Major and Trace Element Analytical Methods of the National Status and Trends Program: 2000-2006

NOAA Technical Memorandum NOS NCCOS 29

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Cover photograph: mussel bed at Throgs Neck, NY.

Citation for this Report

Kimbrough, K. L., and G. G. Lauenstein (Editors). 2006. Major and Trace Element Analytical Methods of the National Status and Trends Program: 2000-2006. Silver Spring, MD. NOAA Technical Memorandum NOS NCCOS 29, 19 pp.

Major and Trace Element Analytical Methods of the National Status and Trends Program: Update 2000 - 2006

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1305 East-West Highway
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NOAA Technical Memorandum NOS NCCOS 29

March 2007

United States Department of Commerce	National Oceanic and Atmospheric Administration	National Ocean Service
Carlos M. Gutierrez Secretary	Conrad C. Lautenbacher, Jr. Administrator	John H. Dunnigan Assistant Administrator

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PREFACE

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This document contains analytical methods that detail the procedures for determining major and trace element concentrations in bivalve tissue and sediment samples collected as part of the National Status and Trends Program (NS&T) for the years 2000-2006. Previously published NOAA Technical Memoranda NOS ORCA 71 and 130 (Lauenstein and Cantillo, 1993; Lauenstein and Cantillo, 1998) detail trace element analyses for the years 1984-1992 and 1993-1996, respectively, and include ancillary, histopathology, and contaminant (organic and trace element) analytical methods.

The methods presented in this document for trace element analysis were utilized by the NS&T Mussel Watch and Bioeffects Projects. The Mussel Watch Project has been monitoring contaminants in bivalves and sediment for over 20 years, and is the longest active contaminant monitoring program operating in U.S. costal waters. Approximately 280 Mussel Watch sites are monitored on biennial and decadal timescales using bivalve tissue and sediment, respectively. The Bioeffects Project applies the sediment quality approach, which uses sediment contamination measurements, toxicity tests and benthic macroinfauna quantification to characterize pollution in selected estuaries and coastal embayments. Contaminant assessment is a core function of both projects.

Although only one contract laboratory was used by the NS&T Program during the specified time period, several analytical methods and instruments were employed. The specific analytical method, including instrumentation and detection limit, is noted for each measurement taken and can be found at http://NSandT.noaa.gov. The major and trace elements measured by the NS&T Program include: Al, Si, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Sn, Sb, Ag, Cd, Hg, Tl and Pb.

REFERENCES

Lauenstein, G. G. and A. Y. Cantillo (eds.) (1998) Sampling and analytical methods of the National Status and Trends Program Mussel Watch Project 1993-1996 Update: TERL Trace Element Quantification Techniques, Volume III. NOAA Technical Memorandum NOS ORCA 71, Silver Spring, MD. 219 pp.

Lauenstein, G. G. and A. Y. Cantillo (eds.) (1993) Sampling and analytical methods of the National Status and Trends Program National Benthic Surveillance and Mussel Watch Projects 1984-1992: Comprehensive descriptions of elemental analytical methods, Volume III. NOAA Technical Memorandum NOS ORCA 71, Silver Spring, MD. 219 pp.

TRACE ELEMENT QUANTIFICATION TECHNIQUES: 2000 - 2006

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ABSTRACT

Sample preparation and analysis methods have been developed and refined that allow the accurate and precise determination of major and trace elements in sediment and biological tissue samples. Sample preparation emphasizes homogenization and total digestion steps that minimize contamination. Analyses utilize atomic spectroscopy techniques, including a full suite of quality assurance and quality control samples, with an emphasis on certified reference materials, in order to produce reliable data. These methods allow measurement of both background and elevated concentrations in samples collected as part of NOAA's National Status and Trends Program.

1.0 INTRODUCTION

This method documents the analytical procedures used for major and minor element analysis of marine sediments and tissue samples collected by NOAA's National Status and Trends Program. These procedures were used by the Trace Element Research Laboratory (TERL), Department of Veterinary Integrative Biosciences, Texas A&M University to analyze samples collected from 2000 to 2006.

2.0 EQUIPMENT AND SUPPLIES

2.1 INSTRUMENTATION

Perkin-Elmer model DRC-2. Inductively coupled plasma mass spectrometry (ICP-MS) Perkin-Elmer, Norwalk, CT. Autosampler, Perkin-Elmer AS 93 Plus

Spectro A.I. CIROS inductively coupled plasma optical emission spectrometry (ICP-OES). Spectro A.I., Fitchburg, MA. Autosampler, Spectro A.I. model AS400

Perkin-Elmer SIMAA 6000 graphite furnace atomic absorption spectrometry (GFAAS) Perkin-Elmer, Norwalk, CT. Autosampler, Perkin-Elmer model AS 72

Perkin-Elmer Analyst 100 flame atomic absorption spectrometry (FAAS). Perkin-Elmer, Norwalk, CT

PSA Millennium Excalibur atomic fluorescence spectrometer. PS Analytical, Orpington, Kent, UK. Autosampler, PS Analytical model AS300

Cetac M7500 cold vapor atomic absorption Hg analyzer. Cetac Technologies, Omaha, NE. Autosampler, Cetac model ASX510

OI Analytical MDS 7295 microwave digestion system. OI Analytical, College Station, TX

CPI ModBlock graphite block digestion system. CPI, Santa Rosa, CA

2.2 SUPPLIES

Argon, liquid

Acetylene, welder's grade

Nitrogen, liquid

Oxygen, compressed

Nitrous oxide

Hollow cathode lamps. Perkin-Elmer, Norwalk, CT

Electrodeless discharge lamps (EDL). Perkin-Elmer, Norwalk, CT

Boosted discharge hollow cathode lamps (BDHCL). Photron, Victoria, Australia

Graphite tubes, THGA, Perkin-Elmer B0504033

Autosampler cups, 1.1 mL, polystyrene, Perkin-Elmer N1012010

Autosampler vials, 5 mL polypropylene, 60818-281. VWR Scientific Products, West Chester, PA

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 diameter, Teflon

Balls, 3.5 cm diameter, Teflon

Bench, clean, with HEPA filter. Liberty Industries, East Berlin, CT

Bottles, screw-cap bottles, polyethylene, wide-mouth, 1 oz., Nalgene 2104-0001

Drying oven, 60 °C, NAPCO 332. Curtin-Matheson Scientific, Houston, TX

Drying oven, 130 °C, Thelco

Freeze dryer system, Labconco Freezone 12L. Labconco, Kansas City, MO

Large jars, Teflon lined caps

Pipette tips, for Finnpette, Finntip 62. Labsystems

Pipette tips, polypropylene for Eppendorf pipettes, 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, polystyrene; 5, 15, and 40 dram. Baxter Scientific Products, McGaw Park, IL

Vials, snap-cap, polyethylene, 70 mL. CPI, Santa Rosa, CA

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

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

2.6.1. INORGANIC VENTURES, LAKEWOOD, NJ

Table 1. Baxter Ricca standards, 1000 ppm. Ricca Chemical Co., Arlington, TX

Individual elements standards, 1,000

Element	Stock number
Hg	CGHG1-1

Individual element standards, 10,000 ppm.

Element	Stock number
Ag	CGAG10-1
Al	CGAL10-1
As	CGAS10-1
Cd	CGCD10-1
Cr	CGCR10-1
Cu	CGCU10-1
Fe	CGFE10-1
Mn	CGMN10-1
Ni	CGNI10-1
Pb	CGPB10-1
Sb	CGSB10-1
Se	CGSE10-1
Sn	CGSN10-1
Tl	CGTL10-1
Zn	CGZN10-1

QC-1 mixed standard, 100 ppm: Al, Fe, Zn; 10 ppm: Ba, Be, B, Cd, Ag, Sr
QC-2 mixed standard, 100 ppm: Sb, As, Cr, Co, Cu, Pb, Mn, Mo, Ni, Se, Tl, Sn, Ti, V
ICP-MS custom mixed standard, 10 ppm: Ag, Al, As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, Th, Tl, U, V, Zn

2.6.2 CPI, SANTA ROSA, CA

ICP-MS internal standard, 10 ppm:

Li-6, Rh, Bi, Ho, Sc, Tb, In

3.0 SAMPLE TREATMENT

3.1 OYSTER AND MUSSEL TISSUE

3.1.1 BIVALVE SHUCKING

Whole oysters and mussels were rinsed with distilled water to remove extraneous material and shucked with a stainless steel knife (using care not to touch the tissue). Whole soft tissue was removed with plastic forceps and rinsed with distilled, deionized water to remove sediment particles from gills and exterior tissue surfaces. Soft parts were transferred to a tared Ziploc polyethylene bag, and the number of individuals shucked and placed in the bag was recorded. When soft tissue from all individuals from a site had been collected, they were weighed on a top loading balance to measure the total sample wet weight. The pooled samples were stored in a freezer.

3.1.2 BULK HOMOGENIZING

Ziploc bags containing pooled tissue were removed from the freezer and allowed to thaw. The entire pooled sample was transferred to an acid-washed Teflon jar and 3 large Teflon balls were added. The Teflon lids were securely tightened and the jars placed in Ziploc bags and shaken in an industrial paint shaker for 20 min. After the bulk sample was homogenized, an aliquot of the sample was transferred to a clean 40 dram snap vial and frozen.

3.1.3 FREEZE DRYING

The frozen aliquot from the bulk homogenization step was placed in a freeze drier and allowed to dry for several days, depending upon the total mass of tissue being dried at one time. In some cases it was 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 were thoroughly dried, three small Teflon balls were inserted into each snap cap vial, the lids were affixed, and the samples placed in a Spex shaker mill for 1 min. The Teflon balls were then removed, and the samples stored in closed vials until weighing.

3.1.5 DIGESTION

Approximately 0.2 g samples of dried tissue were weighed to the nearest 0.0001 g and transferred to tared, acid-washed Teflon bombs. A 3 mL aliquot of HNO_3 was added and

the bombs sealed in a digestion system and cooked according to the appropriate method (Section 3.2.4). The samples were allowed to cool and 1 mL of H_2O_2 was added to each sample, then heated to promote the reaction. After the samples were allowed to cool, 1 mL of HCl was added to each sample, and then heated gently. The samples were cooled and 15 mL of deionized distilled water was added. The bombs were closed, mixed by shaking, and weighed to 0.01 g to determine the total solution weight. The digest solution was transferred to labeled 1 oz polyethylene bottles. Solution density was determined by weighing known volumes with calibrated Eppendorf pipettes in order to determine solution volume.

For analysis of Hg, tissue samples were digested using a modified version of the Environmental Protection Agency (EPA) method 245.6. Approximately 0.15 to 0.3 g (dry weight) of sample was weighed into a 70 mL snap cap vial. Concentrated H_2SO_4 (2.5 mL) and 1.5 mL of concentrated HNO_3 were added and the samples heated in a digestion block at 90 - 95 °C for 30 min. After cooling, 10 mL of distilled water, 10 mL of 5% (w/w) $KMnO_4$, and 5 mL of 5% (w/w) of $K_2S_2O_8$ were added to each tube, and the samples left overnight without heating. Before analysis, 5 mL of 10% (w/w) $NH_2OH \cdot HCl$ were added to reduce excess $KMnO_4$ and the volume brought to 40 mL with distilled water.

3.2 BOTTOM SEDIMENT

Bottom sediment samples were prepared for analysis by freeze drying and wet digestion.

3.2.1 HOMOGENIZATION

Wet bulk sediment was stored frozen until sample processing began. Sediment was thawed and homogenized with a clean plastic spatula. A homogeneous aliquot of the bulk sample was transferred to a labeled 40 dram snap cap vial and frozen. The remainder of the sample was archived in the freezer.

3.2.2 FREEZE DRYING

The snap cap vial containing the sediment sub-sample was 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 ranged from 12 - 76 hr.

3.2.3 HOMOGENIZATION OF DRY ALIQUOT

In some cases, homogenization of freeze dried sediment was accomplished by simply placing the snap cap vials in a Spex shaker. When this was not sufficient, the samples were individually ground in alumina mortar and pestles and the powdered samples returned to the vials in which they were freeze dried.

3.2.4 DIGESTION

Approximately 0.2 g of homogenized, dried sediment was weighed to the nearest 0.0001 g and transferred to tared 70 mL snap cap vials. A 3 mL aliquot of HNO_3 was added and the vials were placed in a 95 °C digestion block for a total of approximately 6 hr. During this time, the vials were periodically removed from the block and swirled to mix. After this period, the vials were removed from the block and allowed to cool before 2 mL of concentrated HF was added. The vials were then returned to the block for approximately 2 hr. After cooling, 15 mL of 4% boric acid were added and the vials returned to the block for another 1 to 2 hr. After the samples were allowed to cool, the content of the vials were mixed by shaking, and the vials weighed to 0.01 g to determine the total solution weight. Digest solutions were then transferred to labeled 1 oz polyethylene bottles. Solution density was determined by weighing known volumes with calibrated Eppendorf pipettes in order to determine solution volume.

For analysis of Hg, sediment samples were digested using a modified version of EPA method 245.5. Approximately 0.1 to 1.0 g (dry weight) of sample was weighed into a 70 mL snap cap vial. Concentrated H_2SO_4 (2.5 mL) and 1.5 mL of concentrated HNO_3 were added and the samples heated in a digestion block at 90 - 95 °C for 30 min. After cooling, 10 mL of distilled water, 10 mL of 5% (w/w) $KMnO_4$, and 5 mL of 5% (w/w) of $K_2S_2O_8$ were added to each tube, and the samples again heated in a digestion block at 90 - 95 °C for 30 min. Before analysis, 5 mL of 10% (w/w) $NH_2OH \cdot HCl$ were added to reduce excess $KMnO_4$ and the volume brought to 40 mL with distilled water.

4.0 CALIBRATION AND ANALYSIS

Calibration standards were prepared by serial dilution of commercially available standards using calibrated micropipettes, a top loading balance, deionized distilled water and acids to match the matrix of the samples and methods. Concentrations of working standards were verified by comparison with independent standards traceable to the National Institute of Standards and Technology (NIST) Standard Reference Materials.

In all cases, final working standards were prepared in an acid matrix that matched that of the samples being analyzed. For some elements, it was necessary to further attempt to match the major ion composition of the samples. This was most apparent in graphite furnace AAS when the peak shape of the samples was 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 were prepared in a solution that had Si, Al, Fe, Ca, and Mg added at final concentrations of 3000, 400, 200, 100, and 100 ppb, respectively.

5.0 CALCULATIONS

Trace metal concentrations were 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.

The least-squares fit of the data was calculated, treating Abs (or Abs-sec., emission intensity, mass/charge ratio, etc.) as the dependent variable (y), and concentration as the independent variable (x). If the concentration range extended into the non-linear range, a second order fit was used. The intercept, the first and second order coefficients (if appropriate), and R, the correlation coefficient, were calculated.

$$Abs = a + b\,(conc_{obs})$$

$$conc_{obs} = \frac{Abs - a}{b}$$

where $conc_{obs}$ was the calculated observed concentration, Abs was the instrumental signal (e.g., Absorbance for atomic absorption instruments, emission for ICP-OES, or counts per second for ICP-MS), a was the intercept, and b was the slope of the regression line.

5.1 DILUTION FACTOR

The dilution factor, DF, resulting from sample digestion was calculated using the equation

$$DF = \frac{[(\text{bomb tot.}) - (\text{bomb tare})]}{(\text{spl. wt.}) \times (\text{soln. dens.})}$$

where bomb tare was the tare weight of the digestion vessel (g); bomb tot. was the total weight of the digestion vessel plus digest solution (g); spl. wt. was the weight of the dry sample (g); and soln. dens. was the density of the digest solution (g/cm^3).

5.2 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 $conc_{obs}$ was the concentration observed in the aqueous sample; DL was the detection limit of the analytical technique; DF_{instr} was the dilution factor of the analytical technique, if necessary; and DF_{dign} was the dilution factor of the sample digestion.

6.0 INSTRUMENTAL ANALYSIS

6.1 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 reagent water

INSTRUMENT SETTINGS:

Instrument settings change on a daily basis as sensitivity is optimized. This is especially true for autolens settings and dual detector calibration. The following software settings give typical values for parameters that remain relatively constant in day-to-day operation:

Power: 1400 watts

Plasma gas flow: 15 L/min.

Auxiliary flow: 1.2 L/min.

Nebulizer flow: 1.0 L/min.

Analog stage voltage: -2200 V

Pulse stage voltage: 1200 V

Quadrupole rod offset: -3 V

Cell rod offset: -9 V

RPQ: 0.25

Cell path voltage: -24 V

Sample uptake: 1 mL/min.

Internal standard uptake: 0.1 mL/min.

PROCEDURE:

Scan mode: peak hopping

Dwell time per AMU: 50 msec.

Sweeps/reading: 20

Integration time: 1000 msec.

Replicates: 3

Autolens: On

Blank subtraction: After internal standard

Measurement unit: cps

Mode: Dual (pulse/analog)

Internal standards: Ga, Rh, In, Bi

STANDARDS:

Calibration standards (representative of sample concentration) are prepared from dilutions of NIST-traceable multi-element standards. The low concentration standard is based on instrument sensitivity (e.g., 0.05 ppb for Pb, 0.5 ppb for Al). Mid and high standards are at 20 and 200 ppb, respectively. Other reference materials (NIST 1640 Trace Elements in Water) are used as check standards. Calibration verification is performed periodically with a blank and mid-range standard (20 ppb).

TYPICAL SENSITIVITY:

Sensitivity is approximately 5×10^7 counts per sec. per ppm for In - 115.

CALIBRATION:

Weighted linear, least-squares regression.

7.2 INDUCTIVELY COUPLED PLASMA - OPTICAL EMISSION SPECTROMETRY

Aluminum, arsenic, chromium, copper, iron, manganese, nickel, silver, and zinc in sediments or tissues.

METHOD:

Inductively coupled plasma - optical emission spectrometry

DIGEST MATRIX:

Direct analysis of digestate

INSTRUMENT SETTINGS:

The following software settings give typical values for parameters that remain relatively constant in day-to-day operation:

Power: 1400 watts

Plasma gas flow: 12 L/min.

Auxiliary flow: 1.0 L/min.

Nebulizer flow: 0.7 L/min.

PROCEDURE:

Integration time: 45 sec.

Integration option: "Best SNR"

Internal standards: Au, In, Yb

STANDARDS:

Calibration standards are prepared from dilutions of NIST-traceable single element standards. Calibration verification standards are prepared from dilutions of NIST-traceable multi-element standards. All standards are prepared to match sample matrix.

CALIBRATION:

Weighted linear, least-squares regression.

7.3 ATOMIC FLUORESCENCE SPECTROMETRY

Arsenic and selenium in sediments or tissues

METHOD:

Hydride generation - atomic fluorescence spectrometry

DIGEST MATRIX:

1 to 10 dilution of digestate, final 3N HCl matrix

INSTRUMENT SETTINGS: The following software settings give typical values for parameters that remain relatively constant in day-to-day operation:

ANALYTE:	As	Se
Primary lamp current:	27.5 mA	20 mA
Boost lamp current:	35 mA	25 mA
Gain:	100	10
Pump 1 speed:	100	100
Pump 2 speed:	50	50
Range (ppb):	0 – 50	0 - 10
Mode:	Pk height	Pk area
Typical sensitivity (1 ppb):	20	500

PROCEDURE:

Delay time: 30 sec.

Analysis time: 20 sec.

Memory time: 50 sec.

STANDARDS:

Calibration standards are prepared from dilutions of NIST-traceable single element standards. Calibration verification standards are prepared from dilutions of NIST-traceable multi-element standards. All standards are prepared to match sample matrix.

CALIBRATION: Weighted linear, least-squares regression.

7.4 ATOMIC ABSORPTION SPECTROMETRY

Hg in sediments or tissues

METHOD:

Cold vapor - atomic absorption spectrometry

DIGEST MATRIX:

Direct analysis of digestate

INSTRUMENT SETTINGS:

The following software settings give typical values for parameters that remain relatively constant in day-to-day operation:

Argon flow rate: 150 mL/min.

Pump rate: 50%

Range: 0 – 50 ppb

PROCEDURE:

Sampling time: 23 sec.

Delay time: 53 sec.

Read time: 5 sec.

Replicates: 5

Background read time: 10 – 14 sec.

Rinse time: 70 sec.

STANDARDS:

Calibration standards are prepared from dilutions of NIST-traceable single element standard. Calibration verification standards are prepared from dilutions of a different NIST-traceable single element standard. All standards are prepared in 7% v/v HCl matrix.

CALIBRATION:

Weighted linear, least-squares regression.

7.5 MICROWAVE DIGESTION PROGRAM

Trace metals, including Hg in sediments or tissues

INSTRUMENT SETTINGS:

The following software settings give typical values for parameters that remain relatively constant in day-to-day operation:

PROCEDURE:

Pressurized steps (nitric acid, hydrofluoric acid):

STAGE	POWER (%)	SETTING (psi)	DWELL (min.)	MAX (min.)
1	50	20	2	5
2	75	40	5	6
3	75	60	2	3
4	75	80	2	3
5	75	100	2	3
6	75	120	2	3
7	75	140	15	16

Non-pressurized steps (hydrogen peroxide, hydrochloric acid, boric acid):

POWER (%)	SETTING (°C)	DWELL (min.)	MAX (min.)
25	85	5	10

7.6 DETECTION LIMITS

The analytical detection limits were determined by following procedures outlined in the Federal Register (1984). Method detection limits for specific measurements can be found online at http://NSandT.noaa.gov.

Table 2. Mussel Watch Project tissue major and trace elements, method limits of detection (µg/g dry weight) for 2000 – 2003*.

	Tissue MDL	Sediment MDL
Sample size	**200 mg**	**300 mg**
Element (method)	**n=9**	**n=2**
Ag (ICP-MS)	0.05	0.06
Al (ICP)	6.32	24.6
As (ICP)	2.53	1.97
Cd (ICP)	0.25	0.07
Cr (ICP)	0.63	0.20
Cu (ICP)	0.63	0.20
Fe (ICP)	1.27	9.83
Hg (CVAAS)	0.03	0.02
Mn (ICP)	0.25	0.10
Ni (ICP)	0.63	0.49
Pb (ICP-MS)	0.06	0.07
Sb (ICP-MS)	N/A	0.10
Se (AFS)	0.03	0.03
Si (ICP)	N/A	246
Sn (ICP-MS)	0.13	0.20
Zn (ICP)	1.18	0.20

Note: Tissue MDLs were calculated by averaging the concentration for each analyte for all blanks analyzed with the 2003 samples (not including Great Lakes samples which were analyzed with 2004 samples). Sediment MDLs were calculated by averaging the concentration for each analyte for all blanks analyzed with the 2003 sediments.

* All samples from 2000-2003 were analyzed in 2003.

Table 3. Mussel Watch Project tissue major and trace elements, method limits of detection (µg/g dry weight) for 2004.

Sample Size	Tissue MDL 200 mg n=9	Sediment MDL 300 mg n=2
Ag (ICP-MS)	0.04	0.06
Al (ICP)	4.88	24.6
As (ICP)	1.95	1.97
Cd (ICP)	0.20	0.07
Cr (ICP)	0.49	0.20
Cu (ICP)	0.49	0.20
Fe (ICP)	1.10	9.83
Hg (CVAAS)	0.01	0.02
Mn (ICP)	0.20	0.10
Ni (ICP)	0.49	0.49
Pb (ICP-MS)	0.043	0.07
Sb (ICP-MS)	N/A	0.10
Se (AFS)	0.05	0.03
Si (ICP)	N/A	246
Sn (ICP-MS)	0.09	0.20
Zn (ICP)	0.50	0.20

8.0 REFERENCES

Federal Register. 1984. vol. 49, No. 209:198-199.

United States Department of Commerce

Carlos M. Gutierrez
Secretary

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Vice Admiral Conrad C. Lautenbacher, Jr. USN (Ret.)
Under Secretary of Commerce for Oceans and Atmospheres

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