HCl that accompanies the prereduction to Se (IV).

For Hg cold vapor AAS, the diluent was a mixture with a final concentration of 1N HCl and 1N HNO_3.

3.5. Standards

Standards were prepared using commercial or NIST-prepared standards in solutions that mimic the dilutions applied to the samples, CRMs, and blanks in order to limit differences in analytical sensitivity due to differences in physical and chemical properties between standards and samples (See sections 2.3.1 and 9.1-9.17).

4. CALIBRATION AND COMPUTATION OF ANALYTE CONCENTRATIONS

Calibration for elements analyzed by graphite furnace AAS was done on-line by the microprocessor or computer associated with the spectrophotometer. Four standards were used with analyte concentrations in the ratio of 0:1:2:3. Two replicate injections were analyzed for each standard. After every eight samples, a partial recalibration was performed using the reslope function of the instrument’s calibration software. The “2” or “3” standard was used along with the “0” standard in resloping the calibration curve. A two-coefficient calibration function was always employed to compensate for minor curvature in the relationship between concentration, C, and background corrected absorbance-secs (A). The concentration was calculated using

$$C = \frac{k_1 \, A}{k_2 \, A \; - \; 1}$$

where k_1 and k_2 are constants calculated by the method of least squares (Barnett, 1984). The mean absorbance of the most recent "0" standard was subtracted from both standard and sample absorbance-second measurements before this computation was performed.

Calibration for elements analyzed by flame AAS is done off-line using the expanded absorbance readings from the digital display of the spectrophotometer for each standard. More than three standards and a “0” concentration standard were usually employed. Where the relationship between concentration and absorbance of standards was linear, the concentration in sample solutions was estimated from a least squares fit of

$$C = k_1 + k_2 A \; .$$

If the relationship between absorbance and concentration is non-linear (visual inspection of a graphed calibration curve or r^2 less than 0.995), calibration is performed using an equation of the form

$$\frac{1}{C} = k_1 + k_2 \frac{1}{A}.$$

The mean "0" concentration standard absorbance was subtracted from all standard and sample results before performing the non-linear calibration computation. The "0" concentration standard is not used subsequently in this calibration computation. This equation is equivalent to the online calibration used by the spectrophotometer computer in graphite furnace AAS. This regression, using reciprocals of C and A, weighs the lower concentration standards more heavily than higher standards. This has advantages in estimating concentrations near the detection limit. Standards are reanalyzed after every 10 samples. Drift in the baseline and sensitivity were corrected by linear interpolation of absorbance data collected between analyses of standards.

Calibration for Hg analysis using cold vapor AAS was similar to that for flame AAS. Peak height output from a strip chart recorder corrected for baseline as described above was used to determine absorbance.

The mass of analyte in each blank sample was determined from the product of measured concentration and diluted sample volume. The mean mass of analyte in the blanks was subtracted from the calculated analyte mass in the samples to yield blank-corrected analyte mass. When divided by sample dry weight, this yields the final analyte concentration in the sediment sample.

5. DETECTION LIMITS

The detection limit was defined as three times the standard deviation of the measured concentration of blanks processed as samples. A dry weight of 0.12 g was assumed in calculating detection limits on the basis of sediment dry weight. Typical detection limits are listed in Table III.3.

Table III.3. Typical sediment detection limits.

Element	Detection limit (µg/g dry weight)	Element	Detection limit (µg/g dry weight)
Ag	0.02	Ni	2
Al (%)	0.09	Pb	0.5
As	0.8	Sb	0.8
Cd	0.02	Se	0.05
Cr	2	Si (%)	0.8
Cu	0.8	Sn	0.3
Fe (%)	0.05	Tl	0.3
Hg	0.06	Zn	5
Mn	20		

Table III.4. Sediment methodological changes through time.

Sample Set	Methodological change
First trace element intercomparison exercise	none
1984 sediments (southeast)	I1
Second trace element intercomparison exercise	I2
1985 sediments (southeast)	M1
Third trace element intercomparison exercise	I3
1987 sediments (southeast)	none
1986 sediments (southeast)	none
Fourth trace element intercomparison exercise	I4, I5, M2, M3
1988 sediments (southeast)	P1
1988 sediments (northeast)	none

Sample preparation:

P1 - Microwave digestion replaced bomb digestion to reduce digestion time and limit possible metal contamination from the stainless steel bomb jacket.

Instrumental:

I1 - The Z/3030 with Zeeman background correction replaced the model 603 for graphite furnace analyses. Zeeman background correction greatly improved accuracy and precision.

I2 - Deuterium arc background correction was dropped from flame analyses on the model 603 AAS. It was unnecessary and increased the analytical signal to noise ratio and baseline drift.

I3 - Graphite furnace AAS replaced flame AAS in the analysis of Cu and Cr to lower the detection limits.

I4 - Flow injection analysis for Hg was introduced to increase the speed of analyses which had previously been done by an inefficient batch method.

I5 - Flow injection analysis for Se was introduced to increase the speed of analyses which had previously been done by an inefficient batch method.

Matrix modification:

M1 - 1000 µg Pd/mL replaced 250 µg Pd/mL as the matrix modifier for Sn analysis.

M2 - Matrix modifier for Se, As, and Sb was changed from (500 µg Pd + 500 µg Co)/mL to (2000 µg Pd + 2000 µg Co)/mL to improve precision and accuracy degraded by matrix effects and to make the analysis more robust to variations in atomization temperature and sample composition.

M3 - 4N HNO_3 replaced furnace sediment matrix solution in dilutions of Cu, Cr, and Ni for graphite furnace AAS to avoid degradation of the graphite furnace by boric acid.

6. CHANGES IN ANALYTICAL METHODS OVER TIME

Initial analytical methods used in the Benthic Surveillance Project have evolved to their current status, as described here, through several iterations in response to new knowledge and experience in addressing perceived problems and improving efficiency. The major changes in the past are documented in Table III.4. Changes are paired with the sample sets where they were first employed. Sample sets are in the order of analysis. Reasons for the changes are given in footnotes to the table.

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exercises conducted by National Research Council of Canada, and, particularly, S. Berman, for their significant contributions to the development, testing, and quality of our methods.

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9. INSTRUMENTAL ANALYSES

9.1. Aluminum

METHOD:	Flame Atomic Absorption Spectrophotometry
SAMPLE DIGEST:	Diluted HF/Aqua regia

SPECTROPHOTOMETER SETTINGS:

Lamp:	HCL 30 ma
Wavelength:	309.3 nm
Slit Width:	0.7 nm
Signal Output:	Expanded absorbance
Expansion:	5 times
Integration Time:	3 sec
Replicate Readings:	1
Nebulization:	Flow spoiler
Burner Head:	Single slot, 5 cm, nitrous oxide
Background Correction:	none
Flame:	Nitrous oxide:acetylene; red reducing; nitrous oxide 35, acetylene 55

STANDARDS:	0, 10, 20, 30, and 40 mg Al/L in flame sediment matrix solution with 1500 µg K^+/L (as KCl) added as an ionization suppressant.
DILUENT:	Flame sediment matrix solution with 1500 µg K^+/L. Ten-fold dilutions of all samples, blanks, and CRMs.
CALIBRATION:	Off-line processing of expanded absorbance signals using either a linear least squares regression (default) or a non-linear least squares regression program. Regression coefficients, r^2, of less than 0.995 indicates the possible need for a non-linear regression calibration. Standards are rerun after every 10 samples. Drift in the calibration parameters is corrected by interpolation.
SENSITIVITY:	0.110 absorbance for a 30 mg Al/L standard.

9.2. Antimony

METHOD: Graphite Furnace Atomic Absorption Spectrophotometry

SAMPLE DIGEST: Diluted HF/Aqua regia

SPECTROPHOTOMETER SETTINGS:

Lamp:	HCL 20 ma
Wavelength:	217.6 nm
Slit Width:	0.7 nm
Read Delay:	0 sec
Integration (Read) Time:	4 sec
Replicate Sample Injections:	2

FURNACE CONDITIONS:

Graphite Tube Type:	Pyrolytic, grooved for forked platform
L'vov Platform Type:	Solid pyrolytic, forked
Carrier Gas:	Argon

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas	Read
		Ramp	Hold	Flow (mL/min)	
1	250	15	30	300	-
2	400	20	10	300	-
3	1000	10	10	300	-
4	2400	0	4	0	*
5	2650	1	5	300	-

STANDARDS: 0, 10, 20, and 30 µg Sb/L in furnace sediment matrix solution.

MATRIX MODIFIER: (2000 µg Pd+2000 µg Co)/mL in 4N HNO_3.

INJECTION VOLUME: 20 µL

MATRIX MODIFIER: 5 µL

DILUENT: Furnace sediment matrix solution, if needed.

CALIBRATION: Two-coefficient least squares fitted calibration line performed by instrument microprocessor using the above standards. Reslope after every 8 samples.

TYPICAL SENSITIVITY: 0.065 abs.-sec. for 20 µL of a 30 µg Sb/L standard.

9.3. Arsenic

METHOD: Graphite Furnace Atomic Absorption Spectrophotometry

SAMPLE DIGEST: Diluted HF/Aqua regia

SPECTROPHOTOMETER SETTINGS:

Lamp:	EDL Z/3030 10 watts continuous or Z/5100 6-6.5 watts modulated
Wavelength:	193.7 nm
Slit Width:	0.7 nm
Read Delay:	0 sec
Integration (Read) Time:	4 sec
Replicate Sample Injections:	2

FURNACE CONDITIONS:

Graphite Tube Type:	Pyrolytic, grooved for forked platform
L'vov Platform Type:	Solid pyrolytic, forked
Carrier Gas:	Argon

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas Flow (mL/min)	Read
		Ramp	Hold		
1	250	15	30	300	-
2	400	20	10	300	-
3	1200	10	10	300	-
4	2450	0	4	0	*
5	2650	1	5	300	-

STANDARDS: 0, 20, 40, and 60 µg As/L in furnace sediment matrix solution.

MATRIX MODIFIER: (2000 µg Pd + 2000 µg Co)/mL in 4N HNO_3.

INJECTION VOLUME: 10 µL

MATRIX MODIFIER: 5 µL

DILUENT: Furnace sediment matrix solution.

CALIBRATION: Two-coefficient least squares fitted calibration line performed by instrument microprocessor using the above standards. Reslope after every 8 samples.

TYPICAL SENSITIVITY: 0.220 abs-sec. for 10 µL of a 60 µg As/L standard.

9.4. Cadmium

METHOD: Graphite Furnace Atomic Absorption Spectrophotometry

SAMPLE DIGEST: Diluted HF/Aqua regia

SPECTROPHOTOMETER SETTINGS:

Lamp:	EDL Z/3030 5 watts continuous or Z/5100 3-3.5 watts modulated
Wavelength:	228.8 nm
Slit Width:	0.7 nm
Read Delay:	0 sec
Integration (Read) Time:	5 sec
Replicate Sample Injections:	2

FURNACE CONDITIONS

Graphite Tube Type:	Pyrolytic, grooved for forked platform
L'vov Platform Type:	Solid pyrolytic, forked
Carrier Gas:	Argon

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas Flow (mL/min)	Read
		Ramp	Hold		
1	250	15	30	300	-
2	400	20	10	300	-
3	500	10	20	300	-
4	1700	0	5	0	*
5	2650	1	5	300	-

STANDARDS: 0, 1, 2, and 3 µg Cd/L in furnace sediment matrix solution.

MATRIX MODIFIER: 250 µg Pd/mL in 4N HNO_3.

INJECTION VOLUME: 15 µL

MATRIX MODIFIER: 5 µL

DILUENT: Furnace sediment matrix solution, if necessary.

CALIBRATION: Two-coefficient least squares fitted calibration line performed by instrument microprocessor using above standards. Reslope after every 8 samples.

TYPICAL SENSITIVITY: 0.250 abs.-sec. for 15 µL of a 2 µg Cd/L standard.

9.5. Chromium

METHOD: Graphite Furnace Atomic Absorption Spectrophotometry

SAMPLE DIGEST: Diluted HF/Aqua regia

SPECTROPHOTOMETER SETTINGS:

Lamp:	HCL 25 ma
Wavelength:	357.9 nm
Slit Width:	0.7 nm
Read Delay:	0 sec
Integration (Read) Time:	6 sec
Replicate Sample Injections:	2

FURNACE CONDITIONS:

Graphite Tube Type:	Pyrolytically coated, grooved
L'vov Platform Type:	Solid pyrolytic graphite
Carrier Gas:	Argon

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas Flow (mL/min)	Read
		Ramp	Hold		
1	160	15	20	300	-
2	400	20	10	300	-
3	1000	10	10	300	-
4	2500	0	6	0	*
5	2800	3	6	300	-

STANDARDS: 0, 10, 20, and 30 µg Cr/L in a 1:15 v/v mixture of furnace sediment matrix solution and 4N HNO_3.

MATRIX MODIFIER: none

INJECTION VOLUME: 15 µL

MATRIX MODIFIER: none

DILUENT: 4N HNO_3. A minimum 16-fold dilution was made on all samples, certified reference materials, and blanks.

CALIBRATION: Two-coefficient least squares fitted calibration line performed by instrument microprocessor using the above standards. Reslope after every 8 samples.

TYPICAL SENSITIVITY: 0.400 abs-sec. for 15 µL of 20 µg Cr/L standard.

9.6. Copper

METHOD: Graphite Furnace Atomic Absorption Spectrophotometry

SAMPLE DIGEST: Diluted HF/Aqua regia

SPECTROPHOTOMETER SETTINGS:

Lamp:	HCL, 20 ma
Wavelength:	324.7 nm
Slit Width:	0.7 nm
Read Delay:	0 sec
Integration Time:	6 sec
Replicate Injections:	2

STANDARDS: 0, 20, 40, and 50 µg Cu/L in 1:3 v/v mixture of furnace sediment matrix solution and 4N HNO_3.

DILUENT: 4N HNO_3. A minimum 4-fold dilution was made on all samples, certified reference materials, and blanks.

CALIBRATION: Two-coefficient least squares fitted calibration line performed by instrument microprocessor using the above standards. Reslope after every 8 samples.

SENSITIVITY: 0.340 abs-sec for a 40 µg Cu/L standard.

9.7. Iron

METHOD: Flame Atomic Absorption Spectrophotometry

SAMPLE DIGEST: Diluted HF/Aqua regia

SPECTROPHOTOMETER SETTINGS:

Lamp:	HCL 30 ma
Wavelength:	372.0 nm
Slit Width:	0.2 nm
Signal Output:	Expanded absorbance
Expansion:	1 time
Integration Time:	3 sec
Replicate Readings:	1
Nebulization:	Glass impact bead
Burner Head:	Single slot, 10 cm
Background Correction:	none
Flame:	Air:acetylene, lean blue; air 55, acetylene 25

STANDARDS: 0, 20, 40, 60, and 80 mg Fe/L in flame sediment matrix solution.

DILUENT: Flame sediment matrix solution. Four-fold dilution on all samples.

CALIBRATION: Off-line processing of expanded absorbance signals using either a linear least squares regression (default) or a non-linear least squares regression program. Regression coefficients, r^2, of less than 0.995 indicate the possible need for a nonlinear regression calibration. Standards are rerun after every 10 samples. Drift in the calibration parameters is corrected by interpolation.

SENSITIVITY: 0.490 absorbance for a 60 mg Fe/L standard.

9.8. Lead

METHOD: Graphite Furnace Atomic Absorption Spectrophotometry

SAMPLE DIGEST: Diluted HF/Aqua regia

SPECTROPHOTOMETER SETTINGS:

Lamp:	EDL Z/3030 10 watts continuous or Z/5100 7-7.5 watts modulated
Wavelength:	283.3 nm
Slit Width:	0.7 nm
Read Delay:	0 sec
Integration (Read) Time:	5 sec
Replicate Sample Injections:	2

FURNACE CONDITIONS:

Graphite Tube Type:	Pyrolytic, grooved for forked platform
L'vov Platform Type:	Solid pyrolytic, forked
Carrier Gas:	Argon

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas Flow (mL/min)	Read
		Ramp	Hold		
1	250	15	30	300	-
2	400	20	10	300	-
3	900	10	10	300	-
4	2000	0	5	0	*
5	2650	1	5	300	-

STANDARDS: 0, 40, 80, and 120 µg Pb/L in furnace sediment matrix solution.

MATRIX MODIFIER: 250 µ Pd/L in 4N HNO_3

INJECTION VOLUME: 15 µL

MATRIX MODIFIER: 5 µL

DILUENT: Furnace sediment matrix solution.

CALIBRATION: Two-coefficient least squares fitted calibration line performed by instrument microprocessor using the above standards. Reslope after every 8 samples.

TYPICAL SENSITIVITY: 0.500 abs-sec for 15 µL of 80 µg Pb/L standard.

9.9. Manganese

METHOD: Flame Atomic Absorption Spectrophotometry

SAMPLE DIGEST: Diluted HF/Aqua regia

SPECTROPHOTOMETER SETTINGS:

Lamp:	HCL 20 ma
Wavelength:	279.5 nm
Slit Width:	0.2 nm
Signal Output:	Expanded absorbance
Expansion:	10 times
Integration Time:	1 sec
Replicate Readings:	3
Nebulization:	Glass impact bead
Burner Head:	Single slot, 10 cm
Background Correction:	none
Flame:	Air:acetylene, lean blue; air 55, acetylene 25

STANDARDS: 0, 0.3, 0.6, 0.9, and 1.2 mg Mn/L in furnace sediment matrix solution.

DILUENT: Flame sediment matrix solution. A 4-fold dilution was made on all samples, certified reference materials, and blanks to minimize interference from Si.

CALIBRATION: Off-line processing of expanded absorbance signals using either a linear least squares regression (default) or a non-linear least squares regression program. Regression coefficients, r^2, of less than 0.995 indicate the probable need for a nonlinear regression calibration. Standards are rerun after every 10 samples. Drift in the calibration parameters is corrected by interpolation.

SENSITIVITY: 0.070 absorbance for a 0.9 mg Mn/L standard.

9.10. Mercury

METHOD: Cold vapor atomic absorption spectrophotometry

SAMPLE DIGEST: Diluted HF/Aqua regia

SPECTROPHOTOMETER SETTINGS:

Lamp:	EDL 5 watts
Wavelength:	253.7 nm
Slit Width:	2.0 nm
Signal Output:	Expanded absorbance to strip chart recorder
Expansion:	10 times
Integration time:	0.5 sec
Recorder Time Constant:	TC3 (4 sec)
Background Correction:	none

FLOW INJECTION PARAMETERS:

Pump:	Rainin Rabbit Plus with 4 channel head
Pump Speed:	25 rpm
Tubing Diameters (I.D.):	0.89 mm reductant
	2.29 mm carrier acid/sample
	2.29 mm waste
Gas Flow (nitrogen)	100 cm^3/min (setting 50)
	230 cm^3/min (setting 50)
Injection Volume:	1.0 mL
Gas/Liquid Separator Volume:	3.5 mL
Mixing Loop Volume:	1 mL
Reaction Loop Volume:	1 mL
Cell Length:	13.5 cm
Cell Diameter:	0.6 cm
Cell Volume:	4 cm^3
Reductant:	10% w/v $SnCl_2 \cdot 2H_2O$ in 1N HCl
Carrier Acid:	Mixed 1N HCl + 1N HNO_3

STANDARDS: 0, 1, 2, 3, 5, and 10 ng Hg/L in mixed 1N HCl + 1N HNO_3.

DILUENT: Mixed in HCl + 1N HNO_3, if necessary.

CALIBRATION: Off-line processing of expanded absorbance signals using either a linear least squares regression (default) or a non-linear least squares regression program. Regression coefficients, r^2, of less than 0.995 indicate the probable need for a nonlinear regression calibration. Standards are run after every 10 samples. Drift in the calibration parameters is corrected by interpolation.

SENSITIVITY: 0.080 absorbance for a 10 µg Hg/L standard.

COMMENTS: Recorder peak height is suppressed by the long time constant in order to smooth baseline noise. See Figure III.1 for flow injection diagram.

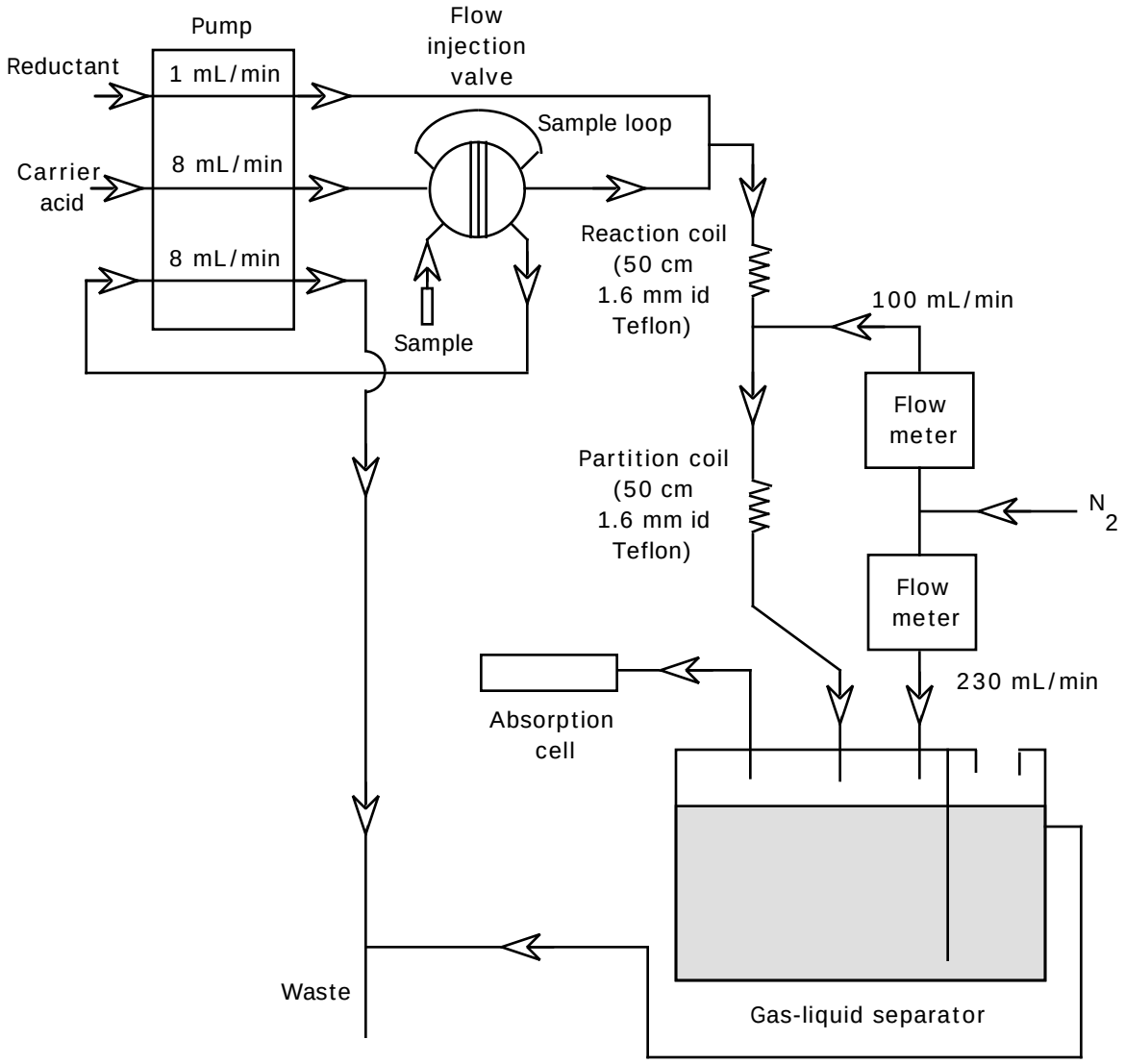

Figure III.1. Flow injection system for sediment mercury analysis.

9.11. Nickel

METHOD: Graphite Furnace Atomic Absorption Spectrophotometry

SAMPLE DIGEST: Diluted HF/Aqua regia

SPECTROPHOTOMETER SETTINGS:

Lamp:	HCL 18 ma
Wavelength:	232.0 nm
Slit Width:	0.2 nm
Read Delay:	0 sec
Integration (Read) Time:	6 sec
Replicate Sample Injections:	2

FURNACE CONDITIONS:

Graphite Tube Type:	Pyrolytic, coated, grooved
L'vov Platform Type:	Solid pyrolytic graphite
Carrier Gas:	Argon

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas Flow (mL/min)	Read
		Ramp	Hold		
1	160	5	20	300	-
2	400	20	10	300	-
3	1000	10	10	300	-
4	2800	0	6	0	*
5	2800	3	6	300	-

STANDARDS: 0, 40, 60, and 80 µg Ni/L in a 1:3 mixture of furnace sediment matrix solution.

MATRIX MODIFIER: none

INJECTION VOLUME: 20 µL

MATRIX MODIFIER: none

DILUENT: 4N HNO_3. A minimum 4-fold dilution was made for all samples, certified reference materials, and blanks.

CALIBRATION: Two-coefficient least squares fitted calibration line performed by instrument microprocessor using the above standards. Reslope after every 8 samples.

TYPICAL SENSITIVITY: 0.660 abs-sec for 20 µL of 80 µg Ni/L standard.

9.12. Selenium

METHOD: Hydride Generation Atomic Absorption Spectrophotometry

SAMPLE DIGEST: Diluted HF/Aqua regia. Two mL diluted sample digests were subsequently diluted 1:1 v:v with 12N HCl and heated for 1 hr at 90°C in closed 5-mL PFA vials to reduce all Se to the +IV oxidation state necessary for hydride generation and analysis.

SPECTROPHOTOMETER SETTINGS:

Lamp:	EDL6 watts
Wavelength:	196.0 nm
Slit Width:	2.0 nm
Signal output:	Expanded absorbance to strip chart recorder
Expansion:	10 times
Recorder time constant:	TC2 (1 sec)
Background Correction:	none
Integration (Read) Time:	0.5 sec
Replicate Sample Injections:	2

FLOW INJECTION PARAMETERS:

Pump:	Rainin Rabbit Plus with 4 channel head
Pump Speed:	25 rpm
Tubing Diameters (I.D.):	
	0.89 mm reductant
	2.29 mm carrier acid/sample
	2.29 mm waste
Gas Flow (nitrogen)	
	130 cm^3/min (setting 60)
	300 cm^3/min (setting 60)
Injection Volume:	0.5 mL
Gas/Liquid Separator Volume:	3.5 mL
Mixing Loop Volume:	1 mL
Reaction Loop Volume:	1 mL
Cell:	Perkin-Elmer MHS-10 system heated in an air:acetylene flame
Cell Length:	16.5 cm
Cell Diameter:	1.2 cm
Cell Volume:	18.7 cm^3
Reductant:	1% w/v $NaBH_4$ in 0.5% w/v NaOH
Carrier Acid:	Mixed 1N HCl + 1N HNO_3

STANDARDS: 0, 1, 2, 3, and 5 µg Se/L in 6N HCl.

DILUENT: 1N HCl

CALIBRATION: Off-line processing of expanded absorbance signals using either a linear least squares regression (default) or a non-linear least squares regression program. Regression coefficients, r^2, of less than 0.995 indicate the probable need for a nonlinear regression calibration. Standards are run after every 10 samples. Drift in the calibration parameters is corrected by interpolation.

TYPICAL SENSITIVITY: 0.100 abs-sec for 5 µg Se/L standard.

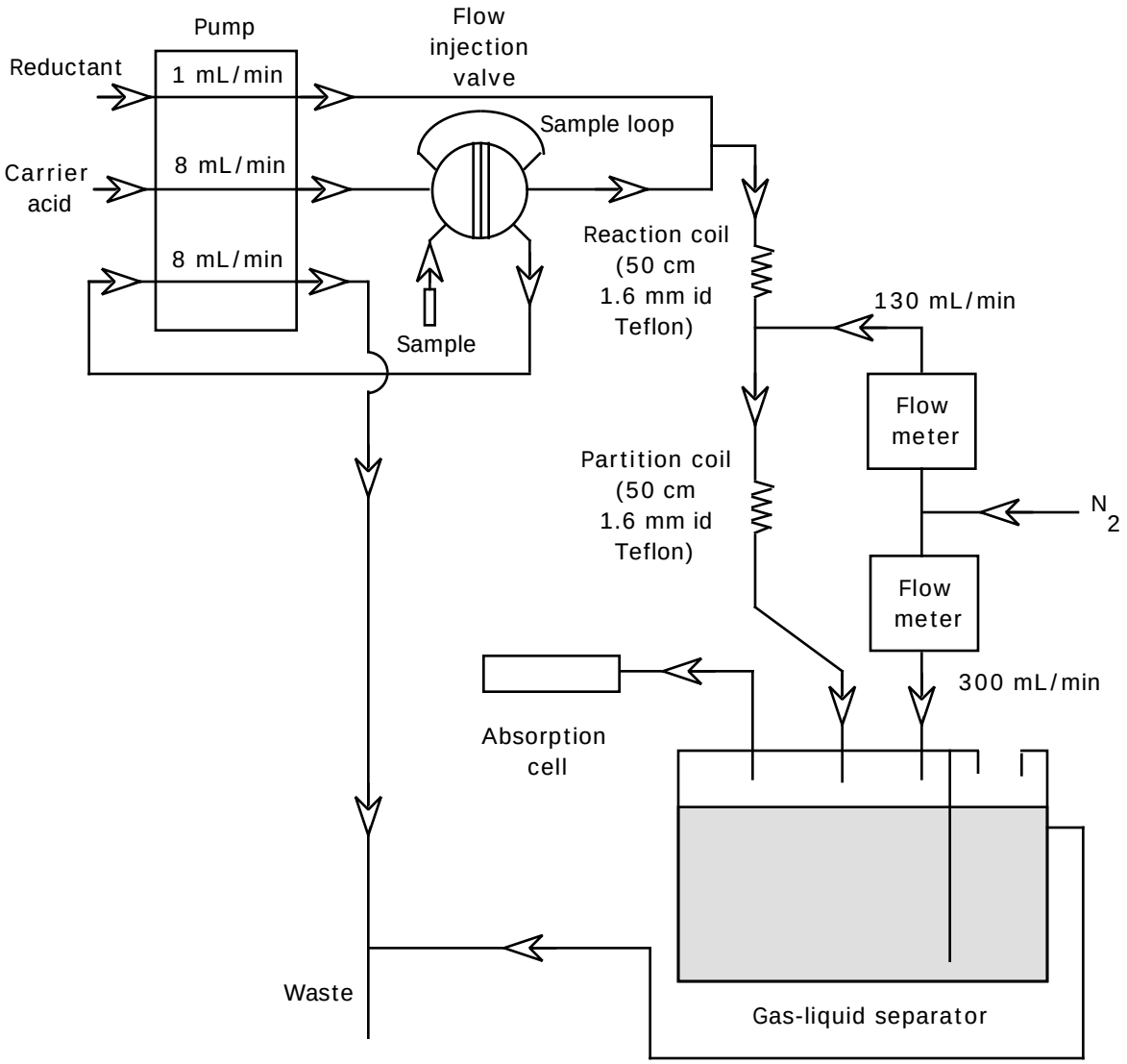

Figure III.2. Flow injection system for selenium analysis.

9.13. Silicon

METHOD: Flame Atomic Absorption Spectrophotometry

SAMPLE DIGEST: Diluted HF/Aqua regia

SPECTROPHOTOMETER SETTINGS:

Lamp:	HCL 30 ma
Wavelength:	251.6 nm
Slit Width:	0.2 nm
Signal Output:	Expanded absorbance
Expansion:	2 times
Integration Time:	3 sec
Replicate Readings:	1
Nebulization:	Flow spoiler
Burner Head:	Single slot, 5 cm
Background Correction:	none
Flame:	Nitrous oxide:acetylene, red reducing; nitrous oxide 35, acetylene 55

STANDARDS: 0, 50, 100, 150, and 200 mg Si/L in flame sediment matrix solution with 1500 µg/L K^+ (as KCl) added as an ionization suppressant.

DILUENT: Flame sediment matrix solution with 1500 µg/L K^+ (as KCl). A 10-fold dilution was made on all samples, certified reference materials, and blanks.

CALIBRATION: Off-line processing of expanded absorbance signals using either a linear least squares regression (default) or a non-linear least squares regression program. Regression coefficients, r^2, of less than 0.995 indicate the probable need for a nonlinear regression calibration. Standards are rerun after every 10 samples. Drift in the calibration parameters is corrected by interpolation.

SENSITIVITY: 0.200 absorbance for a 150 mg Si/L standard.

9.14. Silver

METHOD: Graphite Furnace Atomic Absorption Spectrophotometry

SAMPLE DIGEST: Diluted HF/Aqua regia

SPECTROPHOTOMETER SETTINGS:

Lamp:	HCL 12 ma
Wavelength:	328.1 nm
Slit Width:	0.7 nm
Read Delay:	0 sec
Integration (Read) Time:	4 sec
Replicate Sample Injections:	2

FURNACE CONDITIONS:

Graphite Tube Type:	Pyrolytic, grooved for forked platform
L'vov Platform Type:	Solid pyrolytic, forked
Carrier Gas:	Argon

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas	Read
		Ramp	Hold	Flow (mL/min)	
1	250	15	30	300	-
2	400	20	10	300	-
3	700	10	10	300	-
4	2000	0	4	0	*
5	2650	1	5	300	-

STANDARDS: 0, 1, 2, and 3 µg Ag/L in furnace sediment matrix solution.

MATRIX MODIFIER: 250 µg Pd/mL in 4N HNO_3.

INJECTION VOLUME: 30 µL

MATRIX MODIFIER: 5 µL

DILUENT: Furnace sediment matrix solution, if necessary.

CALIBRATION: Two-coefficient least squares fitted calibration line performed by instrument microprocessor using above standards. Reslope after every 8 samples.

TYPICAL SENSITIVITY: 0.140 abs-sec for 30 µL of a 2 µg Ag/L standard.

9.15. Thallium

METHOD: Graphite Furnace Atomic Absorption Spectrophotometry

SAMPLE DIGEST: Diluted HF/Aqua regia

SPECTROPHOTOMETER SETTINGS:

Lamp:	EDL Z/3030 7 watts continuous or Z/5100 4-4.5 watts modulated
Wavelength:	276.8 nm
Slit Width:	0.7 nm
Read Delay:	0 sec
Integration (Read) Time:	4 sec
Replicate Sample Injections:	2

FURNACE CONDITIONS

Graphite Tube Type:	Pyrolytic, grooved for forked platform
L'vov Platform Type:	Solid pyrolytic, forked
Carrier Gas:	Argon

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas Flow (mL/min)	Read
		Ramp	Hold		
1	250	15	30	300	-
2	400	20	10	300	-
3	600	15	30	300	-
4	1900	0	4	0	*
5	2650	1	3	300	-

STANDARDS: 0, 10, 20, and 30 µg Tl/L in furnace sediment matrix solution.

MATRIX MODIFIERS: (1) 5% w/v ascorbic acid in Milli-Q water
(2) 250 µg Pd/mL in 4N HNO_3

INJECTION VOLUME: 20 µL

MATRIX MODIFIER : 5 µL of (1) + 5 µL of (2).

DILUENT: Furnace sediment matrix solution, if necessary.

CALIBRATION: Two-coefficient least squares fitted calibration line performed by instrument microprocessor using above standards. Reslope after every 8 samples.

TYPICAL SENSITIVITY: 0.100 abs-sec for 20 µL of a 30 µg Tl/L standard.

9.16. Tin

METHOD: Graphite Furnace Atomic Absorption Spectrophotometry

SAMPLE DIGEST: Diluted HF/Aqua regia

SPECTROPHOTOMETER SETTINGS:

Lamp:	EDL Z/3030 8-8.5 watts continuous or Z/5100 5.5-6 watts modulated
Wavelength:	286.3 nm
Slit Width:	0.7 nm
Read Delay:	1 sec
Integration (Read) Time:	3 sec
Replicate Sample Injections:	2

FURNACE CONDITIONS

Graphite Tube Type:	Pyrolytic, grooved for forked platform
L'vov Platform Type:	Solid pyrolytic, forked
Carrier Gas:	Argon

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas Flow (mL/min)	Read
		Ramp	Hold		
1	250	5	40	300	-
2	400	30	10	300	-
3	1000	10	10	300	-
4	2400	0	4	0	*
5	2650	1	3	300	-

STANDARDS: 0, 20, 40, and 60 µg Sn/L in 4N HNO_3.

MATRIX MODIFIER: 1000 µg Pd/mL in 4N HNO_3.

INJECTION VOLUME: 30 µL

MATRIX MODIFIER: 5 µL

DILUENT: Furnace sediment matrix solution, if necessary.

CALIBRATION: Two-coefficient least squares fitted calibration line performed by instrument microprocessor using above standards. Reslope after every 8 samples.

TYPICAL SENSITIVITY: 0.195 abs-sec. for 30 µl of a 60 µg Sn/L standard.

9.17. Zinc

METHOD: Flame Atomic Absorption Spectrophotometry

SAMPLE DIGEST: Diluted HF/Aqua regia

SPECTROPHOTOMETER SETTINGS:

Lamp:	HCL 15 ma
Wavelength:	213.8 nm
Slit Width:	0.7 nm
Signal Output:	Expanded absorbance
Expansion:	1 time
Integration Time:	3 sec
Replicate Readings:	1
Nebulization:	Glass impact bead
Burner Head:	Single slot, 10 cm
Background Correction:	none
Flame:	Air:acetylene, lean blue; air 55, acetylene 25

STANDARDS: 0, 0.3, 0.6, 0.9, and 1.2 mg Zn/L in flame sediment matrix solution.

DILUENT: Flame sediment matrix solution, if needed.

CALIBRATION: Off-line processing of expanded absorbance signals using either a linear least squares regression (default) or a non-linear least squares regression program. R^2 less than 0.995 indicates the probable need for a nonlinear regression calibration. Standards are rerun after every 10 samples. Drift in the calibration parameters is corrected by interpolation.

SENSITIVITY: 0.260 absorbance for a 0.9 mg Zn/L standard.

Analytical Methods for Trace Elements in Fish Liver by Atomic Absorption Spectrophotometry

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ABSTRACT

The methods developed and used for analysis of 15 major and trace elements in teleost fish livers by the NOAA/NMFS/Beaufort Laboratory of the Southeast Fisheries Center as part of the National Benthic Surveillance Surveillance Project of the National Status and Trends (NS&T) Program are described.

1. INTRODUCTION

At the inception of the NS&T National Benthic Surveillance Surveillance Project in 1984, analytical methods were needed for the analysis of 15 elements (Ag, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, Se, Sn, Tl, and Zn) in teleost fish livers. Three laboratories of the NOAA National Marine Fisheries Service (NMFS) participated in the analyses, including the Beaufort Laboratory of the Southeast Fisheries Center. It was important to develop analytical methods that could assure intercomparability of data throughout the nation since each NS&T collaborating laboratory would be analyzing tissue samples collected in its respective region. The Beaufort Laboratory accepted responsibility for development of basic methods for elemental analysis of tissues that would be reflective of the then current state-of-the-art, and that would provide the basis for each laboratory to refine its own methods to fit specific requirements of their samples and instrumentation. Intercomparability of data from the three NMFS laboratories would be assured through analysis of certified reference materials, and annual intercomparison exercises that began in 1985 and continue today under the direction of Dr. Shier Berman of the National Research Council of Canada.

Each of the participating laboratories was equipped, and was familiar with, atomic absorption spectrophotometry (AAS) for elemental analysis, thus providing a common approach to methods development. Data and, therefore, methods for most of the 15 elements in fish liver were reported by early 1984 (Eisler, 1981), often by AAS. Only for Sb, Sn, and Tl were analytical data and methods not available. The principal task was to further develop existing methods within the constraints required by the project. These included:

- Limitations imposed by the often small size of liver samples available for analysis,
- The need to provide dissolution of small tissue samples with reproducible recoveries and minimal process blanks,
- The need to analyze as many as 15 elements in a single dissolved sample, and
- The need to keep the dissolved sample volume small enough to assure analysis of elements with inherently low AAS sensitivities (e.g., Ni and Sb) and expected low concentrations in liver tissue (e.g., Sb, Cr, Ni, and Sn).

Whole livers from some of the smaller fish are often < 0.5 g wet weight and sometimes as small as 0.1 g. Although composite samples could be anticipated, analysis of individual small livers and small dissected pieces of larger livers would be required of the method. The volume of digested sample needed to be at least 10 mL to provide sufficient volume for all 15 elemental analyses from a single digest, and at this volume, detection limits for some elements in liver tissue are approached. The low tissue concentrations for some elements requires a minimal sample volume, and thus constrains the dissolution method to minimize contamination and maximize elemental recoveries. The initial dissolution method used a high temperature pressure vessel heated in a convection oven. The vessel had three walls: a Teflon vial inside a Teflon lined stainless-steel pressure vessel. This functioned well to produce reproducible recoveries and generally low blanks. It was later replaced by a more convenient method using microwave heating in an all Teflon double-walled vessel.

The general method employed is total dissolution of tissue samples using nitric acid at elevated temperature and pressure followed by AAS using flame, graphite furnace, hydride generation, or cold vapor atomization. The basis for development was the literature available in 1984. Although the methods remain substantially as initially developed, they have evolved during the intervening years. The significant differences and the reasons for the changes are presented. Each of the participating NOAA laboratories refined and evolved their methods independently. Some differences undoubtedly exist among the laboratories, and this chapter describes the methods used at Beaufort Laboratory. The results of six tissue intercomparison exercises between 1985 and 1992 indicated good intercomparability of data among the NMFS laboratories.

2. EQUIPMENT AND SUPPLIES

2.1. Equipment

2.1.1. Atomic absorption spectrophotometers

Personal computer, IBM AT with Epson LQ-850 printer
Printer, Printronix model S7024. Anadex, Irvine, CA.
Spectrophotometer, Perkin-Elmer model 603 with manual burner control and deuterium lamp background correction. Perkin-Elmer, Norwalk, CT.
Spectrophotometer, Perkin-Elmer Z/3030 with Perkin-Elmer HGA-600 furnace controller and Perkin-Elmer AS-60 autosampler
Spectrophotometer, Perkin-Elmer Z/5100 with Perkin-Elmer HGA-600 furnace controller and Perkin-Elmer AS-60 autosampler
Strip chart recorder, Perkin-Elmer model R100A

2.1.2. Flow injection system

Connectors and tees, Teflon, variable bore. Omnifit, Atlantic Beach, NY.
Fittings, flangeless. Upchurch Scientific, Oak Harbor, WA.
Flow-meters, panel-mounted with aluminum fittings, 65 mm flow tubes and adjustable valves with maximum air flow rates of 145 mL/min and 333 mL/min. Cole Parmer, Niles, IL.
Gas/liquid separator, custom Teflon and acrylic
Mercury cold vapor absorption cell, custom PFA Teflon, 0.6 mm i.d. by 13.5 mm long
Pump, peristaltic, 4 channel, 0.89 mm and 2.29 mm i.d. PVC pump tubing. Rainin Rabbit, Woburn, MA.
Tubing, Teflon, for reaction and separation coils and intercomponent connections: 1.5-mm o.d., 0.8-mm i.d.; 3.0-mm o.d., 1.5 mm i.d.

Valve, rotary injection, Teflon, manual 6-way with 0.5 and 1.0 mL sample loops. Rheodyne, Cotati, CA.

2.1.3. Lamps and power supplies

Electrodeless Discharge Lamp (EDL) power supply, single lamp. Perkin-Elmer, Norwalk, CT.
Electrodeless Discharge Lamps (EDL), for As, Cd, Hg, Pb, Se, Sn, and Zn. Perkin-Elmer, Norwalk, CT.
Hollow Cathode Lamps (HCL), for Cr, Cu, Fe, Mn, Sb, Tl, and Ag. Perkin-Elmer, Norwalk, CT.
Hollow Cathode Lamps (HCL), for Ni. VWR Scientific, Atlanta, GA.

2.1.4. Sample digestion equipment

Capping station, pressure vessel. CEM Corp., Mathews, NC.
Oven, digestion, microwave , CEM Model MDS 81D
Pressure vessels, 120-mL, perfluoroalkoxy (PFA) Teflon, CEM
Turntable, CEM
Vials, PFA Teflon, 30-mL. Savillex, Minnetonka, MN.

2.1.5. Sample homogenization equipment

Paint shaker, Model MNC-2-C. Miracle Paint Rejuvenator, St. Paul, Mn.
Vials, 30-mL, PFA Teflon. Savillex, Minnetonka, MN.
Spheres, 0.5-inch, Teflon. Cole Parmer, Niles, IL.

2.1.6. General laboratory equipment

Balance, Model GT2100. Ohaus, Florham Park, NJ.
Balance, Model GT4800. Ohaus, Florham Park, NJ.
Balance, Model RP160. Sartorius, McGaw Park, IL.
Deionized water system, Milli-Q. Millipore Corp., Bedford, MA.
Hood, benchtop, laminar flow. Environmental Air, Albuquerque, NM.
Horizontal air flow oven, OV-510A-2. Blue M, Blue Island, IL.
Horizontal air flow oven, OV-510A-3. Blue M, Blue Island, IL.
Hotplate. Thermolyne Cimarec, Dubuque, IA.
Ionizing unit, Staticmaster. Nuclear Products, Grand Island, NY.
Pipets, Pipetman, continuously adjustable, 2-20 µL, 10-100 µL, 20-200 µL, 100-1000 µL, and 500-5000 µL. Gilson, Worthington, OH.

2.2 Supplies

2.2.1. Atomic absorption spectrophotometry

L'vov Platforms; solid pyrolytic, Perkin-Elmer B010-9324
Pyrolytic graphite tubes; grooved, Perkin-Elmer B010-9322
Pyrolytic graphite tubes; with forked platforms, Perkin-Elmer B050-5057

2.2.2. Compressed gases

Acetylene, atomic absorption grade 99.6% purity
Argon, prepurified 99.998% purity
Compressed air
Nitrogen, prepurified 99.998% purity

2.2.3. Plasticware

Bottles, 60-, 125-, 250-, 500-, and 1000-mL, FEP Teflon
Bottles, 125-, 250-, 500-, and 1000-mL, linear polyethylene bottles
Cups, autosampler with external snap caps, 2-mL conical bottom, polyethylene
Pipet tips, polypropylene, for Gilson pipets, clear natural trace metal free
Tubes, culture, with external snap caps, 12 X 75 mm (5-mL), and 17 X 100 mm (15-mL), polystyrene

2.2.4. Dissection tools

Forceps and cutting board, plastic (e.g., Teflon or polypropylene chemically resistant plastic with low metal impurity content)
Knives and scalpels, titanium, made from purified metal

2.2.5. Labware preparation

All containers and utensils coming into contact with the tissue samples were cleaned rigorously to minimize possible contamination. This is especially important in the analyses of Cr, Ni, Pb, and Sn, which are usually in very low concentration in fish livers, and are widely found in shipboard and laboratory environments. Powder-free vinyl gloves were worn during this and all other operations.

The PFA vials used for the digestions were rinsed and scrubbed inside with a brush after each use. They were washed in an automatic laboratory dishwasher using detergent and rinsed in distilled water. The vials were then placed upright in 1-L PFA jars fitted with lids containing ports that can be opened or closed. The jars were filled with concentrated HNO_3 (Baker) and the lids screwed tightly in place. The ports were left open to accommodate expansion and acid evaporation. The jars were heated on a hot plate in an exhaust hood at about 90°C for at least 24 hr. After cooling, the acid was poured off and the jars filled with Milli-Q water, shaken to rinse the vials, and the waste water poured off. This was repeated three times. The vials were removed from the jar and dried at room temperature in a laminar flow clean hood. The vial caps were cleaned similarly but separately. Vials used for tissue digestion and homogenization were cleaned separately and isolated from those used for sediment digestion or standards preparation.

Autosampler (AS 60) cups were placed in 1-L FEP Teflon bottles which were filled with 10% v/v HNO_3 (Baker) in Milli-Q water. They were double sealed in polyethylene Ziplock bags and heated at 60°C for at least 24 hr. After cooling, they were rinsed at least three times with Milli-Q water as described above.

All forceps, scissors, knives, and cutting surfaces which might contact the tissue sample, are washed with 10% v/v HNO_3 (Baker) followed by Milli-Q water just prior to use. Removal of tissue particles from dissecting tools often required washing in detergent (e.g., Micro) prior to acid wash.

2.3. Chemicals and reagents

2.3.1. Atomic absorption standards

Ag: 1000 ppm, Baker 6940-1 and 10,000 ppm NIST SRM 2121. J. T. Baker, Phillipsburg, NJ, and NIST, Gaithersburg, MD.

As: 1000 ppm, Baker 6919-1 and 10,000 ppm NIST SRM 2126
Cd: 1000 ppm, Baker 6924-1 and 10,000 ppm NIST SRM 2121
Cr: 1000 ppm, Baker 6926-1 and 10,000 ppm NIST SRM 2128
Cu: 1000 ppm, Baker 6928-1 and 10,000 ppm NIST SRM 2124
Fe: 1000 ppm, Baker 6929-1 and 10,000 ppm NIST SRM 2124
Hg: 1000 ppm, VWR 737-3 and 1000 ppm, Fisher SO-M-114. VWR, Atlanta, GA, and Fisher Scientific, Pittsburg, PA.
Mn: 1000 ppm, Baker 6933-1 and 10,000 ppm NIST SRM 2128
Ni: 1000 ppm, Baker 6930-1 and 10,000 ppm NIST SRM 2124
Pb: 1000 ppm, Baker 6930-1 and 10,000 ppm NIST SRM 2121
Sb: 1000 ppm, Baker 6918-1 and 10,000 ppm NIST SRM 2126
Se: 1000 ppm, Baker 6938-1 and 10,000 ppm NIST SRM 2126
Sn: 1000 ppm, Baker 6943-1 and 10,000 ppm NIST SRM 2126
Tl: 1000 ppm, Ricca 8390. Ricca Chemicals, Arlington, TX.
Zn: 1000 ppm, Baker 6946-1 and 10,000 ppm NIST SRM 2121

2.3.2. Reagents

Ammonium phosphate, monobasic ($NH_4H_2PO_4$) [7722-76-1], Ultrex 4-4931. J. T. Baker, Phillipsburg, NJ.
Cobalt metal [7440-48-4], powder reagent grade, C-363. Fisher Scientific, Pittsburg, PA.
Hydrochloric acid (HCl) [7647-01-0], concentrated (38%), Instra-analyzed for trace metal analysis. J. T. Baker, Phillipsburg, NJ.
Nitric acid (HNO_3) [7697-37-2], concentrated (70%), Ultra-high purity sub-boiling distilled in Teflon. Seastar Chemicals, Sidney, BC, Canada.
Nitric acid (HNO_3) [7697-37-2], concentrated (70%), Instra-analyzed for trace metal analysis. J. T. Baker, Phillipsburg, NJ.
Palladium metal [7440-05-3], powder, grade 1 puratomic. Johnson Matthey, West Chester, PA.
Stannous chloride ($SnCl_2 \cdot 2H_2O$) [10025-69-1], suitable for mercury analysis, 3980-01. J. T. Baker, Phillipsburg, NJ.

3. SAMPLE TREATMENT

3.1. Sample matrix modification

Chemical modification of the sample matrix is often necessary to achieve unbiased analysis of samples using simple standard solutions in graphite furnace AAS. The development of matrix modifiers has evolved to take advantage of newer approaches or to adapt to specific analytical problems. The current matrix modifiers are described below.

250 µg Pd/mL in 4N HNO_3. This was used in the analysis of Ag, Cd, and Sn and was prepared by diluting 10,000 µg Pd/mL solution 40 fold with 4N HNO_3. The 10,000 µg Pd/mL solution was prepared using Johnson-Matthey Grade 1 Puratomic Pd metal dissolved in concentrated Seastar HNO_3 to which a few drops of Seastar HCl were added to aid dissolution. Heating to 90°C dissolved the Pd metal. The resulting solution was diluted with Milli-Q water to make a 10,000 µg Pd/mL in 4N HNO_3.

(2000 µg Pd + 2000 µg Co)/mL in 4N HNO_3. This solution was used in the analysis of As, Sb, and Se, and was prepared by diluting 10,000 µg Pd/mL and 10,000 µg Co/mL solutions

with 4N Seastar HNO_3. The 10,000 µg Co/mL solution was prepared by dissolving l g Co metal in 100 mL 4N HNO_3.

5% ascorbic acid. This solution was used in conjunction with the 250 µg Pd/mL modifier in the analysis of Tl. It was prepared by dissolving 5 g ascorbic acid (Fisher reagent grade) in 100 mL Milli-Q water.

5% w/v $NH_4H_2PO_4$. This solution was used in the analysis of Pb and was prepared by dissolving 5 g Baker Ultrex ammonium dihydrogen phosphate in 100 mL of 4N HNO_3 (Seastar).

3.2. Sample preparation

3.2.1. Sample drying

All concentrations of trace elements in liver tissues are reported on the basis of tissue dry weight. In the analysis of individual livers, the tissue was dried before nitric acid was added for digestion. Livers were placed in previously tared 30-mL PFA Teflon vials immediately after dissection. The vials were previously cleaned and dried to constant weight at 100°C by heating overnight in a convection oven. During pre-tare drying, the vials caps were loosened. The vials were placed in polypropylene trays with the lid loosely in place.

Livers in their vials were frozen to -90°C and then freeze dried overnight to less than 200 millitorr vacuum. The vial caps were left in place but tightened only one-half to two-thirds turn during freeze drying process. Vials in trays of 10 were placed in polyethylene Ziplock bags which were zipped only two-thirds closed to maintain connection to the vacuum. One such bag was placed inside another and partially zipped from the other side to create a maze-like path. Vials were reweighed after freeze drying and the tissue dry weight determined as the difference from the vial tare. Precision in such weight determination is about 0.0010 g. Reference materials and blanks (no added material) were treated similarly. Weights were determined to 0.0001 g.

Livers analyzed as composites from 10 fish were digested wet and the dry weight determined from the dry-to-wet weight ratio of a separate aliquot. About one gram of liver homogenate puree was pipetted into a tared aluminum weighing pan. The tissue wet weight was determined by difference using a balance with 0.001 g readability. Samples were oven dried overnight at 60°C. The tissue dry weight was determined by difference from the tare weight. The dry weight to wet weight ratio was calculated.

3.2.2. Homogenization of large composite samples

Samples composited from livers of many fish were too large to be digested by our procedure, so a homogeneous subsample was prepared. This was done by placing samples of about 1 g wet weight from each of ten livers directly in a cleaned 30 mL PFA vial.

Table III.5. Volume of nitric acid added to various tissue sample weights.

Tissue weight		
Dry (g)	Wet (g)	Volume of HNO_3 (mL)
< 0.1	< 0.4	2.5
0.1 - 0.2	0.4 to 0.8	5.0
> 0.2	> 0.8	7.5

The actual wet weight of each liver sample added to the vial is determined by repeatedly taring the vial after each addition. Weights are determined to 0.01 g. Two acid-cleaned, 0.5-inch diameter TFE Teflon balls were added to each vial which was then tightly capped. Three vials were placed in a small polyethylene Ziplock bag and three such bags were placed in a special polystyrene foam-lined paint can so that the balls were shaken along the long axis of the PFA vials to homogenize the tissue. The paint can was sealed, attached to the paint shaker, and shaken for ten min.

About 1 mL of the homogenized tissue puree was pipetted into a cleaned, tared 30-mL PFA vial for subsequent digestion. A second aliquot of about the same size was pipetted into a tared aluminum weighing pan for drying and determination of tissue dry weight to wet weight ratio.

3.3. Microwave digestion

3.3.1. Acid additions

Dissolution of tissues was accomplished through oxidation with high purity concentrated HNO_3 (70%, Seastar). The volume of acid used depended on tissue weight. Wet tissues were treated under the assumption that the wet weight to dry weight ratio was 4. The volume of acid used for various tissue sample weights are listed in Table III.5. Samples weighing more than 0.4 g dry weight or 1.6 g wet weight cannot be effectively digested in the 30 mL PFA vials. Certified Reference Material (CRM) weights were targeted at 0.27 g to 0.33 g and received 7.5 mL HNO_3. Blanks containing no sample or CRM material also received 7.5 mL HNO_3 additions.

Pipetting of HNO_3 was done using a 5-mL Gilson pipet with pre-rinsed polyethylene tips in order to minimize contamination. The pipet was disassembled and rinsed immediately after use to prevent corrosion of internal parts.

3.3.2. Digestion

The 30-mL PFA vials containing samples, CRMs, or blanks and added HNO_3 were capped and sealed tightly. The vials were then placed singly in CEM microwave pressure vessels. Five mL of Milli-Q water were added to each pressure vessel, which was then capped and sealed tightly with the capping station. Vessels were placed in alternating positions in the 12-position microwave carousel, and the vent tubes attached from the central chamber. Six samples were digested together using the following program sequence.

1. Close microwave door. Turn on exhaust fan to maximum. Start turntable.

2. Time = 5 min; Power = 30%.
   Cool vials for 20 min; vent each vessel by pressing on exhaust tube.

3. Time = 5 min; Power= 50%
   Cool and vent as in step 2.

4. Time = 5 min; Power = 70%.
   Cool and vent as in step 2.

5. Uncap pressure vessels in an exhaust hood using the capping station. Remove the 30-mL PFA vials from the pressure vessels by floating them out with Milli-Q water. Allow the PFA vials to dry in a laminar flow hood before opening. Dilute sample digests with Milli-Q water as described below.

3.3.3. Initial sample dilution and volume determination

Milli-Q water was added to each digest in a 3:1 v/v ratio of Milli-Q to HNO_3 originally added. Thus, vials with 2.5 mL HNO_3 received 7.5 mL Milli-Q water; vials with 5.0 mL HNO_3 received 15.0 mL Milli-Q water; and vials with 7.5 mL HNO_3 received 22.5 mL Milli-Q water. The diluted digests ranged from about 4N HNO_3 in blanks to 2N HNO_3 in digests with as much as 0.4 g dry weight of tissue. The difference represents the loss of HNO_3 consumed in oxidation of tissue. All subsequent dilutions were made with 3N HNO_3 (Seastar) to approximately match the middle range of acid strengths of initially diluted digests.

Vials and their contents were weighed to 10 mg and the net solution weight calculated as the difference from the vial tare weight. After shaking to mix the vial contents, the solution density was determined. Three 100 µL aliquots of the initially diluted digest solution were pipetted into an AS-60 cup and weighed to 0.1 mg. A calibrated 100 µL Gilson pipet and pre-rinsed pipet tips were used. Pipet tips need not be rinsed between aliquots from the same vial, but new tips must be used for different vials. Weights of the three aliquots had to agree within 1.0 mg, otherwise further aliquots were weighed and the outlying weights rejected. The mean aliquot weight was multiplied by 10 to yield the solution density. Solution volume was calculated as solution weight divided by solution density.

3.4. Alternate bomb digestion

The microwave digestion procedure was developed from an earlier digestion procedure that used large Teflon-lined Parr bombs as pressure vessels and heating in a conventional laboratory oven. This method was modeled on one described by Okamota and Fuwa (1984). The Teflon pressure vessel provided an additional inert barrier to possible metal contamination while using relatively inexpensive PFA vials as primary digestion containers which could be cleaned and weighed in large numbers. The vials could be used for direct weighing of samples and CRMs, initial dilutions, and sample storage. Contamination risks were reduced because digest transfers to other containers for volume determination and storage were unnecessary. Efficiency was increased by eliminating such procedures. For these reasons, we retained the configuration of a digestion vial within an inert pressure vessel when changing to microwave digestion.

Sample preparation and acid additions for the alternate Parr bomb digestion were the same as for the microwave digestion. The 30-mL PFA vials were placed singly in the Teflon liner of the 125-mL Parr bomb with 5 mL of Milli-Q water. After capping, the liner was placed in its

stainless steel bomb jacket which was then assembled according to the manufacturer's instructions. The bombs were heated for 2 hr at 90°C, for 4 hr at 140°C, and cooled overnight. After venting in a fume hood, the PFA vials were removed and treated as in the microwave digestion procedure. In both procedures there was some venting of vapors from the PFA vials into the pressure vessel, but we observed no apparent loss of potentially volatile elements such as mercury.

3.5. Dilution

Any sample or CRM digest whose concentration exceeded that of the highest standard was diluted. Extrapolation of the calibration curve beyond the range of the highest standard was not done. Diluents were selected to mimic the acid matrix of the samples, CRM's, and blanks.

For graphite furnace AAS analyses, the diluent was 4N HNO_3, prepared using 175 g HNO_3 (Seastar) and 375 g Milli-Q water. This acid solution mimics the blank digest composition. The HNO_3 also functioned as a matrix modifier, especially in reducing the possible interference of chloride salts.

For flame and Hg cold vapor AAS analyses, the diluent is 3N HNO_3, prepared using 131 g HNO_3 (Seastar) and 406 g Milli-Q water. This acid solution mimics the CRM digest acid composition. There was a variable loss of HNO_3 utilized in the digestion procedure resulting from the differing amounts of organic matter in samples, CRM's, and blanks, and this resulted in a range of final HNO_3 concentrations. The choice of 3N HNO_3 was a compromise within this range of concentrations. Standards were also prepared in 3N HNO_3 to limit variations in analytical sensitivity due to differences in aspiration, nebulization, and flow rates.

4. CALIBRATION AND COMPUTATION OF ANALYTE CONCENTRATIONS

Calibration for the elements analyzed by graphite furnace AAS was done on line by the microprocessor or computer associated with each spectrophotometer. Four standards in 4N HNO_3 were used with analyte concentrations in the ratio of 0:1:2:3. Two replicate injections were analyzed for each standard. After every eight samples, a partial recalibration was performed using the reslope function of the instrument's calibration software. The "2" or "3" standard was used along with the "0" standard in resloping the calibration curve. A two-coefficient calibration function was always employed to compensate for minor curvature in the relationship between concentration (C) and background corrected absorbance-sec (A). The concentration was calculated using

$$C = \frac{k_1 A}{k_2 A - 1}$$

where k_1 and k_2 are constants calculated by the method of least squares (Barnett, 1984). The mean absorbance of the most recent "0" standard was subtracted from both standard and sample absorbance-second measurements before this computation was performed.

Calibration for elements analyzed by flame AAS was done offline using the mean of three expanded absorbance readings from the digital display of the spectrophotometer for each standard. More than three standards and a "0" concentration standard were usually employed. Where the relationship between concentration and absorbance of standards was linear, the concentration in sample solutions was estimated from a least squares calculation of

Table III.6. Typical tissue detection limits.

Element	Detection limit (µg/g dry weight)	Element	Detection limit (µg/g dry weight)
Ag	0.02	Ni	0.1
As	0.3	Pb	0.1
Cd	0.01	Sb	0.2
Cr	0.05	Se	0.4
Cu	1	Sn	0.2
Fe	5	Tl	0.1
Mn	1	Zn	2
Hg	0.05		

$$C = k_1 + k_2 A.$$

If the relationship between absorbance and concentration was found to be non-linear through visual inspection of a calibration curve or calculation of an r^2 less than 0.995, calibration was performed using an equation of the form

$$\frac{1}{C} = k_1 + k_2 \frac{1}{A} .$$

The mean "0" concentration standard absorbance was subtracted from all standard and sample results before calibration computations. The "0" standard is not used in this calibration computation. This equation is equivalent to the online calibration used by the spectrophotometer computer in graphite furnace AAS. This regression, using reciprocals of C and A, weights the lower standards more heavily than higher standards. This had an advantage when estimating concentrations near the detection limit. Standards were reanalyzed after every ten samples. Drift in baseline and sensitivity were corrected by linear interpolation.

Calibration for Hg analyzed by cold vapor AAS was similar to that for flame AAS. Peak height output from a strip chart recorder corrected for baseline was used to determine expanded absorbance.

The mass of analyte in each blank sample was determined from the product of measured concentration and diluted sample volume. The mean mass of analyte in these blanks was subtracted from the calculated analyte mass in the samples to yield blank-corrected analyte mass. Division by sample dry weight yielded the final analyte concentration in the tissue sample.

5. DETECTION LIMITS

The detection limit was defined as three times the standard deviation of the measured concentration of blanks processed as samples. A dry weight of 0.3 g was assumed in calculating detection limits on the basis of tissue dry weight. Typical detection limits are listed in Table III.6.

Table III.7. Tissue methodological changes through time.

Sample Set	Methodological change
First trace element intercomparison exercise	none
Cycle 1 tissues (southeast)	P1, I1
Second trace element intercomparison exercise	I2
Cycle 2 tissues (southeast)	M1
Cycle 4 tissues (Galveston Bay, St. Johns River, Sapelo Sound)	none
Third trace element intercomparison exercise	none
Cycle 4 tissue (remaining southeast)	none
Cycle 3 tissue (southeast)	none
Cycle 5 tissue (Galveston Bay)	M2, M3, I3
Fourth trace element intercomparison exercise	none
Cycle 5 tissue (Lavaca Bay)	none
Cycle 5 tissue (remaining southeast)	P2
Cycle 5 tissue (northeast)	none

Sample preparation:

P1 - Tissues were freeze dried instead of oven dried to minimize possible mercury losses.

P2 - Microwave digestion replaced bomb digestion to reduce digestion time and limit possible metal contamination from the stainless steel bomb jacket.

Instrumental:

I1 - The Z/3030 with Zeeman background correction replaced the model 603 for graphite furnace analyses. Zeeman background correction greatly improved accuracy and precision.

I2 - Deuterium arc background correction was dropped from flame analyses on the model 603 AAS. It was unnecessary and increased the analytical signal to noise ratio and baseline drift.

I3 - Flow injection analysis for mercury was introduced to increase the speed of analyses which had previously been done by an inefficient batch method.

Matrix modification:

M1 - Selenium digests are diluted a further 4-fold to reduce a matrix effect that biased accuracy.

M2 - Matrix modifier for Se, As, and Sb was changed from (500 µg Pd + 500 µg Co)/mL to (2000 µg Pd + 2000 µg Co)/mL to improve precision and accuracy degraded by matrix effects and to make the analysis more robust to variations in atomization temperature and sample composition.

M3 - 5% ammonium dihydrogen phosphate was substituted for 250 µg Pd/mL as a matrix modifier for lead to improve accuracy by reducing matrix effects.

6. CHANGES IN ANALYTICAL METHODS OVER TIME

Initial analytical methods used in the National Benthic Surveillance Project have evolved to their current status, as described here, through several iterations in response to new knowledge and experience gained in addressing problems and improving efficiency. The major changes in the past are documented in Table III.7. Changes are paired with the sample sets where they were first employed. Sample sets are in the order of analysis. Reasons for the changes are given in Table III.4 footnotes.

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9. INSTRUMENTAL ANALYSES

9.1. Antimony

METHOD: Graphite Furnace Atomic Absorption Spectrophotometry

SAMPLE DIGEST: ~3N HNO_3

SPECTROPHOTOMETER SETTINGS:

Lamp:	HCL 20 ma
Wavelength:	217.6 nm
Slit Width:	0.7 nm
Read Delay:	0 sec
Integration (Read) Time:	4 sec
Replicate Sample Injections:	2

FURNACE CONDITIONS:

Graphite Tube Type:	Pyrolytic, grooved for forked platform
L'vov Platform Type:	Solid pyrolytic, forked
Carrier Gas:	Argon

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas Flow (mL/min)	Read
		Ramp	Hold		
1	250	15	30	300	-
2	1000	30	15	300	-
3	2400	0	4	0	*
4	2650	1	5	300	-

STANDARDS: 0, 10, 20, 30 µg Sb/L in 4N HNO_3.

MATRIX MODIFIER: (2000 µg Pd+2000 µg Co)/mL.

INJECTION VOLUME: 25 µL

MATRIX MODIFIER: 5 µL

DILUENT: 4N HNO_3, if needed.

CALIBRATION: Two-coefficient least squares fitted calibration line performed by instrument microprocessor using the above standards. Reslope after every 8 samples.

TYPICAL SENSITIVITY: 0.085 abs.-sec. for 25 µL of a 30 µg Sb/L standard.

9.2. Arsenic

METHOD: Graphite Furnace Atomic Absorption Spectrophotometry

SAMPLE DIGEST: ~3N HNO_3

SPECTROPHOTOMETER SETTINGS:

Lamp:	EDL Z/3030 10 watts continuous or Z/5100 6-6.5 watts modulated
Wavelength:	193.7 nm
Slit Width:	0.7 nm
Read Delay:	0 sec
Integration (Read) Time:	5 sec
Replicate Sample Injections:	2

FURNACE CONDITIONS:

Graphite Tube Type:	Pyrolytic, grooved for forked platform
L'vov Platform Type:	Solid pyrolytic, forked
Carrier Gas:	Argon

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas	Read
		Ramp	Hold	Flow (mL/min)	
1	250	15	30	300	-
2	1200	30	15	300	-
3	2600	0	5	0	*
4	2650	1	5	300	-

STANDARDS: 0, 60, 120, 180 µg As/L in 4N HNO_3.

MATRIX MODIFIER: (2000 µg Pd + 2000 µg Co)/mL.

INJECTION VOLUME: 10 µL

MATRIX MODIFIER: 5 µL

DILUENT: 4N HNO_3, 2-fold dilutions required of all samples, CRM's, and blanks.

CALIBRATION: Two-coefficient least squares fitted calibration line performed by instrument microprocessor using the above standards. Reslope after every 8 samples.

TYPICAL SENSITIVITY: 0.300 abs-sec. for 10 µL of a 120 µg As/L standard.

9.3. Cadmium

METHOD: Graphite Furnace Atomic Absorption Spectrophotometry

SAMPLE DIGEST: ~3N HNO_3

SPECTROPHOTOMETER SETTINGS:

Lamp:	EDL Z/3030 5 watts continuous or Z/5100 3-3.5 watts modulated
Wavelength:	228.8 nm
Slit Width:	0.7 nm
Read Delay:	0 sec
Integration (Read) Time:	5 sec
Replicate Sample Injections:	2

FURNACE CONDITIONS:

Graphite Tube Type:	Pyrolytic, grooved for forked platform
L'vov Platform Type:	Solid pyrolytic, forked
Carrier Gas:	Argon

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas	Read
		Ramp	Hold	Flow (mL/min)	
1	250	15	30	300	-
2	500	15	30	300	-
3	1700	0	5	0	*
4	2650	1	3	300	-

STANDARDS: 0, 1, 2, and 3 µg Cd/L in 4N HNO_3.

MATRIX MODIFIER: 250 µg Pd/mL in 4N HNO_3.

INJECTION VOLUME: 15 µL

MATRIX MODIFIER: 5 µL

DILUENT: 4N $HN0_3$, if necessary.

CALIBRATION: Two-coefficient least squares fitted calibration line performed by instrument microprocessor using above standards. Reslope after every 8 samples.

TYPICAL SENSITIVITY: 0.250 abs.-sec. for 15 µL of a 2 µg Cd/L standard.

9.4. Chromium

METHOD: Graphite Furnace Atomic Absorption Spectrophotometry

SAMPLE DIGEST: ~3N HNO_3

SPECTROPHOTOMETER SETTINGS:

Lamp:	HCL 25 ma
Wavelength:	357.9 nm
Slit Width:	0.7 nm
Read Delay:	0 sec
Integration (Read) Time:	5 sec
Replicate Sample Injections:	2

FURNACE CONDITIONS:

Graphite Tube Type:	Pyrolytic, grooved for forked platform
L'vov Platform Type:	Solid pyrolytic, forked
Carrier Gas:	Argon

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas Flow (mL/min)	Read
		Ramp	Hold		
1	160	15	30	300	-
2	1000	30	15	300	-
3	2500	0	5	0	*
4	3000	1	6	300	-

STANDARDS: 0, 5, 10, 15 µg Cr/L in 4N HNO_3.

MATRIX MODIFIER: none

INJECTION VOLUME: 30 µL

MATRIX MODIFIER: none

DILUENT: 4N HNO_3, if necessary.

CALIBRATION: Two-coefficient least squares fitted calibration line performed by instrument microprocessor using the above standards. Reslope after every 8 samples.

TYPICAL SENSITIVITY: 0.400 abs-sec. for 30 µL of 15 µg Cr/L standard.

9.5. Copper

METHOD: Flame Atomic Absorption Spectrophotometry

SAMPLE DIGEST: ~3N HNO_3

SPECTROPHOTOMETER SETTINGS:

Lamp:	HCL, 20 ma
Wavelength:	324.7 nm
Slit Width:	0.7 nm
Signal Output:	Expanded absorbance
Expansion:	5 times
Integration Time:	1 sec
Replicate Readings:	3
Nebulization:	Glass impact bead
Burner Head:	Single slot, 10 cm
Background Correction:	none
Flame:	Air:acetylene, lean blue; air 55, acetylene 25

STANDARDS: 0, 0.2, 0.4, 0.8, 1.2, 2.0 mg Cu/L in 3N HNO_3.

DILUENT: 3N HNO_3, if needed.

CALIBRATION: Off-line processing of expanded absorbance signals using either a linear least squares regression (default) or a non-linear least squares regression program. Regression coefficients, r^2, of less than 0.995 indicate the possible need for a nonlinear regression calibration. Standards are rerun after every 10 samples. Drift in the calibration parameters is corrected by interpolation.

SENSITIVITY: 0.160 absorbance for a 2.0 mg Cu/L standard.

9.6. Iron

METHOD: Flame Atomic Absorption Spectrophotometry

SAMPLE DIGEST: ~3N HNO_3

SPECTROPHOTOMETER SETTINGS:

Lamp:	HCL 30 ma
Wavelength:	248.3 nm
Slit Width:	0.2 nm
Signal Output:	Expanded absorbance
Expansion:	1 time
Integration Time:	1 sec
Replicate Readings:	3
Nebulization:	Glass impact bead
Burner Head:	Single slot, 10 cm
Background Correction:	none
Flame:	Air:acetylene, lean blue; air 55, acetylene 25

STANDARDS: 0, 1.0, 2.0, 4.0, 6.0, 10.0 mg Fe/L in 3N HNO_3.

DILUENT: 3N HNO_3, if needed.

CALIBRATION: Off-line processing of expanded absorbance signals using either a linear least squares regression (default) or a non-linear least squares regression program. Regression coefficients, r^2, of less than 0.995 indicate the possible need for a nonlinear regression calibration. Standards are rerun after every 10 samples. Drift in the calibration parameters is corrected by interpolation.

SENSITIVITY: 0.465 absorbance for a 10 mg Fe/L standard.

9.7. Lead

METHOD: Graphite Furnace Atomic Absorption Spectrophotometry

SAMPLE DIGEST: ~3N HNO_3

SPECTROPHOTOMETER SETTINGS:

Lamp:	EDL Z/3030 10 watts continuous or Z/5100 7-7.5 watts modulated
Wavelength:	283.3 nm
Slit Width:	0.7 nm
Read Delay:	0 sec
Integration (Read) Time:	6 sec
Replicate Sample Injections:	2

FURNACE CONDITIONS:

Graphite Tube Type:	Pyrolytic, grooved for forked platform
L'vov Platform Type:	Solid pyrolytic, forked
Carrier Gas:	Argon

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas	Read
		Ramp	Hold	Flow (mL/min)	
1	250	15	30	300	-
2	500	30	15	300	-
3	2000	0	6	0	*
4	2650	1	5	300	-

STANDARDS: 0, 10, 20, 30 µg Pb/L in 4N HNO_3.

MATRIX MODIFIER: 5% w/v $NH_4H_2PO_4$ 4N HNO_3

INJECTION VOLUME: 25 µL

MATRIX MODIFIER: 5 µL

DILUENT: 4N $HN0_3$, if necessary.

CALIBRATION: Two-coefficient least squares fitted calibration line performed by instrument microprocessor using the above standards. Reslope after every 8 samples.

TYPICAL SENSITIVITY: 0.240 abs.-sec. for 25 µL of 30 µg Pb/L standard.

9.8. Manganese

METHOD: Flame Atomic Absorption Spectrophotometry

SAMPLE DIGEST: ~3N HNO_3

SPECTROPHOTOMETER SETTINGS:

Lamp:	HCL 20 ma
Wavelength:	279.5 nm
Slit Width:	0.2 nm
Signal Output:	Expanded absorbance
Expansion:	5 times
Integration Time:	1 sec
Replicate Readings:	3
Nebulization:	Glass impact bead
Burner Head:	Single slot, 10 cm
Background Correction:	none
Flame:	Air:acetylene, lean blue; air 55, acetylene 25

STANDARDS: 0, 0.1, 0.2, 0.4, 0.6, 1.0 mg Mn/L in ~3N HNO_3.

DILUENT: 3N HNO_3, if needed.

CALIBRATION: Off-line processing of expanded absorbance signals using either a linear least squares regression (default) or a non-linear least squares regression program. Regression coefficients, r^2, of less than 0.995 indicate the probable need for a nonlinear regression calibration. Standards are rerun after every 10 samples. Drift in the calibration parameters is corrected by interpolation.

SENSITIVITY: 0.130 absorbance for a 1.0 mg Mn/L standard.

9.9. Mercury

METHOD: Cold vapor atomic absorption spectrophotometry

SAMPLE DIGEST: ~3N HNO_3

SPECTROPHOTOMETER SETTINGS:

Lamp:	EDL 5 watts
Wavelength:	253.7 nm
Slit Width:	0.7 nm
Signal Output:	Expanded absorbance to strip chart recorder
Expansion:	10 times
Integration time:	0.5 sec
Recorder Time Constant:	TC3 (4 sec)
Background Correction:	none

FLOW INJECTION PARAMETERS:

Pump:	Rainin Rabbit Plus with 4 channel head
Pump Speed:	25 rpm
Tubing Diameters (I.D.):	
	0.89 mm reductant
	2.29 mm carrier acid/sample
	2.29 mm waste
Gas Flow(Nitrogen):	
	100 cm^3/min (setting 50)
	230 cm^3/min (setting 50)
Injection Volume:	0.5 mL
Gas/Liquid Separator Volume:	3.5 mL
Mixing Loop Volume:	1 mL
Reaction Loop Volume:	1 mL
Cell Length:	13.5 cm
Cell Diameter:	0.6 cm
Cell Volume:	4 cm^3
Reductant:	10% w/v $SnCl_2 \cdot H_2O$ in 1N HCl
Carrier Acid:	Mixed 1N HCl + 1N HNO_3

STANDARDS: 0, 1, 2, 3, 5, 10, 20, 30, 50, 100 µg Hg/L in mixed 1N HCl + 1N HNO_3.

DILUENT: 3N HNO_3, if necessary.

CALIBRATION: Off-line processing of expanded absorbance signals using either a linear least squares regression (default) or a non-linear least squares regression program. Regression coefficients, r^2, of less than 0.995 indicate the probable need for a nonlinear regression calibration. Standards are run after every 10 samples. Drift in the calibration parameters is corrected by interpolation.

SENSITIVITY: 0.100 absorbance for a 10 µg Hg/L standard.

COMMENTS: Recorder peak height is suppressed by the long time constant in order to smooth baseline noise. See Figure III.3 for flow injection diagram.

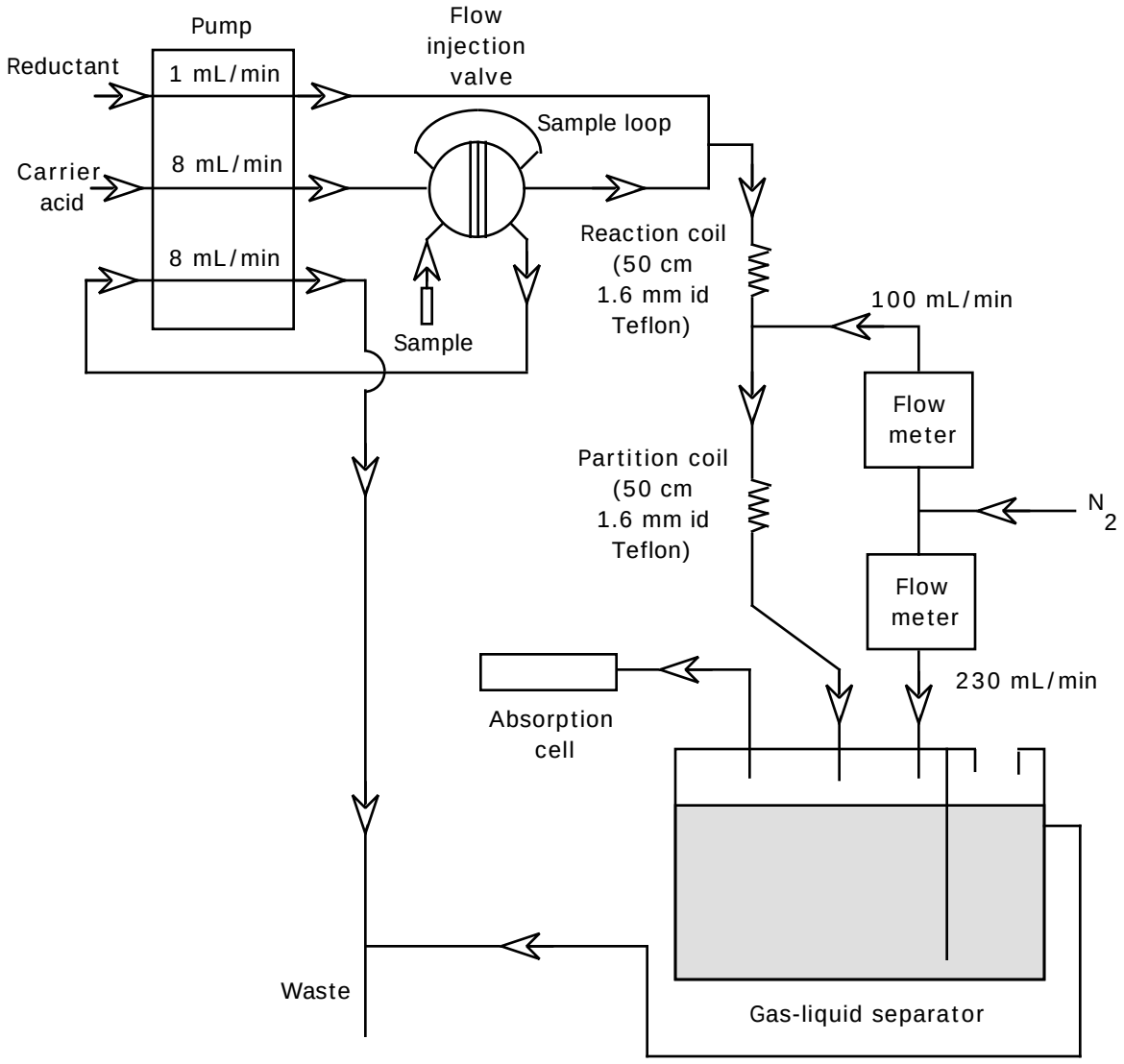

Figure III.3. Flow injection system for tissue mercury analysis.

9.10. Nickel

METHOD: Graphite Furnace Atomic Absorption Spectrophotometry

SAMPLE DIGEST: ~3N HNO_3

SPECTROPHOTOMETER SETTINGS:

Lamp:	HCL 18 ma
Wavelength:	232.0 nm
Slit Width:	0.2 nm
Read Delay:	0 sec
Integration (Read) Time:	6 sec
Replicate Sample Injections:	2

FURNACE CONDITIONS:

Graphite Tube Type:	Pyrolytic, grooved for forked platform
L'vov Platform Type:	Solid pyrolytic, forked
Carrier Gas:	Argon

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas Flow (mL/min)	Read
		Ramp	Hold		
1	160	15	30	300	-
2	1000	30	15	300	-
3	20	1	10	300	-
4	2700	0	6	0	*
5	2700	1	6	300	-

STANDARDS: 0, 10, 20, 30 µg Ni/L in 4N HNO_3.

MATRIX MODIFIER: none

INJECTION VOLUME: 30 µL

MATRIX MODIFIER: none

DILUENT: 4N HNO_3

CALIBRATION: Two-coefficient least squares fitted calibration line performed by instrument microprocessor using the above standards. Reslope after every 8 samples.

TYPICAL SENSITIVITY: 0.260 abs-sec. for 30 µL of 30 µg Ni/L standard.

9.11. Selenium

METHOD: Graphite Furnace Atomic Absorption Spectrophotometry

SAMPLE DIGEST: ~3N HNO_3

SPECTROPHOTOMETER SETTINGS:

Lamp:	EDL Z/3030 6 watts or Z/5100 4-4.5 watts
Wavelength:	196.0 nm
Slit Width:	0.7 nm
Read Delay:	0 sec
Integration (Read) Time:	5 sec
Replicate Sample Injections:	2

FURNACE CONDITIONS:

Graphite Tube Type:	Pyrolytic, grooved for forked platform
L'vov Platform Type:	Solid pyrolytic, forked
Carrier Gas:	Argon

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas	Read
		Ramp	Hold	Flow (mL/min)	
1	250	15	30	300	-
2	700	30	15	300	-
3	2400	0	4	0	*
4	2650	1	3	300	-

STANDARDS: 0, 30, 60, 90 µg Se/L in 4N HNO_3.

MATRIX MODIFIER: (2000 µg Pd + 2000 µg Co)/mL

INJECTION VOLUME: 20 µL

MATRIX MODIFIER : 5 µL

DILUENT: 4N HNO_3, 4-fold dilutions required of all samples, CRM's and blanks.

CALIBRATION: Two-coefficient least squares fitted calibration line performed by instrument microprocessor using the standards. Reslope after every 8 samples.

TYPICAL SENSITIVITY: 0.250 abs-sec. for 20 µL of a 90 µg Se/L standard.

COMMENTS: Sensitivity depends on EDL lamp power and energy output.

9.12. Silver

METHOD: Graphite Furnace Atomic Absorption Spectrophotometry

SAMPLE DIGEST: ~3N HNO_3

SPECTROPHOTOMETER SETTINGS:

Lamp:	HCL 12 ma
Wavelength:	328.1 nm
Slit Width:	0.7 nm
Read Delay:	0 sec
Integration (Read) Time:	4 sec
Replicate Sample Injections:	2

FURNACE CONDITIONS:

Graphite Tube Type:	Pyrolytic, grooved for forked platform
L'vov Platform Type:	Solid pyrolytic, forked
Carrier Gas:	Argon

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas Flow (mL/min)	Read
		Ramp	Hold		
1	250	15	30	300	-
2	500	15	30	300	-
3	1900	0	5	0	*
4	2650	1	3	300	-

STANDARDS: 0, 3, 6, and 9 µg Ag/L in 4N HNO_3.

MATRIX MODIFIER: 250 µg Pd/mL in 4N HNO_3.

INJECTION VOLUME: 20 µL

MATRIX MODIFIER: 5 µL

DILUENT: 4N HNO_3, if necessary.

CALIBRATION: Two-coefficient least squares fitted calibration line performed by instrument microprocessor using above standards. Reslope after every 8 samples.

TYPICAL SENSITIVITY: 0.350 abs-sec. for 20 µL of a 6 µg Ag/L standard.

9.13. Thallium

METHOD: Graphite Furnace Atomic Absorption Spectrophotometry

SAMPLE DIGEST: ~3N HNO_3

SPECTROPHOTOMETER SETTINGS:

Lamp:	EDL Z/3030 7 watts continuous or Z/5100 4-4.5 watts modulated
Wavelength:	276.8 nm
Slit Width:	0.7 nm
Read Delay:	0 sec
Integration (Read) Time:	4 sec
Replicate Sample Injections:	2

FURNACE CONDITIONS

Graphite Tube Type:	Pyrolytic, grooved for forked platform
L'vov Platform Type:	Solid pyrolytic, forked
Carrier Gas:	Argon

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas	Read
		Ramp	Hold	Flow (mL/min)	
1	250	15	30	300	-
2	600	15	30	300	-
3	2100	0	4	0	*
4	2650	1	5	300	-

STANDARDS: 0, 10, 20, and 30 µg Tl/L in 4N HNO_3.

MATRIX MODIFIERS: (1) 5% w/v ascorbic acid in Milli-Q water
(2) 250 µg Pd/mL in 4N HNO_3

INJECTION VOLUME: 15 µL

MATRIX MODIFIER : 5 µL of (1) + 5 µL of (2)

DILUENT: 4N $HN0_3$, if necessary.

CALIBRATION: Two-coefficient least squares fitted calibration line performed by instrument microprocessor using above standards. Reslope after every 8 samples.

TYPICAL SENSITIVITY: 0.080 abs-sec. for 15 µL of a 30 µg Tl/L standard.

9.14. Tin

METHOD: Graphite Furnace Atomic Absorption Spectrophotometry

SAMPLE DIGEST: ~3N HNO_3

SPECTROPHOTOMETER SETTINGS:

Lamp:	EDL Z/3030 8-8.5 watts continuous or Z/5100 5.5-6 watts modulated
Wavelength:	286.3 nm
Slit Width:	0.7 nm
Read Delay:	0 sec
Integration (Read) Time:	4 sec
Replicate Sample Injections:	2

FURNACE CONDITIONS

Graphite Tube Type:	Pyrolytic, grooved for forked platform
L'vov Platform Type:	Solid pyrolytic, forked
Carrier Gas:	Argon

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas	Read
		Ramp	Hold	Flow (mL/min)	
1	250	15	30	300	-
2	500	15	30	300	-
3	2400	0	4	0	*
4	2650	1	5	300	-

STANDARDS: 0, 20, 40, and 60 µg Sn/L in 4N HNO_3.

MATRIX MODIFIER: 250 µg Pd/mL in 4N HNO_3.

INJECTION VOLUME: 25 µL

MATRIX MODIFIER: 5 µL

DILUENT: 4N HNO_3, if necessary.

CALIBRATION: Two-coefficient least squares fitted calibration line performed by instrument microprocessor using above standards. Reslope after every 8 samples.

TYPICAL SENSITIVITY: 0.210 abs-sec. for 25 µl of a 60 µg Sn/L standard.

9.15. Zinc

METHOD: Flame Atomic Absorption Spectrophotometry

SAMPLE DIGEST: ~3N $HN0_3$

SPECTROPHOTOMETER SETTINGS:

Lamp:	HCL 15 ma
Wavelength:	213.8 nm
Slit Width:	0.7 nm
Signal Output:	Expanded absorbance
Expansion:	1 time
Integration Time:	1 sec
Replicate Readings:	3
Nebulization:	Glass impact bead
Burner Head:	Single slot, 10 cm
Background Correction:	none
Flame:	Air:acetylene, lean blue; air 55, acetylene 25

STANDARDS: 0, 0.2, 0.4, 0.8, 1.2, 2.0 mg Zn/L in 3N HNO_3.

DILUENT: 3N HNO_3, if needed.

CALIBRATION: Off-line processing of expanded absorbance signals using either a linear least squares regression (default) or a non-linear least squares regression program. R^2 less than 0.995 indicates the probable need for a nonlinear regression calibration. Standards are rerun after every 10 samples. Drift in the calibration parameters is corrected by interpolation.

SENSITIVITY: 0.570 absorbance for a 2.0 mg Zn/L standard.

Sample Preparation and Analyses of Trace Metals by Atomic Absorption Spectroscopy

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ABSTRACT

The methods used for the atomic absorption analyses of major and trace elements in marine sediments by the NOAA/National Marine Fisheries Service (NMFS) Northwest Fisheries Science Center as part of the National Status and Trends Program are based on those developed by the NMFS Northeast Fisheries Science Center. The methods used for tissues are based on those developed by the NMFS Southeast Fisheries Science Center. The modifications to these methods are described.

1. INTRODUCTION

The methods used for the atomic absorption analyses of major and trace elements in marine sediments by the NOAA/National Marine Fisheries Service (NMFS) Northwest Fisheries Science Center as part of the National Status and Trends Program are based on those developed at the NMFS Northeast Fisheries Science Center by Zdanowicz and Finneran (this document). The methods used for tissues are based on those developed at the NMFS Southeast Fisheries Science Center by Evans and Hanson (this document). The modifications to these methods are described below.

2. EQUIPMENT AND SUPPLIES

2.1. Instrumentation

2.2. Supplies

CEM Model 81D, microwave oven with pressure controller unit and high pressure Teflon digestion vessels. CEM Corp., Matthews, NC.

2.3. Labware

Pippettors, manual, Chempette Digital MacroPipettor. Cole Palmer, Niles, IL.

2.4. Reagents

Acetic acid, ultra pure (CH_3COOH) [64-19-7]. Seastar Chemicals, Sidney, British Columbia.

Ammonium dihydrogen phosphate ($NH_4H_2PO_4$) [7722-76-1], Ultrex. J. T. Baker, Phillipsburg, NJ.

Boric acid (H_3BO_3) [10043-35-3], ultra pure crystalline powder. Aesar/Johnson Matthey, Ward Hill, MA.

Hydrochloric acid (HCl) [7647-01-0], ultra pure. Seastar Chemicals, Sidney, BC, Canada.

Hydrofluoric acid (HF) [7664-39-3], ultra pure. Seastar Chemicals, Sidney, BC, Canada.

Hydrogen peroxide, ultra pure. Fluka Chemical, Ronkondoma, NY.

Magnesium nitrate ($Mg(NO_3)_2 \cdot 6H_20$) [13446-18-9], puratronic. Aesar/Johnson Matthey, Ward Hill, MA.

Nickel nitrate ($Ni(NO_3)_2 \cdot 6H_20$) [13478-00-7], puratronic. Aesar/Johnson Matthey, Ward Hill, MA.

Nitric acid (HNO_3) [7697-37-2], ultra pure. Seastar Chemicals, Sidney, BC, Canada.

Potassium permanganate, $KMnO_4$, (Analyzed Reagent). J. T. Baker, Phillipsburg, NJ.

Single-element Standard Reference Materials. NIST, Gaithersburg, MD.

Sodium borohydride ($NaBH_4$) [16940-66-2], 99% purity. Aldrich Chemical Co., Milwaukee, WI.

Sodium hydroxide (NaOH) [1310-73-2].

Water, high-purity deionized, Milli-Q. Millipore Corporation, Bedford, MA.

2.5. Matrix modifiers and reagents

2.5.1. Magnesium nitrate

$Mg(NO_3)_2$ solutions: [5 and 10 µg $Mg(NO_3)_2$/µL]. This modifier is used in the analysis of Al, Cd, Cr, Pb, Ni, Se, and Sn. The 5 µg $Mg(NO_3)_2$/µL solution is prepared by dissolving 865 mg of $Mg(NO_3)_2 \cdot 6H_20$ in 100 mL of Milli-Q water. The 10 µg $Mg(NO_3)_2$/µL solution is prepared by dissolving 1.73 g of $Mg(NO_3)_2 \cdot 6H_20$ in 100 mL of Milli-Q water.

2.5.2. Nickel nitrate

$Ni(NO_3)_2$. [4 µg Ni^{+2}/µL]. This modifier is used in the analysis of As and Se. The solution is prepared by dissolving 1.982 g of $Ni(NO_3)_2 \cdot 6H_20$ in 100 mL Milli-Q water.

2.5.3. Ammonium hydrogen phosphate

$NH_4H_2PO_4$ [40 µg/µL]. This modifier is used in the analyses of Ag, Cd, and Pb. The solution is prepared by dissolving 4 g of $NH_4H_2PO_4$ in 100 mL Milli-Q water.

2.5.4. Potassium permanganate

5.0% $KMnO_4$. This reagent is used during the analysis of Hg. The solution is prepared by dissolving 5 g of $KMnO_4$ in 100 mL of Milli-Q water.

2.5.5. Sodium borohydride

This reagent is used during the analysis of Hg and Sn. The solution is prepared by dissolving 3 g of $NaBH_4$ in 1% NaOH.

3. SAMPLE PROCESSING

3.1. Tissues

Microwave digestions are conducted in a manner similar to that described by Evans and Hanson (this document), with the following significant exceptions.

3.1.1. Acid addition

Ten milliliters of high-purity concentrated HNO_3 were added to 0.20-0.30 g of tissue (dry wt) and the resulting mixture was allowed to stand at room temperature for two hours before heating.

3.1.2. Microwave digestion

Twelve digestion vessels were processed simultaneously in a 650-watt oven. With the pressure controller set at 90 psi, the following program sequence was used.

Step	Time (min)	Amount Power (%)
1	4	50
2	2	0
3	3	50
4	2	0
5	3	50
6	12	0
7	3	50
8	2	0
9	3	50

The capped, digested samples were stored overnight at approximately 5°C. The vessels containing the digested samples were then uncapped and 1.0 mL of high-purity H_2O_2 was added. After at least 15 min of holding time, a second 1.0 mL aliquot of H_2O_2 was added, followed by another 1.0 mL after a 15 min holding time. After a holding time of 2 hr, a final 1.0 mL of H_2O_2 was added. The sample was recapped and with the pressure controller reset at 90 psi, the following microwave digestion program was used:

Step	Time (min)	Amount Power (%)
1	2	50
2	2	0
3	2	50
4	2	0
5	2	50
6	5	0
7	3	50

Alternating stages with no heating power are needed to keep the pressure resulting from the decomposition of the peroxide from increasing too rapidly.

3.1.3. Sample dilution

The digested samples were cooled to approximately 5°C before being quantitatively transferred to a 25-mL volumetric flask. Each sample was diluted to 25 mL with Milli-Q water. The diluted samples were transferred to a 60-mL low density polyethylene (Nalgene) bottle for storage.

3.2. Sediments

Microwave digestions are conducted in a manner similar to that described by Evans and Hanson (this document), with the following significant exceptions.

3.2.1. Acid addition

Two milliliters of high-purity concentrated aqua regia, freshly made by mixing HCl and HNO_3 in a ratio of 3:1, and 6 mL of high-purity HF, were added to 0.20-0.30 g of sediment (dry wt.).

3.2.2. Microwave digestion

Six digestion vessels were processed simultaneously in a 650-watt oven. With the pressure controller set at 90 psi, the following program sequence was used.

Step	Time (min)	Amount Power (%)
1	2	55
2	23	50
3	90	45

3.2.3. Sample dilution

The digested samples were allowed to cool for approximately one hour, or until the pressure decreased to 20 psi, before being quantitatively transferred to a 50-mL volumetric flask. Each sample was diluted to 50 mL with saturated H_3BO_3. The diluted samples were transferred to a 60-mL low density polyethylene (Nalgene) bottle for storage.

4. CALIBRATION AND COMPUTATION OF ANALYTE CONCENTRATIONS

Calibration standards for each individual element were prepared using the single element spectrometric Standard Reference Materials (SRMs) series. A primary stock solution of 100 µg/mL was prepared for each element by diluting 500 µL of the 10 mg/mL SRM solution to 50 mL maintaining the exact matrix of the original SRM solution. Secondary calibration standards at ng/mL levels were prepared as needed by diluting appropriate aliquots of the 100 µg/mL primary standard using a diluent to match the same matrix as the samples to be analyzed. The diluent used for sediment analyses was a solution of 6 mL concentrated HF and 2 mL aqua regia and brought to volume with saturated H_3BO_3. The diluent used for tissue analyses was a solution of 12 mL concentrated HNO_3 and brought to volume with Milli-Q water.

Calibration for the elements analyzed using graphite furnace and flame atomic absorption spectrometry (GFAAS) was done on-line using the accompanying dedicated computer of the Perkin-Elmer model Z/5100 spectrophotometer. Calibration was done using two independently-made secondary calibration standards from the 100 µg/mL primary standard described above, which were then used to make additional standards with the computerized auto-dilution capability of the spectrophotometer. Using selenium as an example, two secondary standards of 40 and 120 ng/mL were used to give a final calibration curve consisting of five points: 10, 20, 40, 60, and 120 ng/mL. The 10 and 20 ng/mL points were made by the computerized autosampler from the 40 ng/mL standard and the 60 ng/mL from the 120 ng/mL standard. Three replicate injections were analyzed for each standard. Full or partial recalibration was performed as necessary, usually after 15 to 20 samples were analyzed. A partial calibration was performed using the reslope function built into the spectrophotometer software. All calibration curves were drawn through the origin. The calibration curves were routinely calculated using the non-linear equations from the online computer.

Table III.8. Typical method detection limits for 0.3 g digestion samples (µg/g).

	Sediment	Tissue		Sediment	Tissue
Ag	0.01 (HGA)	0.01 (HGA)	Ni	0.1 (HGA)	0.1 (HGA)
Al	500 (Flame)	0.1 (HGA)	Pb	0.1 (HGA)	0.1 (HGA)
As	0.1 (HGA)	0.1 (HGA)	Sb	0.1 (HGA)	0.1 (HGA)
Cd	0.01 (HGA)	0.01 (HGA)	Se	0.1 (HGA)	0.1 (HGA)
Cr	1 (Flame)	0.1 (HGA)	Si	500 (Flame)	
Cu	1 (Flame)	0.1 (HGA)	Sn	0.1 (HGA)	0.1 (MHS)
Hg	0.01 (Vapor)	0.01 (Vapor)	Zn	5 (Flame)	1 (Flame)
Mn	5 (Flame)	0.5 (Flame)			

Calibration curves for those elements analyzed using graphite furnace, flame, hydride, and cold vapor with the Perkin-Elmer model Z/5000 spectrophotometer were calculated using a two-coefficient calibration function and an off-line Apple Macintosh computer. All individual secondary standards for the Model 5000 were made independently from the primary standard.

Typical method detection limits (MDLs) are listed in Table III.8.

5. CONCLUSIONS

The methods of analyses for major and trace elements used in marine sediments by the NMFS Northwest Fisheries Science Center as part of the National Status and Trends Program are based on those developed by the NMFS Northeast Fisheries Science Center. The methods used for tissues are based on those developed by the NMFS Southeast Fisheries Science Center. The modifications to these methods have been described.

6. REFERENCES

In addition to the references listed in Zdanowicz and Finneran (this document), the following citations proved valuable.

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7. SEDIMENT ANALYSIS

7.1. Silver

METHOD: Graphite furnace atomic absorption

INSTRUMENT: Perkin-Elmer Model 5100, Zeeman background correction

SAMPLE DIGESTION: Microwave, 6 mL HF + 2 mL aqua regia; final volume, 50 mL with saturated H_3BO_3.

SAMPLE WEIGHT: 0.2 - 0.3 g (dry weight)

SPECTROPHOTOMETER SETTINGS:

Lamp:	HCL, 10 ma; modulated energy: 65
Wavelength:	328.1 nm
Slit Width:	0.7 nm
Read Delay:	0 sec
Integration Time:	5 sec
Integration:	Peak area
Replicate Injections:	3

FURNACE CONDITIONS:

Pyrolytic grooved graphite tube with L'vov solid pyrolytic platform

Carrier Gas: Argon (prepurified)

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
1	130	5	45	300
2	700	5	40	300
3	20	1	20	300
4	1700	0	5	0
5	2650	1	5	300
6	20	1	10	300

STANDARDS: 0, 0.5, 1.0, 2.0, 3.0, 4.0, and 6.0 ng/mL in HF/aqua regia/boric acid.

MATRIX MODIFIERS: 0.2 mg $NH_4H_2PO_4$ [5 µL of 40 µg $NH_4H_2PO_4$/µL]

INJECTION VOLUME: 20 µL

CALIBRATION: Two-coefficient least squares fit calibration line calculated by instrument computer using above standards. Reslope or calibrate after 10-20 samples.

TYPICAL SENSITIVITY: 0.182 abs-sec for 6 ng/mL standard.

7.2. Aluminum

METHOD: Flame atomic absorption, nitrous oxide flame

INSTRUMENT: Perkin-Elmer Model 5000; deuterium background correction

SAMPLE DIGEST: Microwave, 6 mL HF + 2 mL aqua regia: final volume, 50 mL with saturated H_3BO_3.

SAMPLE WEIGHT: 0.2 - 0.3 g (dry weight)

SPECTROPHOTOMETER SETTINGS:

Lamp:	HCL, 25 ma; continuous energy: 62
Wavelength:	309.3 nm
Slit Width:	0.7 nm
Integration Time:	5 sec
Integration:	Peak area
Replicate Injections:	3
Nebulization:	Glass impact bead
Flame:	N_2O/acetylene, 37:20

STANDARDS: 40, 100, 200, 400, 600, and 800 µg/mL in HF/aqua regia/boric acid.

CALIBRATION: 6 point (standards) best-fit quadratic calibration line.

TYPICAL SENSITIVITY: 0.248 abs-sec for 100 µg/mL standard.

7.3. Arsenic

METHOD: Graphite furnace atomic absorption

INSTRUMENT: Perkin-Elmer Model 5100; Zeeman background correction

SAMPLE DIGEST: Microwave, 6 mL HF + 2 mL aqua regia: final volume, 50 mL with saturated H_3BO_3.

SAMPLE WEIGHT: 0.2 - 0.3 g (dry weight)

SPECTROPHOTOMETER SETTINGS:

Lamp:	EDL, 8 watts, modulated energy: 52
Wavelength:	193.7 nm
Slit Width:	0.7 nm
Read Delay:	0 sec
Integration Time:	5 sec
Integration:	Peak area
Replicate Injections:	3

FURNACE CONDITIONS:

Pyrolytic grooved graphite tube with L'vov solid pyrolytic Platform
Carrier Gas: Argon (prepurified)

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
1	130	5	40	300
2	700	5	45	300
3	20	1	20	300
4	2500	0	4	0
5	2650	1	5	300
6	20	1	10	300

STANDARDS: 0, 15, 30, 60, and 80 ng/mL in HF/aqua regia/boric acid.

MATRIX MODIFIERS: 0.02 mg Ni^{+2} [5 µL of 19.8 µg $Ni(NO_3)_2 \cdot 6H_20$/µL]

INJECTION VOLUME: 20 µL

CALIBRATION: Two-coefficient least squares fit calibration line performed by instrument computer using above standards. Reslope or calibrate after 10-20 samples.

TYPICAL SENSITIVITY: 0.269 abs-sec for 60 ng/mL standard.

7.4. Cadmium

METHOD: Graphite furnace atomic absorption

INSTRUMENT: Perkin-Elmer Model 5100; Zeeman background correction

SAMPLE DIGEST: Microwave, 6 mL HF + 2 mL aqua regia: final volume, 50 mL with saturated H_3BO_3.

SAMPLE WEIGHT: 0.2 - 0.3 g (dry weight)

SPECTROPHOTOMETER SETTINGS:

Lamp:	EDL, 5 watts, modulated energy: 65
Wavelength:	193.7 nm
Slit Width:	0.7 nm
Read Delay:	0 sec
Integration Time:	5 sec
Integration:	Peak area
Replicate Injections:	3

FURNACE CONDITIONS:

Pyrolytic grooved graphite tube with L'vov solid pyrolytic Platform

Carrier Gas: Argon (prepurified)

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
1	130	5	45	300
2	500	5	45	300
3	20	1	20	300
4	1700	0	5	0
5	2650	1	5	300
6	20	1	10	300

STANDARDS: 0, 0.3, 0.6, 1.0, 1.2, and 2.0 ng/mL in HF/aqua regia/boric acid.

MATRIX MODIFIERS: 0.2 mg $NH_4H_2PO_4$ [5 µL of 40 µg $NH_4H_2PO_4$/µL]
2 µL of 5 µg $Mg(NO_3)_2$/µL

INJECTION VOLUME: 20 µL

CALIBRATION: Two-coefficient least squares fit calibration line performed by instrument computer using above standards. Reslope or calibrate after 10-20 samples.

TYPICAL SENSITIVITY: 0.185 abs-sec for 1.2 ng/mL standard.

7.5. Chromium

METHOD: Graphite furnace atomic absorption

INSTRUMENT: Perkin-Elmer Model 5000; no background correction

SAMPLE DIGEST: Microwave, 6 mL HF + 2 mL aqua regia: final volume, 50 mL saturated H_3BO_3.

SAMPLE WEIGHT: 0.2 - 0.3 g (dry weight)

SPECTROPHOTOMETER SETTINGS:

Lamp:	HCL, 25 ma; continuous energy: 65
Wavelength:	357.9 nm
Slit Width:	0.7 nm
Read Delay:	0 sec
Integration Time:	5 sec
Integration:	Peak area
Replicate Injections:	3

FURNACE CONDITIONS:

Pyrolytic grooved graphite tube with L'vov solid pyrolytic platform

Carrier Gas: Argon (prepurified)

FURNACE PROGRAM:

Step	T(°C)	Time (sec)	Internal Gas		
			Ramp	Hold	Flow (mL/min)
1		120	15	30	300
2		450	15	10	300
3		1650	1	10	300
4		2500	0	10	0
5		2600	1	5	300
6		20	1	20	300

STANDARDS: 100, 200, 400, 800, 1000, 1600, 2000, and 4000 ng/mL in HF/aqua regia/boric acid.

MATRIX MODIFIERS: 5 µL of 10 µg $Mg(NO_3)_2$/µL

INJECTION VOLUME: 20 µL

CALIBRATION: 8 point (standards) best fit quadratic calibration line.

TYPICAL SENSITIVITY: 0.909 abs-sec for 100 ng/mL standard.

7.6. Copper

METHOD: Graphite furnace atomic absorption

INSTRUMENT: Perkin-Elmer Model 5000; no background correction

SAMPLE DIGEST: Microwave, 6 mL HF + 2 mL aqua regia: final volume, 50 mL saturated H_3BO_3.

SAMPLE WEIGHT: 0.2 - 0.3 g (dry weight)

SPECTROPHOTOMETER SETTINGS:

Lamp:	HCL, 25 ma; continuous energy: 65
Wavelength:	324.7 nm
Slit Width:	0.7 nm
Read Delay:	0 sec
Integration Time:	5 sec
Integration:	Peak area
Replicate Injections:	3

FURNACE CONDITIONS:

Pyrolytic grooved graphite tube with L'vov solid pyrolytic platform

Carrier Gas: Argon (prepurified)

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
1	120	15	30	300
2	450	15	10	300
3	900	1	10	300
4	2000	0	10	0
5	2400	1	5	300
6	20	1	20	300

STANDARDS: 50, 100, 200, 300, 500, 1000, and 2000 ng/mL in HF/aqua regia/boric acid.

MATRIX MODIFIERS: None

INJECTION VOLUME: 20 µL

CALIBRATION: 7 point (standards) best fit quadratic calibration line.

TYPICAL SENSITIVITY: 0.296 abs-sec for 50 ng/mL standard.

7.7. Iron

METHOD:	Atomic Absorption, Acetylene Flame
INSTRUMENT:	Perkin-Elmer Model 5000; deuterium background correction
SAMPLE DIGEST:	Microwave, 6 mL HF + 2 mL aqua regia: final volume, 50 mL saturated H_3BO_3.
SAMPLE WEIGHT:	0.2 - 0.3 g (dry weight)

SPECTROPHOTOMETER SETTINGS:

Lamp:	HCL, 25 ma; continuous energy: 68
Wavelength:	248.3 nm
Slit Width:	0.7 nm
Integration Time:	5 sec
Integration:	Peak area
Replicate Injections:	3
Nebulization:	Glass impact bead
Flame:	Air/acetylene, 20:30

STANDARDS:	50, 100, 200, 400, 600, 800, and 1000 µg/mL in HF/aqua regia/boric acid.
MATRIX MODIFIERS:	None
CALIBRATION:	7 point (standards) best fit quadratic calibration line.
TYPICAL SENSITIVITY:	0.188 abs-sec for 100 µg/mL standard.

7.8. Iron

METHOD:	Atomic Absorption, Acetylene Flame
INSTRUMENT:	Perkin-Elmer Model 5100; no background correction
SAMPLE DIGEST:	Microwave, 6 mL HF + 2 mL aqua regia: final volume, 50 mL saturated H_3BO_3.
SAMPLE WEIGHT:	0.2 - 0.3 g (dry weight)

SPECTROPHOTOMETER SETTINGS:

Lamp:	HCL, 30 ma; continuous energy: 71
Wavelength:	373.7 nm
Slit Width:	0.2 nm
Integration Time:	5 sec
Integration:	Peak area
Replicate Injections:	3
Nebulization:	Glass impact bead
Flame:	Air/acetylene, 9.9:2.0

STANDARDS:	50, 100, 400, and 600 µg/mL in HF/aqua regia/boric acid.
MATRIX MODIFIERS:	None
CALIBRATION:	Two-coefficient least squares fit calibration line performed by instrument computer using above standards. Reslope or calibrate after 10-20 samples.
TYPICAL SENSITIVITY:	0.257 abs-sec for 100 µg/mL standard.

7.9. Mercury

METHOD: Atomic Absorption, Cold Vapor

INSTRUMENT: Perkin-Elmer Model 5000; deuterium background correction

SAMPLE DIGEST: Microwave 6 mL HF + 2 mL aqua regia: final volume, 50 mL saturated H_3BO_3.

SAMPLE WEIGHT: 0.2 - 0.3 g (dry weight)

SPECTROPHOTOMETER SETTINGS:

Lamp:	EDL, 5 watts; continuous energy: 66
Wavelength:	253.6 nm
Slit Width:	0.7 nm

RECORDER SETTINGS:

Expansion:	1
Integration Time:	Peak height
Recorder Time Constant:	1 sec

VAPOR GENERATION PARAMETERS:

1.5 % HCl (10 mL)
5.0% $KMnO_4$ (approximately 150 µL)
Carrier Gas: argon (maximum flow: 1100 mL/min)
Reductant: 3% $NaBH_4$ in 1% NaOH added until maximum peak height is obtained

STANDARDS: 1.0, 2.0, 4.0, 6.0, 14.0, 20.0 ng/mL in HF/aqua regia/boric acid.

INJECTION VOLUME: 2.0 mL

CALIBRATIONS: 6 point (standards) best fit linear calibration line.

TYPICAL SENSITIVITY: 0.254 abs-sec for 14.0 ng/mL standard.

7.10. Manganese

METHOD:	Atomic Absorption, Acetylene Flame
INSTRUMENT:	Perkin-Elmer Model 5000; deuterium background correction
SAMPLE DIGEST:	Microwave, 6 mL HF + 2 mL aqua regia: final volume, 50 mL saturated H_3BO_3.
SAMPLE WEIGHT:	0.2 - 0.3 g (dry weight)

SPECTROPHOTOMETER SETTINGS:

Lamp:	HCL, 20 ma; continuous energy: 58
Wavelength:	279.5 nm
Slit Width:	0.2 nm
Integration Time:	5 sec
Integration:	Peak area
Replicate Injections:	3
Nebulization:	Glass impact bead
Flame:	Air/acetylene, 25:30

STANDARDS:	0.5, 1.0, 4.0, and 8.0 µg/mL in HF/aqua regia/boric acid.
MATRIX MODIFIERS:	None
CALIBRATION:	4 point (standards) best fit linear calibration line.
TYPICAL SENSITIVITY:	0.224 abs-sec for 4.0 µg/mL standard.

7.11. Nickel

METHOD: Graphite furnace atomic absorption

INSTRUMENT: Perkin-Elmer Model 5000; no background correction

SAMPLE DIGEST: Microwave, 6 mL HF + 2 mL aqua regia: Final volume, 50 mL saturated H_3BO_3.

SAMPLE WEIGHT: 0.2 - 0.3 g (dry weight)

SPECTROPHOTOMETER SETTINGS:

Lamp:	HCL, 25 ma; continuous energy: 52
Wavelength:	232.0 nm
Slit Width:	0.2 nm
Read Delay:	0 sec
Integration Time:	5 sec
Integration:	Peak area
Replicate Injections:	3

FURNACE CONDITIONS:

Pyrolytic grooved graphite tube with L'vov solid pyrolytic platform

Carrier Gas: Argon (prepurified)

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
1	120	15	30	300
2	450	15	10	300
3	1000	1	10	300
4	2400	0	10	0
5	2550	1	5	300
6	20	1	20	300

STANDARDS: 5, 15, 30, 60, 90, 150, and 300 ng/mL in HF/aqua regia/boric acid.

MATRIX MODIFIERS: 5 µL of 10 µg $Mg(NO_3)_2$/µL.

INJECTION VOLUME: 20 µL

CALIBRATION: 7 point (standards) best fit quadratic calibration line.

TYPICAL SENSITIVITY: 0.236 abs-sec for 300 ng/mL standard.

7.12. Lead

METHOD: Graphite furnace atomic absorption

INSTRUMENT: Perkin-Elmer Model 5100; Zeeman background correction

SAMPLE DIGEST: Microwave, 6 mL HF + 2 mL aqua regia: final volume, 50 mL saturated H_3BO_3.

SAMPLE WEIGHT: 0.2 - 0.3 g (dry weight)

SPECTROPHOTOMETER SETTINGS:

Lamp:	EDL, 10 watts, modulated energy: 68
Wavelength:	283.3 nm
Slit Width:	0.7 nm
Read Delay:	0 sec
Integration Time:	5 sec
Integration:	Peak area
Replicate Injections:	3

FURNACE CONDITIONS:

Pyrolytic grooved graphite tube with L'vov solid pyrolytic platform

Carrier Gas: Argon (prepurified)

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
1	130	5	45	300
2	600	5	60	300
3	20	1	20	300
4	1600	0	5	0
5	2650	1	5	300
6	20	1	1 0	300

STANDARDS: 0, 10, 20, 40, 80, and 160 ng/mL HF/aqua regia/boric acid.

MATRIX MODIFIERS: 0.2 mg $NH_4H_2PO_4$ [5 µL of 40 µg/µL]
2 µL of 5 µg $Mg(NO_3)_2$/µL

INJECTION VOLUME: 20 µL

CALIBRATION: Two-coefficient least squares fit calibration line performed by instrument computer using above standards. Reslope or calibrate after 10-20 samples.

TYPICAL SENSITIVITY: 0.204 abs-sec for 40 ng/mL standard.

7.13. Antimony

METHOD: Graphite furnace atomic absorption

INSTRUMENT: Perkin-Elmer Model 5100; Zeeman background correction

SAMPLE DIGEST: Microwave, 6 mL HF + 2 mL aqua regia: final volume, 50 mL saturated H_3BO_3.

SAMPLE WEIGHT: 0.2 - 0.3 g (dry weight)

SPECTROPHOTOMETER SETTINGS:

Lamp:	EDL, 8 watts; continuous energy: 62
Wavelength:	217.6 nm
Slit Width:	2.0 nm
Read Delay:	0 sec
Integration Time:	5 sec
Integration:	Peak area
Replicate Injections:	3

FURNACE CONDITIONS:

Pyrolytic grooved graphite tube with L'vov solid pyrolytic platform

Carrier Gas: Argon (prepurified)

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
1	130	5	45	300
2	900	5	40	300
3	20	1	20	300
4	2200	0	5	0
5	2650	1	5	300
6	20	1	10	300

STANDARDS: 15, 30, 60, and 90 ng/mL in HF/aqua regia/boric acid.

MATRIX MODIFIERS: 0.02 mg Ni^{+2} [5 µL of 19.8 µg $Ni(NO_3)_2 \cdot 6H_20$/µL]

INJECTION VOLUME: 20 µL

CALIBRATION: Two-coefficient least squares fit calibration line performed by instrument computer using above standards. Reslope or calibrate after 10-20 samples.

TYPICAL SENSITIVITY: 0.188 abs-sec for 60 ng/mL std.

7.14. Selenium

METHOD: Graphite furnace atomic absorption

INSTRUMENT: Perkin-Elmer Model 5100; Zeeman background correction

SAMPLE DIGEST: Microwave, 6 mL HF + 2 mL aqua regia: final volume, 50 mL saturated H_3BO_3.

SAMPLE WEIGHT: 0.2 - 0.3 g (dry weight)

SPECTROPHOTOMETER SETTINGS:

Lamp:	EDL, 6 watts, modulated energy: 63
Wavelength:	196.0 nm
Slit Width:	0.7 nm
Read Delay:	0 sec
Integration Time:	5 sec
Integration:	Peak area
Replicate Injections:	3

FURNACE CONDITIONS:

Pyrolytic grooved graphite tube with L'vov solid pyrolytic platform

Carrier Gas: Argon (prepurified)

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
1	130	5	40	300
2	600	5	45	300
3	20	1	20	300
4	2200	0	5	0
5	2650	1	5	300
6	20	1	10	300

STANDARDS: 0,15, 30, 60, 80, and 100 ng/mL in HF/aqua regia/boric acid.

MATRIX MODIFIERS: 5 µL of 4 µg/µL $Ni(NO_3)_2$
5 µL of 5 µg $Mg(NO_3)_2$/µL

INJECTION VOLUME: 20 µL

CALIBRATION: Two-coefficient least squares fit calibration line performed by instrument computer using above standards. Reslope or calibrate after 10-20 samples.

TYPICAL SENSITIVITY: 0.130 abs-sec for 60 ng/mL standard.

7.15. Tin

METHOD: Hydride generation atomic absorption

INSTRUMENT: Perkin-Elmer Model 5000; no background correction

SAMPLE DIGEST: Microwave, 6 mL HF + 2 mL aqua regia: final volume, 50 mL saturated H_3BO_3.

SAMPLE WEIGHT: 0.2 - 0.3 g (dry weight)

HYDRIDE REACTION MIXTURE:

1 mL sample digestate + 50 mL Milli-Q water + 0.5 mL 2 N acetic acid + 3 mL 3% $NaBH_4$ in 1% NaOH. The $NaBH_4$ was added slowly using a syringe.

SPECTROPHOTOMETER SETTINGS:

Lamp:	EDL, 8 watts, continuous energy: 48
Wavelength:	224.6 nm
Slit Width:	0.7 nm
Read Delay:	5 sec
Integration Time:	1 sec
Integration:	Peak area
Replicate Injections:	2

FURNACE CONDITIONS:

Non-grooved, uncoated graphite tube with enlarged port (9/64 inch)

Carrier Gas: Argon (prepurified)

FURNACE PROGRAM (A and B):

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
Introducing the SnH_4 into the graphite tube				
A-1	700	20	360	0
Atomization of the SnH_4				
B-1	300	10	5	300
B-2	2400	0	4	0
B-3	2500	1	4	300
B-4	20	1	20	300

STANDARDS: 5, 10, 20, and 80 ng/L in HF/aqua regia/boric acid.

CALIBRATION: 4 point (standards) best fit quadratic calibration line.

TYPICAL SENSITIVITY: 0.224 abs-sec for 20 ng/L standard.

7.16. Tin

METHOD: Atomic Absorption, Hydride Generation

INSTRUMENT: Perkin-Elmer Model 5000; no background correction

SAMPLE DIGEST: Microwave, 6 mL HF + 2 mL aqua regia: final volume, 50 mL saturated H_3BO_3.

SAMPLE WEIGHT: 0.2 - 0.3 g (dry weight)

SPECTROPHOTOMETER SETTINGS:

Lamp:	EDL, 8 watts; continuous energy: 48
Wavelength:	224.6 nm
Slit Width:	0.7 nm:
Integration Time:	5 sec
Read Delay:	1 sec
Integration:	Peak area
Replicate Injections:	2

FURNACE CONDITIONS:

Non-grooved, uncoated graphite tube, drilled 9/64" bit

RECORDER SETTINGS:

Expansion:	1
Integration Time:	5 sec
Time Constant:	1 sec

VAPOR GENERATION PARAMETERS:

In Chamber/bubbler system (with quartz tip in graphite tube)
50 mL MilliQ water
0.5 mL Acetic acid (2N)
1.0 mL sample
3.0 mL of 3% $NaBH_4$ in 1% NaOH added slowly (45 sec) using a syringe
Carrier Gas: prepurified argon

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
A-1	700	20	360	0
(with quartz tip removed from graphite tube)				
B-1	300	10	5	300
B-2	2400	0	4	0
B-3	2500	1	4	300
B-4	20	1	20	300

STANDARDS: 5, 10, 20, and 80 ng/mL in HF/aqua regia/boric acid.

CALIBRATION:	4 point (standards) best fit linear calibration line.
TYPICAL SENSITIVITY:	0.224 abs-sec for 20 ng/mL standard.

7.17. Zinc

METHOD:	Atomic Absorption, Acetylene Flame
INSTRUMENT:	Perkin-Elmer Model 5000; no background correction
SAMPLE DIGEST:	Microwave, 6 mL HF + 2 mL aqua regia: final volume, 50 mL saturated H_3BO_3.
SAMPLE WEIGHT:	0.2 - 0.3 g (dry weight)

SPECTROPHOTOMETER SETTINGS:

Lamp:	EDL, 7.0 watts; continuous energy: 51
Wavelength:	213.9 nm
Slit Width:	0.7 nm
Integration Time:	5 sec
Integration:	Peak area
Replicate Injections:	3
Nebulization:	Glass impact bead
Flame:	air/acetylene, 20:30

STANDARDS:	0.1, 0.5, 2.0, 4.0, and 8.0 µg/mL in HF/aqua regia/boric acid.
CALIBRATION:	5 point (standards) best fit quadratic calibration line.
TYPICAL SENSITIVITY:	0.345 abs-sec for 2.0 µg/mL standard.

8. TISSUES

8.1. Silver

METHOD: Graphite furnace atomic absorption

INSTRUMENT: Perkin-Elmer Model 5100; Zeeman background correction

SAMPLE DIGEST: Microwave, 10 mL HNO_3 + 4 mL H_2O_2: final volume, 25 mL.

SAMPLE WEIGHT: 0.2 - 0.3 g (dry weight)

SPECTROPHOTOMETER SETTINGS:

Lamp:	HCL, 10 ma;, modulated energy: 65
Wavelength:	328.1 nm
Slit Width:	0.7 nm
Read Delay:	0 sec
Integration Time:	4 sec
Integration:	Peak area
Replicate Injections:	3

FURNACE CONDITIONS:

Pyrolytic grooved graphite tube with L'vov solid pyrolytic platform

Carrier Gas: Argon (prepurified)

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
1	130	5	45	300
2	700	5	40	300
3	20	1	20	300
4	1700	0	5	0
5	2650	1	5	300
6	20	1	10	300

STANDARDS: 0, 0.5, 1.0, 2.0, 4.0, 3.0, and 6.0 ng/mL in HNO_3.

MATRIX MODIFIERS: 0.2 mg $NH_4H_2PO_4$ [5 µL of 40 µg/µL]

INJECTION VOLUME: 20 µL

CALIBRATION: Two-coefficient least squares fit calibration line performed by instrument computer using above standards. Reslope or calibrate after 10-20 samples.

TYPICAL SENSITIVITY: 0.182 abs-sec for 6 ng/mL standard.

8.2. Aluminum

METHOD: Graphite furnace atomic absorption

INSTRUMENT: Perkin-Elmer Model 5000; deuterium background correction

SAMPLE DIGEST: Microwave, 10 mL HNO_3 + 4 mL H_2O_2: final volume, 25 mL.

SAMPLE WEIGHT: 0.2 - 0.3 g (dry weight)

SPECTROPHOTOMETER SETTINGS:

Lamp:	HCL, 25 ma; continuous energy: 62
Wavelength:	309.3 nm
Slit Width:	0.7 nm
Read Delay:	0 sec
Integration Time:	5 sec
Integration:	Peak area
Replicate Injections:	3

FURNACE CONDITIONS:

Pyrolytic grooved graphite tube with L'vov solid pyrolytic platform

Carrier Gas: Argon (prepurified)

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas Flow (mL/min)	
		Ramp	Hold		
1	120		15	30	300
2	450		15	10	300
3	1700		1	10	300
4	2400		0	10	0
5	2500		1	5	300
6	20		1	20	300

STANDARDS: 10, 50, 100, 300, 600, 1000, 2000, and 4000 ng/mL in HNO_3.

MATRIX MODIFIERS: 5 µL of 10 µg $Mg(NO_3)_2$/µL

INJECTION VOLUME: 20 µL

CALIBRATION: 8 point (standards) best fit quadratic calibration line.

TYPICAL SENSITIVITY: 0.205 abs-sec for 300 ng/mL standard.

8.3. Arsenic

METHOD: Graphite furnace atomic absorption

INSTRUMENT: Perkin-Elmer Model 5100; Zeeman background correction

SAMPLE DIGEST: Microwave, 10 mL HNO_3 + 4 mL H_2O_2: final volume, 25 mL.

SAMPLE WEIGHT: 0.2 - 0.3 g (dry weight)

SPECTROPHOTOMETER SETTINGS:

Lamp:	EDL, 8 watts, modulated energy: 65
Wavelength:	193.7 nm
Slit Width:	0.7 nm
Read Delay:	0 sec
Integration Time:	4 sec
Integration:	Peak area
Replicate Injections:	3

FURNACE CONDITIONS:

Pyrolytic grooved graphite tube with L'vov solid pyrolytic platform

Carrier Gas: Argon (prepurified)

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
1	130	5	40	300
2	700	5	45	300
3	20	1	20	300
4	2500	0	5	0
5	2650	1	5	300
6	20	1	10	300

STANDARDS: 0, 15, 30, 60, and 90 ng/mL in HNO_3.

MATRIX MODIFIERS: 0.02 mg Ni^{+2} [5 µL of 19.8 µg $Ni(NO_3)_2 \cdot 6H_20$/µL]

INJECTION VOLUME: 20 µL

CALIBRATION: Two-coefficient least squares fit calibration line performed by instrument computer using above standards. Reslope or calibrate after 10-20 samples.

TYPICAL SENSITIVITY: 0.269 abs-sec for 60 ng/mL standard.

8.4. Cadmium

METHOD: Graphite furnace atomic absorption

INSTRUMENT: Perkin-Elmer Model 5100; Zeeman background correction

SAMPLE DIGEST: Microwave, 10 mL HNO_3 + 4 mL H_2O_2: final volume, 25 mL.

SAMPLE WEIGHT: 0.2 - 0.3 g (dry weight)

SPECTROPHOTOMETER SETTINGS:

Lamp:	EDL, 5 watts, modulated energy: 64
Wavelength:	193.7 nm
Slit Width:	0.7 nm
Read Delay:	0 sec
Integration Time:	4 sec
Integration:	Peak area
Replicate Injections:	3

FURNACE CONDITIONS:

Pyrolytic grooved graphite tube with L'vov solid pyrolytic platform

Carrier Gas: Argon (prepurified)

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
1	130	5	45	300
2	500	5	45	300
3	20	1	20	300
4	1700	0	5	0
5	2650	1	5	300
6	20	1	10	300

STANDARDS: 0, 0.3, 0.6, 1.0, 1.2, and 2.0 ng/mL in HNO_3.

MATRIX MODIFIERS: 0.2 mg $NH_4H_2PO_4$ [5 µL of 40 µg/µL]
2 µL of 5 µg $Mg(NO_3)_2$/µL

INJECTION VOLUME: 20 µL

CALIBRATION: Two-coefficient least squares fit calibration line performed by instrument computer using above standards. Reslope or calibrate after 10-20 samples.

TYPICAL SENSITIVITY: 0.185 abs-sec for 1.2 ng/mL standard.

8.5. Chromium

METHOD: Graphite furnace atomic absorption

INSTRUMENT: Perkin-Elmer Model 5000; no background correction

SAMPLE DIGEST: Microwave, 10 mL HNO_3 + 4 mL H_2O_2: final volume, 25 mL.

SAMPLE WEIGHT: 0.2 - 0.3 g (dry weight)

SPECTROPHOTOMETER SETTINGS:

Lamp:	HCL, 25 ma; continuous energy: 65
Wavelength:	357.9 nm
Slit Width:	0.7 nm
Read Delay:	0 sec
Integration Time:	5 sec
Integration:	Peak area
Replicate Injections:	3

FURNACE CONDITIONS:

Pyrolytic grooved graphite tube with L'vov solid pyrolytic platform

Carrier Gas: Argon (prepurified)

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
1	120	15	30	300
2	450	15	10	300
3	1650	1	10	300
4	2500	0	10	0
5	2600	1	5	300
6	20	1	20	300

STANDARDS: 0.6, 2.0, 4.0, 6.0,10.0, 20.0, 50.0, and 100.0 ng/mL in HNO_3.

MATRIX MODIFIERS: 5 µL of 10 µg $Mg(NO_3)_2$/µL.

INJECTION VOLUME: 20 µL

CALIBRATION: 8 point (standards) best fit linear calibration line.

TYPICAL SENSITIVITY: 0.125 abs-sec for 20.0 ng/mL standard.

8.6. Copper

METHOD: Graphite furnace atomic absorption

INSTRUMENT: Perkin-Elmer Model 5000; no background correction

SAMPLE DIGEST: Microwave, 10 mL HNO_3 + 4 mL H_2O_2: final volume, 25 mL.

SAMPLE WEIGHT: 0.2 - 0.3 g (dry weight)

SPECTROPHOTOMETER SETTINGS:

Lamp:	HCL, 15 ma; continuous energy: 65
Wavelength:	324.7 nm
Slit Width:	0.7 nm
Read Delay:	0 sec
Integration Time:	5 sec
Integration:	Peak area
Replicate Injections:	3

FURNACE CONDITIONS:

Pyrolytic grooved graphite tube with L'vov solid pyrolytic platform.

Carrier Gas: Argon (prepurified)

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
1	120	15	30	300
2	450	15	10	300
3	900	1	10	300
4	2000	0	10	0
5	2400	1	5	300
6	20	1	20	300

STANDARDS: 10, 20, 40, 100, 500, 1000, 2000, and 4000 ng/mL in HNO_3.

MATRIX MODIFIERS: None

INJECTION VOLUME: 20 µL

CALIBRATION: 8 point (standards) best fit quadratic calibration line.

TYPICAL SENSITIVITY: 0.282 abs-sec for 100 ng/mL standard.

8.7. Iron

METHOD: Atomic Absorption, Acetylene Flame

INSTRUMENT: Perkin-Elmer Model 5000; deuterium background correction

SAMPLE DIGEST: Microwave, 10 mL HNO_3 + 4 mL H_2O_2: final volume, 25 mL.

SAMPLE WEIGHT: 0.2 - 0.3 g (dry weight)

SPECTROPHOTOMETER SETTINGS:

Lamp:	HCL, 20 ma; continuous energy: 68
Wavelength:	244.3 nm
Slit Width:	0.7 nm
Integration Time:	5 sec
Integration:	Peak area
Replicate Injections:	3
Nebulization:	Glass impact bead
Flame:	air/acetylene, 20:30

STANDARDS: 0.2, 0.6, 1.0, 2.0, 10.0, 20.0, 40.0, and 100.0 µg/mL in HNO_3.

CALIBRATION: 8 point (standards) best fit quadratic calibration line.

TYPICAL SENSITIVITY: 0.177 abs-sec for 10.0 µg/mL standard.

8.8. Mercury

METHOD: Atomic Absorption, Cold Vapor

INSTRUMENT: Perkin-Elmer Model 5000; deuterium background correction

SAMPLE DIGEST: Microwave 10 mL HNO_3 + 4 mL H_2O_2: final volume 25 mL.

SAMPLE WEIGHT: 0.2 - 0.3 g (dry weight)

SPECTROPHOTOMETER SETTINGS:

Lamp:	EDL, 5 watts; continuous energy: 66
Wavelength:	253.6 nm
Slit Width:	L

RECORDER SETTINGS:

Expansion:	1
Integration Time:	peak height
Recorder Time Constant:	1 sec

VAPOR GENERATION PARAMETERS:

1.5 % HCl (10 mL)
5.0% $KMnO_4$ (approximately 150 µL)
Carrier Gas: argon (maximum flow: 1100 mL/min)
Reductant: 3% $NaBH_4$ in 1% NaOH added until maximum peak height is obtained

STANDARDS: 2, 6, 10, and 16 ng/mL in HNO_3.

INJECTION VOLUME: 2.0 mL

CALIBRATIONS: 8 point (standards) best fit quadratic calibration line.

TYPICAL SENSITIVITY: 0.044 abs-sec for 10.0 ng/mL standard.

8.9. Manganese

METHOD: Atomic Absorption, Acetylene Flame

INSTRUMENT: Perkin-Elmer Model 5000; deuterium background correction

SAMPLE DIGEST: Microwave, 10 mL HNO_3 + 4 mL H_2O_2: final volume, 25 mL.

SAMPLE WEIGHT: 0.2 - 0.3 g (dry weight)

SPECTROPHOTOMETER SETTINGS:

Lamp:	HCL, 20 ma; continuous energy: 68
Wavelength:	279.5 nm
Slit Width:	0.7 nm
Integration Time:	5 sec
Integration:	Peak area
Replicate Injections:	3
Nebulization:	Glass impact bead
Flame:	air/acetylene, 25:30

STANDARDS: 0.02, 0.06, 0.10, 0.30, 0.50, 1.00, 2.00, and 4.00 µg/mL in HNO_3.

CALIBRATION: 8 point (standards) best fit linear calibration line.

TYPICAL SENSITIVITY: 0.397 abs-sec for 0.06 µg/mL standard.

8.10. Nickel

METHOD: Graphite furnace atomic absorption

INSTRUMENT: Perkin-Elmer Model 5000; no background correction

SAMPLE DIGEST: Microwave, 10 mL HNO_3 + 4 mL H_2O_2: final volume, 25 mL.

SAMPLE WEIGHT: 0.2 - 0.3 g (dry weight)

SPECTROPHOTOMETER SETTINGS:

Lamp:	HCL, 25 ma; continuous energy: 52
Wavelength:	232.0 nm
Slit Width:	0.7 nm
Read Delay:	0 sec
Integration Time:	5 sec
Integration:	Peak area
Replicate Injections:	3

FURNACE CONDITIONS:

Pyrolytic grooved graphite tube with L'vov solid pyrolytic platform

Carrier Gas: Argon (prepurified)

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
1	120	15	30	300
2	450	15	10	300
3	1000	1	10	300
4	2400	0	10	0
5	2500	1	5	300
6	20	1	20	300

STANDARDS: 5, 15, 30, 60, 100, and 200 ng/mL in HNO_3.

MATRIX MODIFIERS: 5 µL of 10 µg $Mg(NO_3)_2$/µL.

INJECTION VOLUME: 20 µL

CALIBRATION: 6 point (standards) best fit linear calibration line.

TYPICAL SENSITIVITY: 0.169 abs-sec for 200 ng/mL standard.

8.11. Lead

METHOD: Graphite furnace atomic absorption

INSTRUMENT: Perkin-Elmer Model 5100; Zeeman background correction

SAMPLE DIGEST: Microwave, 10 mL HNO_3 + 4 mL H_2O_2: final volume, 25 mL.

SAMPLE WEIGHT: 0.2 - 0.3 g (dry weight)

SPECTROPHOTOMETER SETTINGS:

Lamp:	EDL, 10 watts, modulated energy: 68
Wavelength:	283.3 nm
Slit Width:	0.7 nm
Read Delay:	0 sec
Integration Time:	4 sec
Integration:	Peak area
Replicate Injections:	3

FURNACE CONDITIONS:

Pyrolytic grooved graphite tube with L'vov solid pyrolytic platform

Carrier Gas: Argon (prepurified)

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
1	130	5	45	300
2	600	5	60	300
3	20	1	20	300
4	1600	0	5	0
5	2650	1	5	300
6	20	1	10	300

STANDARDS: 0, 10, 20, 40, and 80 ng/mL in HNO_3

MATRIX MODIFIERS: 0.2 mg $NH_4H_2PO_4$ [5 µL of 40 µg/µL]
2 µL of 5 µg $Mg(NO_3)_2$/µL

INJECTION VOLUME: 20 µL

CALIBRATION: Two-coefficient least squares fit calibration line performed by instrument computer using above standards. Reslope or calibrate after 10-20 samples.

TYPICAL SENSITIVITY: 0.219 abs-sec for 40 ng/mL standard.

8.12. Antimony

METHOD: Graphite furnace atomic absorption

INSTRUMENT: Perkin-Elmer Model 5000; deuterium background correction

SAMPLE DIGEST: Microwave, 10 mL HNO_3 + 4 mL H_2O_2: final volume, 25 mL.

SAMPLE WEIGHT: 0.2 - 0.3 g (dry weight)

SPECTROPHOTOMETER SETTINGS:

Lamp:	EDL, 8 watts; continuous energy: 62
Wavelength:	217.6 nm
Slit Width:	2.0 nm
Read Delay:	0 sec
Integration Time:	5 sec
Integration:	Peak area
Replicate Injections:	3

FURNACE CONDITIONS:

Pyrolytic grooved graphite tube with L'vov solid pyrolytic platform

Carrier Gas: Argon (prepurified)

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
1	120	15	30	300
2	450	15	10	300
3	1100	1	10	300
4	2400	0	10	0
5	2500	1	5	300
6	20	1	20	300

STANDARDS: 10, 20, 40, 60, 80, and 100 ng/mL in HNO_3.

MATRIX MODIFIERS: 5 µL of 0.4 µg/µL $PdCl_2$.

INJECTION VOLUME: 20 µL

CALIBRATION: 6 point (standards) best fit quadratic calibration line.

TYPICAL SENSITIVITY: 0.091 abs-sec for 100 ng/mL standard.

8.13. Selenium

METHOD: Graphite furnace atomic absorption

INSTRUMENT: Perkin-Elmer Model 5100; Zeeman background correction

SAMPLE DIGEST: Microwave, 10 mL HNO_3 + 4 mL H_2O_2: final volume, 25 mL.

SAMPLE WEIGHT: 0.2 - 0.3 g (dry weight)

SPECTROPHOTOMETER SETTINGS:

Lamp:	EDL, 6 watts, modulated energy: 65
Wavelength:	196.0 nm
Slit Width:	0.7 nm
Read Delay:	0 sec
Integration Time:	5 sec
Integration:	Peak area
Replicate Injections:	3

FURNACE CONDITIONS:

Pyrolytic grooved graphite tube with L'vov solid pyrolytic Platform

Carrier Gas: Argon (prepurified)

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
1	130	5	40	300
2	600	5	45	300
3	20	1	20	300
4	2200	0	5	0
5	2650	1	5	300
6	20	1	10	300

STANDARDS: 0, 15, 30, 60, 80, and 160 ng/mL in HNO_3.

MATRIX MODIFIERS: 0.02 mg Ni^{+2} [5 µL of 4 µg/µL $Ni(NO_3)_2$]
5 µL of 5 µg $Mg(NO_3)_2$/µL

INJECTION VOLUME: 20 µL

CALIBRATION: Two-coefficient least squares fit calibration line performed by instrument computer using above standards. Reslope or calibrate after 10-20 samples.

TYPICAL SENSITIVITY: 0.197 abs-sec for 60 ng/mL standard.

8.14. Tin

METHOD: Graphite furnace atomic absorption

INSTRUMENT: Perkin-Elmer Model 5000; deuterium background correction

SAMPLE DIGEST: Microwave, 10 mL HNO_3 + 4 mL H_2O_2: final volume, 25 mL.

SAMPLE WEIGHT: 0.2 - 0.3 g (dry weight)

SPECTROPHOTOMETER SETTINGS:

Lamp:	EDL, 8 watts, continuous energy: 45
Wavelength:	224.6 nm
Slit Width:	0.7 nm
Read Delay:	0 sec
Integration Time:	5 sec
Integration:	Peak area
Replicate Injections:	3

FURNACE CONDITIONS:

Pyrolytic grooved graphite tube with L'vov solid pyrolytic Platform

Carrier Gas: Argon (prepurified)

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
1	120	15	30	300
2	450	10	10	300
3	900	1	10	300
4	2100	0	10	0
5	2400	1	5	300
6	20	1	20	300

STANDARDS: 4, 6, 10, 20, 50, and 100 ng/mL in HNO_3.

MATRIX MODIFIERS: 5 µL of 10 µg $Mg(NO_3)_2$/µL.

INJECTION VOLUME: 20 µL

CALIBRATION: 6 point (standards) best-fit quadratic calibration line.

TYPICAL SENSITIVITY: 0.161 abs-sec for 100 ng/mL standard.

8.15. Tin

METHOD: Atomic Absorption, Hydride Generation

INSTRUMENT: Perkin-Elmer Model 5000; no background correction

SAMPLE DIGEST: Microwave 10 mL HNO_3 + 4 mL H_2O_2: final volume 25 mL.

SAMPLE WEIGHT: 0.2 - 0.3 g (dry weight)

SPECTROPHOTOMETER SETTINGS:

Lamp:	EDL, 8 watts; continuous energy: 48
Wavelength:	224.6 nm
Slit Width:	L
Read Delay:	1 sec
Integration Time:	5 sec
Integration:	Peak area
Replicate Injections:	2

FURNACE CONDITIONS:

Non-grooved, uncoated graphite tube, drilled 9/64" bit

RECORDER SETTINGS:

Expansion:	1
Integration Time:	5 sec
Time Constant:	1 sec

VAPOR GENERATION PARAMETERS:

In chamber/bubbler system (with quartz tip in graphite tube)
50 mL MilliQ water
0.5 mL acetic acid (2N)
1.0 mL sample
3.0 mL of 3% $NaBH_4$ in 1% NaOH added slowly (45 sec) using a syringe.
Carrier Gas: prepurified argon

FURNACE PROGRAMS (A and B):

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
A-1	700	20	360	0
(with quartz tip removed from graphite tube)				
B-1	300	10	5	300
B-2	2400	0	4	0
B-3	2500	1	4	300
B-4	20	1	20	300

STANDARDS: 4, 6, 10, 20, 30, 50, 100, and 200 ng/mL in HNO_3.

TYPICAL SENSITIVITY: 0.166 abs-sec for 20 ng/mL standard.

8.16. Zinc

METHOD: Atomic Absorption, Acetylene Flame

INSTRUMENT:	Perkin-Elmer Model 5000; no background correction
SAMPLE DIGEST:	Microwave, 10 mL HNO_3 + 4 mL H_2O_2: final volume, 25 mL.
SAMPLE WEIGHT:	0.2 - 0.3 g (dry weight)

SPECTROPHOTOMETER SETTINGS:

Lamp:	EDL, 6.0 watts; continuous energy: 64
Wavelength:	213.9 nm
Slit Width:	0.7 nm
Integration Time:	5 sec
Integration:	Peak area
Replicate Injections:	3
Nebulization:	Glass impact bead
Flame:	Air/acetylene, 20:30

STANDARDS:	0.1, 0.5, 2.0, 6.0, and 10.0 µg/mL in HNO_3.
CALIBRATION:	5 point (standards) best fit quadratic calibration line.
TYPICAL SENSITIVITY:	0.101 abs-sec for 05 µg/mL standard.

GERG Trace Element Quantification Techniques

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1. INTRODUCTION

This report documents the analytical procedures used for major and minor element analysis of marine sediments and tissue samples collected from the Gulf of Mexico coast of the United States as part of the Mussel Watch Project of NOAA's National Status and Trends Program. These procedures were used by the Department of Oceanography at Texas A&M University to analyze samples collected from 1986 to 1990.

2. EQUIPMENT AND SUPPLIES

2.1. Instrumentation

Perkin-Elmer model Z/3030 atomic absorption spectrophotometer. Perkin-Elmer, Norwalk, CT.
- Printer, Apple Imagewriter. Apple Computer, Cupertino, CA.
- Graphite furnace, Perkin-Elmer HGA-600
- Graphite furnace cooling unit:
  - Constant Temperature Circulator Model FK. Haake, Paramus, NJ.
  - IC-6 refrigeration unit, Lauda water bath. Curtin-Matheson, Houston, TX.
- Autosampler, Perkin-Elmer AS-60
- EDL power supply, Perkin-Elmer Model 040-0354

Perkin-Elmer model 306 atomic absorption spectrophotometer
- Background correction, deuterium arc
- Burner (0040-0146) with standard nebulizer, flow spoiler, and single-slot acetylene (0040-0266) and nitrous oxide (0040-0277) burner heads
- Digital absorbance readout

Atomic absorption spectrophotometer Thermo Jarrell Ash Smith-Heiftje 12. Jarrell Ash, Franklin, MA.
- Printer, FACIT 4513 graphics printer
- Graphite furnace, Thermo Jarrell Ash model 188
- Graphite furnace cooling unit, Bernard Constant Temperature Circulator Model 3500SS
- Autosampler, Thermo Jarrell Ash Model 109619
- Burner with standard nebulizer, flow spoiler, and single-slot acetylene head, 121534-02

Mercury Monitor, Model 1235. Laboratory Data Control Analytical, Riviera Beach, FL.
- Wavelength setting, 254 nm
- Absorbance cell, 30 cm
- Recorder, OmniScribe Model A5101-2. Houston Instruments, Houston, TX.

SpectraSpan VI dc-plasma emission spectrophotometer. Applied Research Laboratories/Fison Instruments, Valencia, CA.
- Spectrometer, Czerny-Tumer with Echelle grating
- Plasma, direct current argon with tungsten and pyrolytic carbon electrodes

Data processing, multitasking, computer-controlled operation with statistics and quality assurance

Ortec pure germanium large volume co-axial detectors, GEM-22170S and 23185-P, with 1.68 KeV and 1332.5 KeV resolution, 22% efficient compared to Nal detector. EG&G Ortec, Oak Ridge, TN.

Nuclear Data model 9900 MCA, implemented on a VAX station II-GPX.

2.2. Supplies

Hollow cathode lamps (HCL). Perkin-Elmer, Norwalk, CT.
Electrodeless discharge lamps (EDL). Perkin-Elmer, Norwalk, CT.
Argon, high-purity (99.999%)
Acetylene, industrial
Nitrous oxide
Graphite tubes, pyrolytically coated, grooved, Perkin-Elmer B010-9322
Graphite tubes, pyrolytically coated, ungrooved, Perkin-Elmer B010-9322
Graphite tubes, pyrolytically coated, ungrooved, Thermo Jarrell Ash 124544-01
L'vov graphite platforms, pyrolytically coated, Perkin-Elmer B010-9324
Autosampler cups, 2 ml, polystyrene, B2713-2. Baxter Scientific Products, McGaw Park, IL.

2.3. Labware

Balance, 0.01 g, Fisher 200 Ainsworth toploader. Fisher Scientific, Pittsburgh, PA.
Balance, 0.01 g, Mettler PC2000.
Balance, analytical, 0.0001 g, Mettler H10.
Balls, 1-cm diam., Teflon
Balls, 3.5-cm diam, Teflon
Bench, clean, with HEPA filter. Liberty Industries, East Berlin, CT.
Bottles, screw-cap bottles, polyethylene, wide-mouth, 1-oz., Nalgene 2104-0001
Digestion vessels, 50-mL, Teflon (PFA), 561-R. Savillex, Minnetonka, MN.
Drying oven, 60°C, NAPCO 332. Curtin-Matheson Scientific, Houston, TX.
Drying oven, 130° C, Thelco
Freeze dryer (Virtis 10-100) and vacuum pump (Welch Duo-Seal 1402B80). Virtis Co., Gardner, NY, and Welch, Skokie, IL.
Jars, large, Teflon
Pipette tips, for Finnpette, Finntip 62. Labsystems
Pipette tips, polypropylene for Eppendorf pipets, 10-100 mL Model 22 34190-1 and 200-1000 mL, 22 35 090-1.
Pipette, Finnpette, adjustable, 1000-5000 ml 9402020. Curtin-Matheson Scientific, Houston, TX.
Pipette, transfer, polyethylene.
Pipettes, Eppendorf, fixed volume: 10-mL, 22350102; 25-mL, 22350307; 50-mL, 22350404; 100-mL, 22350501; 200-mL, 22350609; 500-mL, 22350706; 1000-mL, 22350803.
Vials, snap-cap vials, polystyrene, 5-, 15-, and 40-dram. Baxter Scientific Products, McGaw Park, IL.

2.4. Reagents

Ammonium dihydrogen phosphate ($NH_4H_2PO_4$) [7722-76-1], Spectropure Grade, P30. Spex, Edison, NJ.
Ascorbic acid ($C_6H_8O_6$) [50-81-7], A-7506. Sigma, St. Louis, MO.
Boric acid (H_3BO_3) [10043-35-3], 10659, Grade 1. Johnson Matthey, West Chester, PA.
Citric acid ($C_6H_8O_7$) [77-92-9], 0110. J. T. Baker, Phillipsburg, NJ.

Hydrochloric acid (HCl) [7647-01-0], concentrated (37%), Ultrex 6900-05. J. T. Baker, Phillipsburg, NJ.

Hydrofluoric acid (HF) [7664-39-3], concentrated (48%), 9560-06. J. T. Baker, Phillipsburg, NJ.

Magnesium nitrate [$Mg(NO_3)_2 \cdot 6H_20$] [13446-18-9], MG60-50. Spex, Edison, NJ.

Nickel oxide (Ni0) [1313-99-1], powder. Spex, Edison, NJ.

Nitric acid (HNO_3) [7697-37-2], concentrated (70%), 2704-7x6. Mallinckrodt, Paris, KY.

Nitric acid (HNO_3) [7697-37-2], concentrated (70%), Ultrex 6901-05. J. T. Baker, Phillipsburg, NJ.

Palladium metal [7440-05-3], Specpure, 560001. Johnson Matthey, West Chester, PA.

Perchloric acid ($HClO_4$) [7601-90-3], concentrated (70%), Ultrex 4805-01. J. T. Baker, Phillipsburg, NJ.

Stannous chloride, ($SnCl_2 \cdot 2H_2O$) [10025-69-1], 8176. Mallinckrodt, Paris, KY.

Water, redistilled in quartz sub-boiling still.

2.5. Matrix modifiers

Ammonium phosphate: 0.04 g/ml in quartz-distilled water
Ascorbic acid: 2% w/v made with quartz-distilled water
Citric acid: 2% w/v made with quartz-distilled water
Hydroxylamine hydrochloride
Magnesium nitrate: 0.02 g/ml in quartz-distilled water
Palladium nitrate: 1000 mg Pd/ml made by dissolving 0.05 g Pd metal in 2 ml Concentrated Ultrex HNO_3 and diluted to 50 ml with quartz-distilled water

2.6. Standards

Baxter Ricca standards, 1000 ppm. Ricca Chemical Co., Arlington, TX.

Element	Stock number	Element	Stock number
Ag	7100-16UK	Mn	4600-16UK
Al	600-16UK	Ni	5300-16UK
As	800-16UK	Pb	4300-16UK
Cd	1700-16UK	Sb	700-16UK
Cr	2100-16UK	Se	6700-16UK
Cu	2300-16UK	Sn	8500-16UK
Fe	4200-16UK	Zn	9500-16UK
Hg	4800-16UK		

3. SAMPLE TREATMENT

3.1. Oyster tissue

3.1.1. Oyster shucking

Oysters are rinsed with distilled water to remove extraneous material and shucked with a stainless steel knife (using care not to touch the tissue). Tissue is removed with plastic forceps and rinsed with distilled, deionized water to remove sediment particles from gills and exterior tissue surfaces. Oyster soft parts are transferred to a tared Ziploc polyethylene bag, and the number of oysters shucked and placed in the bag is recorded. When all the oysters from a site have been shucked, they are weighed on a top loading balance to measure the total sample wet weight. The pooled samples are placed in a freezer to await further processing.

3.1.2. Bulk homogenizing

Ziploc bags containing pooled frozen oysters are removed from the freezer and allowed to thaw. The entire pooled sample is transferred to an acid-washed Teflon jar and 3 large Teflon balls are added. The Teflon lids are securely tightened and the jars are placed in Ziploc bags and shaken in an industrial paint shaker for 20 minutes. After the bulk sample has been homogenized, an aliquot of the sample is transferred to a clean 40 dram snap vial and frozen.

3.1.3. Freeze drying

The frozen aliquot from the bulk homogenization step is placed in a freeze drier and allowed to dry for several days, depending upon the total mass of oyster tissue being dried at one time. In some cases it is necessary to remove the samples from the freeze drier and drain accumulated water from the trap before continuing with the drying step.

3.1.4. Homogenization of dry aliquot

When samples have been thoroughly dried, three small Teflon balls are inserted into each snap cap vial, the lids are affixed, and the samples are placed in a Spex shaker mill for 1 minute. The Teflon balls are then removed, and the samples stored in closed vials until weighing.

3.1.5. Digestion

Approximately 0.2 gram samples of dried oyster tissue are weighed to the nearest 0.0001 g and transferred to tared, acid-washed Teflon bombs. Three ml of a 3:1 mixture of HNO_3 and $HClO_4$ are added and the bombs are capped loosely and allowed to stand overnight at room temperature. The bombs are then tightened to 18 foot-lbs and placed in a 130 °C oven for a total of approximately 20 hr. During this time, the bombs are periodically removed from the oven, allowed to cool, and vented to release excess pressure. When digestion is complete, the samples are allowed to cool and 18 ml of quartz distilled water is added to each sample. The bombs are closed, mixed by shaking, and weighed to 0.01 g to determine the total solution weight. The digest solution is then transferred to labeled 1 oz polyethylene bottles. Solution density is determined by weighing known volumes with calibrated Eppendorf pipettes in order to determine solution volume.

3.1.6. Displacement volume

Oyster shells are removed from the refrigerator and placed into a displacement cylinder containing distilled water. Water escaping from the cylinder as shells are added is captured in a graduated cylinder. When the water flow ceases the volume of displaced water is recorded. Shells are then removed from the cylinder, placed in plastic bags, and returned to the refrigerator.

3.2. Bottom sediment

Bottom sediment samples are prepared for atomic absorption analysis and activation analysis by freeze drying and wet digestion.

3.2.1. Homogenization

Wet bulk sediment is stored frozen until sample processing begins. Sediment is thawed and then homogenized with a clean plastic spatula. A homogeneous aliquot of the bulk sample is

transferred to a labeled 40 dram snap cap vial and frozen. The remainder of the sample is archived in the freezer.

3.2.2. Freeze drying

The snap cap vial containing the sediment sub-sample is placed in a freeze drier for the period of time required for complete drying. Depending upon the amount of water in the freeze drier, this may range from 12-76 hr.

3.2.3. Homogenization of dry aliquot

In some cases, homogenization of freeze dried sediment can be accomplished by simply placing the snap cap vials in a Spex shaker. When this is not sufficient, the samples are individually ground in alumina mortar and pestles and the powdered samples are returned to the vials in which they were freeze dried.

3.2.4. Digestion

Approximately 0.2 grams of homogenized, dried sediment are weighed to the nearest 0.0001 g and transferred to tared, acid-washed Teflon bombs. Three ml of a 3:1 mixture of HNO_3 and $HClO_4$ are added and the bombs are tightened to 18 foot-lbs and placed in a 130° C oven for a total of approximately 12 hr. During this time, the bombs are periodically removed from the oven, allowed to cool, and vented to release excess pressure. After this period, the bombs are removed from the oven and allowed to cool. Two ml of concentrated HF are added and the bombs are retightened and returned to the oven for 12 hr. After cooling, 18 ml of 4% boric acid are added and the bombs are retightened and returned to the oven for another 12 hr. After the samples are allowed to cool, the bombs are mixed by shaking and weighed to 0.01 g to determine the total solution weight. The digest solution is then transferred to labeled 1 oz polyethylene bottles. Solution density is determined by weighing known volumes with calibrated Eppendorf pipettes in order to determine solution volume. At this point, a 20-fold dilution is made for FAAS analysis of Al, Fe, Mn, Si, and Zn. One ml of digest solution is diluted with 19 ml of an acidified seawater solution containing 2:1:17 proportions of seawater:HNO_3:deionized water.

4. CALIBRATION AND ANALYSIS

Calibration standards are prepared by serial dilution of commercially available atomic absorption standards using calibrated micropipettes, new snap-cap vials, a top loading balance, and 2 N HNO_3. Concentrations of working standards are verified by comparison with US EPA water quality trace metal standards.

In all cases, final working standards are made up in an acid matrix that matches that of the samples being analyzed. For some elements, it is necessary to further attempt to match the major ion composition of the samples; this is most apparent in graphite furnace AAS when the peak shape of the samples is significantly different from that of the standards. For example, the standards may have a relatively broad, Gaussian-shaped peak while the sediment samples may have an extremely sharp peak indicative of rapid volatilization of the metal. In this case, the standards are made up in a solution that has Si, Al, Fe, Ca, and Mg added at final concentrations of 3000, 400, 200, 100, and 100 ppb, respectively.

For graphite furnace atomic absorption analysis, standards were placed in positions 1 - 4 of the autosampler tray, and samples and associated quality control samples in positions 5 - 40.

Matrix modifiers are placed in positions 0 and 40 if necessary. Analysis begins with position 1, thus standards are analyzed first. After the samples in positions 16, 28, and 40, the standards are rerun before sample analysis continues. After one tray is finished, another tray is placed on the autosampler and analysis is begun in position 5.

5. CALCULATIONS

Trace metal concentrations are calculated by comparing analytical signals of unknowns with those of calibration standards, and then multiplying the observed concentration by the instrumental and digestion dilution factors.

Obtain the least-squares fit of the data, treating Abs (or Abs-sec) as the dependent variable ("y"), and concentration as the dependent variable ("x"). If the concentration range extends into the non-linear range, a second order fit must be used. Calculate the intercept, the first and second order coefficients (if appropriate), and R, the correlation coefficient.

$$Abs = a + b\ (conc_{obs})$$

$$conc_{obs} = \frac{Abs - a}{b}$$

5.1. Concentration

The Perkin-Elmer Z3030 used in much of this project incorporates a patented curve-fitting routine, and is described here. In this method, the concentration is determined as

$$C = \frac{K_1\ A + K_3\ A^2}{K_2\ A - 1}$$

where C is the concentration, A is the absorbance-sec, and K_1, K_2, and K_3 are the coefficients determined by solution of simultaneous equations or by the method of least squares.

In our laboratory, the instrument is allowed to auto-select the appropriate equation to fit the data. In all cases, the standard curve is computed from a blank and three standards that are equally spaced from zero to the maximum concentration. For example, concentrations might be 0, 1, 2, and 3 ppb. If the highest standard is within 15% of the value expected from extrapolation of the lowest standard, a 2-coefficient equation is used. If the highest standard is not within 15% of the value expected from extrapolation of the lowest standard, a 3-coefficient equation is used. Because of the number of standards analyzed, the 2-coefficient equation is calculated via least squares regression and the 3-coefficient equation via solution of simultaneous equations. The instrument has the capability to perform a "reslope" based on a single point, however, our recalibrations always involved completely rerunning all standards. Comparison of observed values predicted by the Perkin-Elmer curve fitting routine with those calculated independently by least squares shows insignificant differences that are within rounding errors of the printout.

5.2. Dilution factor

Calculate the dilution factor, DF, resulting from sample digestion using the equation

$$DF = \frac{[(\text{bomb tot}) - (\text{bomb tare})]}{(\text{spl wt}) \times (\text{soln dens})}$$

where bomb tare is the tare weight of the digestion vessel (g); bomb tot is the total weight of the digestion vessel plus digest solution (g); spl wt is the weight of the dry sample (g); and soln dens is the density of the digest solution (g/cm^3).

5.3. Concentration

The concentration in the original sample was calculated according to the relationship:

If $conc_{obs} < DL$, final concentration $\leq (DL)\ (DF_{instr})\ (DF_{dign})$

If $conc_{obs} \geq DL$, final concentration = $(conc_{obs})\ (DF_{instr})\ (DF_{dign})$

where $conc_{obs}$ is the concentration observed in the aqueous sample. DL is the detection limit of the analytical technique; DF_{instr} is the dilution factor of the analytical technique, if necessary; and DF_{dign} is the dilution factor of the sample digestion.

6. INSTRUMENTAL ANALYSIS

6.1. Mercury

METHOD: Cold vapor atomic absorption

INSTRUMENTATION: Laboratory Data Control Model 1205 Spectrophotometer with 30-cm path length gas cell.

ATOMIC ABSORPTION SPECTROPHOTOMETER SETTINGS:

Wavelength:	254 nm
Lamp:	Low pressure, hot cathode Hg lamp
Peak measurement:	Peak height (absorbance)
Range:	0.2 absorbance units
Output:	To strip chart recorder, 10 mV full scale

Reaction Conditions:

Sample volume:	1 ml
Reductant:	10% $SnCl_2$
Reductant volume	0.1 ml
Reaction vessel	25 ml Erlenmeyer flask

STANDARDS: 0, 0.5, 1.0, and 2.0 ppb prepared from 1000 ppm Ricca standard in 0.2 M HNO_3 / 0.1 M HCl.

APPROXIMATE SENSITIVITY: Approximately 0.160 Abs for 1 mL of 2 ng/mL solution.

6.2. Aluminum

METHOD: Flame atomic absorption

INSTRUMENTATION: Atomic absorption spectrophotometer Perkin-Elmer 306

ATOMIC ABSORPTION SPECTROPHOTOMETER SETTINGS:

Wavelength:	309.3 nm
Slit width:	0.7 nm
Lamp:	Al HCL, 10 mA
Background correction:	Deuterium arc
Peak measurement:	Peak height (absorbance)
Read mode:	Peak

FLAME SETTINGS:

Fuel:	Acetylene
Oxidant:	Nitrous oxide
Flame:	Oxidizing
Burner:	Single slot, 5.5 cm, parallel

STANDARDS: 0, 10, 30, and 50 ppm prepared from 1000 ppm Ricca standard in 0.2 M HNO_3.

MATRIX MODIFIERS: Samples and standards are spiked with La (prepared from $LaCl_3$) to a final concentration of 1000-2000 ppm La to suppress ionization interferences.

APPROXIMATE SENSITIVITY: 50 µg/ml gives approximately 0.200 Abs.

6.3. Copper

METHOD: Flame atomic absorption

INSTRUMENTATION: Atomic absorption spectrophotometer Perkin-Elmer 306

ATOMIC ABSORPTION SPECTROPHOTOMETER SETTINGS:

Wavelength:	324.7 nm
Slit width:	0.7 nm
Lamp:	Cu HCL, 15 mA
Background correction:	deuterium arc
Peak measurement:	Peak height (absorbance)
Read mode:	Peak

FLAME SETTINGS:

Fuel:	Acetylene
Oxidant:	Air
Flame:	Oxidizing
Burner:	Single slot, 10 cm, parallel

STANDARDS: 0, 1, 2.5, and 5 ppm prepared from 1000 ppm Ricca standard in 0.2 M HNO_3.

APPROXIMATE SENSITIVITY: 2 µg/ml gives approximately 0.125 Abs.

6.4. Iron

METHOD: Flame atomic absorption

INSTRUMENTATION: Atomic absorption spectrophotometer Perkin-Elmer 306

ATOMIC ABSORPTION SPECTROPHOTOMETER SETTINGS:

Wavelength:	248.3 nm
Slit width:	0.2 nm
Lamp:	Fe HCL, 18 mA
Background correction:	Deuterium arc
Peak measurement:	Peak height (absorbance)
Read mode:	Peak

FLAME SETTINGS:

Fuel:	Acetylene
Oxidant:	Air
Flame:	Oxidizing
Burner:	Single slot, 10 cm, parallel

STANDARDS: 0, 0.5, 1.0, 2.0, 3.0, 4.0, and 5.0 ppm prepared from 1000 ppm Ricca standard in 0.2 M HNO_3.

APPROXIMATE SENSITIVITY: 3 µg/ml gives approximately 0.100 Abs.

6.5. Manganese

METHOD: Flame atomic absorption

INSTRUMENTATION: Atomic absorption spectrophotometer Perkin-Elmer 306

ATOMIC ABSORPTION SPECTROPHOTOMETER SETTINGS:

Wavelength:	279.5 nm
Slit width:	0.2 nm
Lamp:	Mn HCL, 20 mA
Background correction:	Deuterium arc
Peak measurement:	Peak height (absorbance)
Read mode:	Peak

FLAME SETTINGS:

Fuel:	Acetylene
Oxidant:	Air
Flame:	Oxidizing
Burner:	Single slot, 10 cm, parallel

STANDARDS: 0, 0.4, 0.8, and 1.2 ppm prepared from 1000 ppm Ricca standard in 0.2 M HNO_3.

APPROXIMATE SENSITIVITY: 1 µg/ml gives approximately 0.100 Abs.

6.6. Zinc

METHOD: Flame atomic absorption

INSTRUMENTATION: Atomic absorption spectrophotometer Perkin-Elmer 306

ATOMIC ABSORPTION SPECTROPHOTOMETER SETTINGS:

Wavelength:	213.9 nm
Slit width:	0.7 nm
Lamp:	Zn HCL, 15 mA
Background correction:	Deuterium arc
Peak measurement:	Peak height (absorbance)
Read mode:	Peak

FLAME SETTINGS:

Fuel:	Acetylene
Oxidant:	Air
Flame:	Oxidizing
Burner:	Single slot, 10 cm, parallel

STANDARDS: 0, 0.5, 1.0, and 2.0 ppm prepared from 1000 ppm Ricca standard in 0.2 M HNO_3.

APPROXIMATE SENSITIVITY: 1 µg/ml gives approximately 0.190 Abs.

6.7. Silver

METHOD: Graphite furnace atomic absorption

INSTRUMENTATION:

Spectrophotometer:	Perkin-Elmer Z3030
Graphite furnace:	Perkin-Elmer HGA 600
Autosampler:	Perkin-Elmer AS 60
Printer:	Apple Imagewriter

ATOMIC ABSORPTION SPECTROPHOTOMETER SETTINGS:

Wavelength:	328.1 nm
Slit width:	0.7 nm
Lamp:	Ag HCL, 10 mA
Background correction:	Zeeman effect
Peak measurement:	Peak area
Read delay:	0 sec
Read time:	5 sec
Output:	To printer

GRAPHITE FURNACE SETTINGS:

Tube/platform:	L'vov platform, pyrolytically coated
Carrier gas:	Argon (high purity)

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
1	130	10	50	200
2	900	10	20	200
3	100	1	5	200
4	1400	0	5	0
5	2500	1	4	300

AUTOSAMPLER PROGRAM:

Solution:	Volume (µL):
Sample	20
Blank	0
Modifier 1	10
Modifier 2	0

Number of injections: 1
Recalibrate after positions: 16, 28, and 40

STANDARDS: 0, 3, 6, and 9 ppb prepared from 1000 ppm Ricca standard in 0.2 M HNO_3.

MATRIX MODIFIERS: (1) 2.5 % ammonium phosphate in 1 M HNO_3; prepared from SPEX ammonium dihydrogen orthophosphate
(2) none

APPROXIMATE SENSITIVITY: Approximately 0.130 A-sec for 20 µL of 3 ng/mL.

6.8. Arsenic

METHOD: Graphite furnace atomic absorption

INSTRUMENTATION:

Spectrophotometer:	Perkin-Elmer Z3030
Graphite furnace:	Perkin-Elmer HGA 600
Autosampler:	Perkin-Elmer AS 60
Printer:	Apple Imagewriter

ATOMIC ABSORPTION SPECTROPHOTOMETER SETTINGS:

Wavelengths:	193.7 nm
	197.0 nm (samples with high Al)
Slit width:	0.7 nm
Lamp:	As EDL, 8 W
Background correction:	Zeeman effect
Peak measurement:	Peak area
Read delay:	0 sec
Read time:	4 sec
Output:	To printer

GRAPHITE FURNACE SETTINGS:

Tube/platform:	L'vov platform, pyrolytically coated
Carrier gas:	Argon (high purity)

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
1	130	10	50	200
2	1300	10	10	200
3	100	1	5	200
4	2400	0	4	0
5	2400	1	5	300

AUTOSAMPLER PROGRAM:

Solution:	Volume (µL):
Sample	20
Blank	0
Modifier 1	10
Modifier 2	0

Number of injections: 1
Recalibrate after positions: 16, 28, and 40

STANDARDS:	0, 20, 40, and 60 ppb prepared from 1000 ppm Ricca standard in 0.2 M HNO_3.
MATRIX MODIFIERS	(1) 1:1:1 citric acid (2%): palladium (1000 ppm): Ni (4000 ppm) (2) none
APPROXIMATE SENSITIVITY:	Approximately 0.200 A-sec for 20 µL of 40 ng/mL at 193.7 nm; and 0.100 A-sec at 197.0 nm.

6.9. Cadmium

METHOD: Graphite furnace atomic absorption

INSTRUMENTATION:

Spectrophotometer:	Perkin-Elmer Z3030
Graphite furnace:	Perkin-Elmer HGA 600
Autosampler:	Perkin-Elmer AS 60
Printer:	Apple Imagewriter

ATOMIC ABSORPTION SPECTROPHOTOMETER SETTINGS:

Wavelength:	228.8 nm
Slit width:	0.7 nm
Lamp:	Cd EDL, 5 W
Background correction:	Zeeman effect
Peak measurement:	Peak area
Read delay:	0 sec
Read time:	5 sec
Output:	To printer

GRAPHITE FURNACE SETTINGS:

Tube/platform:	L'vov platform, pyrolytically coated
Carrier gas:	Argon (high purity)

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
1	130	10	35	300
2	350	10	20	300
3	100	1	5	300
4	1300	0	5	0
5	2300	1	4	300

AUTOSAMPLER PROGRAM:

Solution:	Volume (µL):
Sample	10
Blank	0
Modifier 1	5
Modifier 2	0

Number of injections: 1
Recalibrate after positions: 16, 28, and 40

STANDARDS: 0, 1, 2.5, and 4 ppb prepared from 1000 ppm Ricca standard in 0.2M HNO_3.

MATRIX MODIFIERS: (1) 2% citric acid
(2) none

APPROXIMATE SENSITIVITY: Approximately 0.110 A-sec for 10 µL of 1.4 ng/mL.

6.10. Chromium

METHOD: Graphite furnace atomic absorption

INSTRUMENTATION:

Spectrophotometer:	Perkin-Elmer Z3030
Graphite furnace:	Perkin-Elmer HGA 600
Autosampler:	Perkin-Elmer AS 60
Printer:	Apple Imagewriter

ATOMIC ABSORPTION SPECTROPHOTOMETER SETTINGS:

Wavelength:	357.9 nm
Slit width:	0.7 nm
Lamp:	Cr HCL, 25 mA
Background correction:	Zeeman effect
Peak measurement:	Peak area
Read delay:	0 sec
Read time:	5 sec
Output:	To printer

GRAPHITE FURNACE SETTINGS:

Tube/platform:	L'vov platform, pyrolytically coated
Carrier gas:	Argon (high purity)

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
1	130	10	50	200
2	1000	10	20	200
3	100	1	5	200
4	2400	0	5	0
5	2500	1	4	300

AUTOSAMPLER PROGRAM:

Solution:	Volume (µL):
Sample	15
Blank	0
Modifier 1	15
Modifier 2	0

Number of injections: 1
Recalibrate after positions: 16, 28, and 40

STANDARDS: 0, 7, 14, and 21 ppb prepared from 1000 ppm Ricca standard in 0.2 M HNO_3.

MATRIX MODIFIERS: (1) Dilute NH_3, prepared in quartz-distilled water by isothermal distillation
(2) none

APPROXIMATE SENSITIVITY: Approximately 0.160 A-sec with 15 µL of 7 ng/ml.

6.11. Copper

METHOD: Graphite furnace atomic absorption

INSTRUMENTATION:

Spectrophotometer:	Perkin-Elmer Z3030
Graphite furnace:	Perkin-Elmer HGA 600
Autosampler:	Perkin-Elmer AS 60
Printer:	Apple Imagewriter

ATOMIC ABSORPTION SPECTROPHOTOMETER SETTINGS:

Wavelength:	324.8 nm
Slit width:	0.7 nm
Lamp:	Cu HCL, 15 mA
Background correction:	Zeeman effect
Peak measurement:	Peak area
Read delay:	0 sec
Read time:	5 sec
Output:	To printer

GRAPHITE FURNACE SETTINGS:

Tube/platform:	L'vov platform, pyrolytically coated
Carrier gas:	Argon (high purity)

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
1	110	10	35	200
2	500	10	20	200
3	100	1	5	200
4	1600	0	5	0
5	2500	1	4	300

AUTOSAMPLER PROGRAM:

Solution:	Volume (µL):
Sample	10
Blank	0
Modifier 1	5
Modifier 2	0

Number of injections: 1
Recalibrate after positions: 16, 28, and 40

STANDARDS: 0, 20, 40, and 60 ppb prepared from 1000 ppm Ricca standard in 0.2 M HNO_3.

MATRIX MODIFIERS: (1) Citric acid (2%)
(2) none

APPROXIMATE SENSITIVITY: Approximately 0.100 A-sec for 10 µL of 20 ng/mL.

6.12. Nickel

METHOD: Graphite furnace atomic absorption

INSTRUMENTATION:

Spectrophotometer:	Perkin-Elmer Z3030
Graphite furnace:	Perkin-Elmer HGA 600
Autosampler:	Perkin-Elmer AS 60
Printer:	Apple Imagewriter

ATOMIC ABSORPTION SPECTROPHOTOMETER SETTINGS:

Wavelength:	232 nm
Slit width:	0.2 nm
Lamp:	Ni HCL, 25 mA
Background correction:	Zeeman effect
Peak measurement:	Peak area
Read delay:	0 sec
Read time:	5 sec
Output:	To printer

GRAPHITE FURNACE SETTINGS:

Tube/platform:	L'vov platform, pyrolytically coated
Carrier gas:	Argon (high purity)

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas Flow (mL/min)	
		Ramp	Hold		
1	130	10	40	200	
2	1000	10	20	200	
3	100	1	5	200	
4	2200	0	4	0	*
5	2500	1	5	300	

AUTOSAMPLER PROGRAM:

Solution:	Volume (µL):
Sample	20
Blank	0
Modifier 1	5
Modifier 2	0

Number of injections: 1
Recalibrate after positions: 16, 28, and 40

STANDARDS: 0, 15, 30, and 45 ppb prepared from 1000 ppm Ricca standard in 0.2 M HNO_3.

MATRIX MODIFIERS: (1) 2:2:1 Pd (1000 ppm) : La (1000 ppm) : $MgNO_3$ (2 %)
(2) none

APPROXIMATE SENSITIVITY: Approximately 0.150 A-sec for 20 µL of 30 ng/mL.

6.13. Lead

METHOD: Graphite furnace atomic absorption

INSTRUMENTATION:

Spectrophotometer:	Perkin-Elmer Z3030
Graphite furnace:	Perkin-Elmer HGA 600
Autosampler:	Perkin-Elmer AS 60
Printer:	Apple Imagewriter

ATOMIC ABSORPTION SPECTROPHOTOMETER SETTINGS:

Wavelength:	283.3 nm
Slit width:	0.7 nm
Lamp:	Pb EDL, 10 W
Background correction:	Zeeman effect
Peak measurement:	Peak area
Read delay:	0 sec
Read time:	5 sec
Output:	To printer

GRAPHITE FURNACE SETTINGS:

Tube/platform:	L'vov platform, pyrolytically coated
Carrier gas:	Argon (high purity)

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
1	130	10	45	200
2	800	10	15	200
3	100	1	5	200
4	1800	0	5	0
5	2500	1	5	300

AUTOSAMPLER PROGRAM:

Solution:	Volume (µL):
Sample	20
Blank	0
Modifier 1	10
Modifier 2	0

Number of injections: 1
Recalibrate after positions: 16, 28, and 40

STANDARDS: 0, 10, 20, and 30 ppb prepared from 1000 ppm Ricca standard in 0.2 M HNO_3.

MATRIX MODIFIERS: (1) 1:1 ammonium phosphate (4%, prepared from ammonium dihydrogen orthophosphate) and citric acid (2 %)
(2) none

APPROXIMATE SENSITIVITY: Approximately 0.160 A-sec for 20 µL of 30 ng/mL.

6.14. Selenium

METHOD: Graphite furnace atomic absorption

INSTRUMENTATION:

Spectrophotometer:	Perkin-Elmer Z3030
Graphite furnace:	Perkin-Elmer HGA 600
Autosampler:	Perkin-Elmer AS 60
Printer:	Apple Imagewriter

ATOMIC ABSORPTION SPECTROPHOTOMETER SETTINGS:

Wavelength:	196.0 nm
Slit width:	0.7 nm
Lamp:	Se EDL, 6 W
Background correction:	Zeeman effect
Peak measurement:	Peak area
Read delay:	0 sec
Read time:	5 sec
Output:	To printer

GRAPHITE FURNACE SETTINGS:

Tube/platform:	L'vov platform, pyrolytically coated
Carrier gas:	Argon (high purity)

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
1	130	10	50	200
2	900	10	15	200
3	100	1	5	200
4	2300	0	5	0
5	2500	1	4	300

AUTOSAMPLER PROGRAM:

Solution:	Volume (µL):
Sample	20
Blank	0
Modifier 1	10
Modifier 2	0

Number of injections: 1
Recalibrate after positions: 16, 28, and 40

STANDARDS: 0, 25, 50, and 75 ppb prepared from 1000 ppm Ricca standard in 0.2 M HNO_3.

MATRIX MODIFIERS: (1) 5:3:1 Pd (1000 ppm) : Ni (4000 ppm) : hydroxylamine hydrochloride (2%)
(2) none

APPROXIMATE SENSITIVITY: Approximately 0.140 A-sec for 20 µL of 50 ng/mL.

6.15. Tin

METHOD: Graphite furnace atomic absorption

INSTRUMENTATION:

Spectrophotometer:	Perkin-Elmer Z3030
Graphite furnace:	Perkin-Elmer HGA 600
Autosampler:	Perkin-Elmer AS 60
Printer:	Apple Imagewriter

ATOMIC ABSORPTION SPECTROPHOTOMETER SETTINGS:

Wavelength:	286.3 nm
Slit width:	0.7 nm
Lamp:	Sn EDL, 8 W
Background correction:	Zeeman effect
Peak measurement:	Peak area
Read delay:	0 sec
Read time:	5 sec
Output:	To printer

GRAPHITE FURNACE SETTINGS:

Tube/platform:	L'vov platform, pyrolytically coated
Carrier gas:	Argon (high purity)

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
1	130	10	50	200
2	800	10	10	200
3	100	1	5	200
4	2100	0	5	0
5	2300	1	4	300

AUTOSAMPLER PROGRAM:

Solution:	Volume (µL):
Sample	20
Blank	0
Modifier 1	10
Modifier 2	0

Number of injections: 1
Recalibrate after positions: 16, 28, and 40

STANDARDS: 0, 10, 25, and 50 ppb prepared from 1000 ppm Ricca standard in 0.2M HCl.

MATRIX MODIFIERS: (1) 1:1 magnesium nitrate (0.2 %) and ammonium phosphate (4%, prepared from ammonium dihydrogen orthophosphate)
(2) none

APPROXIMATE SENSITIVITY: Approximately 0.200 A-sec for 20 µL of 50 ng/ml.

6.16. Aluminum

METHOD: Instrumental neutron activation analysis for Al in sediments

INSTRUMENTATION:

TRIGA 1 MW reactor
Ortec high-resolution germanium detector
Nuclear Data Genie MCA

IRRADIATION CONDITIONS:

Position:	Pneumatics
Nominal neutron flux:	1×10^{13} neutrons/cm^2/sec
Length of irradiation:	30 sec
Cooling period:	15 min
Peak measurement:	Net peak area using Nuclear Data peak program

COUNTING CONDITIONS:

Counting position:	2-10 cm
g-ray peak energy:	1779 KeV
Count time:	300 sec

STANDARDS:

Pure element standards:	0.01 g prepared from 1000 ppm Ricca standard.
Matrix standards:	0.1 g of: TAMU HS2*, USGS GXR-5, NBS 1646, NRC BCSS-1.

SAMPLE PREPARATION: Approximately 0.1 g weighed to nearest 0.0001 g into 0.4-dram polyethylene vials.

APPROXIMATE SENSITIVITY: Depends upon background; 100 µg results in approximately 1000 counts with associated counting error of 10 %; with typical background and 0.1 g sample size, this corresponds to 0.1% Al.

* TAMU HS2 is a "house" reference sediment standard collected using a box corer in the Mississippi river delta. The sediment was washed several times in distilled water to remove dissolved salts, freeze dried, ground with a mortar and pestle, and homogenized.

6.17. Chromium

METHOD: Instrumental neutron activation analysis for Cr in sediments

INSTRUMENTATION:

TRIGA 1 MW reactor
Ortec high-resolution germanium detector
Nuclear Data Genie MCA

IRRADIATION CONDITIONS:

Position:	Rotisserie
Nominal neutron flux:	1×10^{13} neutrons/cm^2/sec
Length of irradiation:	14 hr
Cooling period:	10 days
Peak measurement:	Net peak area using Nuclear Data peak program

COUNTING CONDITIONS:

Counting position:	10 cm
g-ray peak energy:	320.1 KeV
Count time:	60 min

STANDARDS:

Pure element standards:	1000 µg prepared from 1000 ppm Ricca standard.
Matrix standards:	0.5 g of: TAMU HS2, USGS GXR-5, NBS 1646, NRC BCSS-1.

SAMPLE PREPARATION: Approximately 0.5 g weighed to nearest 0.0001 g into 0.4-dram polyethylene vials.

APPROXIMATE SENSITIVITY: Depends upon background; 1 µg results in approximately 1000 counts with associated counting error of 15%; with typical background and 0.5 g sample size, this corresponds to 2 ppm Cr.

6.18. Iron

METHOD: Instrumental neutron activation analysis for Fe in sediments

INSTRUMENTATION:

TRIGA 1 MW reactor
Ortec high-resolution germanium detector
Nuclear Data Genie MCA

IRRADIATION CONDITIONS:

Position:	Rotisserie
Nominal neutron flux:	1×10^{13} neutrons/cm^2/sec
Length of irradiation:	14 hr
Cooling period:	10 days
Peak measurement:	Net peak area using Nuclear Data peak program

COUNTING CONDITIONS:

Counting position:	10 cm
g-ray peak energy:	1099.2 KeV
Count time:	60 min

STANDARDS:

Pure element standards:	0.01 g prepared from 1000 ppm Ricca standard.
Matrix standards:	0.5 g of: TAMU HS2, USGS GXR-5, NBS 1646, NRC BCSS-1.

SAMPLE PREPARATION: Approximately 0.5 g weighed to nearest 0.0001 g into 0.4-dram polyethylene vials.

APPROXIMATE SENSITIVITY: Depends upon background; 150 µg results in approximately 1000 counts with associated counting error of 10%; with typical background and 0.5 g sample size, this corresponds to 300 ppm Fe.

6.19. Manganese

METHOD: Instrumental neutron activation analysis for Mn in sediments

INSTRUMENTATION:

TRIGA 1 MW reactor
Ortec high-resolution germanium detector
Nuclear Data Genie MCA

IRRADIATION CONDITIONS:

Position:	Pneumatics
Nominal neutron flux:	1 x 10^{13} neutrons/cm^2/sec
Length of irradiation:	30 sec
Cooling period:	15 min
Peak measurement:	Net peak area using Nuclear Data peak program

COUNTING CONDITIONS:

Counting position:	2-10 cm
g-ray peak energy:	846.8 KeV
Count time:	300 sec

STANDARDS:

Pure element standards:	1000 µg prepared from 1000 ppm Ricca standard.
Matrix standards:	0.1 g of TAMU HS2, USGS GXR-5, NBS 1646, NRC BCSS-1.

SAMPLE PREPARATION: Approximately 0.1 g weighed to nearest 0.0001 g into 0.4-dram polyethylene vials.

APPROXIMATE SENSITIVITY: Depends upon background: 1 µg results in approximately 1000 counts with associated counting error of 10 %; with typical background and 0.1 g sample size, this corresponds to 10 ppm Mn.

Analysis of Marine Sediment and Bivalve Tissue by X-Ray Fluorescence, Atomic Absorption and Inductively Coupled Plasma Mass Spectrometry

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ABSTRACT

Analytical chemistry techniques including atomic absorption spectrophotometry, inductively coupled plasma mass spectrometry (ICP-MS) and energy dispersive x-ray fluorescence (XRF) have been applied to the analysis of 17 elements in aquatic sediment and bivalve tissue in support of the NOAA NS&T Program. Complete acid digestion of samples at elevated pressure and temperature in a sealed Teflon container minimizes contamination and loss of elements. Multielemental techniques such as ICP-MS and XRF provide sensitive, accurate, and precise results for a variety of elements at a reasonable cost.

1. INTRODUCTION

Methods used for analysis of 17 metals in estuarine sediments and tissues were developed as part of the Mussel Watch Project of the National Status and Trends (NS&T) Program. The total digestion procedure used for sediments, without loss of volatile elements, was developed by Taylor and Presley at Texas A&M University (TAMU) (this volume). The digestion procedure for tissues was either a modification of the microwave digestion method described by Patterson, Veillon, and Kingston (1988) or a modified TAMU procedure. Metals were analyzed predominantly by graphite furnace atomic absorption (GFAA) spectrometry and x-ray fluorescence (XRF). Mercury was analyzed by cold vapor atomic absorption (CVAA) and Sn was analyzed using a hydride generation procedure. Selected metals were determined by inductively-coupled plasma mass spectrometry (ICP-MS). The primary objective in developing each instrumental method was to keep the method as simple and straightforward as possible while producing acceptable accuracy and precision.

It is expected that users of the instrumental methods described below will modify certain parameters to suit their particular instrumentation and equipment due to variations in performance between instruments. Such variations are caused by differences in furnace calibration, lamp intensities, nebulizer characteristics, and other parameters.

2. EQUIPMENT AND SUPPLIES

2.1. Instrumentation

Perkin-Elmer model Z/5000 spectrophotometer. Perkin-Elmer, Norwalk, CT.

Dual lamp EDL power supply
Model 500 graphite furnace atomizer with Zeeman background correction system
Model 3600 data terminal
Model AS40 autosampler

Perkin-Elmer model Z/3030 spectrophotometer

Dual lamp EDL power supply
Model 600 graphite furnace atomizer with Zeeman background correction system
Model AS60 autosampler
Model PRS 100 printer

Laboratory Data Control atomic absorption spectrophotometer, LDC UV 1235. Laboratory Data Control, Division of Milton Roy Co., Riviera, FL.

Dual-voltage variable auto transformer (Statco model 2PF1010)
Flow meter, 0-150 mm. Cole-Parmer Instrument Co., Chicago, IL.
Integrator CR6A. Shimadzu, Columbia, MD.

CEM Microwave digestion system (model MDS-81D). CEM Corp., Mathews, NC.

Pressure monitor. CEM Corp., Mathews, NC.

KEVEX x-ray fluorescence excitation and detection subsystem, 0810Z. Fisons Instruments, San Carlos, CA.

Canberra series 80 multichannel analyzer. Canberra Nuclear Products, Merider, CT.
Digital PDP-11/34A computer operating system
Digital RL01 floppy disc drive
Digital RL01 hard disc drive
Digital video terminal (model 102)
KEVEX 4620 detector bias supply
KEVEX high voltage generator
PHA/LTC model 8623 amplifier
Versatec printer/plotter. Versatec Inc., Santa Clara, CA.

VG Plasma Quad 2+ inductively-coupled plasma mass spectrometer. Fisons Instruments, Danvers, MA.

Perkin-Elmer model 5000 inductively coupled plasma mass spectrometer

2.2. Supplies

Air mixture
Argon, 99.999% purity
Electrodeless discharge lamps (EDL)
Electron multiplier, model 4870V, Galileo channeltron. Galileo Inc., Sturbridge, MA.
Four-way valve, SRV-4. Pharmacia Co., Piscataway, NJ.
Gold foil, Speyer, Inc.
Graphite tubes, pyrolytically coated, grooved, Perkin-Elmer B0121-092. Perkin-Elmer, Norwalk, CT.
Graphite tubes, pyrolytically coated, non-grooved, Perkin-Elmer B0135-653. Perkin-Elmer, Norwalk, CT.
Helium
Hollow cathode lamps (HCL)
Hydrogen
Laboratory press, 3.2-cm diameter, 27,000 kg
Nitrogen, ultra-pure
Platforms, pyrolytically coated L'vov, Perkin-Elmer B0121-091
Quartz torch
Sample cones, nickel
Skimmer cones, nickel
Thin film standards. Micro Matter, Eastsound, WA
UV source lamp, LDC G4T4\1. Laboratory Data Control, Division of Milton Roy Co., Riviera, FL.

2.3. Labware

Balance, Mettler model AC100 and H30, Sartorius MCI LAB LC1200 S

Bomb lids, 120-mL, Teflon perfluoralkoxy (PFA), double-ported, 0104-4-2. Savillex, Minnetonka, MN.

Bombs, 60-mL, Teflon perfluoralkoxy (PFA) bomb, 561R2; 120-mL, Teflon perfluoralkoxy (PFA), 577. Savillex, Minnetonka, MN.

Capping station. CEM Corp., Mathews, NC.

Cups, 2-mL, polystyrene, B2713-2. Baxter, McGaw Park, IL.

Flask, volumetric, polyethylene, 100-mL

Freeze dryers, 6206-0101. Virtis Co., Gardiner, NY.

Jars, 125-mL, polystyrene, 8002. Spex Industries, Edison, NJ.

Methacrylate balls, 3112. Spex Industries, Edison, NJ.

Mixer/Mills, model 8000. Spex Industries, Edison, NJ.

Oven, stainless steel, Imperial II Radiant Heat Oven. Lab Line Inc., Melrose Park, IL.

Pipets, macro and micro

Polyethylene tubing, 7420. Clay Adams Co., Parsippany, NJ.

Spatulas

Stopwatch or timer

Syringe needles, 3-mL, 72-38D. Pharmaseal Inc., Glendale, CA.

Teflon tubing, 1-mm i.d.

Test tube, 5-inch, glass

Vials, 20-mL, polyethylene, threaded, with screw caps, Kimble 66022-241

Vials, dry grinding, ceramic, 8003. Spex Industries, Edison, NJ.

Polyethylene vials were cleaned by soaking for five days in 5% HNO_3, at room temperature, rinsed with deionized water and dried in Class 100 laminar flow hoods. All other plasticware was soaked for three days in 10% HNO_3 at room temperature, rinsed with deionized water, and dried as above. Teflon bombs were soaked for two days in 50% concentrated HNO_3.

2.4. Reagents

All reagents are ultrapure grades except where so designated.

Acetic acid (CH_3COOH) [64-19-7], glacial (99%), 9524-33. J. T. Baker, Phillipsburg, NJ.

Ammonium dihydrogen phosphate ($NH_4H_2PO_4$) [7722-76-1], Ultrex 7-9431. J. T. Baker, Phillipsburg, NJ.

Ammonium nitrate (NH_4NO_3) [6484-52-2], solid, reagent grade, 729-1. J. T. Baker, Phillipsburg, NJ.

Ascorbic acid ($C_6H_8O_6$) [50-81-7], solid, reagent grade, 581-5. J. T. Baker, Phillipsburg, NJ.

Atomic absorption standards, 1000 µg/mL. High-Purity Standards, Inc., Charleston, SC

Hydrochloric acid (HCl) [7647-01-0], concentrated (37%), Instra-analyzed, 9530-33. J. T. Baker, Phillipsburg, NJ.

Hydrofluoric acid (HF) [7664-39-3], Instra-analyzed, 9563-01. J. T. Baker, Phillipsburg, NJ.

Magnesium nitrate [$Mg(NO_3)_2 \cdot 6H_2O$] [13446-18-9], solid, Puratonic Grade. Johnson Matthey Chemicals, West Chester, PA.

Nickel nitrate [$Ni(NO_3)_2 \cdot 6H_2O$] [13478-00-7], solid, Puratonic Grade. Johnson Matthey Chemicals, West Chester, PA.

Nitric acid (HNO_3) [7697-37-2], concentrated (70%), Instra-analyzed, 9598-33. J. T. Baker, Phillipsburg, NJ.

Perchloric acid ($HClO_4$) [7601-90-3], concentrated (70%), 230. G. Frederick Smith, Columbus, OH.

Soda lime [variable mixture of NaOH and $CaO/Ca(OH)_2$] [8006-28-8], 4-8 mesh, used as acid fume trap in CVAA, 3448-01. J. T. Baker, Phillipsburg, NJ.

Stannous chloride ($SnCl_2 \cdot 2H_2O$) [10025-69-1], 3980-01. J. T. Baker, Phillipsburg, NJ.

Sulfuric acid (H_2SO_4) [7664-93-9], concentrated (98%), Instra-analyzed, 9673-33. J. T. Baker, Phillipsburg, NJ.

Water, deionized, 10 megohm-cm resistivity.

2.5. Solvents and matrix modifiers

Ammonium phosphate: 2%, monobasic, 2 g of $NH_4H_2PO_4$ and 0.200 g of $Mg(NO_3)_2$ per liter of deionized water.

Ammonium phosphate: 4%, monobasic, 4 g $NH_4H_2PO_4$ and 13 g NH_4NO_3 diluted to 100 mL with deionized water.

Magnesium nitrate solution: 250 mg/L of deionized water.

0.10 M Nickel nitrate: 2.91 g $Ni(NO_3)_2 \cdot 6H_2O$ in 100 mL of deionized water.

2 N Acetic acid: Dilute 11.5 mL of glacial acetic acid (99.7%) to 100 mL with deionized water.

Sulfuric acid modifier solution: Dilute 1 mL of concentrated sulfuric acid to 99 mL with deionized water and add 10 µL of 0.1 M $Ni(NO_3)_2 \cdot 6H_2O$.

3. SAMPLE TREATMENT

3.1. Drying and homogenization

3.1.1. Sediments

Sediments were collected with a grab sampler that collects the top 2 cm of surface sediment. Sample aliquots were weighed, freeze-dried for approximately 5 days to constant weight in 125-mL polystyrene Spex jars in a freeze dryer, and reweighed to determine percent dry weight. Approximately 3 g were ground for 5 min using a Spex ceramic ball mill. Aliquots of 0.5 g were used for X-ray fluorescence, or digested for atomic absorption or ICP-MS analysis.

3.1.2. Tissues

Bivalves were hand-collected and shucked at the lab. Tissues were freeze-dried in Spex jars and homogenized using methacrylate balls in a Spex mixer/mill.

3.2. Digestion

Battelle used minor modifications of the total digestion techniques for sediments and tissues developed by Taylor and Presley (this volume).

Two reagent blanks and three standard reference material samples are included in each analytical string of 50 samples. Reagent blanks contain no sediment or tissue and are processed like the samples.

3.2.1. Sediments

Approximately 200 ± 7 mg of homogenized ground dried sediment was weighed into a tared 60-mL Teflon digestion bomb. One mL of 4:1 $HNO_3/HClO_4$ was added to each bomb and the lid tightened at the capping station.

The bombs were heated in the oven at 130 ± 10°C for 4 hr and allowed to cool.

Three mL of concentrated HF were added to each bomb, rinsing the walls of the bomb to insure that all solids were washed down into the acid mixture. The lid was tightened at the capping station.

The bombs were heated in the oven at 130 ± 10°C for 8 hr and allowed to cool.

The bombs were opened and the digestates diluted to approximately 20 mL with deionized water.

The solutions were weighed in the Teflon bombs and the volume calculated using a density factor of 1.05 g/mL.

The contents of each bomb were transferred quantitatively to a 20-mL polyethylene screw-cap vial for storage prior to analysis.

Digestates can be analyzed directly by GFAA or CVAA. Before analysis by ICP-MS, a 10-mL aliquot was transferred to a Teflon bomb and dried slowly, uncovered, on a hot plate (203°C) in a perchloric acid hood to eliminate chloride and fluoride. White fumes are indicative of successful elimination of these elements. The dried digestate was dissolved in 1 mL of 10% HNO_3 and heated again to dryness. The dried digestate is dissolved again with 1 mL of 10% HNO_3 and 9 mL of deionized water.

3.2.2. Tissues

Approximately 500 ± 15 mg of homogenized, dried sediment was weighed into a tared 60-mL Teflon digestion bomb. Three mL of 4:1 $HNO_3/HClO_4$ was added to each bomb and the lid screwed on but not tightened.

The bombs were placed in a cold water bath in a perchloric hood and the water bath was heated slowly to 60 ± 3°C. Perchloric acid ignites in the presence of organics compounds if heated rapidly. The temperature was raised to 95 ± 5°C to eliminate NO_x fumes. The total heating time was 3 to 4 hr.

The bombs were allowed to cool. The lids were tightened at the capping station.

The bombs were heated in the oven at 130 ± 10°C for 4 hr and allowed to cool.

The bombs were opened and the digestates diluted to approximately 20 mL with deionized water.

The solutions were weighed in the Teflon bombs and the volume calculated using a density factor of 1.04 g/mL.

Digestates were analyzed directly by GFAA and CVAA, or diluted 10:1 for ICP-MS analysis.

3.3. Microwave digestion

The microwave digestion was conducted in a CEM model MDS-81D oven equipped with a 12-sample carousel and a pressure monitor. The pressure monitor tube was connected to one of the digestion bombs allowing the pressure to be monitored during the entire digestion. The carousel rotated in an alternating direction so the pressure monitoring tube was not twisted.

Approximately 300 ± 5 mg of dried, homogenized sample was weighed into a tared 120-mL Teflon digestion bomb. Five mL of concentrated HNO_3 were added to each bomb and the lids tightened at the capping station.

The digestion program should allow a minimum of 20 minutes at 85-95 psi.

When digestion was completed, the bombs were allowed to cool and the pressure released slowly and carefully.

Each sample was transferred quantitatively to a tared polyethylene scintillation vial. Each bomb was rinsed three times with 5-mL portions of deionized water and the rinsings added to the vial. The lid was rinsed with one additional 5-mL portion of deionized water and the rinsing added to the vial.

The vials were weighed and the average density of three representative digestates per matrix was determined. The final volume of each sample was calculated by dividing the digestate weight by the average density.

4. CALIBRATION

Calibration standards were prepared by serial dilution of commercially available atomic absorption standards using class-A glass pipets, volumetric flasks, and 10% HNO_3. Some metals, such as Sb and Sn, require use of a different acid diluent. Final working standards are prepared in 1% HNO_3 or the appropriate acid diluent, using micropipets and glass volumetric flasks. The element concentrations in each standard should be sufficient to cover the appropriate range of sample concentrations and produce good measurement precision and accurately define the slope of the response curve. Concentrations of commercial standards are verified by comparison with National Institute of Standards and Technology (NIST) spectrophotometric standards.

5. SPECTRAL INTERFERENCES

Spectral interferences may be minimized by sample dilution, use of an alternate analyte wavelength, or selective volatilization of the analyte. Non-spectral interferences may be detected and compensated for using the method of standard additions. Matrix modifiers that are used include $Mg(NO_3)_2$, $NH_4H_2PO_4$, $Ni(NO_3)_2$, and H_2SO_4. Their specific use is described in the instrumental analysis section for each element.

6. CALCULATIONS

6.1. Graphite furnace and ICP-MS

Sample concentrations are determined from calibration results and from the dilution factors using the following equation:

$$\text{Concentration } (\mu g/g \text{ dry wt}) = \frac{(S_A - B_A)\ m\ S_V}{1000\ (S_{DW})\ (DF)}$$

where S_A is the sample absorbance or intensity value, B_A is the procedural blank absorbance or intensity value, m is the slope of standard addition calibration line, S_V is the sample volume, S_{DW} is the sample dry weight in grams, and DF is the dilution factor.

6.2. Cold vapor atomic absorption

Sample concentrations are determined from calibration results and from the dilution factors involved in instrumental analysis and sample digestion according to the following equation:

$$\text{Concentration } (\mu g/g \text{ dry wt}) = \frac{(S_A - B_A)\ m\ S_V}{1000\ \ (S_{DW})\ (DF)}$$

where S_A is the sample absorbance value, B_A is the procedural blank absorbance value, m is the slope of the calibration line, S_V is the sample volume, S_{DW} is the sample dry weight in grams, and DF is the dilution factor.

6.3. X-ray fluorescence

This procedure uses energy dispersive x-ray fluorescence spectroscopy to quantify elemental concentrations in sediment and tissue samples (Nielson *et al.*, 1982). The backscatter/fundamental parameter approach using the SAP3 computer code incorporates thin film standards and scattering rations to produce matrix corrections (Nielson and Sanders, 1982).

Thin film standards are used for the determination of intensity in count/min/µg (element)/cm^2 versus element energy in KeV. Thin film standards produced by vapor deposit of the elements on Mylar or polycarbonate substrate are available from Micro Matter of Eastsound, Washington. These standards are traceable to the U.S. National Institute of Standards and Technology.

The peak analysis and elemental concentration sections of the computer program (SAP3) use arrays of fundamental physical parameters of x-ray energies, mass adsorption coefficients, cross sections, fluorescence yields, absorption edge, and jump ratios to perform the matrix corrections for relating net peak intensities to element concentrations. These arrays are read into the computer from a disc file when the program in initiated. Each excitation source has its own unique disc file or library. Thin film sensitivities or calibration factors of the spectrometer using the intended excitation source is also part of the library.

7. CONCLUSIONS

A variety of analytical instruments provide the optimum method for the analysis of 17 elements in sediment and bivalve tissue. The advantage of XRF is that the sample does not require digestion but is analyzed as a dry powder. Crustal elements such as Al, Cr, Fe, Ni, and Si, that are difficult to dissolve in sediment, can be quantified by XRF. Also, Se and As can be difficult to quantify in tissue digestates by MS but can be quantified simpler by XRF. ICP-MS has the advantage of simultaneous analysis of many elements with detection limits much lower than the XRF and similar to those of GFAA. Elements that are particularly sensitive and relatively interference free by ICP-MS include Ag, Cd, Pb, Sb, Sn, and Tl. Cold vapor atomic absorption with gold amalgamation is a very sensitive and reliable technique for Hg analysis. Care must be taken to avoid leakage at high pressure or Hg can be lost during digestion. With the use of the sealed Teflon digestion vessel, mercury can be analyzed from the same digestion as the other metals.

The advantage of freeze drying both sediment and tissue is that the dry material is easily ground or homogenized. No Hg loss occurs during freeze drying. The microwave digestion with nitric acid is an ideal matrix for ICP-MS analysis of tissue. Sediment digestates must receive special treatment to remove silicon, fluoride and perchloric acid before analysis by ICP-MS. Analysis by GFM requires matrix modifiers and standardization of the instrument by method of addition to the sample matrix to provide accurate results.

8. REFERENCES

Nielson, K. K., and R. W. Sanders (1982) The SAP3 computer program for quantitative multi-element analysis by energy-dispersive x-ray fluorescence. PNL-4173, Battelle Pacific Northwest Laboratory, Richland, WA. 120 pp.

Nielson, K. K., R. W. Sanders, and J. C. Evans (1982) Analysis of steels by energy-dispersive x-ray fluorescence with fundamental parameters. Anal. Chem., 54(11):1782-6.

Patterson, K. Y., C. Veillon, and H. M. Kingston (1988) Microwave digestion of biological samples. In: Introduction to Microwave Sample Preparation. H. M. Kingston and L. B. Jassie (eds.). 155-66. ACS Professional Reference Book, American Chemical Society, Washington, DC.

9. INSTRUMENTAL ANALYSIS

9.1. Atomic absorption spectrometry

9.1.1. Aluminum

Graphite furnace atomic absorption for tissue

METHOD: Graphite furnace atomic absorption

DIGEST MATRIX: ~15% 4:1 HNO_3:$HClO_4$ by volume.

INSTRUMENT SETTINGS:

Wavelength:	309.3 nm
Lamp:	HCL, 25 ma (Perkin-Elmer 0303-6009)
Tube:	Non-platform, pyrolytically coated
Carrier gas:	Argon
Slit width:	0.7
Background correction:	Zeeman
Signal mode:	Peak height
Scale expansion:	None
Read time:	5 sec
Output:	Recorded from spectrophotometer display

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
Dry 1	80	9	1	300
Dry 2	140	45	5	300
Dry 3	250	20	5	300
Char	1600	45	25	300
Atomize	2300	0	4	50
Cleanout	2650	1	3	300
Cool	20	1	10	300

STANDARDS: Addition calibration using 22.2, 43.5, and 83.3 µg/L Al to CRM DOLT-1 tissue digestate. Method of standard addition.

TYPICAL SENSITIVITY: Absorbance is approximately 0.100 for 0.4 µg Al standard.

CALIBRATION: Peak height versus concentration of standards used to compute the slope, intercept, and correlation coefficient of calibration line using linear, least-squares regression.

INJECTION VOLUME: 5 µL

MATRIX MODIFIER: 5 µL of 2% $NH_4H_2PO_4$.

9.1.2. Chromium

Graphite furnace atomic absorption for tissue

METHOD: Graphite furnace atomic absorption

DIGEST MATRIX: ~15% 4:1 HNO_3:$HClO_4$ by volume.

INSTRUMENT SETTINGS:

Wavelength:	357.9 nm
Lamp:	HCL, 25 ma (Perkin-Elmer 0303-6021)
Tube:	Pyro, non-platform
Carrier gas:	Argon
Slit width:	0.7
Background correction:	Zeeman
Signal mode:	Peak height
Scale expansion:	None
Read time:	5 sec
Output:	Recorded from spectrophotometer display

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
Dry 1	80	9	1	300
Dry 2	140	45	5	300
Dry 3	250	20	5	300
Char	1500	20	25	300
Atomize	2500	0	4	0
Cleanout	2650	1	3	300
Cool	20	1	10	300

STANDARDS: Method of standard addition calibration using 20.0, 33.3, and 66.7 µg/L Cr to CRM DOLT-1 tissue digestate.

TYPICAL SENSITIVITY: Absorbance is approximately 0.200 for 0.165 µg Cr standard.

CALIBRATION: Peak height versus concentration of standards used to compute the slope, intercept, and correlation coefficient of calibration line using linear, least-squares regression.

INJECTION VOLUME: 5 µL

MATRIX MODIFICATION: 5 µL of 250 mg/L Mg as $Mg(NO_3)_2$.

9.1.3. Nickel

Graphite furnace atomic absorption for tissues

METHOD: Graphite Furnace Atomic Absorption

DIGEST MATRIX: ~15% 4:1 HNO_3:$HClO_4$ by volume.

INSTRUMENT SETTINGS:

Wavelength:	232.0 nm
Lamp:	HCL, 35 ma (Perkin-Elmer 0303-6047)
Tube:	Pyro, non-platform
Carrier gas:	Argon
Slit width:	0.2
Background correction:	Zeeman
Signal mode:	Peak height
Scale expansion:	None
Read time:	5 sec
Output:	To printer

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
Dry 1	80	9	1	300
Dry 2	140	45	5	300
Dry 3	250	20	5	300
Char	1200	20	20	300
Atomize	2300	0	4	0
Cleanout	2650	1	3	300
Cool	20	1	10	300

STANDARDS: Method of standard addition calibration using 24.39, 47.62, and 90.91 µg/L Ni to CRM DOLT-1 digestate.

TYPICAL SENSITIVITY: Absorbance is approximately 0.100 for 0.6 µg Ni standard.

CALIBRATION: Peak height of standard versus concentration of standard. Compute the slope, intercept, and correlation coefficient using linear, least-squares regression.

INJECTION VOLUME: 5 µL

MATRIX MODIFICATION: 5 µL of 2% $NH_4H_2PO_4$.

MODIFIER VOLUME: 5 µL

9.1.4. Selenium

Graphite furnace atomic absorption for sediment

METHOD: Graphite Furnace Atomic Absorption

DIGEST MATRIX: ~4% 4:1 HNO_3:$HClO_4$ + 12% HF by volume.

INSTRUMENT SETTINGS:

Wavelength:	195.9 nm
Lamp:	EDL, 6 watts (Perkin-Elmer 0303-6262)
Tube:	L'vov, pyro coated
Carrier gas:	Argon
Slit width:	2.0
Background correction:	Zeeman
Signal mode:	Peak height
Scale expansion:	None
Read time:	5 sec
Output:	Recorded from spectrophotometer display

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
Dry 1	80	9	1	300
Dry 2	140	45	5	300
Dry 3	250	20	5	300
Char	1300	20	20	300
Atomize	2100	0	4	0
Cleanout	2650	1	3	300
Cool	20	1	10	300

STANDARDS: Method of standard addition calibration using 47.6, 90.9, and 130.4 µg/L Se to CRM MESS-1 sediment digestate.

TYPICAL SENSITIVITY: Absorbance is approximately 0.100 for 1.0 µg Se standard.

CALIBRATION: Peak height of standard versus concentration of standard. Compute the slope, intercept, and correlation coefficient using linear, least-squares regression.

INJECTION VOLUME: 20 µL

MATRIX MODIFICATION: 10 µL of 0.1 M $Ni(NO_3)_2$.

9.1.5. Silver

9.1.5.1. Graphite furnace atomic absorption for tissue

METHOD: Graphite Furnace Atomic Absorption

DIGEST MATRIX: ~15% 4:1 HNO_3:$HClO_4$ by volume.

INSTRUMENT SETTINGS:

Wavelength:	327.9 nm
Lamp:	HCL, 12 ma (Perkin-Elmer 0303-6064)
Tube:	L'vov, pyro coated
Carrier gas:	Argon
Slit width:	0.7
Background correction:	Zeeman
Signal mode:	Peak height
Scale expansion:	None
Read time:	4 sec
Output:	To printer

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
Dry 1	80	9	1	300
Dry 2	140	45	5	300
Dry 3	250	20	5	300
Char	800	20	20	300
Atomize	2100	0	4	0
Cleanout	2650	1	3	300
Cool	20	1	10	300

STANDARDS: Addition calibration using 0.99, 1.96, and 4.76 µg/L Ag to CRM DOLT-1 tissue digestate.

TYPICAL SENSITIVITY: Absorbance is approximately 0.100 for 0.03 µg Ag standard.

CALIBRATION: Peak height of standard versus concentration of standard. Compute the slope, intercept, and correlation coefficient using linear, least-squares regression.

INJECTION VOLUME: 10 µL

MATRIX MODIFICATION: 5 µL of 2% $NH_4H_2PO_4$.

9.1.5.2. Graphite furnace atomic absorption for sediment

METHOD: Graphite Furnace Atomic Absorption

DIGEST MATRIX: ~4% 4:1 HNO_3:$HClO_4$ +12% HF by volume.

INSTRUMENT SETTINGS:

Wavelength:	327.9 nm
Lamp:	HCL, 12 ma (Perkin-Elmer 0303-6064)
Tube:	L'vov, pyro coated
Carrier gas:	Argon
Slit width:	0.7
Background correction:	Zeeman
Signal mode:	Peak height
Scale expansion:	None
Read time:	4 sec
Output:	To printer

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
Dry 1	80	9	1	300
Dry 2	140	45	5	300
Dry 3	250	20	5	300
Char	800	20	20	300
Atomize	2100	0	4	0
Cleanout	2650	1	3	300
Cool	20	1	10	300

STANDARDS: Addition calibration using 2.44, 4.76, and 9.09 µg/L Ag to SRM 1646 sediment digestate.

TYPICAL SENSITIVITY: Absorbance is approximately 0.120 for 0.05 µg Ag standard.

CALIBRATION: Peak height of standard versus concentration of standard. Compute the slope, intercept, and correlation coefficient using linear, least-squares regression.

INJECTION VOLUME: 10 µL

MATRIX MODIFICATION: 5 µL of 2% $NH_4H_2PO_4$.

9.1.6. Cadmium

9.1.6.1. Graphite furnace atomic absorption for tissue

METHOD: Graphite Furnace Atomic Absorption

DIGEST MATRIX: ~15% 4:1 HNO_3:$HClO_4$ by volume.

INSTRUMENT SETTINGS:

Wavelength:	228.9 nm
Lamp:	EDL, 5 watts (Perkin-Elmer 0303-60216)
Tube:	L'vov, pyro coated
Carrier gas:	Argon
Slit width:	0.7
Background correction:	Zeeman
Signal mode:	Peak area
Scale expansion:	None
Read time:	4 sec
Output:	To printer

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
Dry 1	80	9	1	300
Dry 2	140	45	5	300
Dry 3	250	20	5	300
Char	800	20	20	300
Atomize	1800	0	4	0
Cleanout	2650	1	3	300
Cool	20	1	10	300

STANDARDS: Addition calibration using 0.96, 2.37, and 4.62 µg/L Cd to SRM 1566a tissue digestate.

TYPICAL SENSITIVITY: Absorbance is approximately 0.100 for 0.02 µg Cd standard.

CALIBRATION: Peak area of standard versus concentration of standard. Compute the slope, intercept and correlation coefficient using linear, least-squares regression.

INJECTION VOLUME: 5 µL

MATRIX MODIFICATION: 10 µL of 2% $NH_4H_2PO_4$.

Cadmium

9.1.6.2. Graphite furnace atomic absorption for sediment

METHOD: Graphite Furnace Atomic Absorption

DIGEST MATRIX: ~4% 4:1 HNO_3:$HClO_4$ + 12% HF by volume.

INSTRUMENT SETTINGS:

Wavelength:	228.8 nm
Lamp:	EDL, 5 watts (Perkin-Elmer 0303-6216)
Tube:	L'vov, pyro coated
Carrier gas:	Argon
Slit width:	0.7
Background correction:	Zeeman
Signal mode:	Peak area
Scale expansion:	None
Read time:	4 sec
Output:	To printer

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
Dry 1	80	9	1	300
Dry 2	140	45	5	300
Dry 3	250	20	5	300
Char	800	20	20	300
Atomize	1800	0	4	0
Cleanout	2650	1	3	300
Cool	20	1	10	300

STANDARDS: Addition calibration using 0.90, 2.22, and 4.35 µg/L Cd to SRM 1646 sediment digestate.

TYPICAL SENSITIVITY: Absorbance is approximately 0.100 for 0.015 µg Cd standard.

CALIBRATION: Peak area of standard versus concentration of standard. Compute the slope, intercept, and correlation coefficient using linear, least-squares regression.

INJECTION VOLUME: 5 µL

MATRIX MODIFICATION: 10 µL of 2% $NH_4H_2PO_4$.

9.1.7. Tin

9.1.7.1. Hydride generation atomic absorption for tissue

METHOD: Graphite Furnace Atomic Absorption by Hydride Generation

DIGEST MATRIX: ~15% 4:1 HNO_3:$HClO_4$ by volume.

INSTRUMENT SETTINGS:

Wavelength:	286.5 nm
Lamp:	EDL, 8 watts (Perkin-Elmer 0303-6274)
Tube:	Non-platform, non-coated
Carrier gas:	Argon
Slit width:	0.7
Background correction:	Zeeman
Signal mode:	Peak height
Scale expansion:	None
Read time:	4 sec
Output:	To printer

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
Dry 1	700	10	99	0
Dry 2	700	1	99	0
Dry 3	700	1	99	0
Dry 4	700	1	99	0
Dry 5	700	1	99	0
Cool 1	350	5	5	300
Atomize	2300	0	4	0
Cleanout	2600	1	4	300
Cool 2	20	1	10	300

STANDARDS: Spike addition at 1.0, 2.5, and 5.0 ng Sn.

TYPICAL SENSITIVITY: Absorbance is approximately 0.150 for a 2.0 ng Sn spike.

CALIBRATION: Peak height of standard versus concentration of standard. Compute the slope, intercept, and correlation coefficient using linear, least-squares regression.

INJECTION VOLUME: 0.5 mL

MATRIX MODIFICATION: 0.5 mL of 2 N acetic acid.

NOTES: See hydride generation method for Sn. Note that the auto sampler is not used in this technique, and 50 mL of DI water is used as a carrier for the Sn standard, the modifier, and the borohydride.

Tin

9.1.7.2. Hydride generation atomic absorption for sediment

METHOD: Graphite furnace atomic absorption by hydride generation

DIGEST MATRIX: ~4% 4:1 HNO_3:$HClO_4$ + 12% HF by volume.

INSTRUMENT SETTINGS:

Wavelength:	286.5 nm
Lamp:	EDL, 8 watts (Perkin-Elmer 0303-6274)
Tube:	Non-platform, non-coated
Carrier gas:	Argon
Slit width:	0.7
Background correction:	Zeeman
Signal mode:	Peak height
Scale expansion:	None
Read time:	4 sec
Output:	To printer

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
Dry 1	700	10	99	0
Dry 2	700	1	99	0
Dry 3	700	1	99	0
Dry 4	700	1	99	0
Dry 5	700	1	99	0
Cool 1	350	5	5	300
Atomize	2300	0	4	0
Cleanout	2600	1	4	300
Cool 2	20	1	10	300

STANDARDS: Method of standard addition calibration at 1, 2.5, and 5.0 ng Sn to SRM 1646 sediment digestate.

TYPICAL SENSITIVITY: Absorbance is approximately 0.100 for a 3.0 ng Sn spike.

CALIBRATION: Peak height of standard versus concentration of standard. Compute the slope, intercept, and correlation coefficient using linear, least-squares regression.

INJECTION VOLUME: 0.100 mL

MATRIX MODIFICATION: 0.25 mL of 2 N acetic acid.

NOTES: See hydride generation method for Sn. Note that the auto sampler is not used in this technique, and 50 mL of DI water is used as a carrier for the Sn standard, the modifier, and the borohydride.

9.1.8. Antimony

9.1.8.1. Graphite furnace atomic absorption for tissue

METHOD: Graphite Furnace Atomic Absorption

DIGEST MATRIX: ~15% 4:1 HNO_3:$HClO_4$ by volume.

INSTRUMENT SETTINGS:

Wavelength:	217.8 nm
Lamp:	EDL, 8 watts (Perkin-Elmer 0303-6210)
Tube:	L'vov, coated
Carrier gas:	Argon
Slit width:	0.7
Background correction:	Zeeman
Signal mode:	Peak area
Scale expansion:	None
Read time:	4 sec
Output:	To printer

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
Dry 1	80	9	1	300
Dry 2	140	45	5	300
Dry 3	250	20	5	300
Char	1000	20	25	300
Atomize	2400	0	4	0
Cleanout	2650	1	3	300
Cool	20	1	10	300

STANDARDS: Addition calibration at 47.6, 90.9, and 130.4 µg/L Sb to SRM 1566a tissue digestate.

TYPICAL SENSITIVITY: Absorbance is approximately 0.100 for 3 µg Sb standard.

CALIBRATION: Peak area of standard versus concentration of standard. Compute the slope, intercept, and correlation coefficient using linear, least-squares regression.

INJECTION VOLUME: 20 µL

MATRIX MODIFICATION: 5 µL of 0.1 M $Ni(NO_3)_2$.

9.1.8.2. Graphite furnace atomic absorption for sediment

METHOD: Graphite Furnace Atomic Absorption

DIGEST MATRIX: ~4% 4:1 HNO_3:$HClO_4$ + 12% HF by volume.

INSTRUMENT SETTINGS:

Wavelength:	217.8 nm
Lamp:	EDL, 8 watts (Perkin-Elmer 0303-6210)
Tube:	L'vov, coated
Carrier gas:	Argon
Slit width:	0.7
Background correction:	Zeeman
Signal mode:	Peak height
Scale expansion:	None
Read time:	4 sec
Output:	To printer

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
Dry 1	80	9	1	300
Dry 2	140	45	5	300
Dry 3	250	20	5	300
Char	1200	20	20	300
Atomize	2500	0	4	0
Cleanout	2650	1	3	300
Cool	20	1	10	300

STANDARDS: Addition calibration at 42.9, 81.8, and 117.4 µg/L Sb to CRM MESS-1 sediment digestate.

TYPICAL SENSITIVITY: Absorbance is approximately 0.100 for 0.8 µg Sb standard.

CALIBRATION: Peak height of standard versus concentration of standard. Compute the slope, intercept, and correlation coefficient using linear, least-squares regression.

INJECTION VOLUME: 10 µL

MATRIX MODIFICATION: 10 µL of 0.1M $Ni(NO_3)_2$.

9.1.9. Mercury

Cold vapor/gold foil amalgam for tissue or sediment

METHOD:	Cold vapor/gold foil amalgam
DIGEST MATRIX:	~15% 4:1 HNO_3 and $HClO_4$ by volume for tissues. ~4% 4:1 HNO_3 and $HClO_4$ + 12% HF by volume for sediments.

INSTRUMENT SETTINGS:

Reaction volume:	0.020 -1 mL
Diluent:	1% HNO_3
Carrier Gas:	N_2
Flow rate:	300 mL/min (purge), 100 mL/min (trap burn)
Scale expansion:	Attenuation - mid-range
Integration time:	1 min
Output:	Shimadzu Integrator

REDUCTANT:	10% $SnCl_2$ in 10% H_2SO_4
STANDARDS:	0, 0.5, 1.0, 2.5, 5.0, and 10.0 ng Hg from a 100 ng/mL standard in 1% HNO_3 using High Purity standards. Use aliquots of 0, 5, 10, 25, 50 and 100 µL.
TYPICAL SENSITIVITY:	0.01 µg/g Hg.
CALIBRATION:	Instrument read-out is in peak area and input is in ng Hg, so calibration curve is based on Hg input versus Hg output reading. The slope, intercept, and correlation coefficient are calculated using linear, least-squares regression.
INJECTION VOLUME:	0.005 to 1 mL
REDUCTANT VOLUME:	0.5 mL
MATRIX MODIFICATION:	None

9.1.10. Thallium

9.1.10.1. Graphite furnace atomic absorption for tissue

METHOD: Graphite Furnace Atomic Absorption

DIGEST MATRIX: ~15% 4:1 HNO_3:$HClO_4$ by volume.

INSTRUMENT SETTINGS:

Wavelength:	276.8 nm
Lamp:	EDL, 7 watts (Perkin-Elmer 0303-6271)
Tube:	L'vov, coated
Carrier gas:	Argon
Slit width:	0.7
Background correction:	Zeeman
Signal mode:	Peak area
Scale expansion:	None
Read time:	4 sec
Output:	To printer

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
Dry 1	80	9	1	300
Dry 2	140	45	5	300
Dry 3	250	20	5	300
Char	600	20	25	300
Atomize	1700	0	4	0
Cleanout	2650	1	3	300
Cool	20	1	10	300

STANDARDS: Method of standard addition calibration at 24.4, 47.6, and 90.0 µg/L Tl to SRM 1566a tissue digestate.

TYPICAL SENSITIVITY: Absorbance is approximately 0.100 for 1.25 µg Tl standard.

CALIBRATION: Peak area of standard versus concentration of standard. Compute the slope, intercept, and correlation coefficient using linear, least-squares regression.

INJECTION VOLUME: 25 µL

MATRIX MODIFICATION: 5 µL of 1% H_2SO_4.

9.1.10.2. Graphite furnace atomic absorption for sediment

METHOD: Graphite furnace atomic absorption

DIGEST MATRIX: ~4% 4:1 HNO_3:$HClO_4$ + 12% HF by volume.

INSTRUMENT SETTINGS:

Wavelength:	276.9 nm
Lamp:	EDL, 7 watts (Perkin-Elmer 0303-6271)
Tube:	L'vov, coated
Carrier gas:	Argon
Slit width:	0.7
Background correction:	Zeeman
Signal mode:	Peak area
Scale expansion:	None
Read time:	4 sec
Output:	To printer

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
Dry 1	80	9	1	300
Dry 2	140	45	5	300
Dry 3	250	20	5	300
Char	600	20	25	300
Atomize	1700	0	4	0
Cleanout	2650	1	3	300
Cool	20	1	10	300

STANDARDS: Method of standard addition calibration at 24.4, 47.6, and 90.0 µg/L Tl to SRM 1646 sediment digestate.

TYPICAL SENSITIVITY: Absorbance is approximately 0.060 for 1.25 µg Tl standard.

CALIBRATION: Peak area of standard versus concentration of standard. Compute the slope, intercept, and correlation coefficient using linear, least-squares regression.

INJECTION VOLUME: 25 µL

MATRIX MODIFICATION: 10 µL of 1% H_2SO_4 + 10 µL 0.1 M $Ni(NO_3)_2$.

9.1.11. Lead

Graphite furnace atomic absorption for tissue

METHOD: Graphite Furnace Atomic Absorption

DIGEST MATRIX: ~15% 4:1 HNO_3:$HClO_4$ by volume.

INSTRUMENT SETTINGS:

Wavelength:	283.3 nm
Lamp:	EDL, 5 ma (Perkin-Elmer 0303-6039)
Tube:	L'vov, coated
Carrier gas:	Argon
Slit width:	0.7
Background correction:	Zeeman
Signal mode:	Peak height
Scale expansion:	None
Read time:	5 sec
Output:	Recorded from Spectrophotometer display

FURNACE PROGRAM:

Step	T(°C)	Time (sec)		Internal Gas
		Ramp	Hold	Flow (mL/min)
Dry 1	80	9	1	300
Dry 2	140	45	5	300
Dry 3	250	20	5	300
Char	800	20	20	300
Atomize	2100	0	4	0
Cleanout	2650	1	3	300
Cool	20	1	10	300

STANDARDS: Method of standard addition calibration at 9.9, 19.6, and 24.4 µg/L Pb to CRM DOLT-1 tissue digestate.

TYPICAL SENSITIVITY: Absorbance is approximately 0.160 for 0.25 µg Pb standard.

CALIBRATION: Peak height of standard versus concentration of standard. Compute the slope, intercept, and correlation coefficient using linear, least-squares regression.

INJECTION VOLUME: 5 µL

MATRIX MODIFICATION: 10 µL of 2% $NH_4H_2PO_4$.

9.2. Inductively coupled plasma mass spectrometry

Silver, aluminum, chromium, cadmium, nickel, lead, antimony, and tin in sediments or tissues

METHOD: Inductively coupled plasma mass spectrometry

DIGEST MATRIX: 1 to 10 dilution of digestate with deionized water plus 0.1 mL of 1 ppm In standard.

INSTRUMENT SETTINGS: Instrument settings change on a daily basis as sensitivity is optimized. This is especially true of lens settings. The following gives general ranges on parameters that remain relatively constant in day-to-day operation:

Power:	1250-1500 watts
Coolant flow:	13-14 L/min.
Auxiliary flow:	0.5-1.0 L/min.
Nebulizer flow:	0.85-1.0 L/min.
EM voltage:	2000-3000 volts
Sample uptake:	0.5-1.5 mL/min.
Integration method:	Constant area
Integration area:	0.8
Background counts:	35
Dead time:	40 nsec
Quad slew factor:	0.10

PROCEDURE:

Element menu:	tissue2
Mass range:	25.98 to 212.05 amu
Number of channels:	2048
Number of sweeps:	100
Dwell time:	320 µsec
Collector type:	pulse
Internal standards:	In
Skipped mass regions:	28.00 - 43.00, 63.00 - 105.00, 125.00 - 200

STANDARDS: Appropriate calibration standards (representative of sample concentration) are prepared from dilutions of NIST single- and/or multi-element standards. Other reference materials (NIST or second party single/multi-element standards) are used as check standards. Method of standard addition can be used to produce instrumental response curve.

TYPICAL SENSITIVITY: Sensitivity is approximately 5 x 10^4 million counts per sec per ppm for In^{115}.

CALIBRATION: Constant area integration (using 0.8 of total peak) versus concentration of standard. Compute the slope, intercept, and correlation coefficient using linear, least-squares regression.

9.3. X-Ray fluorescence

Elements in sediment:	Al, As, Cr, Cu, Fe, Mn, Ni, Pb, Si, and Zn.
Elements in tissue:	As, Cu, Fe, Mn, Se, Si, and Zn.
METHOD:	X-ray fluorescence
Sample preparation:	0.5 g dried and homogenized sediment or tissue pressed in a pellet, 2 cm in diameter.

INSTRUMENT SETTINGS:

Gain:	PHA/LTC for Series 80 MCA
Secondary target:	Zr
Target gain:	25 eV/channel
Resolution:	182 eV at 6.4 KeV
Timing counter:	12 µsec
Bias:	-1000 V
Live time:	1500 sec
Dead time:	$\leq$ 40%
Tungsten tube voltage:	40 V
Tube current:	20 milliamps

Analytical Procedures Followed by Science Applications International Corporation for Trace and Major Element Analyses

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Battelle Ocean Sciences
Marine Chemistry
Duxbury, MA

1. INTRODUCTION

During Year 1 (1986) of the Mussel Watch Project, two analytical laboratories performed the trace and major element analyses on tissue and sediment samples. Battelle's Pacific Northwest Laboratory in Sequim, WA, prepared and analyzed all samples collected on the East Coast, and those collected in Oregon, Washington, and Alaska. Science Applications International Corporation (SAIC), La Jolla, CA, performed similar analyses on samples collected from the California coast. A summary of laboratory responsibilities is found in Table III.9. The analytical methods used for each element by Battelle and SAIC for each year of the Mussel Watch Project are summarized in Tables III.10 to III.12. The analytical methods used by SAIC are described below. These methods have been summarized from information in Battelle's Quality Assurance Work Plans and Final Reports to NOAA for 1986 through 1989 of the National Status and Trends Program Mussel Watch Project.

2. TRACE METAL ANALYSIS

2.1. Equipment and reagents

2.1.1. Instruments

Perkin-Elmer 603 atomic absorption spectrophotometer. Perkin-Elmer, Norwalk, CT.
- HGA-2200 graphite furnace
- Perkin-Elmer Model 056 recorder
- Autosampler, model AS-1
- Deuterium lamp background corrector
- Electrodeless discharge lamps

Perkin-Elmer 5100PC absorption spectrophotometer
- HGA-600 graphite furnace
- Autosampler, model AS-60
- Zeeman background corrector
- Electrodeless discharge dual lamp power supply
- Epson Equity 3+ color computer with printer. Wakefield, MA.

Mercury monitor, Laboratory Data Control, model 1235

Hitachi 100-80 uv/visible spectrophotometer. Hitachi Instruments, Danbury, CT.

Air/acetylene burner for (flame atomic absorption analysis)

Nitrous oxide/acetylene burner for (flame atomic absorption analysis)

Table III.9. Summary of laboratory responsibilities.

Sample Origin	Laboratory			
	Year 1986	Year 1987	Year 1988	Year 1989
East Coast (all sites)	Battelle	Battelle	Battelle	Battelle
West Coast				
California	SAIC	SAIC	SAIC*	SAIC**
Oregon	Battelle	Battelle	Battelle	Battelle
Washington	Battelle	Battelle	Battelle	Battelle
Alaska	Battelle	Battelle	NS	NS
Hawaii	Battelle	Battelle	NS	NS

* Sn analyzed by Battelle. ** Se and Sn analyzed by Battelle. NS - Not Sampled

Table III.10. Analytical methods for trace elements used by Battelle and SAIC, 1986.

Element	Battelle		SAIC	
	Tissue	Sediment	Tissue	Sediment
Al	GFAA	XRF	GFAA/FAA	FAA
Ag	GFAA	GFAA	GFAA	GFAA
As	XRF	XRF	GFAA	GFAA
Cd	GFAA	GFAA	GFAA/FAA	GFAA
Cr	GFAA	XRF	GFAA	GFAA
Cu	XRF	XRF	GFAA/FAA	GFAA
Fe	XRF	XRF	FAA	FAA
Hg	CVAA	CVAA	CVAA	CVAA
Mn	XRF	XRF	GFAA/FAA	FAA
Ni	GFAA	XRF	GFAA	GFAA
Pb	GFAA	XRF	GFAA	GFAA
Sb	NA	NA	GFAA	GFAA
Se	XRF	GFAA	GFAA	GFAA
Si	XRF	XRF	COLOR	COLOR
Sn	HAA	HAA	GFAA	GFAA
Tl	GFAA	GFAA	GFAA	GFAA
Zn	XRF	XRF	FAA	FAA

GFAA - Graphite furnace atomic absorption spectrometry. HAA - Hydride generation atomic absorption spectrometry. CVAA - Cold vapor atomic absorption spectrometry. FAA - Flame atomic absorption spectrometry. XRF - X-Ray fluorescence spectrometry. NAA - Neutron activation analysis. COLOR - Colorimetry.

Table III.11. Analytical methods for trace elements used by Battelle and SAIC, 1987.

Element	Battelle		SAIC	
	Tissue	Sediment	Tissue	Sediment
Al	GFAA	XRF	GFAA/FAA	FAA
Ag	GFAA	GFAA	GFAA	GFAA
As	XRF	XRF	GFAA	GFAA
Cd	GFAA	GFAA	GFAA	GFAA
Cr	GFAA	XRF	GFAA	GFAA
Cu	XRF	XRF	GFAA/FAA	GFAA
Fe	XRF	XRF	GFAA/FAA	GFAA/FAA
Hg	CVAA	CVAA	CVAA	CVAA
Mn	XRF	XRF	GFAA/FAA	GFAA/FAA
Ni	GFAA	XRF	GFAA	GFAA
Pb	GFAA	XRF	GFAA	GFAA
Sb	NA	NA	GFAA	GFAA
Se	XRF	GFAA	GFAA	GFAA
Si	XRF	XRF	COLOR	COLOR
Sn	HAA	HAA	GFAA	GFAA
Tl	GFAA	GFAA	GFAA	GFAA
Zn	XRF	XRF	FAA	FAA

GFAA - Graphite furnace atomic absorption spectrometry. HAA - Hydride generation atomic absorption spectrometry. CVAA - Cold vapor atomic absorption spectrometry. FAA - Flame atomic absorption spectrometry. XRF - X-Ray fluorescence spectrometry. NAA - Neutron activation analysis. COLOR - Colorimetry.

2.1.2. Labware

Autoclave
Balance
Bottles, 50 mL, borosilicate
Bottles, polyethylene
Bottles, polyethylene, 60-mL
Flasks, volumetric, 50 mL, polypropylene
Jars, 60 mL, polyethylene
Mill, Mixer-Mill. Spex Industries, Edison, NJ.
Tubes, centrifuge, 25 mL, Oak Ridge style, Teflon
Virtis Unitrap II freeze-dryer. Gardiner, NY.

2.1.2. Reagents

[*Sources and purity of some reagents not available. Ed. Note.*]

Hydrochloric acid (HCl) [7647-01-0], concentrated (semi-conductor grade). J. T. Baker, Phillipsburg, NJ.
Hydrofluoric acid (HF) [7664-39-3], concentrated. J. T. Baker, Phillipsburg, NJ.
NIST SRM series 3100 spectrometric solutions. NIST, Gaithersburg, MD.
NIST SRM series 3133 spectrometric solutions. NIST, Gaithersburg, MD.
Nitric acid (HNO_3) [7697-37-2], concentrated (semi-conductor grade). J. T. Baker, Phillipsburg, NJ.
Nitric acid (HNO_3) [7697-37-2], double distilled from Vycor. G. Frederick Smith Chemicals, Columbus, OH.
Potassium permanganate ($KMnO_4$) [7722-64-7], (Hg free).
Sodium chloride (NaCl) [7647-14-5].

Table III.12. Analytical methods for trace elements used by Battelle and SAIC, 1988 and 1989.

Element	Battelle		SAIC	
	Tissue	Sediment	Tissue	Sediment
Al	GFAA	XRF	GFAA	GFAA
Ag	GFAA	GFAA	GFAA	GFAA
As	XRF	XRF	GFAA	GFAA
Cd	GFAA	GFAA	GFAA	GFAA
Cr	GFAA	XRF	GFAA	GFAA
Cu	XRF	XRF	GFAA	GFAA
Fe	XRF	XRF	FAA	FAA
Hg	CVAA	CVAA	CVAA	CVAA
Ni	GFAA	XRF	GFAA	GFAA
Pb	GFAA	XRF	GFAA	GFAA
Se	XRF	GFAA	GFAA Δ	GFAA Δ
Sn	HAA	HAA	◊	◊
Zn	XRF	XRF	FAA	FAA

GFAA - Graphite furnace atomic absorption spectrometry. HAA - Hydride generation atomic absorption spectrometry. CVAA - Cold vapor atomic absorption spectrometry. FAA - Flame atomic absorption spectrometry. XRF - X-Ray fluorescence spectrometry. NAA - Neutron activation analysis. Δ Se analyzed by Battelle for Year 4. ◊ Sn analyzed by Battelle for Years 3 and 4.

Standards, atomic absorption standards, 1000 ppm. Fisher Scientific, Pittsburgh, PA.

Stannous chloride ($SnCl_2 \cdot 2H_2O$) [10025-69-1]

Sulfuric acid (H_2SO_4) [8014-95-7], semi-conductor grade.

Water, Milli-Q. Millipore Corp., Bedford, MA.

2.2. Bivalve tissues digestion - SAIC

2.2.1. For all elements except Hg

The following methodology was used for sample processing for the analyses of all elements except mercury.

All bivalve specimens were sized and shucked prior to analytical processing. Bivalve specimens were shucked and the entire tissue mass of each animal placed in a sufficiently large, labeled polyethylene bottle. The bottles were tightly capped and the samples frozen. The samples were then macerated using a stirrer with a polypropylene shaft and cutting blades, and blended for a minimum of 10 min or until the samples appeared to be a homogenized slurry. Approximately 2 g of each sample were then weighed into 50-mL borosilicate bottles and reserved for later Hg analysis. An additional 50 g of each sample was transferred to labeled preweighed 60-mL polypropylene jars, the wet weights recorded, and the samples frozen. Sample aliquots were taken to a constant dry weight using a Virtis Unitrap II freeze-dryer. The sample dry weights were recorded and dry:wet weight ratios calculated. The dry and wet weights were used to convert the wet weights of the Hg samples to dry weights, since wet samples were used for Hg analysis. Wet samples were used for Hg analysis due to possible loss of Hg during the drying

process. Following the drying process, samples were ground to a homogeneous powder in their original containers using a Spex Mixer-Mill.

The samples were digested following a modification of Gorsuch (1970) and Risby (1979). Approximately 1.0 g of the dry sample from each station was placed in a 25-mL screw cap Teflon centrifuge tube. Five mL of concentrated nitric acid was added to each sample and the tubes capped prior to overnight digestion at room temperature. The next day, the tubes were loosely capped and placed in a 95°C water bath in the fume hood for 2 hr. The samples were swirled often. The caps were tightened and the samples placed in an autoclave for 2 hr at 115°C. The samples were removed from the autoclave, cooled, and transferred to 50-mL polypropylene volumetric flasks. The flasks were brought to volume with Milli-Q water and the samples transferred to labeled 60-mL polyethylene bottles and stored until analysis.

2.2.2. For Hg analysis

The following methodology, modified from EPA (1983), was used for preparation of Hg samples. Five milliliters of concentrated nitric acid (semi-conductor grade) was added to the samples, in 2 g borosilicate bottles. The sample bottles were capped and allowed to digest overnight at room temperature. Five milliliters of concentrated H_2SO_4 were then added to each sample. The sample bottles were loosely capped and heated in a 95°C water bath for 2 hr. The bottles were allowed to cool and approximately 10 mL of a saturated solution of $KMnO_4$ (Hg-free) was added until a purple color persisted. The samples were reheated for 1 hr, allowed to cool, tightly capped, and refrigerated until analysis.

2.3. Surficial sediments

2.3.1. For all elements except Hg

For all elements except Hg, samples were thawed, allowed to warm to room temperature, and homogenized while wet. Approximately 20 g of each sample was transferred to labeled 60-mL polyethylene bottles and stored frozen for later Hg analysis. An additional 50-g aliquot of each sample was transferred to labeled preweighed 60-mL polypropylene jars, the wet weight recorded, and the samples frozen. Unused portions of the samples were refrozen and archived. Sample aliquots, except those for Hg, were taken to a constant dry weight using a Virtis Unitrap II freeze-dryer. The sample dry weights were determined and the resulting dry:wet ratios were used to convert the wet weights of the Hg samples to dry weights. The dried samples were ground to a homogeneous powder in their original containers using a Spex Mixer-Mill.

Samples were digested following modifications of Eggimann and Betzer (1976) and Johnson and Maxwell (1981). Approximately 0.2-g aliquots of homogenized sediment were placed in 25-mL screw-cap Teflon centrifuge tubes. Four milliliters of concentrated HCl and 2 mL of concentrated HNO_3 were added to each tube. The tubes were loosely capped and placed in a 95°C water bath in fume hood for 2 h and frequently swirled. The samples were cooled, and 3 mL of concentrated HF were added. The bottles were re-capped tightly. Samples were placed in an autoclave at 115°C for 2 hr. The samples were cooled, transferred to 50-mL polypropylene volumetric flasks, and brought to volume with Milli-Q water. The samples were then transferred to labeled 60-mL polyethylene bottles and stored until analyzed.

2.3.2. For Hg analysis

Sample preparation for Hg analysis followed a modification of EPA Method 245.1 (1983). Approximately 1 g wet weight of the samples was weighed into labeled 50-mL borosilicate bottles. Five milliliters of concentrated HNO_3 and 5 mL of concentrated H_2SO_4 were added to each sample. The bottles were loosely capped and heated in a 95°C water bath for 2 hr, swirling often. Samples were cooled, the caps tightened, and refrigerated until analysis.

2.4. Sample analysis

The following equipment and techniques were used by SAIC to determine trace element concentrations in bivalve tissues and surficial sediments.

2.4.1. Graphite furnace atomic absorption spectrometry

Atomic absorption spectrophotometry (AAS) (using the graphite furnace according to the manufacturer's conditions) was used to analyze samples which had analyte concentrations not detectable by flame atomic absorption. A Perkin-Elmer No. 603 AAS equipped with an HGA-2200 graphite furnace, an AS-1 autosampler, a deuterium (D_2) lamp background corrector, electrodeless discharge lamps, and a Perkin-Elmer No. 056 Recorder were used. The D_2 background corrector was used for all analyses.* Standard additions were routinely performed along with standard calibrations. All sample values were calculated using the method of additions.

Manufacturer's instrument operating conditions were followed. AAS working standards were prepared from a mixed 10-ppm stock in 1% HNO_3 using Fisher 1000 ppm standards. Silver standards were prepared separately from a Fisher 1000-ppm standard.

2.4.2. Flame atomic absorption spectrometry

Samples not requiring the sensitivity of the graphite furnace atomic absorption were analyzed by flame atomic absorption. The Perkin-Elmer No. 603 was modified with air/acetylene and nitrous oxide/acetylene burners for flame analysis. A deuterium (D_2) lamp background corrector included with this instrument was used for all analyses. Standard additions and standard calibrations were performed regularly. AAS working standards were prepared from a mixed 10-ppm stock in 1% HNO_3 using Fisher 1000-ppm standards. Silver standards were prepared separately from a Fisher 1000-ppm standard.

2.4.3. Cold vapor atomic absorption spectrometry

Hg was determined by cold vapor atomic absorption spectrophotometry (CVAA) using a Laboratory Data Control No. 1235 Mercury Monitor equipped with a Perkin-Elmer 023 Recorder. A modification of EPA Method 245 (1983) was followed for analysis. Samples were reduced to destroy the excess $KMnO_4$ using a 10% solution of NH_2OH/HCl in 10% sodium chloride (NaCl). Next, the samples were reduced to the Hg° state using a 20% solution of stannous chloride ($SnCl_2$) in 3N HCl. The resulting Hg vapor was purged with a nitrogen (N_2) vapor through the above system. Working standards were prepared from a 10 ppm stock in 1% HNO_3 using a Fisher 1000-ppm standard. Standard additions were routinely performed.

* During Year 4, additional instrumentation was used to analyze sediments and tissues by GFAA. The second instrument was a computer-controlled Perkin-Elmer 5100PC equipped with a HGA-600 graphite furnace, AS-60 autosampler, Zeeman background correction, electrodeless discharge dual lamp power supply, and an Epson 3+ color computer with printer.

2.4.4. Colorimetry

Sample aliquots of the original digestates were diluted appropriately and analyzed colorimetrically forming a silicomolybdate complex (Strickland and Parsons, 1972). The sample absorbance was read at 810 nm, using 1-cm cells and a Hitachi No. 100-80 UV/Visible spectrophotometer. Working standards were prepared from a 10-ppm stock in 1% HNO_3 using a Fisher 1000-ppm standard. Standard additions were routinely performed.

3. REFERENCES

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