Section C

METALS

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INTRODUCTION

The following sections are divided into various topics including:

1. Sample Preparation
2. Instrumental Analysis
3. Specific Elemental Conditions

The intent of these methods is not to exclude other techniques but, rather, to provide information on the most commonly used protocols. Other acceptable techniques are encouraged providing equivalent or better performance can be established.

The routine methods proposed in the manual include various atomic spectroscopy techniques. Not all elements have been covered for each technique even though it may be practical to use that method. For instance, ICP is well suited for the analysis of calcium although only atomic absorption is described in the element specific section. Refer to the ICP section 2.4 for a list of capabilities and the associated detection levels.

Additionally, not all elements are represented in this manual currently. Future revisions will likely include these methods as well as any updated information available.

1. SAMPLE PREPARATION

1.0.1 Introduction

Environmental samples submitted to a laboratory for metals analyses are subject to a variety of special handling needs and precautions. The following serves to alert the analyst to most of the common concerns encountered. Refer to the QA/QC section for additional information.

1.0.2 Sample Contamination

Due to the abundance and mobility of many metals, caution must always be taken to eliminate potential contamination sources. This includes all materials that contact the samples, exposure to dust and fumes and reagents used in the preservation, preparation and analysis procedures. All procedures must be reviewed and appropriate measures taken to address these concerns. Concurrent analysis of method blanks must be carried out to monitor contamination.

1.0.3 Sample Homogeneity

The ability to obtain a representative subsample for analysis is one of the most important steps in the measurement process. The analyst must always ensure that samples are properly homogenized and subsampled prior to analysis. If a unique physical property prohibits this, the analyst must note this information and alert others of this concern.

1.0.4 Unique Characteristics

Many samples contain physical or chemical attributes that can affect the performance of the analysis method used. Since most analytical protocols do not address unusual sample characteristics, the analyst must occasionally make modifications to procedures. These modifications must be validated through an appropriate method validation procedure.

1.0.5 Sample/Extract Stability

The stability of metals must be considered before, during and after sample preparation. Losses of some volatile elements could occur during drying and heating operations. In addition, chemical and physical changes such as precipitation, absorption, adsorption, oxidation, etc., should be considered at all times. As a general rule, samples should be prepared and analyzed as soon as practical after submission to the laboratory. Guidelines such as the “EPA Holding Times” exist for many parameters indicating typical stability of elements in solution.

1.1 Aqueous Samples

Revision Date: Sept 15, 2017

1.1.1 Digestion for Total Metals in Water - Prescriptive

Parameter	Total Metals in Water
Analytical Method	Nitric – Hydrochloric acid digestion, Instrumental analysis

Introduction

This method was prepared for BC MOE by the BCELTAC to provide improved consistency of results for total metals in water. All definitive elements of the method have been prescribed to minimize inter-laboratory variability.

This method uses a prescribed mixture of nitric and hydrochloric acids with a standardized digestion time and temperature. Laboratories are allowed some flexibility regarding apparatus and heating methods, but variations in acid type or concentration, digestion time, or digestion temperature are not permitted.

This method is BC MOE approved for the digestion of 37 metals in waters, including mercury (subject to performance requirements being met). However, other methods are also available for mercury, including potassium permanganate / potassium persulfate digestion and bromine monochloride oxidation.

Method Summary

Samples are digested with a mixture of nitric and hydrochloric acids. Instrumental analysis of sample extracts can be performed by a variety of analytical methods.

This method provides the sample preparation procedure for the analysis of total metals. Total metals include all metals, inorganically and organically bound, both dissolved and particulate (APHA 3030A). The terms total metals and total recoverable metals are used interchangeably and are defined as the concentration of analyte measured in an unfiltered aqueous sample following treatment by refluxing with hot dilute mineral acid (US EPA 200.2).

Digestion by this procedure is required for total metals analysis of any water sample with turbidity >1 NTU, or for any sample that is visibly coloured, or that has any noticeable odour. Colourless samples with no apparent odour that are verified by measurement to have turbidity <1 NTU are either analyzed as received or are digested.

This method is prescriptive. It must be followed exactly as described. Where minor deviations are permitted, this is indicated in the text.

MDL(s) and EMS Analyte Code(s)

This method is applicable to the following parameters:

Analyte	CAS Number	EMS Code	Analyte	CAS Number	EMS Code
Aluminum	7429-90-5	AL-T	Molybdenum	7439-98-7	MO-T
Antimony	7440-36-0	SB-T	Nickel	7440-02-0	NI-T
Arsenic	7440-38-2	AS-T	Phosphorus	7723-14-0	P-T
Barium	7440-39-3	BA-T	Potassium	7440-09-7	K-T
Beryllium	7440-41-7	BE-T	Selenium	7782-49-2	SE-T
Bismuth	7440-69-9	BI-T	Silicon	7440-21-3	SI-T
Boron	7440-42-8	B-T	Silver	7440-22-4	AG-T
Cadmium	7440-43-9	CD-T	Sodium	7440-23-5	NA-T
Calcium	7440-70-2	CA-T	Strontium	7440-24-6	SR-T
Chromium	7440-47-3	CR-T	Sulfur	7704-34-9	S-T
Cobalt	7440-48-4	CO-T	Thallium	7440-28-0	TL-T
Copper	7440-50-8	CU-T	Thorium	7440-29-1	TH-T
Iron	7439-89-6	FE-T	Tin	7440-31-5	SN-T
Lead	7439-92-1	PB-T	Titanium	7440-32-6	TI-T
Lithium	7439-93-2	LI-T	Tungsten	7440-33-7	W-T
Magnesium	7439-95-4	MG-T	Uranium	7440-61.1	U-T
Manganese	7439-96-5	MN-T	Vanadium	7440-62-2	V-T
Mercury	7439-97-6	HG-T	Zinc	7440-66-6	ZN-T

Other metals may be analyzed by this method if acceptable performance is demonstrated and validated.

EMS Method Code

Refer to EMS Parameter Dictionary on the Ministry of Environment and Climate Change Strategy website for all current EMS codes.

Method Limitation

This digestion procedure may not be sufficiently vigorous to solubilize all particulate metals in the sample. Even in these cases, this method does provide a conservative measure of environmentally or ecologically available metals.

This method is suitable for digestion of water samples containing silver concentrations of up to 0.1 mg/L (US EPA 200.2). Samples containing higher levels of silver must be diluted prior to digestion by this procedure.

The solubility and stability of barium is limited in the presence of free sulfate using this method (US EPA 200.2).

This method is not suitable for the determination of volatile low boiling point organo-mercury compounds (US EPA 200.2).

Matrix

Water, including fresh water, seawater, brackish water, and wastewater.

Interferences and Precautions

The interferences encountered will differ depending on the instrumental method used to analyze the sample extracts. Interferences should be clearly outlined and controlled in the analysis procedure. High concentrations of acids may cause physical interferences with some instrumental techniques.

Sample Handling and Preservation

Sampling should be done by qualified personnel. Samples must be collected and stored such that degradation or alteration of the sample is minimized.

Metals other than Mercury: Collect samples in clean high-density polyethylene (HDPE), glass, or Polytetrafluoroethylene (PTFE) containers. Preserve in the field with nitric acid to pH < 2. Treatment of samples with approximately 3 mL of 1:3 HNO_3 : Deionized water per 250 mL sample is recommended. Adding nitric acid to the original sample container at the laboratory within 14 days of sampling is an acceptable alternative to field preservation (equilibrate ≥ 16 hours prior to sub-sampling).

Mercury: Collect samples using only glass or PTFE containers. Field-preserve with HCl to pH < 2. Adding BrCl to the original sample container at the laboratory within 28 days of sampling is an acceptable alternative to field preservation (use ≥ 5 mL BrCl solution per litre of sample, equilibrate ≥ 24 hours prior to sub-sampling).

Stability

Holding Time:

Metals (excluding Mercury): 6 months.

Mercury: 28 days.

Results reported for samples digested beyond holding times must be qualified.

Storage: No storage temperature requirement (US EPA 40CFR May 18, 2012).

Equipment and Supplies

1. Heating source (e.g., block digester, hotplate, water bath) capable of maintaining a sample extract temperature of 95 ± 5°C).
2. Acid dispensers.
3. Vapour refluxing cover to fit digestion vessel (e.g., reflux cover, watch glass, etc.).
4. Digestion Vessels (e.g., block digester tube, beaker, flask, etc.).
5. Gloves.
6. Filters (optional; filtration through large pore size filters, e.g., 20 – 25 µm, may be necessary for filtration of some samples prior to analysis).
7. Filter funnels (optional).
8. Glass thermometer or suitable temperature sensor.

Reagents

1. Nitric Acid (HNO_3), concentrated (67 - 70%), ACS or reagent grade minimum.
2. Hydrochloric Acid (HCl), concentrated (36 - 40%), ACS or reagent grade minimum.
3. Water, de-ionized (ASTM Type I or equivalent recommended).

Safety

Wear appropriate PPE (Personal Protective Equipment) including lab coat, gloves, and safety glasses. Add acid to samples and perform digestions under a fume hood.

Procedure

Samples are prepared and digested using the following procedures:

No-Digestion Option for Samples with Low Turbidity

Digestion is not required for single-phase samples with measured turbidity <1 NTU with no visible colour and no discernable odour. To qualify for this exception, measured turbidity values from the raw (unacidified) cut, or from the acidified total metals cut must be measured and recorded. If the raw cut is used for turbidity measurement, visually confirm that no precipitates exist in the acidified portion.

For samples that were not acidified in the field, acidify with HNO_3 to pH <2. Shake the sample to mix. Let samples stand in their original containers for at least 16 hours prior to analysis to allow potentially adsorbed metals to re-dissolve. Apply appropriate qualifiers to any total metals samples that have not been allowed to equilibrate for this time. No further preparation is required.

Digestion is required for all samples that do not meet the above criteria for turbidity, colour, odour and phase.

Sample Preparation - Digestion

For samples that were not acidified in the field, acidify with HNO_3 to pH < 2. Shake the sample to mix. Let samples stand in their original containers for at least 16 hours prior to analysis to allow potentially adsorbed metals to re-dissolve. Apply appropriate qualifiers to any total metals samples that have not been allowed to equilibrate for this time.

The following procedure uses a 50 mL sub-sample. Sample volume may be scaled up or down if the ratios of HNO_3 or HCl to sample are not changed.

1. Shake the sample well to homogenize before sub-sampling for digestion.
2. Take a 50 ± 1 mL sub-sample and dispense the sample into a digestion vessel, which must be fitted with a reflux cap and which must be capable of supporting open vessel reflux action. Examples of digestion vessels fitted with a reflux cap include a beaker fitted with a watch glass, or an Erlenmeyer flask or digestion tube fitted with a reflux cover or watch glass. Include Method Blanks, Lab Duplicates and Reference Materials or Laboratory Control Samples with each batch of samples.
3. Add 1.0 ± 0.1 mL conc. HNO_3 and 0.50 ± 0.05 mL conc. HCl to each sample (assuming 50 mL sample size).
4. Prepare a Method Blank for every batch of samples. Add 50 ± 1 mL of de-ionized water into a digestion vessel. Add 1.0 ± 0.1 mL of conc. HNO_3 and 0.50 ± 0.05 mL conc. HCl to the water.
5. Prepare a Reference Material or Laboratory Control Sample for every batch of samples. Add 50 ± 1 mL of the RM or LCS solution into a digestion vessel. Add 1.0 ± 0.1 mL of conc. HNO_3 and 0.50 ± 0.05 mL conc. HCl to the water.
6. Prepare at least one duplicate for every batch of samples.
7. Cover samples with a reflux cover or watch glass and digest for 2.0 – 2.5 hours at 95 ± 5°C (this excludes the time needed to pre-heat the samples to 95°C). The heat for digestion must maintain the sample extract temperature at 95 ± 5°C. This refers to the temperature of the sample extract in a digestion vessel covered with a reflux cap, not the temperature setting on the heating source, and not the temperature of an uncovered digestion vessel. It is recommended that the sample extract temperature be monitored and recorded with each batch, using 50 ± 1 mL de-ionized water with 1.0 ± 0.1 mL conc. HNO_3 and 0.50 ± 0.05 mL conc. HCl.
8. After 2.0 – 2.5 hours at 95 ± 5°C, remove the samples from heat source and let cool for at least 30 minutes (this will reduce any potential harmful fumes from the sample).
9. Remove the reflux cover or watch glass and reconstitute sample(s) back to 50 ± 1 mL with de-ionized water. Shake samples to mix. It is not necessary to rinse the condensation from the reflux cover or watch glass back into the sample tube.
10. Analyze the digested sample using appropriate analytical methods. If significant solids are present in the sample after digestion, decant, centrifuge, or filter the sample prior to analysis to prevent sample introduction issues. If any sample extracts are filtered, the method blank must also be filtered.
11. Record and report any anomalies observed during the digestion and analysis.

Quality Control

Summary of QC Requirements		
QC Component	Minimum Frequency	Minimum Data Quality Objectives
Method Blank (MB)	One per batch (max 20 samples)	Less than reported DL
Lab Control Sample (LCS)	One per batch (max 20 samples)	80 – 120%
Lab Duplicates (DUP)	One per batch (max 20 samples)	≤ 20% RPD [or within 2x reported DL for low level results]
Matrix Spike (MS) or Reference Material (RM)	One per batch (max 20 samples)	70 – 130%
Field Duplicates	Recommended	None specified
If DQOs are not met, repeat testing or report qualified test results. DQOs do not apply to MS results where sample background exceeds spike amount.		

Method Validation Requirements

Initial Method Validation requirements as outlined below must be completed before this method may be used to generate results for unknown samples. The method must be re-evaluated periodically (every two years is recommended as a suitable frequency). Prepared validation samples must be analyzed by all instrument methods used for routine analysis.

Demonstration of Accuracy and Precision

Prepare and analyze at least 8 replicates of a Reference Material or Laboratory Control Sample.

Where the above Reference Material or Laboratory Control Sample is utilized for routine QC purposes, re-validations should be conducted using all routine QC data available for the review period.

Accuracy is measured as Percent Difference from the targets for the Reference Material or Laboratory Control Sample. For each metal, average accuracy must be within 90-110% of the targets, for results ≥ 5 times the Reported Detection Limit. Precision must be <10% RSD for results ≥ 5 times the Reported Detection Limit.

References

1. US EPA Method 200.2, Sample Preparation Procedure for Spectrochemical Determination of Total Recoverable Elements, National Exposure Research Laboratory, Office of Water, US EPA, Cincinnati, OH, October 1999.
2. APHA 3030A, Preliminary Treatment of Samples – Introduction, 2004.
3. US EPA 40CFR, Table II, Required Containers, Preservation Techniques, and Holding Times, May 18, 2012.

Revision History	Sept 15, 2017	Added tungsten (new substance in the 2017 CSR).
	Nov 6, 2015	Updated “total metals” definition reference to APHA 3030A. Updated EPA 40CFR reference to 2012 version. Removed requirement that 1% solids by weight must be digested with SALM procedure. Added recommendation for Matrix Spike in QC section. Updated preservations for mercury to current BC MOE requirements.
	Oct 1, 2003	Replaces BC Lab Manual Methods (December 31, 2000) “Nitric Acid Digestion for Water Samples” and “Nitric Acid Digestion for Turbid Water Samples”. Effective October 1, 2013, the use of this method is required for listed metals, other than mercury, for BC CSR analysis purposes.

1.1.2 Sample Preparation for Dissolved Metals or Mercury in Water – PBM

Parameter	Dissolved Metals in Water.
Analytical Method	Membrane filtration, acid preservation, instrumental analysis.
Introduction	This method was prepared for the BC Ministry of Environment and Climate Change Strategy (BC ENV) by the BCELTAC to ensure consistency of results for dissolved metals in water. All definitive elements of the method have been prescribed to minimize inter-laboratory variability. This method is BC ENV approved for the preparation of 35 dissolved metals in waters. This method is not applicable to the determination of speciated metals such as hexavalent chromium.
Method Summary	Samples are field-filtered (before preservation) through a 0.45 µm membrane. General metals samples are preserved with nitric acid. Mercury samples are preserved with hydrochloric acid or bromine monochloride (BrCl). BrCl is not recommended for use in the field. Instrumental analysis of sample extracts can be performed by a variety of BC ENV approved analytical methods. Samples must be filtered in the field as close as possible to the time of collection (preferably within 15 minutes). This is particularly important for groundwaters where exposure to atmospheric conditions can trigger redox reactions that cause certain metals to precipitate (particularly iron). If precipitation of iron oxides occurs, many other heavy metals may precipitate or co-precipitate, potentially causing substantially low bias for many metallic elements. In extreme cases, some elements may be 100% removed from solution due to precipitation or co-precipitation caused by delay of filtration. Acid preservation of filtered samples (using nitric acid for general metals, or hydrochloric acid for mercury) is normally performed in the field, but may alternatively be performed in the lab (within 14 days of sample collection for general metals, or within 28 days for mercury using BrCl). BrCl (bromine monochloride) is not normally recommended as a field preservative for safety reasons. Upon arrival at the laboratory, minimal preparation is required for field-filtered and preserved samples, except that additional acid may be added prior to analysis to ensure pH is < 2 and for matrix-matching purposes. Lab-filtered samples may not provide reliable measures of dissolved metals concentrations. Lab-filtered samples must be qualified on lab reports and are not acceptable for compliance testing for CSR or permittee purposes. If a visible precipitate is evident at the laboratory after filtration and preservation, the sample must be digested prior to analysis, using an applicable BC ENV approved digestion method for metals or mercury (as applicable). This method is performance-based. Laboratories may adopt alternative options to improve performance or efficiency if all stated performance requirements and prescribed (mandatory) elements are met.

MDL(s) and EMS Analyte Code(s)*

This method is applicable to the following parameters:

Parameter	EMS Code	Parameter	EMS Code	Parameter	EMS Code
Aluminum	AL-D	Iron	FE-D	Silver	AG-D
Antimony	SB-D	Lead	PB-D	Sodium	NA-D
Arsenic	AS-D	Lithium	LI-D	Strontium	SR-D
Barium	BA-D	Magnesium	MG-D	Thallium	TL-D
Beryllium	BE-D	Manganese	MN-D	Thorium	TH-D
Bismuth	BI-D	Mercury	HG-D	Tin	SN-D
Boron	B-D	Molybdenum	MO-D	Titanium	TI-D
Cadmium	CD-D	Nickel	NI-D	Tungsten	W-D
Calcium	CA-D	Phosphorus	P-D	Uranium	U-D
Chromium	CR-D	Potassium	K-D	Vanadium	V-D
Cobalt	CO-D	Selenium	SE-D	Zinc	ZN-D
Copper	CU-D	Silicon	SI-D		

Other metals may be analyzed by this method if acceptable performance is demonstrated and validated.

EMS Method Code*

* Refer to EMS Parameter Dictionary on the Ministry of Environment and Climate Change Strategy website for all current EMS codes.

Matrix

Water, including fresh water, seawater, brackish water, and wastewater.

Interferences and Precautions

The interferences encountered will differ depending on the instrumental method used to analyze the sample extracts. Interferences should be clearly outlined and controlled in the analysis procedure. High concentrations of acids may cause physical interferences with some instrumental techniques.

Sample Handling and Preservation

Sampling should be done by qualified personnel. Samples must be collected and stored such that degradation or alteration of the sample is minimized. For further details, refer to the BC Field Sampling Manual.

The sample must be filtered through a 0.45 µm pore diameter membrane filter at the time of collection, or as soon thereafter as practically possible (preferably within 15 minutes).

Note: Membrane filters are typically made from polycarbonate or cellulose esters, though other materials are acceptable if demonstrated to be suitable for use. Pre-filters are also acceptable for highly turbid samples if demonstrated to be suitable. To reduce the possibility of false positives from contamination, it is highly recommended that the environmental practitioner either use filters that are supplied by the laboratory or provide the laboratory with samples of their chosen filters for testing prior to use.

Metals other than Mercury: Collect samples in clean high-density polyethylene (HDPE), glass, or Polytetrafluoroethylene (PTFE) containers. Preserve in the field (or in the laboratory) with nitric acid to pH < 2. Treatment of samples with approximately 1 mL of 1:4 HNO_3* per 100 mL sample is recommended. For laboratory preservation, add nitric acid to the original sample container within 14 days of sampling , then equilibrate ≥ 16 hours prior to sub-sampling.

Mercury: Collect samples using only glass or PTFE containers. Field-preserve with HCl to pH < 2. Adding BrCl to the original sample container at the laboratory within 28 days of sampling is an acceptable alternative to field preservation (use ≥ 0.5 mL BrCl solution per 100 mL of sample and equilibrate ≥ 24 hours prior to sub-sampling; prepare BrCl solution as per BC Lab Manual method for Total and Dissolved Mercury in Water by Bromine Monochloride Digestion).

* Note: 1:4 HNO_3 is equivalent to 18 %wt/wt HNO_3. Nitric acid concentrations exceeding 20 wt% triggers additional TDG shipping restrictions (cannot be shipped by passenger airline).

Holding Time:

Metals, excluding Mercury: 180 days from sampling (if preserved to $pH < 2$ with HNO_3)

Mercury; 28 days from sampling (if preserved to $pH < 2$ with HCl or BrCl)

Results reported for samples analyzed beyond the holding time must be qualified.

Holding Time:

Metals, excluding Mercury: 180 days from sampling (if preserved to $pH < 2$ with HNO_3)

Mercury; 28 days from sampling (if preserved to $pH < 2$ with HCl or BrCl)

Results reported for samples analyzed beyond the holding time must be qualified.

Storage: No storage temperature requirement (US EPA 40CFR May 18, 2012).

Procedure

If the laboratory's client or sample submission paperwork indicates that the sample was not filtered prior to arrival at the laboratory, proceed with filtration at the laboratory as soon as is practical. Lab-filtered dissolved metals samples must always be qualified due to the potential for low biased results, regardless of how quickly after receipt the filtration is conducted. Dissolved metals or mercury samples that are lab-filtered may be low-biased and may not reflect conditions at time of sampling.

For filtration, use 0.45 µm filters that have been previously tested to be metals-free (i.e. < MRL for analytes of interest) by filtering deionized water. Positive pressure (e.g., syringe) or vacuum filtration are acceptable, provided that the materials that contact the sample have been tested for suitability. Use a portion of the sample to rinse the filter assembly, discard this portion and collect the required volume of filtrate. Add the appropriate volume of nitric acid (for general metals) or hydrochloric acid (for mercury) to achieve $pH < 2$.

If the sample was field-filtered but not acid-preserved prior to arrival at the laboratory, samples may be preserved in the laboratory without consequence (refer to Sample Handling and Preservation section for guidance).

Prior to sub-sampling and analysis, perform a visual assessment of each filtered and acid-preserved sample. If a precipitate is evident, the sample must be digested prior to analysis using an applicable BC ENV approved digestion method, e.g., "Digestion for Total Metals in Water – Prescriptive" or "Total and Dissolved Mercury in Water by Bromine Monochloride Digestion – PBM". Results are still reported as "dissolved" metals or mercury.

Conduct instrumental analysis using an appropriate BC ENV approved method. Specific preparation steps are dependent on the analytical technique.

Performance Requirements

Any analytical method options selected for this analysis must meet or exceed the performance requirements specified below.

Accuracy and Precision requirements are distinct from daily QC requirements and apply to measures of long-term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method re-validation studies. For Initial Validations, averages of at least 8 Lab Control Samples or RMs must be assessed. Ongoing Re-validations (performance reviews) should assess QC data encompassing longer timeframes (e.g., 6 months to 1 year). A minimum frequency of 2 years is recommended for Ongoing Re-validations.

Accuracy Requirement: Laboratories must demonstrate method accuracy (measured as average recovery) of 85-125% or better for Lab Control Samples or Reference Materials at concentrations above ten times the MDL.

Precision Requirement: Laboratories must demonstrate method precision equal to or better than 10% relative standard deviation for clean matrix spikes at concentrations above ten times the MDL.

Sensitivity Requirement: Where possible, the method should support Reporting Limits (and MDLs) that are less than 1/5 of applicable numerical standards. The method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

Quality Control

Summary of QC Requirements

QC Component	Minimum Frequency	Minimum Data Quality Objectives
Field Filtration Blank	Strongly Recommended	One per sampling event
Method Blank (MB)	One per batch (max 20 samples)	Less than reported DL
Lab Control Sample (LCS)	One per batch (max 20 samples)	80 – 120%
Lab Duplicates (DUP)	One per batch (max 20 samples)	≤ 20% RPD [or within 2x reported DL for low level results]
Matrix Spike (MS) or Reference Material (RM)	One per batch (max 20 samples)	70 – 130%
Field Duplicates	Recommended	None specified

If DQOs are not met, repeat testing or report qualified test results. DQOs do not apply to MS results where sample background exceeds spike amount.

Prescribed Elements

The following components of this method are mandatory:

1. Dissolved metals samples must be field-filtered for suitability to CSR or permittee applications for compliance testing or any applications under ministry jurisdiction. Samples that are filtered and preserved in the laboratory must be qualified, e.g., “dissolved metals sample was lab-filtered; test results may be low-biased and are unsuitable for CSR or permittee compliance monitoring”.
2. Samples must not be preserved prior to filtration.
3. Filtration must be performed using 0.45 µm membrane filters. It is strongly recommended to utilize filters that have been previously tested for trace metal impurities to verify suitability (filters should not contribute background levels of metals above method reporting limits).
4. In rare occasions where a visible precipitate is evident after filtration and preservation, the sample must be digested prior to analysis using an applicable BC ENV approved digestion method for metals or mercury (as applicable). If digestion is conducted due to visible particulate, qualify test results, e.g., “field filtered dissolved metals sample required digestion due to presence of visible particulate”. This qualifier is for information purposes only and does not necessarily indicate a data quality issue. This occurrence may indicate precipitation of dissolved metals has occurred or could indicate improper field filtration.

5. Samples that are field-filtered but not field-preserved must be preserved at the lab in their original containers. For general metals, add HNO_3 to the original container to achieve pH < 2 within 14 days of sampling, then equilibrate for at least 16 hours prior to sub-sampling or analysis. For mercury, add BrCl to the original container within 28 days of sampling, then equilibrate for at least 24 hours prior to sub-sampling and analysis.
6. All stated Sample Handling and Preservation requirements, Performance Requirements, and Quality Control requirements must be met.
7. Samples analyzed beyond the stated holding time must be qualified. Refer to latest version of “BC ENV Sample Preservation and Hold Time Requirements” for updates.

Apart from these limitations, and provided performance requirements are met, laboratories may introduce modifications to this method to improve quality or efficiency.

References

1. EPA Method 200.8 “Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma - Mass Spectrometry”, Revision 5.4, U.S. Environmental Protection Agency, May 1994.
2. British Columbia Field Sampling Manual – Part E: Water and Wastewater Sampling, 2013.
3. APHA 3030 B, Preliminary Treatment of Samples – Filtration for Dissolved and Suspended Metals, 2004.
4. US EPA 40CFR, Table II, Required Containers, Preservation Techniques, and Holding Times, May 18, 2012.

Revision History

Dec 20, 2019 First version of method for publication in BC Lab Manual. This method formalizes BC ENV policy that field filtration is required for dissolved metals (for CSR or permittee compliance monitoring).

1.1.3 Total and Dissolved Mercury in Water by Bromine Monochloride Digestion – PBM

Parameter	Total and Dissolved Mercury in Water
Analytical Method	Bromine monochloride digestion (followed by appropriate instrumental analysis).
Introduction	This method is applicable to the analysis of total or dissolved mercury in water samples. Bromine monochloride is an extremely strong oxidizer, and is highly efficient at converting elemental, organic, and inorganic mercury species (including particulate bound species) to Hg(II). Full oxidation of all mercury species is necessary to facilitate complete reaction with stannous chloride ($SnCl_2$), as used by cold vapour atomic absorption or atomic fluorescence spectroscopic methods.
Method Summary	Samples are digested with bromine monochloride. Instrumental analysis of sample extracts can be performed by a variety of analytical methods (e.g., cold vapour atomic absorption or fluorescence spectrometry with $SnCl_2$ reduction). This method is performance-based. Laboratories may adopt alternative options to improve performance or efficiency provided that all stated performance requirements and prescribed (mandatory) elements are met.

MDL and EMS Codes

Analyte	Approx. MDL (units)	EMS Code
Total Mercury	0.00001 mg/L	HG-T
Dissolved Mercury	0.00001 mg/L	HG-D

Matrix	Water, including fresh water, marine water, brackish water, and wastewater.
Interferences and Precautions	The interferences encountered will differ depending on the instrumental method used to analyze the sample extracts. These interferences should be clearly outlined and controlled in the analysis procedure. Samples high in organic matrices (e.g., sewage effluent), may require higher levels of BrCl and longer oxidation times, or elevated temperatures (e.g., place sealed bottles in oven at 50°C for 6 hours). Sample oxidation must be continued until complete, which is determined by observation of a permanent yellow colour remaining in the sample, or by the use of starch iodide indicating paper to test for residual free oxidizer. If necessary, these types of samples can be diluted prior to digestion with BrCl. It is critical that significant care is taken to avoid contamination when collecting and analyzing samples for trace levels of mercury. Refer to US EPA 1669 Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels. Gold and iodide (at levels above 3 mg/L) have been reported as interferences (US EPA 1631E). Pre-reducing the sample with $SnCl_2$ can minimize the interference from iodide. Clean room conditions are recommended for sample handling and preparation steps prior to trace level mercury analyses (e.g., below ~ 0.00001 mg/L).
Sample Handling and Preservation	Sample containers: Glass or PTFE only. Mercury vapours can diffuse through HDPE containers, which can cause either high or low biases. Preservation: HCl to pH <2 or BrCl (field). Total mercury samples should be field preserved with HCl or BrCl. Dissolved mercury samples should be field filtered (0.45µm) and field preserved with HCl or BrCl (lab-filtered results may be low biased

and must be qualified). For total mercury and for dissolved mercury if field filtered, an acceptable alternative is to add BrCl to the original sample container (within 28 days of sampling, 5 mL BrCl solution per L of sample), and to let the sample oxidize for at least 24 hours prior to sub-sampling or analysis.

Sample collection in HDPE containers and/or preservation with HNO_3 are no longer considered to be recommended practices due to recently highlighted stability issues. Samples received in HDPE containers or preserved with HNO_3 must be qualified.

When samples for dissolved mercury are filtered, filter blanks should be prepared under the same conditions and analyzed together with the samples.

Field preservation with BrCl is not recommended due to the hazards associated with this reagent.

Stability

Holding Time: Total and Dissolved Mercury: 28 days from sampling.

Results reported for samples digested or analyzed beyond holding times must be qualified.

Storage: No storage temperature requirement.

Equipment and Supplies

1. Acid and reagent dispensers
2. Digestion vessels
3. Gloves
4. Spatula
5. Balance, minimum 2 decimal place

Reagents

1. Nitric acid (HNO_3), concentrated (67 - 70%), ACS or reagent grade minimum.
2. Hydrochloric acid (HCl), concentrated (36-40%), ACS or reagent grade minimum.
3. Water, de-ionized (ASTM Type I or equivalent recommended).
4. Potassium bromate ($KBrO_3$), ACS or reagent grade minimum.
5. Potassium bromide (KBr), ACS or reagent grade minimum.
6. Hydroxylamine hydrochloride ($NH_2OH \cdot HCl$), ACS or reagent grade minimum.
7. Stannous chloride ($SnCl_2$), ACS or reagent grade minimum.

As per US EPA 1631E, it is permissible to use quantities of reagents and procedures other than those suggested in this method, as long as equivalent performance is demonstrated by the laboratory.

<u>Preparation of Bromine Monochloride (BrCl) Solution:</u>

In a fume hood, dissolve 27 ± 1 g of KBr in 2.5 ± 0.1 L of HCl. Stir for approximately 1 hr in a fume hood using a clean magnetic stir bar, while slowly adding 38 ± 1 g $KBrO_3$ to the acid. The solution colour should change from yellow to red to orange, after all of the $KBrO_3$ has been added. Loosely cap the bottle and allow stirring for another hour before tightening the lid.

WARNING: Free halogens (Cl_2, Br_2, BrCl) are generated from this process, which are released from the bottle. The addition of $KBrO_3$ must be performed slowly in a fume hood!

Alternatively, commercially prepared BrCl solution may be used, as long as the same reagent concentrations are maintained, or equivalent performance is demonstrated by the laboratory.

<u>Preparation of Hydroxylamine Hydrochloride ($NH_2OH \cdot HCl$) Solution:</u>

Dissolve 300 ± 5 g of $NH_2OH \cdot HCl$ in reagent water and dilute to a 1.0 L final volume. If necessary, this solution may be purified by the addition of 1.0 ± 0.1 mL of $SnCl_2$ solution and purging overnight with nitrogen.

Safety

Wear appropriate PPE (Personal Protective Equipment) including lab coat, gloves, and safety glasses. Add acid to samples and perform digestions under a fume hood.

Due to the toxicological and physical properties of Hg, pure standards should be handled only by trained personnel thoroughly familiar with the handling and cautionary procedures and associated risks.

Procedure

For dissolved mercury analysis, filter an unacidified sample through a 0.45 µm filter (preferably done in the field), followed by acidification with HNO_3 or HCl to pH < 2 and/or addition of BrCl.

Samples preserved with acid have the potential to lose mercury to coagulated organic materials in the water or condensed on the walls of the bottle. It is recommended to add BrCl directly to the original sample bottle at the laboratory (prior to sub-sampling) if BrCl was not added in the field, even if the sample has been field preserved with HCl.

Include Method Blanks, Lab Duplicates, Matrix Spikes, and Reference Materials or Laboratory Control Samples with each batch of samples.

Sample Preparation - Digestion

1. Per 100 mL of sample, add 0.50 ± 0.05 mL BrCl solution for clear and filtered samples, or 1.0 ± 0.1 mL BrCl solution for brown and turbid samples. If sample containers dedicated to mercury analysis are available, BrCl should preferably be added directly to the sample container (previously filtered, in the case of dissolved mercury). If sample containers will be shared for other metals analyses in addition to mercury, shake the preserved sample well and treat a sub-sample with BrCl. Cap the sample bottle or digestion vessel (for sub-samples), and digest at room temperature for a minimum of 30 minutes (as per US EPA 245.7, 2005). A permanent yellow colour must persist, otherwise more BrCl must be added and the digestion repeated. Use starch iodide paper to verify excess BrCl in highly coloured samples.
2. After the BrCl oxidation is complete, add 0.20 - 0.25 mL of hydroxylamine hydrochloride solution per 100 mL of sample, and cap the bottle or digestion vessel. Swirl the sample. As the BrCl is destroyed, the yellow colour will disappear. Allow the sample to react for a minimum of 5 minutes with periodic swirling.
3. Analyze the final extract using appropriate analytical methods (e.g., cold vapour atomic absorption or atomic fluorescence spectrometry with $SnCl_2$ reduction).

Record any anomalies observed during the digestion and analysis.

Performance Requirements

Any analytical method options selected for this analysis must meet or exceed the performance requirements specified below.

Accuracy and Precision requirements apply to measures of long-term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method re-validation studies. They do not constitute acceptance criteria or Data Quality Objectives for individual Quality Control samples. For Initial Validations, averages of at least 8 spikes or CRMs must be assessed (preferably taken from multiple analytical batches). Ongoing re-validations (performance reviews) should assess QC data encompassing longer timeframes (e.g., 6 months to 1 year). A minimum frequency of 2 years is recommended for ongoing re-validations.

Accuracy Requirement: Laboratories must demonstrate method accuracy (measured as average recovery) of 90 – 110% or better for clean matrix spikes or certified reference materials at concentrations above ten times the MDL.

Precision Requirement: Laboratories must demonstrate method precision equal to or better than 10% relative standard deviation for clean matrix spikes at concentrations above ten times the MDL.

Sensitivity Requirement: Where possible, the method should generate Method Detection Limits that are less than 1/5 of applicable numerical standards. The method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

Quality Control

Summary of QC Requirements

Method QC Component	Minimum Frequency	Minimum Data Quality Objectives*
Method Blank	1 per batch (max 20 samples)	Less than reported DL
Reference Material or Laboratory Control Sample	1 per batch (max 20 samples)	80 – 120%
Matrix Spike	1 per batch (max 20 samples)	70 – 130%
Lab Duplicate	1 per batch (max 20 samples)	≤ 20% RPD
Field Duplicate	Recommended	None Specified

* Minimum DQOs apply to individual QC samples, not averages, and only at levels above 10x MDL. Laboratories must report qualified data when DQOs are not met, unless other evidence demonstrates that the quality of associated sample data has not been adversely affected.

Prescribed Elements

The following components of this method are mandatory:

1. Completeness of BrCl digestion must be verified by ensuring that digested samples retain a permanent yellow colour, or by testing with a starch iodide indicating paper.
2. All Sample Handling, Preservation, Hold Time, Performance Requirements, and Quality Control requirements must be met.

Apart from these limitations, and provided performance requirements are met, laboratories may introduce modifications to this method in order to improve quality or efficiency.

Note that other BC MOE approved sample preparation procedures are also available for total and dissolved mercury in waters.

References

1. US EPA Method 1631, Revision E, Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry, Office of Water, US EPA, Aug 2002.

2. US EPA Method 245.7, Revision 2.0, Mercury in Water by Cold Vapor Atomic Fluorescence Spectrometry, Office of Water, US EPA, February 2005.

3. US EPA Method 1669, Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels, Office of Water, US EPA, July 1996.

4. US EPA 40 CFR Part 136, March 2007.

Revision History

October 1, 2013	New method added to BC Lab Manual. The effective date for this method is October 1, 2013. A requirement for the use of new sample container and preservation requirements for mercury in water (as described in this method) is also effective October 1, 2013.

1.1.4 Total Mercury Digestion

Sample Type:	Fresh Water Wastewater Marine Water
Container:	Containers are glass with a tightly fitting lid, or Teflon™.
Preservation:	Unfiltered-field: add 4 mL HNO_3 (see section 2.1.6) per litre or 20% (w/v) $K_2Cr_2O_7$ in 1:1 HNO_3, 2mL/L Unfiltered-lab: add 4 mL HNO_3 (see section 2.1.6) per litre or 20% (w/v) $K_2Cr_20_7$ in 1:1 HNO_3, 2mL/L
Principle of Method:	The water sample undergoes a strongly oxidizing digestion to dissolve all the mercury, break down organics and eliminate any sulfide present in the sample. The sample is then introduced to: a) CVAAS
Apparatus:	(see section 2.1.5) a) Water bath -minimum temperature requirement: 95°C b) Fume hood c) Glassware -300 mL BOD bottles (or equivalent)
Reagents:	a) Deionized distilled water b) Sulfuric acid (H_2SO_4), concentrated, reagent grade c) Nitric acid (HNO_3), concentrated, reagent grade d) Potassium permanganate ($KMnO_4$), 5% w/v, mercury-free e) Potassium persulfate ($K_2S_2O_8$), 5% w/v, reagent grade f) Sodium chloride-hydroxylamine sulfate, 12% w/v, reagent grade

Procedure
Sample Preparation: Samples are prepared in batches (25-35) dictated by the size of the water bath accommodating the glassware containing the samples.

Each batch encompasses:

a) Sample replicates - 10% of samples in duplicate, minimum of one duplicate per batch.
b) Quality control samples - 5% of samples, minimum of one per batch - containing elements of known concentrations.
c) Two reagent blanks - 5% of samples, not to exceed two per batch and minimum of one per batch.
d) Calibration standards, minimum of three per batch, bracketing the expected concentration of the samples.

All are subjected to the same reagents and treatment for digestion as follows:
a) Pipette 100 mL of sample, or an aliquot diluted to 100 mL, into a 300 mL BOD bottle.
b) Add 5 mL concentrated H_2SO_4, 2.5 mL of concentrated HNO_3, and 15 mL 5% $KMnO_4$ solution to each bottle. Mix well after each addition.
c) Ensure purple color persists for at least 15 minutes. If not, add additional portions of 5% $KMnO_4$ solution, mixing well after each addition, until the purple color persists for longer than 15 minutes.
    1. Add 8 mL 5% $K_2S_2O_8$ solution to each bottle.
    2. Heat bottles in a 95°C water bath for 2 hours.
    3. Allow the samples to cool.
d) Add 6 mL 12% sodium chloride-hydroxylamine sulfate to reduce excess $KMnO_4$.
    1. Proceed immediately to analyze the solution.

Instrumental Analysis:	The sample is now prepared for analysis by CVAAS. See the specific instrumental analysis section (section 2.3) for details.

1.2 Non-Aqueous Samples

Revision Date: Sept 15, 2017

1.2.1 Strong Acid Leachable Metals (SALM) in Soil - Prescriptive

Parameter	Metals in Soil and Sediment
Analytical Method	Nitric – Hydrochloric acid digestion, Instrumental analysis

Introduction

This revised method was prepared for BC MOE by the BCELTAC to provide improved consistency of results for metals in soil, in support of the Waste Management Act, Contaminated Sites Regulation (CSR). All definitive elements of the method have been prescribed to minimize inter-laboratory variability, particularly for incompletely recovered elements like barium.

The BC CSR includes Water and Soil as matrix types, but Soil is only broadly defined (CSR, section 1). Carter's definition of Soil (Reference: Carter) as being "less than 2 mm" material is used for this method.

This method may also be used for marine and freshwater sediment applications, where sediment is defined as being "less than 63 µm" material. However, by default, laboratories are instructed to apply the method on the "less than 2 mm" fraction, except by special request.

This method uses a mixture of nitric acid, hydrochloric acid, and de-ionized water, with a standardized digestion time and temperature. Laboratories are allowed some flexibility regarding apparatus and heating methods, but variations in acid mixture composition, digestion time, or digestion temperature are not permitted.

Method Summary

Samples are dried at ≤ 60°C, sieved, and digested with a mixture of nitric acid, hydrochloric acid, and de-ionized water. Instrumental analysis of sample extracts can be performed by a variety of analytical methods.

This method provides the sample preparation procedure for the analysis of Total Metals, as referenced within the BC CSR. Total Metals does not imply a complete dissolution of silicate materials, as would occur with digestions using perchloric and hydrofluoric acids. The strong acid leach prescribed by this method is intended to dissolve those metals that may be environmentally available. The method achieves near complete recoveries of some important metals, but many others are only partially recovered (see Table 1 for examples). Metals not dissolved with this method are unlikely to be of environmental consequence.

This method is prescriptive. It must be followed exactly as described. Where minor deviations are permitted, this is indicated in the text. All results must be reported on a dry weight basis.

MDL(s) and EMS Analyte Code(s)*

This method is applicable to the following parameters:

Parameter	CAS Number	EMS Code	Parameter	CAS Number	EMS Code
Aluminum	7429-90-5	AL-T	Molybdenum	7439-98-7	MO-T
Antimony	7440-36-0	SB-T	Nickel	7440-02-0	NI-T
Arsenic	7440-38-2	AS-T	Phosphorus	7723-14-0	P-T
Barium	7440-39-3	BA-T	Potassium	7440-09-7	K-T
Beryllium	7440-41-7	BE-T	Selenium	7782-49-2	SE-T
Boron	7440-42-8	B-T	Silver	7440-22-4	AG-T
Cadmium	7440-43-9	CD-T	Sodium	7440-23-5	NA-T
Calcium	7440-70-2	CA-T	Strontium	7440-24-6	SR-T
Chromium	7440-47-3	CR-T	Sulfur	7704-34-9	S-T
Cobalt	7440-48-4	CO-T	Thallium	7440-28-0	TL-T
Copper	7440-50-8	CU-T	Thorium	7440-29-1	TH-T
Iron	7439-89-6	FE-T	Tin	7440-31-5	SN-T
Lead	7439-92-1	PB-T	Titanium	7440-32-6	TI-T
Lithium	7439-93-2	LI-T	Tungsten	7440-33-7	W-T
Magnesium	7439-95-4	MG-T	Uranium	7440-61.1	U-T
Manganese	7439-96-5	MN-T	Vanadium	7440-62-2	V-T
Mercury	7439-97-6	HG-T	Zinc	7440-66-6	ZN-T

Other metals may be analyzed by this method if acceptable performance is demonstrated and validated. This method is not suitable for the determination of silica or silicon.

EMS Method Code*

FS82

Refer to EMS Parameter Dictionary on the Ministry of Environment and Climate Change Strategy website for all current EMS codes.

Method Limitations

This method does not dissolve all silicate materials and may result in a partial extraction, depending on the sample matrix, for some metals, including, but not limited to aluminum, barium, beryllium, chromium, strontium, titanium, thallium, tungsten, and vanadium.

Unpublished studies by some BC laboratories have shown that dissolved antimony and tin may re-sorb to undigested solids over time after the sample extract has been diluted. Once the solids have been removed from the sample extract, antimony and tin are more stable.

This method is suitable for the digestion of samples with silver concentrations of up to 0.5 mg/L in the extract after dilution to final volume, which is equivalent to 50 mg/kg in soils, based on a 1 g sample size and 100 mL final volume (Reference: US EPA 200.2).

This method is suitable for digesting samples with tin concentrations of up to 100 mg/L in the sample extract after dilution to final volume, which is equivalent to 1% in soils, using a 1 g sample size and 100 mL final volume (Reference: US EPA 200.2).

The solubility and stability of barium is limited in the presence of free sulfate using this method (Reference: US EPA 200.2).

This method does not adequately recover elemental sulfur and is not appropriate for the assessment of BC CSR standards for elemental sulfur in soil.

Matrix

Soil and sediment.

Interferences and Precautions

The interferences encountered will differ depending on the instrumental method used to analyze the sample extracts. These interferences should be clearly outlined and controlled in the analysis procedure. High concentrations of acids may cause physical interferences with some instrumental techniques.

Sample Handling and Preservation

Sampling should be done by qualified personnel. Samples must be collected and stored such that degradation or alteration of the sample is minimized. Collect the sample in a clean polyethylene or glass container, and tightly cap immediately after sampling.

Preservation: None.

Stability

Holding Time:

Metals (except Mercury): 180 days.

Mercury: 28 days.

When tin and antimony analyses are required, the sample extracts must be separated from the undigested solids within 4 hours of diluting to final volume. The decanted or filtered sample extract must be analyzed within 7 days.

Results reported for samples digested beyond holding times must be qualified.

Storage: For mercury, store at ≤ 6°C unless dried (freezing is permitted but is not recommended due to the potential for container breakage). For all other metals, there is no requirement for storage temperature (ambient storage temperature conditions are suitable).

The potential for loss of mercury by storage at ambient temperature is due to conversion of Hg(II) to volatile Hg(0) by microbial activity. Dried soils are stable at ambient temperature for at least 28 days (refer to References, Bull Environ Contam Toxicol (2015) 94:570–576).

Equipment and Supplies

1. Heating source (e.g., block digester, hotplate, water bath) capable of maintaining a sample extract temperature of 95 ± 5°C).
2. Balance, minimum 3 place.
3. Drying oven (not required).
4. Sieve, 2 mm (ASTM-E11 Sieve No. 10, US Sieve No. 10, Tyler 9 Mesh) or Sieve, 63 µm (ASTM-E11 Sieve No. 230, US Sieve No. 230, Tyler 250 Mesh). It is recommended that a stainless steel screen/sieve with all tin solder be used. Sieves must not be constructed of brass or contain lead solder. Polypropylene or nylon sieves may also be used.
5. Acid dispensers.
6. Vapor refluxing cover to fit digestion vessel (e.g., reflux cover, watch glass etc.).
7. Digestion vessels (e.g., block digester tube, beaker, flask, etc.).
8. Gloves.
9. Spatula.

Reagents

1. Nitric acid (HNO_3) conc. (67 - 70%), reagent grade minimum.
2. Nitric acid (1+1) – add 500 mL concentrated HNO_3 to 400 mL de-ionized water and dilute to 1 L.
3. Hydrochloric acid (HCl) conc. (34 - 37%), reagent grade minimum.
4. Hydrochloric acid (1+1) – add 500 mL concentrated HCl to 400 mL de-ionized water and dilute to 1 L.
5. Water, de-ionized (ASTM Type I or equivalent recommended).

Safety

Nitric and hydrochloric acid must not be premixed; they should be added individually to each sample vessel. Mixtures of nitric and hydrochloric acid must not be stored in closed containers.

Wear appropriate PPE (Personal Protective Equipment) including lab coat, gloves, and safety glasses. Add acids to samples and perform digestions under a fume hood.

Procedure

Samples are prepared and digested using the following procedures:

Sample Homogenization and Sub-Sampling

1. Inspect the sample and record any unusual or significant characteristics (e.g., lead shot pellets, metal turnings, nails, shells, etc.).
2. Remove any obviously foreign material such as vegetation.
3. If the sample has separated into visually discrete layers (e.g., aqueous, organic, and sediment phases), the entire sample must be homogenized prior to sub-sampling. The aqueous phase must not be decanted.

   Note: Special project requirements may involve alternative procedures such as decanting of the aqueous fraction. Indicate any departures or deviations from the prescribed method with a qualifying statement in the laboratory report.
4. Homogenize the entire sample by vigorous stirring using a spatula. If it is not possible to homogenize the sample in the container it was received in, the sample can be transferred to a larger container prior to homogenization. Clean the spatula and mixing container between samples.
5. Where moisture determination is required, a separate sub-sample must be taken prior to drying and sieving.

Sample Preparation – Drying

1. Dry the sample to a constant weight at a temperature of ≤ 60°C. Freeze drying is acceptable.

   Note: Sample drying temperature must not exceed 60°C to minimize volatilization of analytes such as mercury (Reference: US EPA 200.2).
2. Alternatively, moist or wet samples may be wet-sieved. If a sample is sieved when moist, a moisture determination must be done on the sieved portion (not on the “as received” sample) in order to convert results to dry weight.

Sample Preparation – Sieving

1. Sieve each sample through a 2 mm sieve. By special request, some sediment applications may require the use of a 63 µm sieve. If a 63 µm sieve is used, this must be indicated on the laboratory report. DO NOT pulverize samples to pass through either sieve type. Easily friable materials (dried clay clods, disintegrating rock, etc.) should be disaggregated prior to screening. Where necessary, non-pulverizing disaggregating tools like rolling mills, mortar and pestle, or flail grinders may be used.
2. Where available, it is recommended that a minimum of 25 grams of sample is sieved to ensure representative sub-sampling for the digestion stage.
3. Discard the portion of sample that did not pass through the sieve.
4. Field sampling personnel may pre-screen the samples in the field.

Sample Preparation - Digestion

1. Weigh 1.0 ± 0.1 g (dry weight) of sample into a digestion vessel, which must be fitted with a cap that supports open vessel reflux action (e.g., hotblock digestion tube, beaker, or Erlenmeyer flask with watch glass). At minimum, include Method Blanks, Lab Duplicates, and Reference Materials with each

batch of samples. Laboratory Control Samples are also recommended. Weights must be recorded using a minimum 3 place balance.

Note: In cases where one gram of sieved sample is not available, perform the analysis as described, and qualify the results (results for poorly recovered metals like Barium may be increased).

2. Add 5,0 ± 0.5 mL de-ionized water, 2.50 ± 0.25 mL concentrated HNO_3, and 2.50 ± 0.25 mL concentrated HCl. Alternatively, add 5.0 ± 0.5 mL of HNO_3 (1+1) and 5.0 ± 0.5 mL of HCl (1+1).
3. Add a reflux cap to the top of the digestion vessel. Swirl acid and sample to mix gently. It is permitted to allow samples to cold digest prior to heating to reduce any potential effervescence from reactive samples.
4. Digest samples for 2 hours ± 15 minutes at a temperature of 95 ± 5°C at atmospheric pressure. A digestion block or water bath are the preferred methods of heating. The heat for digestion must maintain the sample extract temperature at 95 ± 5°C. This refers to the temperature of the sample extract in a digestion vessel covered with a reflux cap, not the temperature setting on the heating source, and not the temperature of an uncovered digestion vessel. It is recommended that the sample extract temperature be monitored and recorded with each batch.
5. Allow the sample to cool and dilute the entire sample with de-ionized water to the volume required for the analysis. The dilution volume will depend on the analytical method and objectives. Typical final dilution volumes will be 25 mL, 50 mL, or 100 mL. Include all undigested solid material as part of the final diluted volume. Sample extracts should not be stored in glass.
6. When tin and antimony analyses are required, sample extracts must be separated from the undigested solids within 4 hours of diluting to final volume. The decanted or filtered sample extract must be analyzed within 7 days. These steps are necessary to minimize tin and antimony losses due to re-sorption.
7. Analyze the final extract using appropriate analytical methods and report the results on a dry weight basis.

Report any anomalies observed during the digestion and analysis.

Quality Control

Summary of QC Requirements		
Method QC Component	Minimum Frequency	Minimum Data Quality Objectives*
Method Blank	1 per batch (max 20 samples)	Less than reported DL
Reference Material	1 per batch (max 20 samples)	70 - 130% of the laboratory's long term mean value (see validation section for additional requirements)
Laboratory Control Sample	1 per batch (max 20 samples)	80 - 120%
Lab Duplicates	1 per batch (max 20 samples)	≤ 30% RPD for all metals except those indicated below; [or within 2x reported DL for low level results] ≤ 40% RPD (Ag, Al, Ba, Hg, K, Mo, Na, Pb, Sn, Sr, Ti, W, Zr)
Field Duplicates	Recommended	None Specified
* If DQOs are not met, repeat testing or report qualified test results. The stated recovery DQOs do not apply to RM parameters where target levels are below 10x MDL (use locally derived DQOs).		

Reference Material requirements: Any suitable RM (including in-house RMs) may be utilized for this method for routine Quality Control purposes, but the RMs listed below under validation requirements are recommended. RMs provide QC data that includes digestion elements of the method and which is representative of method performance for typical samples.

Laboratory Control Sample: An LCS for this method is a digested spiked Method Blank (no blank matrix exists for metals in soils). An LCS has more precisely defined targets than soil RMs, can cover all parameters reported by the method, and allows for better and more precise Quality Control of basic elements of the method (e.g., volumetric precision and controls and instrumental analysis).

Method Validation Requirements

Initial Method Validation requirements as outlined below must be completed before this method may be used to generate results for unknown samples. The method must be re-evaluated periodically (every two years is recommended as a suitable frequency). Prepared validation samples must be analyzed by all instrument methods used for routine analysis.

Demonstration of Accuracy and Precision:

Prepare and analyze at least 8 replicates of at least two of the following Certified Reference Materials:

- NRC PACS-2
- CCRMP TILL-1
- CCRMP TILL-3
- SCP Science SS-2

Where the above RMs are utilized for routine QC purposes, re-validations should be conducted using all routine QC data available for the review period.

Accuracy is measured as Percent Recovery versus the Interim Targets outlined in Table 1. For each metal, average accuracy must be within 70-130% of the Interim Targets, for results ≥ 5 times the Reported Detection Limit. Precision must be <15% RSD for results ≥ 5 times the Reported Detection Limit.

The Interim SALM Targets and DQOs may be re-assessed in the future if RMs become unavailable or if otherwise required.

References

1. US EPA Method 200.2, Sample Preparation Procedure for Spectrochemical Determination of Total Recoverable Elements, National Exposure Research Laboratory, Office of Water, US EPA, Cincinnati, OH, October 1999.
2. Soil Sampling and Methods of Analysis, Carter, M.R., editor, for Canadian Society of Soil Science, Lewis Publishers, 1993.
3. The Influence of Sample Drying Procedures on Mercury Concentrations Analyzed in Soils, Maria Hojdova et. al., Bull Environ Contam Toxicol (2015) 94:570–576.

Revision History

Sept 15, 2017	Added tungsten (a new substance in the 2017 CSR). Minor changes for compliance with CCME guidance manual including requirement for LCS QC (previously recommended) and change of storage temperature from ambient to ≤6°C for Hg (unless dried). Acid and water reagent volume tolerances standardized at +/-10%. Method limitation comment added for elemental sulfur.
Nov 6, 2015	Changed storage temperatures to be consistent with current BC MOE requirements. Removed requirement for minimum one-hour cold digestion (not necessary with version 2 of SALM method). Added LCS to QC and Procedure sections (recommended). Removed unnecessary references.
July 7, 2009	Version 2 of BC SALM Method for 2009 BC Lab Manual. Method revised from performance based to prescriptive. All key defining elements of the method are now prescribed. New interim RM targets assigned.
Feb 2001	Version one of BC SALM Method was introduced. Incorporated into Lab Manual November 2002.

TABLE 1. Interim Target Values for Reference Materials using BC SALM(a)

Parameter	CCRMP TILL-1 Certified (“Total”)	CCRMP TILL-1 SALM Interim Target	CCRMP TILL-3 Certified (“Total”)	CCRMP TILL-3 SALM Interim Target	NRC PACS-2 Certified (“Total”)	NRC PACS-2 SALM Interim Target	SCP Science SS-2 EPA3050A Digestion Targets	SCP Science SS-2 SALM Interim Target
Aluminum - Al (%)	7.25	1.82	6.45	1.15	6.62	1.75	1.33	1.37
Antimony - Sb (mg/kg)	7.8	6.27	0.9	0.724	11.3	7.3	-	4.16
Arsenic - As (mg/kg)	18	15.4	87	82.1	26.2	23.3	75	88.4
Barium - Ba (mg/kg)	702	80.6	489	40	-	294	215	224
Beryllium - Be (mg/kg)	2.4	0.544	2.0	0.369	1.0	0.408	-	-
Boron - B (mg/kg)	-	-	-	-	-	38.1	-	-
Cadmium - Cd (mg/kg)	< 0.2(b)	-	< 0.2(b)	-	2.11	1.98	-	2.2
Calcium - Ca (%)	1.94	0.332	1.88	0.517	1.96	0.779	11.3	12.3
Chromium - Cr (mg/kg)	65	27.2	123	63.1	90.7	48.1	34	34.6
Cobalt - Co (mg/kg)	18	12.5	15	10.4	11.5	8.75	12	13.1
Copper - Cu (mg/kg)	47	44.9	22	19.8	310	297	191	211
Iron - Fe (%)	4.81	3.33	2.78	2.02	4.09	3.12	2.10	2.53
Lead - Pb (mg/kg)	22	14.4	26	17.3	183	167	126	132
Lithium - Li (mg/kg)	15	-	21	-	32.2	-	14	14.3
Magnesium - Mg (%)	1.30	0.583	1.03	0.609	1.47	0.99	1.11	1.24
Manganese - Mn (mg/kg)	1420	1100	520	315	440	253	457	511
Mercury - Hg (mg/kg)	0.092(b)	0.098	0.107(b)	0.11	3.04	2.88	-	0.33
Molybdenum - Mo (mg/kg)	2	0.738	2	0.619	5.43	4.57	-	2.94
Nickel - Ni (mg/kg)	24	17.4	39	31.7	39.5	31.6	54	63
Phosphorus - P (%)	0.0930	0.0796	0.0490	0.042	0.096	0.0838	0.0752	0.0832
Potassium - K (%)	1.84	0.0619	2.01	0.0965	1.24	0.323	0.342	0.342
Selenium - Se (mg/kg)	-	-	-	-	0.92	-	-	-
Silver - Ag (mg/kg)	0.2(b)	-	1.6(b)	1.75	1.22	-	-	1.1
Sodium - Na (%)	2.01	0.0340	1.96	0.027	3.45	1.86	0.0558	-
Strontium - Sr (mg/kg)	291	11.6	300	20.3	276	68	214	232
Sulfur - S (%)	< 0.05	-	< 0.05	-	1.29	1.22	-	-
Thallium - Tl (mg/kg)	-	-	-	-	0.6(c)	-	-	0.38
Thorium - Th (mg/kg)	5.6	-	4.6	-	-	-	-	-
Tin - Sn (mg/kg)	-	-	-	-	19.8	19.1	-	0.74
Titanium - Ti (%)	0.599	0.0764	0.291	0.0645	0.443	0.09	0.0850	0.0969
Uranium - U (mg/kg)	2.2	-	2.1	-	3(c)	-	-	1.34
Vanadium - V (mg/kg)	99	54.9	62	33.5	133	74.4	34	39.9
Zinc - Zn (mg/kg)	98	67.5	56	40.2	364	337	467	546

(a) Interim Targets from “Report on Results of 2007 Inter-laboratory Study to Re-establish Data Quality Objective for BCMOE Strong Acid Leachable Metals (SALM) in Soil Method, Prepared for the BC Ministry of Environment, JRD Consulting Company, 2007 June 20. Interim Targets for SS-2 RM are single lab values provided to BCLQAAC.

(b) Parameter not listed as “Total”. Listed as “Summary of partial extraction elements concentrated HNO_3 – concentrated HCl”.

(c) Parameter not certified, provided as informational value.

1.2.2 Digestion of Biota (Tissues, Vegetation)

Sample Preparation

Samples can be processed wet or dry, and can follow a number of processing schemes which may include:

a) dissection - isolation of target tissue; i.e., liver, muscle (animal), root systems (plants), etc.
b) drying and lipid removal.
c) homogenizing and sub-sampling.

The specifics of the processing scheme will depend on a number of variables which may include intended use of data generated, nature of samples to be analyzed, the specific list of elements to be determined and requirements of applicable regulation.

Analytical Method:

ICP-AES, HVICP-AES, FAAS, CVAAS, GFAAS and HVAAS.

Introduction:

The trend in biological sampling is to choose a species of plant or animal which can be used as an indicator of human-induced environmental impact. To the analyst this may involve the determination of a number of heavy metals in, for example, one single small clam, leaves, or sections or organs of mammals, fish, or invertebrates.

Method Summary:

There are two main ashing techniques to decompose biota samples. The oldest and simplest method is dry ashing, carried out by heating the tissue in a muffle furnace at 400-800°C in the presence of air. This technique can lead to a variable loss of many elements, including, Hg, B, Pb, Zn, Cd, Ca, In, Tl, As, Sb, Fe, Cr, and Cu. The addition of fluxes reduces these losses in many cases but increases the risk of contaminating the samples with the elements of interest. Wet ashing (acid digestion) techniques employing liquid reagents which are most often applied to biological samples. Relatively low temperatures are used to achieve decomposition so that losses through volatilization, adsorption and reaction with vessel materials are limited to only a few elements. For this reason, substances, which are particularly difficult to decompose are occasionally not completely solubilized or require such a large amount of reagent that the blank values exceed permissible limits. Other reagents which may be used are; nitric acid alone or in combination with hydrogen peroxide or perchloric acid.

Matrix:

Plant tissue and animal tissue.

Interferences and Precautions:

Note: Standard laboratory safety precautions must be followed.

Volatile chlorides such as Hg^{+2}, Sb^{+3} and Se^{+4} tend to be lost from HCl solutions; in contrast, Cr^{+3} tends to be lost from perchloric acid solutions at temperatures above 150°C through the formation of chromyl chloride (CrO_2Cl_2). As^{+3}, Sn^{+2}, Ru and Os can be volatilized when samples are fumed with perchloric or sulfuric acid. When metals are dissolved in non-oxidizing acids, As and Sb may escape as hydrides.

Some vegetation contains silicates which may not fully dissolve unless a small amount of HF is used.

Sample Handling and Preservation:

For all biota the best preservation technique is to freeze the sample. Freeze-thaw cycles must be avoided to prevent the loss of interstitial and intercellular fluids.

Apparatus, Materials and Reagents:

See References.

Quality Control:	Many biological reference materials (RMs) are available. The RM and sample matrixes should be matched as closely as possible.	
Revision History:	February 14, 1994:	Publication in 1994 Laboratory Manual.
	March 1997:	Additional digestion procedures published in Supplement #1. Nitric acid digestion procedure formats from 1994 Laboratory Manual replaced by 2 nitric acid digestion procedures from 1997 Supplement. Also, metals in soils/sediment procedure from 1994 Laboratory Manual deleted and replaced by both Aqua Regia digestion (preferred) and perchloric digestion procedures from the 1997 Supplement.
	December 31, 2000:	SEAM codes removed. Container restriction for mercury samples added. Minor editing.

1.2.3 Metals in Animal Tissue and Vegetation (Biota) - Prescriptive

Parameter	Metals in Tissue and Vegetation (Biota)
Analytical Method	Nitric acid, Hydrochloric acid, and Hydrogen peroxide digestion (followed by appropriate instrumental analysis).
Introduction	This method was prepared for BC MOE by the BCELTAC to provide improved interlaboratory consistency of results for metals in tissue and vegetation. All definitive elements of the method have been prescribed to minimize inter-laboratory variability. This method uses a mixture of nitric acid, hydrochloric acid, and hydrogen peroxide, with a standardized digestion time and temperature. Laboratories are allowed some flexibility regarding apparatus and heating methods, but variations in acid mixture composition, digestion time, or digestion temperature are not permitted.
Method Summary	Samples are homogenized and digested with a mixture of nitric acid, hydrochloric acid, and hydrogen peroxide. Instrumental analysis of sample extracts can be performed by a variety of analytical methods. This method provides the sample preparation procedure for the analysis of Total Metals but does not imply a complete dissolution of some materials, as would occur with digestions using perchloric and hydrofluoric acids. The strong acid leach prescribed by this method is intended to provide a conservative estimate of the concentrations of metals that may be bio-available (for example, through mammalian digestion processes). The method achieves near complete recoveries of most toxicologically important metals, but some elements associated with recalcitrant minerals (e.g., aluminosilicates) are only partially recovered, especially those that originate from dust, soil, or sand particles that can be present in some types of biota samples. This method is prescriptive. It must be followed exactly as described. Where minor deviations are permitted, this is indicated in the text.
Method Limitations	This method does not dissolve all materials and may result in a partial extraction, depending on the sample matrix, for some metals, including, but not limited to aluminum, chromium, iron, nickel, strontium, tin, titanium, uranium, and vanadium, especially when these elements are present in refractory mineral forms.

Analytes and EMS Codes

This method is applicable to the following parameters:

Analyte	EMS Code	Analyte	EMS Code	Analyte	EMS Code
Aluminum	AL-T	Iron	FE-T	Silver	AG-T
Antimony	SB-T	Lead	PB-T	Sodium	NA-T
Arsenic	AS-T	Lithium	LI-T	Strontium	SR-T
Barium	BA-T	Magnesium	MG-T	Sulfur	S-T
Beryllium	BE-T	Manganese	MN-T	Thallium	TL-T
Boron	B-T	Mercury	HG-T	Thorium	TH-T
Cadmium	CD-T	Molybdenum	MO-T	Tin	SN-T
Calcium	CA-T	Nickel	NI-T	Titanium	TI-T
Chromium	CR-T	Phosphorus	P-T	Uranium	U-T
Cobalt	CO-T	Potassium	K-T	Vanadium	V-T
Copper	CU-T	Selenium	SE-T	Zinc	ZN-T

Other metals may be analyzed by this method if acceptable performance is demonstrated and validated. This method is not suitable for the determination of silica or silicon.

Reported results must be clearly indicated as being in either dry weight and/or wet weight concentration units, depending on the application, as requested by the data-user. The default Ministry preference is for animal tissues to be reported on a wet weight basis (e.g., “mg/kg wwt”), and for vegetation to be reported on a dry weight basis (e.g., “mg/kg” or “mg/kg dwt”). Biota samples with excessively high moisture contents (i.e., >90% moisture, which may occur in periphyton, macrophyte, benthic invertebrates, eggs, etc.) should be dried at ≤ 60° or freeze dried and weighed prior to digestion to minimize the error associated with moisture corrections.

Matrix

Tissue and vegetation (biota).

Interferences and Precautions

The interferences encountered will differ depending on the instrumental method used to analyze the sample extracts. Applicable interferences should be clearly identified and controlled in the analysis procedure. High concentrations of acids may cause physical interferences with some instrumental techniques.

Equipment used for sample homogenization, including various types of homogenizer probes, grinders, food processors, knife blades, may have the potential for the contamination of metals including, but not limited to aluminum, chromium, iron, manganese, molybdenum, nickel, tin, and vanadium. Such equipment must be tested and validated to ensure it does not introduce significant metallic contaminants to samples.

Sample Handling and Preservation

Sampling should be done by qualified personnel. Samples must be collected and stored such that degradation or alteration of the sample is minimized. Collect the sample in a clean plastic or glass container, appropriately sealed. Paper bags are suitable collection containers for vegetation where samples will be dried prior to digestion and where test results will be reported on a dry weight basis.

Where practical, submission of a minimum of 20 wet grams of animal tissue or 5 grams of low moisture vegetation is recommended.

The decision as to which components of animal tissue samples (e.g., organs, muscle tissue, skin, whole sample, etc.) is critical to this analysis. Specific instructions for the preparation of vegetation samples can also be critical (e.g., whether to include or exclude dirt residues, etc.). Ensure that clients have been adequately consulted for specific instructions.

Stability

Preservation: none.

Holding time:

Metals (except Mercury): 2 years if frozen at ≤ -18°C (Reference: Puget Sound Protocols). Freezing is optional for freeze-dried tissue samples and for vegetation that is dried prior to digestion and reported on a dry weight basis; in these cases, samples may be stored up to 6 months at ambient temperature (based on BC MOE soil guidelines).

Mercury: 1 year if frozen at ≤ -18°C (Reference: US EPA 1631E Appendix). Freezing is optional for freeze dried tissue samples and for vegetation that is dried prior to digestion and reported on a dry weight basis; in these cases, samples may be stored up to 28 days at ambient temperature (based on BC MOE soil guidelines).

Results reported for samples digested beyond holding times must be qualified.

Storage: Samples must be kept cool (≤ 10°C) during transport. Biota samples where freezing is required (e.g., animal tissues, high moisture vegetation like berries, etc.) should be frozen as soon as possible, preferably within 48 hours of sampling, or digestion should be initiated within 96 hours of sampling.

Where practical, it is recommended for tissue dissections to be conducted prior to freezing, unless the whole sample will be homogenized.

Equipment and Supplies

1. Heating source (e.g., block digester, hotplate, water bath) capable of maintaining a sample extract temperature of 95 ± 5°C
2. Balance (capable of weighing to at least 3 significant figures)
3. Drying oven (may not be required)
4. Freezer (may not be required)
5. Freeze Dryer (may not be required)
6. Acid dispensers
7. Vapour refluxing cover to fit digestion vessel (e.g., reflux cap, watch glass etc.)
8. Digestion Vessels (e.g., block digester tube, beaker, flask, etc.)
9. Gloves
10. Spatula
11. Equipment for sample homogenization

Reagents

1. Nitric acid (HNO_3), concentrated (67 - 70%), reagent grade minimum
2. Hydrochloric acid (HCl), concentrated (34 - 37%), reagent grade minimum
3. Hydrogen peroxide (H_2O_2) 30%, reagent grade minimum
4. Water, de-ionized (ASTM Type I or equivalent recommended)

Safety

Nitric and hydrochloric acid must not be premixed; they should be added individually to each sample vessel. Mixtures of nitric and hydrochloric acid must not be stored in closed containers. When mixing concentrated acids with water, slowly and carefully add the acids to water. Adding water to concentrated acids is a hazard and can cause a violent exothermic reaction.

Wear appropriate PPE (Personal Protective Equipment) including lab coat, gloves, and safety glasses. Add reagents to samples and perform digestions under a fume hood.

Procedure

Sample Preparation – Drying and Homogenization

1. Depending on project requirements, samples may require drying prior to homogenization. Where drying is required, dry the sample at a temperature of ≤ 60°C. Freeze drying is acceptable.
2. Note: Sample drying temperature must not exceed 60°C to minimize evaporative loss of volatile analytes such as mercury (Reference: Puget Sound Protocols).
3. Homogenize the dried or as-received sample to a paste-like consistency either manually or mechanically using suitable equipment.

Sample Preparation - Digestion

The following procedure is based on the digestion of approximately 5 grams of wet sample or 1 gram of dry sample. The amount of sample digested can be scaled up or down as long as the acid ratios are maintained (9 parts HNO_3 : 1 part HCl). The default minimum total amount of reagents listed below may be used for sample weights up to 7.5 wet grams or 1.5 dry grams. For sample weights larger than this, increase the total amount of reagents.

1. Weigh approximately 5 grams of wet sample or 1 gram of dry sample into a digestion vessel, which must be fitted with a reflux cap and which must be capable of supporting reflux action. Examples of digestion vessels fitted with a reflux cap include a beaker, Erlenmeyer flask, or digestion tube fitted with a watch glass. Include Method Blanks, Lab Duplicates, and Reference Materials with each batch of samples. Weights must be recorded using a balance capable of weighing to at least 3 significant figures.
2. Add a minimum of 9 mL concentrated HNO_3, and a minimum of 1 mL concentrated HCl (per ~5 grams wet sample or ~1 gram dry sample). Optionally, 4 ± 0.5 mL of de-ionized water can be added to dried CRMs to be representative of the typical water content of wet tissue samples. Adding water to the CRMs may prevent excessive reactivity after acid addition.
3. Add a reflux cap to the top of the digestion vessel. Swirl acid and sample to mix gently. To reduce the reactivity of samples during initial heating, it is recommended to allow samples to equilibrate with the acid mixture at room temperature for a minimum of 1 hour prior to heating.
4. Digest samples for 2 hours ± 15 minutes at a temperature of 95 ± 5°C at atmospheric pressure. A hotblock or waterbath are the preferred methods of heating. The heat for digestion must maintain the sample extract temperature at 95 ± 5°C. This refers to the temperature of the sample extract in a digestion vessel covered with a reflux cap, not the temperature setting on the heating source, and not the temperature of an uncovered digestion vessel. It is recommended that the sample extract temperature be monitored and recorded with each batch.
5. Allow the sample to cool and add a minimum of 4 mL 30% H_2O_2. It is acceptable to add the H_2O_2 in multiple additions.
6. Digest samples for a minimum of 1 hour at a temperature of 95 ± 5°C.
7. Dilute the entire sample with de-ionized water to the volume required for the analysis. The dilution volume will depend on the analytical method and

objectives. Typical final dilution volumes for most instrumental techniques range from 25 mL to 100 mL. Include all undigested solid material as part of the final diluted volume.

8. Analyze the final extract using appropriate analytical methods and report the results on a dry weight and/or wet weight basis, depending on the application, as requested by the data-user. Refer to *Analytes and EMS Codes* section for Ministry preferences on reporting units for biota.
9. Report any anomalies observed during the digestion and analysis.

Quality Control

Summary of QC Requirements		
Method QC Component	Minimum Frequency	Minimum Data Quality Objectives*
Method Blank	1 per batch (max 20 samples)	Less than reported DL
Reference Material	1 per batch (max 20 samples)	70 – 130% of the laboratory's long term mean value or of certified targets for the method (if available)
Lab Duplicates	1 per batch (max 20 samples) where sufficient sample is available	≤ 40% RPD for all metals except those indicated below ≤ 60% RPD (for Ca & Sr)
Field Duplicates	Recommended	None Specified

* Minimum DQOs apply to individual QC samples at levels above 10x MDL. Report qualified data when DQOs are not met.

Reference Material requirements: Any suitable RM (including in-house RMs) may be utilized for this method for routine Quality Control purposes.

Method Validation Requirements

If metallic instruments or equipment are used to process or homogenize test samples, validation studies must be conducted to ensure that significant metallic contaminants are not introduced to test samples.

Specific method validation requirements for accuracy and precision may be established after interlaboratory consensus targets for appropriate Reference Materials have been established for this method by interlaboratory study or round robin.

References

1. US EPA Method 200.3, Sample Preparation Procedure for Spectrochemical Determination of Total Recoverable Elements in Biological Tissues, United States Environmental Protection Agency, 1996.
2. Recommended Guidelines for Measuring Metals in Puget Sound Marine Water, Sediment and Tissue Samples, Prepared for the US EPA, Puget Sound Water Quality Action Team, Olympia Washington, 1997.
3. US EPA Appendix to Method 1631, Total Mercury in Tissue, Sludge, Sediment, and Soil by Acid Digestion and BrCl Oxidation, United States Environmental Protection Agency, 1991.

Revision History

Aug 15, 2014: New prescriptive method added to BC Lab Manual to improve interlaboratory consistency. Effective date of this method is Jan 1, 2015.

2. INSTRUMENTAL ANALYSIS

2.1 Atomic Absorption – Direct Flame and Graphite Furnace Methods

2.1.1 Introduction

Metals in solution may be readily determined by atomic absorption spectroscopy. The method is simple, rapid, and applicable to a large number of metals in drinking, surface, and saline waters, and domestic and industrial wastes. While drinking waters free of particulate matter may be analyzed directly, domestic and industrial wastes require processing to solubilize suspended material. Sludge, sediments and other solid samples may also be analyzed after proper pretreatment.

Detection limits, sensitivity and optimum concentration ranges of the metals will vary with the various makes and models of atomic absorption spectrometers. The data shown in Table C-1, however, provide some indication of the actual concentration ranges measurable by direct aspiration and furnace techniques. In the majority of instances, the concentration range shown in the table under direct aspiration may be extended much lower with scale expansion and, conversely, extended upwards by using a less sensitive wavelength or by rotating the burner head. Detection limits by direct aspiration may also be extended through concentration of the sample and/or through solvent extraction techniques. Lower concentrations may also be determined using furnace techniques. The concentration ranges given in Table C-1 are somewhat dependent on equipment, such as the type of spectrometer and furnace accessory, the energy source and the degree of electrical expansion of the output signal. When using furnace techniques, however, the analyst should be cautioned as to possible chemical reactions occurring at elevated temperatures which may result in either suppression or enhancement of the analysis element. To ensure valid data with furnace techniques, the analyst must examine each matrix for interference effects and, if detected, treat accordingly using either successive dilution, matrix modification or method of standard additions.

Where direct aspiration atomic absorption techniques do not provide adequate sensitivity, in addition to the furnace procedure, reference is made to specialized procedures such as the gaseous hydride method for arsenic and selenium, the cold vapour technique for mercury, and the chelation-extraction procedure for selected metals. Reference to approved colorimetric methods is also made.

Atomic spectroscopy procedures are provided as the methods of choice; however, other instrumental methods have also been shown to be capable of producing precise and accurate analytical data. These instrumental techniques include mass spectroscopy, X-ray fluorescence, neutron activation, and anodic stripping, to name but a few. The above-mentioned techniques are presently considered as alternate test procedures providing they meet or exceed individual performance requirements.

2.1.2 Method Summary

In direct aspiration atomic absorption spectroscopy, a sample is aspirated and atomized in a flame. A light beam from a hollow cathode lamp, whose cathode is made of the element to be determined, is directed through the flame into a monochromator, and onto a detector that measures the amount of light absorbed. Absorption depends upon the presence of free unexcited ground state atoms in the flame. Since the wavelength of the light beam is characteristic of only the metal being determined, the light energy absorbed by the flame is a measure of the concentration of that metal in the sample. This principle is the basis of atomic absorption spectroscopy. It should be noted that alternate light sources include electrodeless discharge or “Super” lamps.

TABLE C-1

Atomic Absorption Concentration Ranges(1)

	Direct Aspiration				Furnace Procedure (4,5)		
Metal	Detection Limit mg/L	Sensitivity* mg/L	Optimum Concentration Range mg/L		Detection Limit mg/L	Optimum Concentration Range mg/L	
Aluminum	0.1	1	5	50	0.003	0.02	0.2
Antimony	0.2	0.5	1	40	0.003	0.02	0.3
Arsenic (2)	0.0001		0.0005	0.02	0.001	0.005	0.1
Barium (p)	0.1	0.4	1	20	0.002	0.01	0.2
Beryllium	0.005	0.025	0.05	2	0.0002	0.001	0.03
Cadmium	0.005	0.025	0.05	2	0.0001	0.0005	0.01
Calcium	0.01	0.08	0.2	7			
Chromium	0.05	0.25	0.5	10	0.001	0.005	0.1
Cobalt	0.05	0.2	0.5	5	0.001	0.005	0.1
Copper	0.02	0.1	0.2	5	0.001	0.005	0.1
Gold	0.1	0.25	0.5	20	0.001	0.005	0.1
Iridium (p)	3	8	20	500	0.030	0.1	1.5
Iron	0.03	0.12	0.3	5	0.001	0.001	0.1
Lead	0.1	0.5	1	20	0.001	0.005	0.1
Magnesium	0.001	0.007	0.02	0.5			
Manganese	0.01	0.05	0.1	3	0.0002	0.001	0.03
Mercury (3)	0.0002		0.0002	0.01			
Molybdenum (p)	0.1	0.4	1	40	0.001	0.003	0.06
Nickel (p)	0.03	0.15	0.3	5	0.001	0.005	0.1
Osmium	0.3	1	2	100	0.020	0.05	0.5
Palladium	0.1	0.25	0.5	15	0.005	0.02	0.4
Platinum (p)	0.2	2	5	75	0.020	0.1	2
Potassium	0.01	0.04	0.1	2			
Rhenium (p)	5	15	50	1000	0.20	0.5	5
Rhodium (p)	0.05	0.3	1	30	0.005	0.02	0.4
Ruthenium	0.2	0.5	1	50	0.020	0.1	2
Selenium (2)	0.0005		0.001	0.02	0.002	0.005	0.1
Silver	0.01	0.06	0.1	4	0.0002	0.001	0.025
Sodium	0.002	0.015	0.03	1			
Thallium	0.1	0.5	1	20	0.001	0.005	0.1
Tin	0.5	5	10	300	0.005	0.02	0.3
Titanium (p)	0.5	2	5	100	0.010	0.05	0.5
Vanadium (p)	0.2	0.8	2	100	0.005	0.01	0.2
Zinc	0.005	0.02	0.05	1	0.00005	0.0002	0.004

1) The concentrations shown are not contrived values and should be obtainable with any satisfactory atomic absorption spectrophotometer.

2) Gaseous hydride method.

3) Cold vapour technique.

4) For furnace sensitivity values consult instrument operating manual.

5) The listed furnace values are those expected when using a 20 µL injection and normal gas flow except in the case of arsenic and selenium where gas interrupt is used. The symbol (p) indicates the use of pyrolytic graphite with the furnace procedure.

* The concentration in milligrams of metal per litre that produces an absorption of 1%.

Although methods have been reported for the analysis of solids by atomic absorption spectroscopy (Spectrochim Acta, 24B 53, 1969) the technique generally is limited to metals in solution or solubilized through some form of sample processing.

i. Preliminary treatment of wastewater and/or industrial effluents is usually necessary because of the complexity and variability of the sample matrix. Suspended material must be subjected to a solubilization process before analysis. This process may vary because of the metals to be determined and the nature of the sample being analyzed. When the breakdown of organic material is required, the process should include a wet digestion with nitric acid.

ii. In those instances where complete characterization of a sample is desired, the suspended material must be analyzed separately. This may be accomplished by filtration and acid digestion of the suspended material. Metallic constituents in this suspended matter will then contribute to the total concentrations present. The sample should be filtered as soon as possible after collection and the filtrate acidified immediately.

iii. The total sample may also be treated with acid without prior filtration to measure what may be termed “total recoverable” concentrations.

When using the furnace technique in conjunction with an atomic absorption spectrometer, a representative aliquot of a sample is placed in the graphite tube in the furnace, evaporated to dryness, charred and atomized. As a greater percentage of available analyte atoms are vaporized and dissociated for absorption in the tube technique than in the flame technique, the use of small sample volumes or detection of low concentrations of elements is possible. The principle is essentially the same as with direct aspiration atomic absorption except a furnace, rather than a flame, is used to atomize the sample. Radiation from a given excited element is passed through the vapour containing ground state atoms of that element. The intensity of the transmitted radiation decreases in proportion to the amount of the ground state element in the vapour.

The metal atoms to be measured are placed in the beam of radiation by increasing the temperature of the furnace, thereby causing the injected specimen to be volatilized. A monochromator isolates the characteristic radiation from the hollow cathode lamp and a photosensitive device measures the attenuated transmitted radiation.

2.1.3 Definition of Terms

Optimum Concentration Range: A range, defined by limits expressed in concentration, below which scale expansion must be used and above which curve correction should be considered. This range will vary with the sensitivity of the instrument and the operating conditions employed.

Detection Limit: Detection limits can be expressed as either an instrumental or method parameter. The limiting factor of the former using acid water standards would be the signal-to-noise ratio and degree of scale expansion used; the latter would be more affected by the sample matrix and preparation procedure used. The Scientific Apparatus Makers Association (SAMA) has approved the following definition for detection limit: that concentration of an element which would yield an absorbance equal to twice the standard deviation of a series of measurements of a solution, the concentration of which is distinctly detectable above, but close to, blank absorbance measurement. The detection limit values listed in Table C-I and on the individual analysis sheets are to be considered minimum working limits achievable with the procedures given in this manual. These values may differ from the optimum detection limit values reported by the various instrument manufacturers.

2.1.4 Interferences

2.1.4.1 Direct Aspiration

The most troublesome type of interference in atomic absorption spectroscopy is usually termed “chemical” and is caused by lack of absorption of atoms bound in molecular combination in the flame. This phenomenon can occur when the flame is not sufficiently hot to dissociate the molecule, as in the case of phosphate interference with magnesium, or because the dissociated atom is immediately oxidized to a compound that will not dissociate further at the temperature of the flame. The addition of lanthanum will overcome the phosphate interference in magnesium, calcium and barium determinations. Similarly, silica interference in the determination of manganese can be eliminated by the addition of calcium. Chemical interferences may also be eliminated by separating the metal from the interfering material. While competing agents are primarily employed to increase the sensitivity of the analysis, they may also be used to eliminate or reduce interferences.

The presence of high dissolved solids in the sample may result in an interference from non-atomic absorbance such as light scattering. If background correction is not available, a non-absorbing wavelength should be checked. Preferably, samples containing high levels of dissolved solids should be extracted.

Ionization interferences occur where the flame temperature is sufficiently high to generate the removal of an electron from a neutral atom, giving a positively charged ion. This type of interference can generally be controlled by the addition, to both standard and sample solutions, of a large excess of any easily ionized element.

Although quite rare, spectral interference can occur when an absorbing wavelength of an element present in the sample but not being determined falls within the width of the absorption line of the element of interest. The results of the determination will then be erroneously high, due to the contribution of the interfering element to the atomic absorption signal. Also, interference can occur when resonant energy from another element in a multi-element lamp or a metal impurity in the lamp cathode falls within the bandpass of the slit setting and that metal is present in the sample. This type of interference may sometimes be reduced by narrowing the slit width.

2.1.4.2 Flameless Atomization

Although the problem of oxide formation is greatly reduced with furnace procedures because atomization occurs in an inert atmosphere, the technique is still subject to chemical and matrix interferences. The composition of the sample matrix can have a major effect on the analysis. Those effects must be determined and taken into consideration in the analysis of each different matrix encountered. To help verify the absence of matrix or chemical interference use the following serial dilution procedure. Withdraw from the sample two equal aliquots and dilute to the same predetermined volume. (The dilution volume should be based on the analysis of the undiluted sample. Preferably, the dilution should then be 1:4 while keeping in mind the optimum concentration range of the analysis. Under no circumstances should the dilution be less than 1:1). The diluted aliquots should then be analyzed and the results, multiplied by the dilution factor, should be compared to the original determination. Agreement of the results (within ± 10%) indicates the absence of interference. Comparison of the actual signal from the spike to the expected response from the analyte in an aqueous standard should help confirm the finding from the dilution analysis. Those samples which indicate the presence of an interferent should be treated in one or more of the following ways:

a) The samples should be successively diluted and reanalyzed to determine if the interference can be eliminated.

b) The matrix of the sample should be modified in the furnace. Examples are the addition of ammonium nitrate to remove alkali chlorides, ammonium phosphate to retain cadmium, and nickel nitrate for arsenic and selenium analyses. Platinum or palladium is a proven matrix modifier for many furnace elements. The mixing of hydrogen with the inert purge gas has also been used to suppress chemical interference. Hydrogen acts as a reducing agent and aids in molecular dissociation.

c) Analyze the sample by method of standard additions while noting the precautions and limitations of its use.

Gases generated in the furnace during atomization may have molecular absorption bands encompassing the analytical wavelength. When this occurs, either the use of background correction or choosing an alternate wavelength outside the absorption band should eliminate this interference. Non-specific broad band absorption interference can also be compensated for with background correction.

Continuum background correction cannot correct for all types of background interference. When the background interference cannot be compensated for, chemically remove the analyte or use an alternate form of background correction; e.g., Zeeman background correction.

Interference from a smoke-producing sample matrix can sometimes be reduced by extending the charring time at a higher temperature or utilizing an ashing cycle in the presence of air. Care must be taken, however, to prevent loss of the analyte.

Samples containing large amounts of organic materials should be oxidized by conventional acid digestion prior to being placed in the furnace. In this way broad band absorption will be minimized.

From anion interference studies in the graphite furnace it is generally accepted that nitrate is the preferred anion. Therefore, nitric acid is preferable for any digestion or solubilization step. If another acid in addition to HNO_3 is required, a minimum amount should be used. This applies particularly to hydrochloric and, to a lesser extent, sulfuric and phosphoric acids.

Carbide formation resulting from the chemical environment of the furnace has been observed with certain elements that form carbides at high temperatures. Molybdenum may be cited as an example. When this takes place, the metal will be released very slowly from the carbide as atomization continues. For molybdenum, the analyst may be required to atomize for 30 seconds or more before the signal returns to baseline levels. This problem is greatly reduced and the sensitivity increased with the use of pyrolytically-coated graphite. Ionization interferences have not been reported to date with furnace techniques. For comments on spectral interference see section 2.1.4.1.

Contamination of the sample can be a major source of error because of the extreme sensitivities achieved with the furnace. The sample preparation work area should be kept scrupulously clean. All glassware should be cleaned as directed in part 2.1.5 of this manual. It is very important that special attention be given to reagent blanks in both analysis and the correction of analytical results. Lastly, pyrolytic graphite, because of the production process and handling, can become contaminated. As many as five or possibly ten high temperature burns may be required to clean the tube before use.

2.1.5 Apparatus

1. Atomic Absorption Spectrometer: Single or dual channel, single or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provision for interfacing with a strip chart recorder or computer work station.
2. Burner: The burner recommended by the particular instrument manufacturer should be used. For certain elements a nitrous oxide burner is required.
3. Hollow cathode lamps: Single element lamps are preferred but multi-element lamps may be used. Electrodeless discharge lamps or “super” lamps may also be used when available.
4. Graphite furnace: Any furnace device capable of reaching the specified temperatures is satisfactory.
5. Strip chart recorder: A recorder is strongly recommended for furnace work so that there will be permanent record and any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can be easily recognized.
6. Pressure-reducing valves: The supplies of fuel and oxidant shall be maintained at pressures somewhat higher than the controlled operating pressure of the instrument by suitable valves.
7. Containers: All glassware, linear polyethylene, polypropylene or Teflon containers, including sample bottles, should be washed with detergent then rinsed with tap water, 1:1 nitric acid, tap water, 1:1 hydrochloric acid, tap water, and deionized distilled water, in that order.

2.1.6 Reagents

1. Type II water (ASTM D1193): Use Type II water for the preparation of all reagents and calibration standards and as dilution water.
2. Concentrated nitric acid (HNO_3): Use a spectrograde acid certified for AA use. Prepare a 1:1 dilution with Type II water by adding the concentrated acid to an equal volume of water.
3. Hydrochloric acid (HCl, 1:1): Use a spectrograde acid certified for AA use. Prepare a 1:1 dilution with Type II water by adding the concentrated acid to an equal volume of water.
4. Fuel and oxidant: Commercial grade acetylene is generally acceptable. Air may be supplied from a compressed air line, a laboratory compressor, or a cylinder of compressed air. Reagent grade nitrous oxide is also required for certain determinations. Standard, commercially available argon and nitrogen are required for furnace work.
5. Stock standard metal solutions: Stock standard solutions are prepared from high purity metals, oxides, or nonhygroscopic reagent-grade salts using Type II water and redistilled nitric or hydrochloric acids. (See individual methods for specific instructions.) Sulfuric or phosphoric acids should be avoided as they produce an adverse effect on many elements. The stock solutions are prepared at concentrations of 1,000mg of the metal per litre. Commercially available standard solutions may also be used. Where the sample viscosity, surface tension, and components cannot be accurately matched with standards, the method of standard addition (MSA) may be used. This method has been described in detail in section 2.1.7.
6. Calibration standards: For those instruments which do not read out directly in concentration, a calibration curve is prepared to cover the appropriate concentration range. Usually, this means the preparation of standards which produce an absorbance of 0.0 to 0.7. Calibration standards are prepared by diluting the stock metal solutions at the time of analysis. For best results, calibration standards should be prepared fresh each time a batch of samples is analyzed. Prepare a blank and at least three calibration standards in graduated amounts in the appropriate range of the linear part of the curve. The calibration standards should be prepared using the same type of acid or combination of acids and at the same concentration as will be found in the samples following processing. Beginning with the blank and working toward the highest standard, aspirate the solutions and record the readings. Repeat the operation with both the calibration standards and the samples a sufficient number of times to secure a reliable average reading for each solution. Calibration standards for furnace procedures should be prepared as described on the individual sheets for that metal or as described in a specific instrument manual.

2.1.7 Preparation of a Standard Addition Plot

In this method, equal volumes of sample are added to a deionized distilled water blank and to three standards containing different known amounts of the test element. The volume of the blank and the standards must be the same. The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated back to zero absorbance, the point of interception of the abscissa is the concentration of the unknown. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate. An example of a plot so obtained is shown in Figure 1.

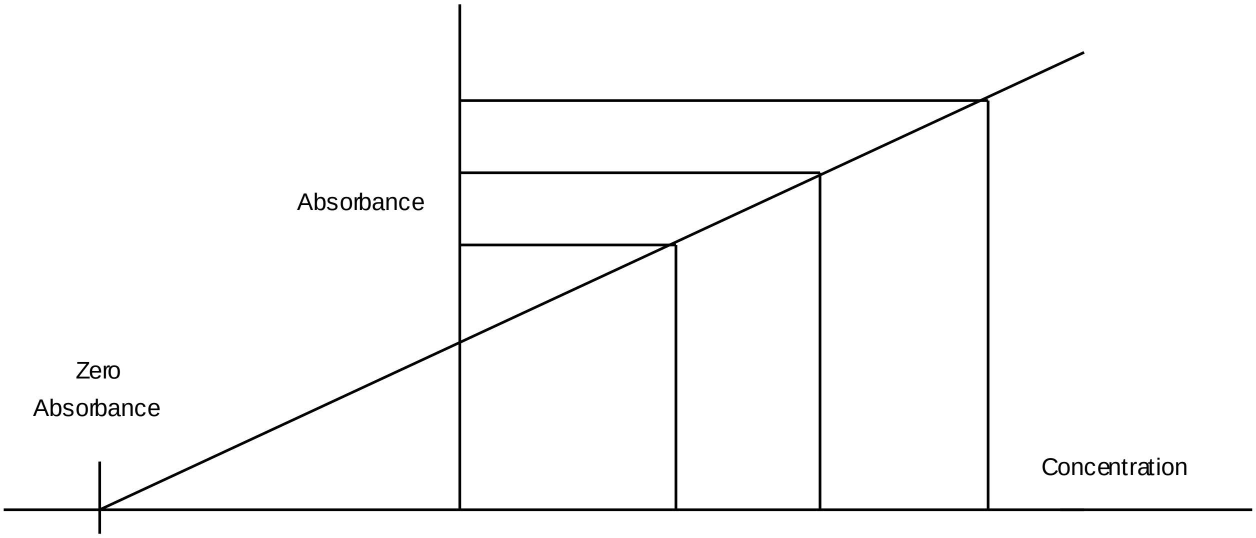


Figure 1. Standard Addition Plot

Conc. of sample	Addn 0	Addn 1	Addn 2	Addn 3
	No Addn	Addn of 50% of Expected Amount	Addn of 100% of Expected Amount	Addn of 150% of Expected Amount

The method of standard additions can be very useful; however, for the results to be valid the following limitations must be taken into consideration:

1. The absorbance plot of sample and standards must be linear over the concentration range of concern. For best results the slope of the plot should be the same as the slope of the aqueous standard curve. If the slope is significantly different (more than 20%) caution should be exercised.
2. The effect of the interference should not vary as the ratio of analyte concentration to sample matrix changes and the standard addition should respond in a similar manner to the analyte.
3. The determination must be free of spectral interference and corrected for non-specific background interference.

2.1.8 General Procedure for Analysis by Atomic Absorption

2.1.8.1 Direct Aspiration

Differences between the various makes and models of satisfactory atomic absorption spectrometers prevent the formulation of detailed instructions applicable to every instrument. The analyst should follow the manufacturer's operating instructions for the particular instrument. In general, after choosing the proper hollow cathode lamp for the analysis, the lamp should be allowed to warm up for a minimum of 15 minutes unless operated in a double beam mode. During this period, align the instrument, position the monochromator at the correct wavelength, select the proper monochromator slit width, and adjust the hollow cathode current according to the manufacturer's recommendation. Subsequently, light the flame and regulate the flow of fuel and oxidant, adjust the burner and nebulizer flow rate for maximum percent absorption and stability, and balance the photometer. Run a series of standards of the element under analysis and construct a calibration curve by plotting the concentrations of the standards against the absorbance. For those instruments which read directly in concentration set the curve corrector to read out the proper concentration. Aspirate the samples and determine the concentrations either directly, or from the calibration curve. Standards must be run each time a sample or series of samples are run.

Calculation - Direct determination of liquid samples:

Read the metal value in mg/L from the calibration curve or directly from the readout system of the instrument.

1. <u>If dilution of sample was required</u>:

   mg metal/L in sample = A (C+B) / C

   where: A = mg/L of metal in diluted sample from calibration curve
   B = mL of deionized water used for dilution
   C = mL of sample aliquot

2. <u>For samples containing particulates</u>:

   mg metal/L in sample = A (V / C)

   where: A = mg/L of metal in processed sample from calibration curve
   V = final volume of the processed sample in mL
   C = mL of sample aliquot processed

3. <u>For solid samples</u>: report all concentrations as mg/kg dry weight:

   Dry sample:

   $$\text{mg metal/kg sample} = \frac{A \times V}{D}$$

   where: A = mg/L of metal in processed sample from calibration curve
   V = final volume of the processed sample in mL
   D = weight of dry sample in gram

   Wet sample:

   $$\text{mg metal/kg sample} = \frac{A \times V}{W \times P}$$

   where: A = mg/L of metal in processed sample from calibration curve
   V = final volume of the processed sample in mL
   W = weight of wet sample in grams
   P = % solids in wet sample

2.1.8.2 Furnace Procedure

Furnace devices (flameless atomization) are a most useful means of extending detection limits. Because of the differences between various makes and models of satisfactory instruments, no detailed operating instructions can be given for each instrument. Instead, the analyst should follow the instructions provided by the manufacturer of the particular instrument. In addition, the following points may be helpful.

1. Background correction is important when using flameless atomization, especially below 350nm. Certain samples, when atomized, may absorb or scatter light from the lamp. This can be caused by the presence of gaseous molecular species, salt particles, or smoke in the sample beam. If no correction is made, sample absorbance will be greater than it should be, and the analytical result will be erroneously high. Zeeman background correction is effective in overcoming composition or structured background interferences. It is particularly useful when analyzing for As in the presence of Al and when analyzing for Se in the presence of Fe.
2. Memory effects occur when the analyte is not totally volatilized during atomization. This condition depends on several factors: volatility of the element and its chemical form, whether pyrolytic graphite is used, the rate of atomization, and furnace design. This situation is detected through blank burns. The tube should be cleaned by operating the furnace at full power for the required time period, as needed, at regular intervals during the series of determinations.
3. Inject a measured microliter aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.
4. To verify the absence of interference, follow the serial dilution procedure given in section 2.1.4.2.
5. A check standard should be run after approximately every 10 sample injections. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced. Tube life depends on sample matrix and atomization temperature. A conservative estimate would be that a tube will last at least 50 firings. A pyrolytic coating will extend that estimated life by a factor of three.

   Calculation: Read the metal value in µg/L from the calibration curve or directly from the readout system of the instrument.

   1. If different size furnace injection volumes are used for samples and standards:

      $$\mu g\ metal/L\ of\ sample = Z\,(S/U)$$

      where: Z = µg/L of metal read from calibration curve or readout system
      S = µL of standard injected into furnace for calibration curve
      U = µL of sample injected for analysis

   2. If dilution of sample was required but sample injection volume is the same as for the standard:

      $$\mu g\ metal/L\ of\ sample = Z\,(C+B)/C$$

      where: Z = µg/L of metal in diluted aliquot from calibration curve
      B = mL of deionized distilled water used for dilution
      C = mL of sample aliquot

   3. For sample containing particulates:

      $$\mu g\ metal/L\ of\ sample = Z\,(V/C)$$

      where: Z = µg/L of metal in processed sample from calibration curve
      V = final volume of processed sample in mL
      C = mL of sample aliquot processed

4. For solid samples: Report all concentration as mg/kg dry weight

Dry sample:

mg metal /kg sample = (Z x V/ 1000) / D

where: Z = µg/L of metal in processed sample from calibration curve
V = final volume of processed sample in mL
D = weight of dry sample in grams

Wet sample:

mg metal/kg sample = (Z x V/ 1000) / (WxP)

where: Z = µg/L of metal in processed sample from calibration curve
V = final volume of processed sample in mL
W = weight of wet sample in grams
P = % solids in wet sample

2.1.9 Quality Control for Water Analysis

1. Minimum Requirements
   - i. All quality control data should be maintained and available for easy reference or inspection.
   - ii. An unknown performance sample (when available) must be analyzed once per year for the metals measured. Results must be within the control limits established by good laboratory practice. If problems arise, they should be corrected, and a follow-up performance sample should be analyzed.
2. Minimum Daily Control
   - i. After a calibration curve composed of a minimum of a reagent blank and three standards has been prepared subsequent calibration curves must be verified by use of at least a reagent blank and one standard at or near the median concentration level (MCL). Daily checks must be within ±10 percent of original curve.
   - ii. If 20 or more samples per day are analyzed, the working standard curve must be verified by running an additional standard at or near the MCL every 20 samples. Checks must be within ±10 percent of original curve.
3. Optional Requirements
   - i. A current service contract should be in effect on balances and the atomic absorption spectrometer.
   - ii. Class S weights should be available to make periodic checks on balances.
   - iii. Chemicals should be dated upon receipt and replaced as needed or before shelf life has been exceeded.
   - iv. A known reference sample (when available) should be analyzed once per quarter for the metals measured. The measured value should be within the control limits established by good laboratory practice.
   - v. At least one duplicate sample should be run every 10 samples, or with each set of samples, to verify precision of the method. Checks should be within the control limit established by good laboratory practice.
   - vi. Standard deviation should be obtained and documented for all measurements being conducted.
   - vii. Quality control charts or a tabulation of mean and standard deviation should be used to document validity of data on a daily basis.

2.2 Hydride Vapour Generation Sample Introduction (HVAAS/HVICP)

2.2.1 Introduction

The determination of small traces of a number of metallic hydride-forming elements (especially As, Sb, Se) has been of importance in toxicology for many years. In many fields of industry, in geochemistry and in metallurgy, the trace determination of these elements is also of importance.

It is generally agreed that, because of its simplicity and specificity, atomic absorption spectroscopy or atomic emission spectroscopy, together with a hydride generation sample introduction system, best meets the requirements for the economical determination of trace concentrations of these elements.[1]

2.2.2 Method Summary

Hydride vapour generation sample introduction systems utilize a chemical reduction to form a volatile hydride with the metal of interest. This volatile hydride is then swept into either a heated reaction cell, or directly into the plasma of an ICP, where the metal of interest is freed from the hydride.

Standard FAAS (heated reaction cell) or ICP is then carried out on the volatile metallic species.[1]

See Section 2.1 and 2.4 for details on FAAS and ICP.

2.2.3 Interferences

The following metals, compounds and conditions may interfere:

- easily reduced metals, i.e., copper, silver, mercury, etc.
- high concentrations of transition metals (>200 mg/L).
- oxidizing agents remaining following sample digestion, i.e., oxides of nitrogen.[2]
- oxidation state of element: sample may require a pre-treatment prior to analysis using a reducing agent such as potassium iodide (KI).

2.2.4 General Procedure

Sodium borohydride solution is used as the reductant for the determination of metallic hydride-forming elements. Sodium borohydride liberates hydrogen on contact with acids. The reaction mechanisms involved in the reduction of metal ions are complicated and almost certainly take place via the formation of intermediate radicals. The following equation represents a simplification of the reduction and free volatile metal forming mechanism:

$$M^{n+} + nBH_4^- \text{ ---> } MH_n \text{ (gas)} + H_2 \text{ (gas)} + n/2\ B_2H_6$$

$$MH_n + \text{heat (900-1000°C) ---> } M$$

M is a metallic element which forms a volatile hydride (ie, arsenic, bismuth, antimony, selenium, tin, tellurium, etc).

The sample solution is first treated to convert the metal of interest to ionic form in acidic solution. Reductant is then dispensed into the sample solution where it reacts with liberated hydrogen. A carrier gas (eg, argon) flushes the hydride into a heated reaction cell or directly into the plasma of an ICP where it is decomposed and the absorption or emission of the metal is measured. Where a reaction cell is used, it is heated to between 900°C and 1000°C.[1]

2.3 Cold Vapour Generation Sample Introduction (CVAAS)

2.3.1 Introduction

The determination of small traces of mercury has been of importance in toxicology for many years. In many fields of industry, in geochemistry and in metallurgy, the trace determination of this element is also of importance.

It is generally agreed that, because of its simplicity and specificity, atomic absorption spectroscopy, together with a cold vapour generation sample introduction system, best meets the requirements for the economical determination of trace concentrations of mercury.[1]

2.3.2 Method Summary

Cold vapour generation sample introduction systems utilize a chemical reduction to form a volatile metal species. This volatile species is then swept into a cell positioned in the path of a standard AAS. Concentration is then determined at a specific wavelength.[1]

2.3.3 Interferences and Precautions

Any produced vapour which absorbs at the same wavelength as the metal of interest will interfere.[3]

2.3.4 General Procedure

Stannous chloride is used as the reductant for the determination of room temperature volatile metallic elements (ie, mercury). Stannous chloride reduces the metal of interest to its elemental form.

The reaction mechanisms involved in the reduction of metal ions are complicated and almost certainly take place via the formation of intermediate radicals. The following equation represents a simplification of the reduction and volatilization of mercury:

$$Hg^{2+} + Sn^{2+} \text{--->} Hg\ (gas) + Sn^{4+}$$

The sample is first treated to convert mercury to ionic form in acidic solution. Reductant (usually tin) is then dispensed into the sample solution to produce volatile elemental mercury. A carrier gas (eg, argon) flushes the volatile mercury into a cell positioned in the light path of an AAS and concentration is determined by standard AAS technique. [1]

2.4 Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES)

2.4.1 Introduction

ICP-AES is a rapid multi-element technique which is capable of the simultaneous determination of major, minor, and trace elements in solution. Reference 1 is recommended as an excellent source of information on this topic. Some advantages of this technique include:

1. A large linear dynamic range of 5 to 6 decades for each analytical line which permits both trace and major elements to be analyzed in the same sample dilution.
2. The low sample volume (5 to 20 mL) required for the simultaneous determination of up to 70 elements (depending on the instrument).
3. A low susceptibility to chemical and matrix interferences.
4. The versatility to add a hydride generator, ultrasonic nebulizer, graphite furnace or laser ablation system to increase sensitivity even further.

Some disadvantages include:

1. A high initial instrument cost.
2. A high initial investment in data handling software.
3. Clogging of some pneumatic nebulizer systems.
4. Spectral interferences - (see interference section 2.1.4).

2.4.2 Method Summary

Atomic emission spectrometry (AES), atomic absorption spectrometry (AAS), and atomic fluorescence spectrometry (AFS) all measure atomic spectra in the ultraviolet, visible, and near infrared region of the electromagnetic spectrum. All three methods must atomize the sample prior to excitation and measurement. In AES, the inductively coupled plasma (ICP) provides the energy for atomization and excitation. The method is applicable to aqueous samples and to digests of sediments, soils, and biota.

2.4.3 Detection Limits

The Detection Limit (DL) is a statistical figure of merit. It can be defined as the smallest signal equal to 2 - 6 times the standard deviation of the background signal and, in deionized water, this definition gives a fair estimation of the instrument DL. Errors associated with Inter Element Correction (IEC) factors are thought to be in the order of ±5% [2, 3] although Millward and Kluckner [4] found that ±2.5% is probably more likely. The EDL (Effective Detection Limit) can then be calculated as follows:

$$EDL = (d^2 + \sum(0.05t)^2)^{1/2}$$

where d = 3 times standard deviation of base noise
t = concentration of interfering element times the IEC factor

Experience indicates that as the matrix becomes more complex, the EDL rises. The above calculation, although not perfect, quantitates to some extent what is observed in practice. In any event, the method of determining EDLs should accompany any data generated by any analytical technique.

Table C-2 indicates the detection power of ICP-AES for an argon ICP operated with a pneumatic nebulizer 1. The detection limits are on a 2 times standard deviation basis. These DLs can vary by a factor of 10 or more depending on:

1. Source - 27 MHz vs 40 MHz
2. Nebulizer - pneumatic vs ultrasonic vs hydride
3. Operating Conditions - compromise vs optimal
4. Differences in spectral bandwidth
5. Prominent line chosen
6. Concomitants - pure water vs sediment digests

Table C-2

Element		Detection Limit µg/L	Element		Detection Limit µg/L	Element		Detection Limit µg/L
Aluminum	Al	10-30	Indium	In	30-100	Ruthenium	Ru	30-100
Antimony	Sb	30-100	Iridium	Ir	30-100	Scandium	Sc	3-10
Arsenic	As	30-100	Iron	Fe	3-10	Selenium	Se	30-10
Barium	Ba	3-10	Lanthanum	La	10-30	Silicon	Si	30-100
Beryllium	Be	3	Lead	Pb	30-100	Silver	Ag	3-10
Bismuth	Bi	30-100	Lithium	Li	3-10	Sodium	Na	10-30
Boron	B	3	Lutetium	Lu	3-10	Strontium	Sr	3-10
Cadmium	Cd	10-30	Magnesium	Mg	3-10	Tantalum	Ta	10-30
Calcium	Ca	10-30	Manganese	Mn	3	Tellurium	Te	100-300
Carbon	C	30-100	Mercury	Hg	30-100	Terbium	Tb	30-100
Cerium	Ce	30-100	Molybdenum	Mo	3-10	Thallium	Tl	30-100
Chromium	Cr	3-10	Neodymium	Nd	30-100	Thorium	Th	30-100
Cobalt	Co	3-10	Nickel	Ni	10-30	Thulium	Tm	3-10
Copper	Cu	3-10	Niobium	Nb	30-100	Tin	Sn	30-100
Dysprosium	Dy	10-30	Osmium	Os	3	Titanium	Ti	3-10
Erbium	Er	10-30	Palladium	Pd	30-100	Tungsten	W	30-100
Europium	Eu	3-10	Phosphorus	P	30-100	Uranium	U	100-300
Gadolinium	Gd	10-30	Platinum	Pt	30-100	Vanadium	V	3-10
Gallium	Ga	30-100	Potassium	K	30-300	Ytterbium	Yb	3-10
Germanium	Ge	30-100	Praseodymium	Pr	30-100	Yttrium	Y	3-10
Gold	Au	10-30	Rhenium	Re	10-30	Zinc	Zn	3-10
Hafnium	Hf	10-30	Rhodium	Rh	30-100	Zirconium	Zr	10-30
Holmium	Ho	3-10						

2.4.4 Interferences and Precautions

1. Physical

   Samples containing high concentrations of acids and/or dissolved solids will affect surface tension and hence sample uptake, droplet size distribution, and aerosol transport to the plasma. High dissolved solids can also cause salt build-up at the tip of some pneumatic nebulizers. Sample uptake variations due to viscosity differences can be controlled with a peristaltic pump. Salt build-up can be controlled by wetting the argon prior to nebulization, using a tip washer, or diluting the sample. Changes in droplet size distribution cannot be compensated for as easily, other than matching the standard and sample matrix, which is difficult if the sample matrix is unknown.

2. Chemical [5]

   Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant with the ICP technique. If observed, they can be minimized by careful selection of operating conditions (incident power, viewing height, nebulizer argon flow, etc.), by buffering of the sample, by matrix matching, and by internal standard procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.

3. Spectral

   ICP-AES suffers more from spectral interferences and less from chemical interferences than FAAS where the opposite is true. Spectral interferences classify as [1]:
   - Stray light
   - Continua and line wings contributed by the constituents of the sample
   - Spectral lines and molecular bands contributed by the discharge atmosphere and the solvent
   - Spectral lines and molecular bands contributed by the constituents of the sample

   The effect of the above interferences is background enhancement which can be categorized as:
   - Simple or “flat” background
   - Sloping background
   - Direct line overlap
   - Complex line overlap

   All of the background changes can be corrected to some degree by measuring the background off-peak then subtracting the value(s) from the peak and/or subtracting empirically calculated inter-element corrections. This topic is broad and complex but there are many excellent texts and papers which cover spectral interferences in ICP-AES. For instance, EPA method 200.7 gives suggested background correction positions for a number of specified analysis lines. The ICP spectroscopist must carefully choose background correction positions for their particular instrument and analysis requirements.

2.4.5 General Procedure

1. Aerosol Production

Nebulizers are the weak point in ICP and are at the root of many ICP problems. The function of the nebulizer is to convert the solution to a fine, uniform aerosol. The aerosol will consist of droplets with a range of sizes but most of the aerosol mass should be in the smaller size range.

Pneumatic nebulizers are common and can be divided into two types - concentric (e.g., Meinhard) and Cross-flow (eg. MAX). Grid nebulizers (e.g., Hildebrand) are becoming more common. Special nebulizers are available such as the Babington (e.g., GMK) for samples containing high concentrations of dissolved solids and the Fritted Disc for LC-ICP-AES applications.

Ultrasonic nebulizers have been introduced commercially in the last few years. Their efficiency at producing an aerosol is typically 10 times the efficiency of the pneumatic nebulizers. Because of the increase in material reaching the plasma, detection limits for many elements exceed pneumatic nebulizer detection limits by a factor of 10. However, the upper concentration range for these elements is decreased by a factor of 10.

The solution to be analyzed is either fed to the nebulizer by a pump or is pulled through as a result of reduced pressure at the nozzle (Venturi effect).

As for AAS, electrothermal atomizers can be connected to ICP. These devices can be metal (boat or filament) or graphite (yarn, rod or furnace).

2. Spray Chambers

The aerosol which is produced by the nebulizer consists of various size droplets. The function of the spray chamber is to sort out the larger droplets and allow the finer droplets through to the plasma. A major part of the primary aerosol is lost to chamber surfaces - in the order of 98 - 99.5% [1].

The most common spray chamber is the dual concentric or Scott chamber. Cyclone chambers are starting to become popular. These sort droplets by imparting a spiral motion to the aerosol so that the larger droplets strike the wall of the chamber preferentially.

3. Torches

The most critical component of the ICP assembly is the torch and although there are many different designs, the torch type in most common use for argon plasmas is the three concentric tube “Fassel” torch. Over the years the Fassel torch has been refined to reflect the following performance requirements [1]:

1. Easy ignition of the plasma.
2. Continuous, stable plasma generation with a minimum influence of the injected sample, primarily the absence of risks of extinguishing the plasma and formation of deposits in the torch.
3. A sufficiently high sample flow through the plasma tunnel to the observation zone.
4. An optimum sample heating efficiency by a long residence time of the sample in the plasma.
5. A low gas consumption rate.
6. Minimal power requirements to reduce size and cost of the RF power supply.

The torch is placed in a water-cooled induction coil of an RF generator. Two or three gas flows are introduced into the tubes of the torch and the flowing gas is made electrically conductive by Tesla sparks.

The RF current through the coil generates oscillating magnetic fields which induce electric currents in the conducting gas, which in turn heats up due to resistance and forms the plasma. The aerosol from the nebulizer/spray chamber is introduced into the centre of the plasma where it becomes volatilized and atomized. The resulting spectral lines are separated and their intensity measured by the spectrometer.

4. Spectrometer Systems

Spectral information from the ICP can be separated in two different ways. Sequential spectrometers employ a monochrometer and various drive systems (Sine Bar, Direct, Magnetic, Encoding) under computer control to scan the spectrum, stopping at lines of interest. Scan rate and integration time at each selected line can be varied. Various peak-finding methods (Single, Moving Window, Peak Area Fitting, Side Line Indexing) are used to ensure the requested peak is presented to the detector. Flexibility is the main advantage of sequential spectrometers.

Simultaneous or Direct Reading Spectrometers are commonly based on concave grating mounts: Rowland Circle, Paschen-Runge or Seya-Namioka or on an Echelle mount. Line selection must precede the purchase of the instrument, keeping in mind that, due to physical limitations, line selection compromises may be necessary. Speed is the main advantage of simultaneous spectrometers.

Characteristics of the ideal spectrometer system for ICP-AES are as follows [1]:

1. Record all spectral information simultaneously.
2. Rapid signal acquisition and recovery.
3. Provide high contrast (high resolution, low stray light).
4. Possess a wide dynamic range - at least 106.
5. Provide accurate, precise wavelength identification and selection for analysis.
6. Highly stable, insensitive to environmental changes (temperature, humidity, vibration).
7. Provide means to identify and correct for interferences including displaying spectra for operator.
8. Measure and subtract background.
9. Provide a permanent record of spectra and analysis results.
10. Computerized operation: control, readout, storage, data manipulation, statistical analysis, report generation.

5. Method Validation

Method validation must be performed initially and whenever instrumental modifications are incorporated. Method validation checks include determination of precision, accuracy, detection limit, calibration curve linearity, and analytical range.

As these items are easily measured it is recommended that they be monitored on a regular basis. For example, measurement of precision and detection limit could be monitored weekly, or daily if desired.

It should be noted that the responses of some ICP emission lines are not linear. Where the use of an alternate analysis line is not possible (e.g., in a fixed - channel instrument). Computer curve correction may be employed. Curvature of some lines is sensitive to operating conditions; the validity of computer curve correction should be confirmed by regular analysis of QC solutions.

The extent of the upper range of each ICP channel must be known; detector and measurement electronic parameters will limit the upper analysis range. Detectors may “saturate”, for some elements at concentrations under 50 mg/L.

6. Long Term Stability of ICP Conditions

It is desirable to ensure that inter-element correction factors, line curvature, analytical ranges, and other parameters remain constant. This may be done by setting the ratio of the intensities of an "atom" line and an "ion" line to a constant value. This is usually accomplished by aspirating a solution containing the two elements of interest and adjusting the nebulizer argon flow rate using a mass flow controller until the desired intensities are observed. [6, 7]

7. Daily Instrument Calibration

Most ICP standardization schemes employ "two-point" calibration using a "blank" or "zero" solution and a single "high-level" concentration for each element. The "high-level" points range generally from 0.5 to 100 mg/L, although 1.0 to 10.0 mg/L levels are typical.

Since an ICP may analyze over thirty elements simultaneously, it is important to monitor the integrity of the mixed calibration solutions, since element concentrations may vary due to contamination or precipitation. A hardcopy of instrument responses for each element should be produced and examined daily. Also, analysis of calibration verification solutions should be carried out prior to sample analysis by analyzing a check standard prepared independently from the calibration solutions. Acceptance criteria for the verification standard should be within approximately 5% of the "real" value.

It is also important to monitor the stability of calibration over the "long term" by analyzing a check or calibration standard after every 10 samples. This not only monitors instrument stability but ensures that other factors such as nebulizer clogging do not go undetected.

2.4.6 Precision

Precision represents the reproducibility of measurement and is usually expressed in terms of percent relative standard deviation (RSD). At the detection limit (DL) the RSD will be higher than at levels above the DL. For example, when the DL is set at:

2 times standard deviation - RSD is 50%
3 times standard deviation - RSD is 33%
5 times standard deviation - RSD is 10%

At levels equalling a few hundred times the DL, short term precision of 0.5 - 2% can be obtained depending on [1]:

- nebulizer
- ICP system
- spectrometer
- analyte
- sample type
- definition of "short term"
- "enthusiasm" of the analyst

2.4.7 Accuracy

Accuracy or agreement between measured and "true" value can best be determined using Standard Reference Materials (SRM's).

2.4.8 Quality Control

To ensure accuracy and precision, quality control blanks, duplicates, spikes, and certified reference materials must be incorporated into the analysis scheme. It should be noted that a wide variety of certified reference materials for water, geologicals, and biological materials are available at levels suitable for ICP analysis.

2.4.9 References

1. P. W. J. M. Boumans, Ed., Inductively Coupled Plasma Emission Spectroscopy, Parts I and II, Chemical Analysis 90. John Wiley & Sons Pub., (1987).
2. M. Thompson & J. N. Walsh, Ed., Handbook of Inductively Coupled Plasma Spectrometry, 2nd ed., Chapman & Hall Pub., (1989).
3. S. E. Church, Geostand. Newslett., Vol. 2, p. 133, (1981).
4. Christopher G. Millward & Paul D. Kluckner, JAAS, Vol. 6, Feb., (1991).
5. EPA Method 6010A, Revision 1, November (1990).
6. Botto, R.I., Long-term Stability of Spectral Interference Calibrations for Inductively Coupled Plasma Atomic Emission Spectrometry, Analytical Chemistry, 54:1654 (1982).
7. Methods for Chemical Analysis of Water and Wastes, EPA-600, 4-79-020, March, 1983, Method 200.7.
8. Instructions - MHS-20 Mercury/Hydride System, Publication 338-A2-M 294/12.79. Bodenseewerk Perkin-Elmer & Co. GMBH/Uberlingen. 1979.
9. Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods. Publication #SW-846 Revision 0. United States Environmental Protection Agency, Washington, DC. 3rd edition, 1986.
10. Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods (Revised). Publication #SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd edition 1990.
11. Instructions - MHS-20 Mercury/Hydride System, Publication 338-A2-M 294/12.79. Bodenseewerk Perkin-Elmer & Co. GMBH/UBERLINGEN. 1979.
12. Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods (Revised). Publication #SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd edition, 1990.

2.4.10 Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes removed. Minor editing.

Revision Date: December 31, 2000

2.5 Metal Analysis of Solids by ICP

Parameter	Metals
Analytical Method	D+G; acid digestion; ICP
Introduction	Inductively Coupled Argon Plasma - Atomic Emission Spectrometry (ICP) is a rapid multi-element scanning technique for the analysis of elements including metals. This analysis is applicable to a large list of elements within the periodic table but for the purposes of this method, 25 of the more commonly analyzed metals will be targeted.
Method Summary	The soil or sediment sample is initially homogenized to ensure representative sub-aliquots will be digested and analyzed. An accurate weight of soil is acid digested and the resulting digestate is analyzed for metals by ICP.

MDL

Target Element	Detection Limit (ug/g)
Aluminum	10
Antimony	10
Arsenic	30
Barium	0.1
Beryllium	1
Boron	0.5
Cadmium	5
Calcium	1
Chromium	2
Cobalt	1
Copper	1
Iron	2
Lead	10
Magnesium	0.1
Manganese	0.2
Molybdenum	4
Nickel	2
Phosphorus	20
Silver	2
Sodium	5
Strontium	0.1
Tin	5
Titanium	0.3
Vanadium	0.5
Zinc	1

Detection Limits have been derived by multiplying (weight / volume) factors by the estimated instrument detection limits in solution. These limits are only given as guidelines and are dependent on the specific instrument configuration.

Matrix	Soil, solids, (marine) sediments.
Interferences and Precautions	Not available.
Sample Handling and Preservation	Container - Acid Washed Polyethylene Bottle. Digested soils are already in an acid medium and require no extra preservation chemicals.

Stability	Metallic elements in acid digested soil samples have a holding time of six months.
Instrumentation/ Calibration and Analysis Procedures	Refer to Specific Instrument Operations Manuals, EPA Method 6010A.
Precision	Refer to EPA Method 6010A and Section 2.5.6 of the ICP-AES method in the B.C. Laboratory Manual for further explanations.
Accuracy	Refer to EPA Method 6010A and Section 2.5.7 of the ICP-AES method in the B.C. Laboratory Manual for further explanations.
Quality Control	For each analytical batch include a minimum of the following: a) Two method blanks b) 10% Duplication (minimum of one) c) One Standard Reference Material
References	a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 18th edition, 1992 Section 3120 B. b) Methods for Chemical Analysis of Water and Wastes, EPA-600 4-79-020, March 1983, Method 200.7. c) Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods (Revised). Publication # SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd Edition, 1990.

2.6 Trace Metals Analysis by ICP-MS – PBM

Parameter

Metals including major ions and trace metals

Analytical Method

Analysis by ICP-MS

Introduction

This method is applicable to metals in filtered or digested waters, and to total recoverable metals in solid samples, tissues, and other matrices which have gone through appropriate digestion procedures.

Method Summary

This method describes the multi-elemental determination of trace elements by ICP-MS. It is used to measure dissolved metals in water, total metals in water, total recoverable metals in solid samples such as soil, sediment, and vegetation from a Strong Acid Leachable (SALM) digestate, or other acceptable digestion procedures.

The method measures ions produced by a radio-frequency inductively coupled plasma. Analyte species originating in a liquid are nebulized and the resulting aerosol transported by argon gas into the plasma torch. The metal ions produced are entrained in the plasma gas and extracted, by means of a differentially pumped vacuum interface, into a mass spectrometer. The metal ions produced in the plasma are sorted according to their mass-to-charge ratios by a quadrupole or magnetic sector mass spectrometer having a minimum resolution capability of 1 AMU peak width at 5% peak height. The ions transmitted through the quadrupole are quantified by a detector and the ion information is processed by a data handling system.

This method is performance-based. Laboratories may adopt alternative options to improve performance or efficiency provided that all stated performance requirements and prescribed (mandatory) elements are met.

MDL(s) and EMS Analyte Code(s)

This method is applicable to the following parameters:

Parameter	CAS Number	EMS Code	Parameter	CAS Number	EMS Code
Aluminum	7429-90-5	AL-x	Molybdenum	7439-98-7	MO-x
Antimony	7440-36-0	SB-x	Nickel	7440-02-0	NI-x
Arsenic	7440-38-2	AS-x	Phosphorus	7723-14-0	P-x
Barium	7440-39-3	BA-x	Potassium	7440-09-7	K-x
Beryllium	7440-41-7	BE-x	Selenium	7782-49-2	SE-x
Bismuth	7440-69-9	BI-x	Silicon	7440-21-3	SI-x
Boron	7440-42-8	B-x	Silver	7440-22-4	AG-x
Cadmium	7440-43-9	CD-x	Sodium	7440-23-5	NA-x
Calcium	7440-70-2	CA-x	Strontium	7440-24-6	SR-x
Chromium	7440-47-3	CR-x	Sulfur	7704-34-9	S-x
Cobalt	7440-48-4	CO-x	Thallium	7440-28-0	TL-x
Copper	7440-50-8	CU-x	Thorium	7440-29-1	TH-x
Iron	7439-89-6	FE-x	Tin	7440-31-5	SN-x
Lead	7439-92-1	PB-x	Titanium	7440-32-6	TI-x
Lithium	7439-93-2	LI-x	Tungsten	7440-33-7	W-x
Magnesium	7439-95-4	MG-x	Uranium	7440-61.1	U-x
Manganese	7439-96-5	MN-x	Vanadium	7440-62-2	V-x
Mercury	7439-97-6	HG-x	Zinc	7440-66-6	ZN-x

“x” in EMS codes may be T or D dependent upon Total or Dissolved as reported parameter.

Other metals may be analyzed by this method if acceptable performance is demonstrated and validated.

EMS Method Code

Refer to EMS Parameter Dictionary on the Ministry of Environment and Climate Change Strategy website for all current EMS codes.

Matrix

Water, soils, sediments, sludges, solids, air filters, animal and plant tissues with appropriate digestion or leachate procedures applied.

Interferences and Precautions

Interferences associated with ICP-MS analysis may be classified as physical, isobaric (elemental or polyatomic), memory (carryover) or contamination in nature.

a) Physical interferences can be reduced by using internal standards which compensate for the matrix effect. High levels of dissolved solids in the sample will increase deposition of material on the extraction and/or skimmer cones, reducing the effective diameter of the orifices and therefore ion transmission. Dissolved solids of no more than 0.2% have been recommended.

b) Both the isobaric and molecular ion interferences must be fully investigated and understood prior to the introduction of this methodology. When they cannot be avoided by the selection of alternative analytical isotopes, appropriate corrections must be made to the data. Equations for the correction of data should be established at the time of the analytical run sequence, as the polyatomic ion interferences will be highly dependent on the sample matrix and chosen instrument conditions.

c) Memory effects can result from sample deposition on the extraction and skimmer cones, and from the buildup of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the element and can be minimized by flushing the system with a rinse blank between samples. The possibility of memory interferences should be recognized within an analytical run and suitable rinse times should be used to reduce them. The rinse times necessary for a particular element should be estimated prior to analysis.

Interferences may also result from contaminants in acids, reagents, glassware, and other sample processing hardware that lead to artifacts and/or elevated baseline. All materials used should be routinely monitored and demonstrated to be free of interferences under the conditions of the analysis.

Sample Handling and Preservation

Refer to the “Summary of Sample Preservation and Hold Time Requirements” table found in Section A of the British Columbia Environmental Laboratory Manual.

Stability

Refer to the “Summary of Sample Preservation and Hold Time Requirements” table found in Section A of the British Columbia Environmental Laboratory Manual.

Procedure

Reagents:

Reagents may contain elemental impurities that might affect the integrity of analytical data. Owing to the high sensitivity of ICP-MS, high-purity reagents should be used whenever possible.

Digestion:

Refer to British Columbia Environmental Laboratory Manual for appropriate sample preparation procedures.

Where the Laboratory Manual does not prescribe digestion procedures, other appropriate digestion methods may be used provided performance requirements are met.

Instrumental Analysis:

Detailed instrumental procedures are not provided in this method. The procedures described in the following reference are suitable for general guidance:

- EPA Method 200.8 “Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma - Mass Spectrometry”, Revision 5.4, U.S. Environmental Protection Agency, May 1994.
- EPA SW846 Method 6020A “Inductively Coupled Plasma - Mass Spectrometry”, Revision 1, U.S. Environmental Protection Agency, February 2007.

This method is applicable only to ICP-MS analysis. Refer to USEPA Method 200.8 or 6020A for guidelines on establishing quantitation and confirmation ions for trace metal analytes

The use of internal standards is required. Internal standards can vastly improve method accuracy and precision. Instrument drift as well as suppressions or enhancements of instrument response caused by the sample matrix must be corrected for by the use of internal standards. Refer to EPA Method 200.8 for recommended internal standard criteria.

Performance Requirements

Any analytical method options selected for this analysis must meet or exceed the method validation performance requirements specified below:

Accuracy and Precision requirements apply to measures of long-term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method re-validation studies. They do not constitute acceptance criteria or Data Quality Objectives for individual Quality Control samples.

For Initial Validations, averages of at least 8 spikes or certified reference materials (CRMs) must be assessed (preferably taken from multiple analytical batches).

Ongoing re-validations (performance reviews) should assess QC data encompassing longer timeframes (e.g., 6 months to 1 year). A minimum frequency of 2 years is recommended for Ongoing Re-validations.

Accuracy Requirement: Refer to British Columbia Environmental Laboratory Manual for appropriate sample preparation procedures.

Precision Requirement: Refer to British Columbia Environmental Laboratory Manual for appropriate sample preparation procedures.

Sensitivity Requirement: Where possible, the method should generate Method Detection Limits that are less than 1/5 of applicable numerical standards. The method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

Linear Dynamic Range: Linear range studies are to be performed during the initial validation of the method to determine the upper limit of linearity on the specific ICP-MS instrument. It must be determined from a linear calibration. The LDR should be determined by analysing at least 3 different standard concentrations for each analyte and the observed analyte concentration is within 90-110% of the stated concentration of the standard. Note that the LDR concentration may not be the upper limit of the element, but rather the upper concentration examined. If a sample concentration exceeds the LDR, it must be diluted and reanalysed. The frequency of the LDR determination is subject to the individual laboratory's Quality Management System.

Internal Standard Recovery Range: The absolute response of any internal standard must not deviate more than 50-130% from the original response in the calibration blank. Deviations outside this range must be investigated and reanalysed.

Interference Analysis: Laboratories must show evidence that elemental isobaric and polyatomic interference have been fully investigated and corrected for in the reporting of data by this technique.

Elemental Isobaric Interference: Atoms or elements having the same atomic weights are naturally occurring and therefore must be compensated for isobaric overlap. This should be automatically corrected in the instrument software or using post analysis corrections.

Polyatomic Isobaric Interference: Polyatomic ions are formed from samples containing high concentrations of particular elements (i.e., Oxides, Halides, etc.). These interferences may be automatically corrected in the instrument software, or using post analysis corrections, while others may be corrected by using an alternative isotope or removed by collision/reaction cell or high-resolution technologies. Daily optimisation of the nebulizer gas pressure reduces the formation of oxides.

Quality Control

Summaryof QC Requirements		
QC Component	Minimum Frequency	Minimum Data Quality Objectives
Instrument Blank (IB)	One per 20 samples	Less than reported DL
Calibration Verification Standard (CVS)	One per batch	90-110% recovery (after internal standard correction)
Continuing Calibration Verification (CCV)	1 per 20 samples and at the end of each run.	85-115% recovery (after internal standard correction) for mid-level standards.
If DQOs are not met, repeat testing for bracketed samples or report qualified test results.		

Instrument Blank: Required. Minimum one per batch of 20 samples or less, or as necessary to ensure contamination control.

Calibration Verification Standard (CVS): Required. A control standard from a source separate from the calibration standard must be analyzed to monitor calibration accuracy.

Continuing Calibration Verification (CCV): Required. Calibration standards (typically a mid-point standard) must be analyzed periodically throughout the instrument run to monitor calibration drift (at least 1 per 20 samples). A control standard may serve the same purpose.

Prescribed Elements

The following components of this method are mandatory:

a) This method is applicable only to analysis by ICP-MS.

b) Initial calibrations must be done daily.

c) Internal standards must be used. Internal standards must cover all analytes within a 70 amu range, except for analytes with masses ≥ 210 amu, where interal standard mass must be within 80 amu. Where practical, internal standards used should generally have masses within 50 amu of assigned analytes.

d) All Performance Requirements and Quality Control requirements must be met.

Apart from these limitations, and provided performance requirements are met, laboratories may introduce modifications to this method in order to improve quality or efficiency.

References

a) EPA Method 200.8 “Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma - Mass Spectrometry”, Revision 5.4, U.S. Environmental Protection Agency, May 1994.

b) EPA SW846 Method 6020B “Inductively Coupled Plasma - Mass Spectrometry”, Revision 2, U.S. Environmental Protection Agency, July 2014.

Revision History	Sept 15, 2017	Added tungsten (a new substance in the 2017 CSR). Added thorium as it is already in the Total Metals in Water digestion method and sulfur as it is already in the SALM method. Made minor updates to the QC table to reflect current naming convention (CVS added). Internal standard amu range changed to 70 amu, and 80 amu for high mass analytes (≥ 210 amu). Internal standard acceptance limits changed to 50-130% (composite value between EPA 200.8 and EPA 6020B limits).
	Oct 1, 2013	Trace Metals Analysis by ICP-MS – PBM method added to 2013 version of BC Lab Manual, effective October 1, 2013.
	May 24, 2011	First version of BC Lab Manual ICPMS method (PBM format).

3. SPECIFIC ELEMENTAL CONDITIONS

Note: FA = Field acidified LA = Lab acidified
FF = Field filtered LF = Lab filtered

Revision Date: December 31, 2000

Aluminum (Atomic Absorption - Direct Aspiration)

Parameter	Aluminum, total Aluminum, dissolved
Sample Preparation	See section 1.0, the sample preparation section.
Analytical Method	See section 2.1, the AA methods section.
EMS Code	FA: HNO_3: AA (total) Al-T X073 LA: HNO_3: AA (total) Al-T X351 FF, FA: HNO_3: AA (dissolved) Al-D X203 LF, LA: HNO_3: AA (dissolved) Al-D X085
Method Summary	Aqueous solutions of metals are aspirated into a flame and atomized. The absorption of light, at a wavelength specific to the element being analyzed, is measured and the concentration of the analyte is determined by comparison with standards.
MDL	Given an aqueous sample free of interferences, the instrumental performance characteristics are: MDL: 0.1 mg/L Range: 0.1-50.0 mg/L See Table C-1 in section 2.1, the AA methods section, for additional information.
Matrix	Water, wastewater, marine water.
Interferences and Precautions	See section 2.1.4 of the AA methods section of this manual. Ionization should be controlled by the addition of potassium chloride to a level of 0.1%. The Al signal can be enhanced by the presence of Fe, Ti, fluoroborate and acetic acid.
Sample Handling and Preservation	See section 1.0, the sample preparation section of this manual.
Stability	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
Instrument Parameters	Source: Al hollow cathode lamp Wavelength: 309.3 nm (primary); 396.2 nm (alternate) Type of Flame: nitrous oxide-acetylene Background Correction: recommended
Apparatus, Materials and Reagents	See sections 2.1.5 and 2.1.6 of this manual.
Precision	None listed.
Accuracy	None listed.
Quality Control	See section 2.1.9, QA/QC Guidelines in this manual.

References	a)	Standard Methods for the Examination of Water and Wastewater APHA, AWWA, WEF, 18th edition, 1992, Method 3111 B/D.
	b)	Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods (Revised). Publication #SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd Edition 1990.

Revision History	February 14, 1994:	Publication in 1994 Laboratory Manual.
	December 31, 2000:	SEAM codes replaced by EMS codes. Sample matrix added.

Antimony (Atomic Absorption - Direct Aspiration)

Parameter	Antimony, total Antimony, dissolved
Sample Preparation	See section 1.0, the sample preparation section.
Analytical Method	See section 2.1, the AA methods section.
EMS Code	FA: HNO_3: AA (total) Sb-T X073 LA: HNO_3: AA (total) Sb-T X351 FF, FA: HNO_3: AA (dissolved) Sb-D X203 LF, LA: HNO_3:AA (dissolved) Sb-D X085
Introduction	Antimony and its compounds have been reported to cause dermatitis, keratitis, conjunctivitis and nasal septal ulceration by contact, fumes, or dust.
Method Summary	Aqueous solutions of metals are aspirated into a flame and atomized. The absorption of light, at a wavelength specific to the element being analyzed, is measured and the concentration of the analyte is determined by comparison with standards.
MDL	Given an aqueous sample free of interferences, the instrumental performance characteristics are: MDL: 0.2 mg/L Range: 0.20-40.0 mg/L See Table C-1 in section 2.1, the AA methods section, for additional information.
Matrix	Water, wastewater, and marine water.
Interferences and Precautions	See section 2.1.4 of the AA methods section of this manual. A decrease in absorption occurs with increasing acid concentration. To avoid this effect, matrix-match the acid concentration of the samples and standards.
Sample Handling and Preservation	See section 1.0, the sample preparation section of this manual.
Stability	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
Instrument Parameters	Source: Sb EDL or hollow cathode lamp Wavelength: 217.6 nm (primary) Type of Flame: air/acetylene Background Correction: recommended
Apparatus, Materials and Reagents	See section 2.1.5 and 2.1.6 of this manual.
Precision	None listed.
Accuracy	None listed.
Quality Control	See section 2.1.9, QA/QC Guidelines in this manual.

References	a)	Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992, Method 3111 B/D.
	b)	Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods (Revised). Publication #SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd Edition 1990.
Revision History	February 14, 1994:	Publication in 1994 Laboratory Manual.
	December 31, 2000:	SEAM codes replaced by EMS codes. Sample matrix added.

Antimony (Atomic Absorption - Gaseous Hydride)

Parameter	Antimony, total Antimony, dissolved	
Sample Preparation	See section 1.0, the sample preparation section.	
Analytical Method	See section 2.1, the AA methods section, and section 2.2 the hydride AA method section.	
EMS Code	FA: HNO_3: HVAAS (total)	Sb-T X289
	LA: HNO_3: HVAAS (total)	Sb-T X354
	FA: HCl: HVAAS (total)	Sb-T X345
	LA: HCl: HVAAS (total)	Sb-T X355
	FF, FA: HNO_3: HVAAS (dissolved)	Sb-D X202
	LF, LA: HNO_3: HVAAS (dissolved)	Sb-D X359
	FF, FA: HCl: HVAAS (dissolved)	Sb-D X348
	LF, LA: HCl: HVAAS (dissolved)	Sb-D X360
Introduction	Antimony and its compounds have been reported to cause dermatitis, keratitis, conjunctivitis, and nasal septal ulceration by contact, fumes, or dust.	
Method Summary	Antimony is converted to a gaseous hydride and analyzed by atomization in a heated quartz tube. Conversion to hydrides allows antimony to be detected with greater sensitivity.	
MDL	Given an aqueous sample free of interferences, the instrumental performance characteristics are: MDL: 0.0001 mg/L Range: 0.0001-0.010 mg/L See Table C-1 in section 2.1, the AA methods section, for additional information.	
Matrix	Water, wastewater, marine water.	
Interferences and Precautions	See section 2.2.3 in the hydride AA section of this manual.	
Sample Handling and Preservation	See section 1.0, the sample preparation section of this manual.	
Stability	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.	
Instrument Parameters	Source: Sb EDL or hollow cathode lamp Wavelength: 217.6 nm Background Correction: not required	
Apparatus, Materials and Reagents	See section 2.2 and section 2.1.5 and 2.1.6 of this manual.	
Precision	None listed.	
Accuracy	None listed.	
Quality Control	See section 2.1.9, QA/QC Guidelines in this manual.	

References

a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 18th edition, 1992.

b) Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods (Revised). Publication #SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd Edition 1990.

Revision History	February 14, 1994:	Publication in 1994 Laboratory Manual.
	December 31, 2000:	SEAM codes replaced by EMS codes. Sample matrix added.

Antimony (Atomic Absorption - Graphite Furnace)

Parameter	Antimony, total Antimony, dissolved
Sample Preparation	See section 1.0, the sample preparation section.
Analytical Method	See section 2.1, the AA methods section.
EMS Code	FA: HNO_3: GFAA (total) Sb-T X072 LA: HNO_3: GFAA (total) Sb-T X179 FF, FA: HNO_3: GFAA (dissolved) Sb-D X116 LF, LA: HNO_3: GFAA (dissolved) Sb-D X357
Introduction	Antimony and its compounds have been reported to cause dermatitis, keratitis, conjunctivitis and nasal septal ulceration by contact, fumes, or dust.
Method Summary	A discrete sample volume is introduced into the graphite sample boat which is heated in stages to accommodate drying of the solution, charring and volatization of organics and other matrix components, and finally, atomization of the analyte into the light path of the spectrometer. The absorption of light, at a wavelength specific to the element being analyzed, is measured and the concentration of the analyte is determined by comparison with standards.
MDL	Given an aqueous sample free of interferences, the instrumental performance characteristics are: MDL: 0.003 mg/L Range: 0.003-0.30 mg/L See Table C-1 in section 2.1, the AA methods section, for additional information.
Matrix	Water, wastewater, marine water.
Interferences and Precautions	See section 2.1.4 of the AA Methods section of this manual. High lead concentration may cause a measurable spectral interference on the 217.6 nm line. If this interference is expected, the secondary wavelength should be employed or Zeeman background correction used.
Sample Handling and Preservation	See section 1.0, the sample preparation section of this manual.
Stability	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
Instrument Parameters	Source: Sb EDL or hollow cathode lamp Wavelength: 217.6 nm Background Correction: recommended
Apparatus, Materials and Reagents	See sections 2.1.5 and 2.1.6 of this manual.
Precision	None listed.
Accuracy	None listed.
Quality Control	See section 2.1.9, QA/QC Guidelines in this manual.

References	a)	Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992, Method 3111 B.
	b)	Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods (Revised). Publication #SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd Edition 1990.

Revision History	February 14, 1994:	Publication in 1994 Laboratory Manual.
	December 31, 2000:	SEAM codes replaced by EMS codes. Sample matrix added.

Antimony (Atomic Emission - Inductively Coupled Argon Plasma {ICAP})

Parameter	Antimony, total Antimony, dissolved
Sample Preparation	See section 1.0, the sample preparation section.
Analytical Method	See section 2.4, the ICP-AES method section.
EMS Code	FA: HNO_3: ICAP (total) Sb-T X349 LA: HNO_3: ICAP (total) Sb-T X352 FF, FA: HNO_3: ICAP (dissolved) Sb-D X350 LF, LA: HNO_3: ICAP (dissolved) Sb-D X356
Introduction	Antimony and its compounds have been reported to cause dermatitis, keratitis, conjunctivitis, and nasal septal ulceration by contact, fumes, or dust.
Method Summary	Aqueous solutions of metals are converted to aerosols in the nebulizer of the ICP and injected directly into a high temperature plasma (6000 to 8000°K). The highly efficient ionization produces ionic emission spectra and wavelengths specific to the elements of interest can be monitored either simultaneously or sequentially.
MDL	Given an aqueous sample free of interferences, the instrumental performance characteristics are: MDL: 0.05 mg/L Range: 0.05-1000 mg/L See Table C-2 in section 2.4, the ICP method section, for additional information.
Matrix	Water, wastewater, marine water.
Interferences and Precautions	See section 2.4.4, the ICP-AES section of this manual.
Sample Handling and Preservation	See section 1.0, the sample preparation section of this manual.
Stability	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
Instrument Parameters	Wavelength: 206.8 nm Background Correction: recommended
Apparatus, Materials and Reagents	See section 2.4, the ICP-AES methods section in this manual.
Precision	None listed.
Accuracy	None listed.
Quality Control	See section 2.1.9, QA/QC Guidelines in this manual.

References	a)	Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992, Method 3120B.
	b)	Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods (Revised). Publication #SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd Edition 1990.
Revision History	February 14, 1994:	Publication in 1994 Laboratory Manual.
	December 31, 2000:	SEAM codes replaced by EMS codes. Sample matrix added.

Arsenic (Atomic Absorption - Direct Aspiration)

Parameter	Arsenic, total Arsenic, dissolved
Sample Preparation	See section 1.0, the sample preparation section.
Analytical Method	See section 2.1, the AA methods section.
EMS Code	FA: HNO_3: AA (total) As-T X073 LA: HNO_3: AA (total) As-T X351 FF, FA: HNO_3: AA (dissolved) As-D X203 LF, LA: HNO_3: AA (dissolved) As-D X085
Introduction	The determination of trace amounts of arsenic in water and wastewater is crucial because it is a highly toxic material. The main sources of arsenic contamination in water and wastewater are coal, petroleum, detergents, and pesticides.
Method Summary	Aqueous solutions of metals are aspirated into a flame and atomized. The absorption of light, at a wavelength specific to the element being analyzed, is measured and the concentration of the analyte is determined by comparison with standards.
MDL	Given an aqueous sample free of interferences, the instrumental performance characteristics are: MDL: 0.20 mg/L Range: 0.2-100mg/L See Table C-1 in section 2.1, the AA methods section, for additional information.
Matrix	Water, wastewater, marine water.
Interferences and Precautions	See section 2.1.4 of the AA Methods section of this manual. Background interferences occur with the use of both the air-acetylene and the nitrous oxide-acetylene flames, but particularly with the air-acetylene flame, where at least 60% of the light energy is absorbed. The nitrous oxide-acetylene flame may be preferred due to its reduced background interferences, although sensitivity is also decreased. Background correction should be used with both flames and will improve the signal to noise ratio. A sample with high total salt content (greater than 1%) will produce apparent absorption at the 193.7 nm arsenic line, even when the metal is absent. It is therefore necessary to check readings for background absorption. A suitable line for this purpose is the non-absorbing mercury line at 194.2 nm.
Sample Handling and Preservation	See section 1.0, the sample preparation section of this manual.
Stability	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
Instrument Parameters	Source: As EDL or hollow cathode lamp Wavelength: 193.7 nm Type of flame: air/acetylene Background correction: recommended
Apparatus, Materials and Reagents	See section 2.1.5 and 2.1.6 of this manual.
Precision	None listed.

Accuracy	None listed.
Quality Control	See section 2.1.9, QA/QC Guidelines in this manual.
References	a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992, Method 3111 B/D. b) Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods (Revised). Publication #SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd Edition 1990.
Revision History	February 14, 1994: Publication in 1994 Laboratory Manual. December 31, 2000: SEAM codes replaced by EMS codes.

Arsenic (Atomic Absorption - Gaseous Hydride)

Parameter	Arsenic, total Arsenic, dissolved	
Sample Preparation	See section 1.0, the sample preparation section.	
Analytical Method	See section 2.1, the AA methods section, and section 2.2, the hydride AA method section.	
EMS Code	FA: HNO_3: HVAAS (total)	As-T X289
	LA: HNO_3: HVAAS (total)	As-T X354
	FA: HCl: HVAAS (total)	As-T X345
	LA: HCl: HVAAS (total)	As-T X355
	FF, FA: HNO_3: HVAAS (dissolved)	As-D X202
	LF, LA: HNO_3: HVAAS (dissolved)	As-D X359
	FF, FA: HCl: HVAAS (dissolved)	As-D X348
	LF, LA: HCl: HVAAS (dissolved)	As-D X360
Introduction	The determination of trace amounts of arsenic in water and wastewater is crucial because it is a highly toxic material. The main sources of arsenic contamination in water and wastewater are coal, petroleum, detergents, and pesticides.	
Method Summary	Arsenic is converted to a gaseous hydride and analyzed by atomization in a heated quartz tube. Conversion to hydrides allows Arsenic to be detected with greater sensitivity.	
MDL	Given an aqueous sample free of interferences, the instrumental performance characteristics are: MDL: 0.0002 mg/L Range: 0.0002-0.020 mg/L See Table C-1 in section 2.1, the AA method section, for additional information.	
Matrix	Water, wastewater, marine water.	
Interferences and Precautions	See section 2.2.3 of the hydride AA methods section of this manual. High concentrations of chromium, cobalt, copper, mercury, molybdenum, nickel, and silver can cause analytical interferences. Traces of nitric acid left following the sample work-up can result in analytical interferences. Elemental arsenic and many of its compounds are volatile; therefore, certain samples may be subject to losses of arsenic during sample preparation.	
Stability	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.	
Instrument Parameters	Source: As EDL or hollow cathode lamp Wavelength: 193.7 nm Background Correction: not required	
Apparatus, Materials and Reagents	See section 2.2.3 and section 2.1.5 and 2.1.6 of this manual.	
Precision	None listed.	
Accuracy	None listed.	
Quality Control	See section 2.1.9, QA/QC Guidelines in this manual.	

References

a) B.C. Ministry of Environment, Laboratory Manual p. 97, 1989.

b) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 18th edition, 1992.

c) Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods (Revised). Publication #SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd Edition 1990.

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes. Sample matrix added.

Arsenic (Atomic Emission - Inductively Coupled Argon Plasma {ICAP})

Parameter	Arsenic, total Arsenic, dissolved
Sample Preparation	See section 1.0, the sample preparation section.
Analytical Method	See section 2.4, the ICP-AES method section.
EMS Code	FA: HNO_3: ICAP (total) As-T X349 LA: HNO_3: ICAP (total) As-T X352 FF, FA: HNO_3: ICAP (dissolved) As-D X350 LF, LA: HNO_3: ICAP (dissolved) As-D X356
Introduction	The determination of trace amounts of arsenic in water and wastewater is crucial because it is a highly toxic material. The main sources of arsenic contamination in water and wastewater are coal, petroleum, detergents, and pesticides.
Method Summary	Aqueous solutions of metals are converted to aerosols in the nebulizer of the ICP and injected directly into a high temperature plasma (6000 to 8000°K). This highly efficient ionization produces ionic emission spectra and wavelengths specific to the elements of interest can be monitored either simultaneously or sequentially.
MDL	Given an aqueous sample free of interferences, the instrumental performance characteristics are: MDL: 0.050 mg/L Range: 0.05-1000 mg/L See Table C-2 in section 2.4, the ICP method section, for additional information.
Matrix	Water, wastewater, marine water.
Interferences and Precautions	See section 2.4.4 of the ICP-AES section of this manual.
Sample Handling and Preservation	See section 1.0, the sample preparation section of this manual.
Stability	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
Instrument Parameters	Wavelength: 193.8 nm (primary) Background Correction: recommended
Apparatus, Materials and Reagents	See section 2.4 of this manual.
Precision	None listed.
Accuracy	None listed.
Quality Control	See section 2.1.9, QA/QC Guidelines in this manual.

References	a)	Standard Method for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992, Method 3120 B.
	b)	Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods (Revised). Publication #SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd Edition 1990.

Revision History	February 14, 1994:	Publication in 1994 Laboratory Manual.
	December 31, 2000:	SEAM codes replaced by EMS codes. Sample matrix added.

Arsenic Analysis of Solids by HVGAA

Parameter As-T - Arsenic Total

Sample Preparation Nitric-perchloric acid digestion

Analytical Method N/P Digestion: Hydride Generation

Atomic Absorption Spectrophotometry

EMS Codes As-T 1194 Hydride Atom. Absorption Spec

Method Summary The sample undergoes a nitric-perchloric acid hydrochloric acid digestion to break down all organically bound arsenic. The digestate is diluted 1:1 with 50% HCl. This solution is mixed with sodium borohydride which releases the volatile hydride of arsenic. The hydride is separated from the aqueous solution and introduced to a flame heated quartz absorption cell. Atomic absorption is measured at 193.77 nm.

MDL 0.2 μg/g

Matrix Soil, solids, (marine) sediments.

Stability Digested samples are stable for 6 months.

Procedure

Apparatus

a) Digest block
b) Glassware

Instrumentation A system consisting of:

a) Peristaltic pump
b) Hydride generator, (mixing coils and phase separator)
c) Quartz absorption cell
d) Atomic absorption spectrophotometer

Reagents Digest:

a) Hydrochloric Acid (HCl) conc., analytical grade.
b) Potassium persulfate solution, 4%: Dissolve 40 g of potassium persulfate, analytical grade $K_2S_2O_8$, in DI and dilute to 1 litre.

Analysis:

a) Sodium Borohydride solution, 1.5%: Dissolve 15 g of $NaBH_4$, analytical grade, and 1 g NaOH, analytical grade in 1 litre of deionized water. Filter through Whatman #41 filter paper.

Standards

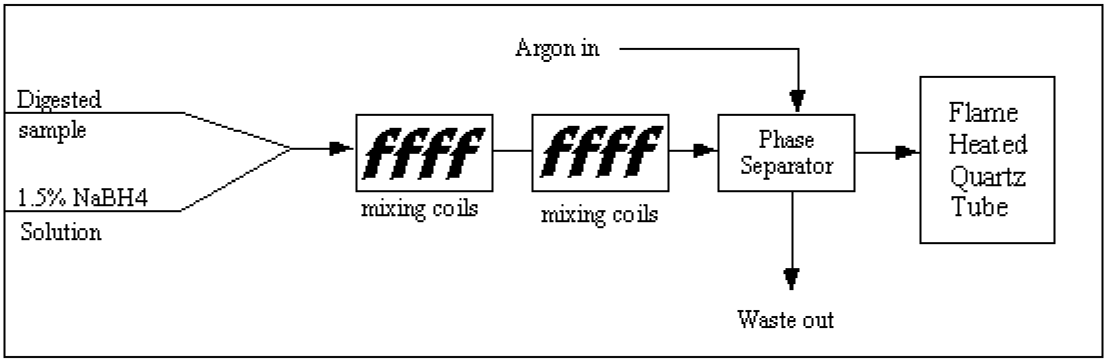
a) Stock Arsenic Calibration standards, 1000 mg/L; available commercially, or: 1000 mg/L As can be prepared by dissolving 1.320 g Arsenic Trioxide, As_2O_3, analytical grade, in 10 mL deionized water containing 4g NaOH, dilute to 500 mL with DI, adjust pH to slightly acidic with HCl and dilute to 1 litre with DI.

b) Prepare 10 mg/L stock As. Dilute 5 mL of 1000 mg/L As to 500 mL with DI. Prepare 1 mg/L stock As, dilute 10 mL of 10 mg/L stock solution to 100 mL with DI.

c) Prepare 1 litre of working standards: 0.005, 0.010, 0.025, 0.040 and 0.050 mg/L As by diluting 0.5, 1.0, 2.5, 4.0 and 5 mLs and 10 mLs of 1 mg/L stock and 10 mLs of 10 mg/L stock to 1 litre with DI.

Procedure	See "Digestion of Soils for metals Analysis".
Instrumental Analysis	a) Set up the Atomic Absorption Spectrophotometer according to the operating instructions. b) Install Arsenic electrodeless discharge lamp (EDL) and allow to warm up for at least 30 minutes.
Calculations	Absorbances are read from the instrument and electronically captured into a Data Collection software package where concentration is calculated based on Beers Law.
Hydride Generation System	a) Sample tubing: black/purple; flowrate: 6.8 mL/min. b) NaBH4 tubing: black/black; flowrate: 0.8 mL/min. c) Pump speed: maximum 11 RPM. d) Argon flowrate: 0.5 LPM.

Diagram of Hydride Generation System:



Precision	Synthetic samples at concentrations of 3 and 10 mg/L As gave coefficients of variation of 2% and 2% respectively.
Accuracy	To be determined.
Quality Control	a) Arsenic Quality Control Stock Solutions, 1000 mg/L. This solution is to be obtained from an alternate supplier than the calibration stock. b) QCA for As: Solution containing 0.035 mg/L. c) QCB for As: Solution containing 0.005 mg/L. d) QC sample QH: 0.020 mg/L As.
References	a) Standard Methods for the Examination of Water and Wastewater, 17th Edition, 1989. Section 3114; p. 3-43 to 3-53.
Revision History:	March 1997: Published in Supplement Manual #1. November 2002: EMS code assigned.

Arsenic, Cadmium and Lead in Solids by GFAA

Parameter

Arsenic, Cadmium and Lead

Sample Preparation

See Section 1.0 for sample preparation.

Analytical Method

Analysis of acid digested geological samples for metals by atomic absorption spectrophotometry with a graphite furnace attachment.

EMS Code

EMS codes to be defined on request.

Method Summary

Analyte is electro-thermally heated to dry, char and then atomize within the confines of a graphitic carbon tube. Absorbance is measured at the atomization stage. Because the atom cloud generated at the atomization stage is confined, relatively small quantities of analyte are required to produce a significant signal level thus permitting the detection of picogram levels of metals in various samples. Background correction is performed to negate the effect of changing matrices.

Compounds Determined and Detection Limits

Element	Detection Limit (µg/g)
Arsenic	0.5
Cadmium	0.05
Lead	0.5

Detection limits have been calculated by multiplying the determined solution detection limits by a common weight to volume factor.

Matrix

Soil, solids, (marine) sediments.

Stability and Sample Storage

Soil digestates are stored in acid washed polypropylene bottles. Metals are considered to be stable in solution for six months at room temperature.

Reagents

a) Ultrapure water
b) "Trace Metal" grade nitric acid
c) "Trace Metal" grade hydrochloric acid
d) "Trace Metals grade hydrogen peroxide
e) "Ultrapure" nitric acid. Seastar or equivalent
f) Palladium (Granular) Aldrich 20,399-8 or equivalent
g) Nickel Solution, 1000 mg/L, Certified Atomic Absorption Standard Solution, obtained from Fisher Scientific or other suitable supplier.

Note: Palladium and Nickel are used as matrix modifiers in specific analyses. Please refer to specific instrumental analysis techniques for instructions on uses of matrix modifiers.

Preparation of Graphite Furnace AA Calibration Standard Solutions

Note: Please see specific instrument operation manual for procedures. in preparing calibration standard solutions.

Apparatus

Atomic Absorption Spectrophotometer equipped with a graphite furnace atomizer attachment. Please refer to specific instrument manufacturers' for other peripheral devices required for correct instrument set-up.

Examples are

PC's, printers
EDL or Super Lamp Power Supplies
Auto-samplers
Hollow Cathode Lamps
Hollow Cathode Super Lamps
Electrodless Discharge Lamps (EDL)
Other required items include but are not limited to the following:
Graphite tubes
Graphite electrodes

Micropipette with disposal tips1000 mL, 250 mL, 100 mL Volumetric Flasks for dilutions (note1)
50 mL, 25 mL, 10 mL, 5 mL, 1 mL, 0.5 mL pipettes for dilutions (note 1)
50 mL graduated cylinder
Disposal sample cups for systems with autosamplers.

Note 1: All glassware should be Class A and acid washed prior to use.

Analysis Procedure

Refer to specific instrument operations manuals for set-up and analysis procedures.

Quality Control Section

Analysis of Soils

a) Digestion Blanks

b) Duplicates: If sample size permits, at a minimum frequency of 10%

c) Certified Reference Materials: If available, an SRM is run which matches the sample matrix type. Available Environmental Sediments Certified Reference Materials include:

- National Institute of Standards & Technology (NIST) 1646a Estuarine Sediment
- National Research Council of Canada Estuarine Sediments: MESS-1, BCSS-1, PACS-1.

Daily Instrument Checks

Several graphite furnaces have built in QC checks. These include but are not limited to:

a) Monitoring of calibration curve - at regular intervals the calibration is checked automatically. If the standard changes by over 20% from the previous calibration the run is stopped.

b) When two or more replicates are run for each sample, the sample will be repeated if the % RSD is over 20%. If the % RSD is still over 20% the sample will be flagged.

c) Internal Spiking - The instrument will make its own spike by adding a preset quantity of standard solution to a sample. If the spike recovery is not within the range of 80 to 120 % recovery, the spike is flagged.

Safety Notes

a) These instruments use high voltage in their operation. Unplug instrument or take other appropriate precautions when servicing.

b) Many of the reagents used in analysis techniques are hazardous. Use in accordance with guidelines set out in the MSDS for each compound.

c) Heat, vapors and fumes generated by furnace methods can be hazardous, toxic, or otherwise injurious to personnel.

ALWAYS switch the exhaust fan on BEFORE operating the graphite tube atomizer.

d) Hazardous ultraviolet radiation can be emitted by the atomizer, hollow cathode super lamps and electrodeless discharge lamps. This radiation can cause serious damage to the eyes.

ALWAYS wear safety glasses manufactured to an approved standard and which are certified or otherwise warranted to protect the eyes from ultraviolet radiation.

e) When the graphite tube automizer is operating, the magnet, atomizer chimney and immediate surrounds can present heat hazards which can result in burns to personnel.

Never touch the magnet, atomizer chimney or the atomizer assembly while the graphite tube atomizer is operating. Wear protective gloves when working near the magnet.

f) The magnet produces a variable field of 8000 gauss RMS at mains frequency in the workhead during the read stage.

To avoid interference with heart pacemakers or magnetic storage media, keep them at least 300 mm from the magnet.

g) The graphite tube atomizer gas supply system is designed for use with inert gases and air. The system is not designed for use with pure hydrogen.

NEVER use pure hydrogen with the graphite tube atomizer since this could result in leakage and potentially explosive accumulation of hydrogen.

You may, however, use a proprietary, prepackaged mixture of 95% argon and 5% hydrogen.

NEVER attempt to create your own mixture of hydrogen and inert gas through the GTA system.

Method References

a) Analytical Methods for Atomic Absorption Spectroscopy - Perkin Elmer (1976).

b) Analytical Methods Using the HGA Graphite Furnace - Perkin Elmer (1975).

c) Analytical Methods for Zeeman Graphite Tube Atomizer - Varian (1986).

d) Advanced Furnace Training Manual.

e) Atomic Absorption Newsletter (Various Issues).

f) Varian Instruments at Work (Various Issues).

Revision History:

March 1997:	Published in Manual Supplement #1.
November 2002:	Method adopted from Supplement #1.

Soluble Barium by Calcium Chloride Extraction - Prescriptive

Parameter	Soluble Barium ($CaCl_2$)
Analytical Method	1M Calcium Chloride extraction

Introduction

This method is intended to provide quantification of soluble barium species, without extracting insoluble and/or sequestered barium (e.g., barite). It is intended to support CSR regulations for barium for sites where detailed documentary evidence of barite usage exists.

The method uses excess calcium ions to increase barium solubility in solution, and to encourage displacement of barium from cation exchange sites.

Method Summary

This method is prescriptive. It must be followed exactly as described. Where minor deviations are permitted, this is indicated in the text.

Samples are dried at low temperature and sieved using a 2 mm (10 mesh) sieve. Solid samples are extracted for 2 hours with 1.0 M $CaCl_2$ at a 10:1 ratio of extraction solvent to solid. The extract is filtered and analyzed for barium using an appropriately sensitive and precise analytical method for barium (e.g., ICP-AES or ICP-MS).

MDL and EMS Codes

Analyte	Approx. MDL	EMS Code
Soluble Barium ($CaCl_2$)	2 mg/kg	Not available

Matrix

Soil, sediment, drilling waste solids, waste.

Interferences and Precautions

Samples with high petroleum or non-petroleum hydrocarbon content (Oil and Grease) may require specialized sample pre-treatment using solvent extraction.

Extracts from this method are very high in salt content, and normally require dilution prior to analysis by most techniques.

Sample Handling and Preservation

Collect samples in a clean polyethylene or glass container. No preservation is required.

Stability

Holding and Storage Time: Soils may be stored at room temperature or refrigerated at ≤6°C for up to 6 months.

Extracts must be stored at room temperature and must be analyzed within 7 days of extraction.

Procedure

Samples are prepared using the following procedures. All procedures are mandatory elements, unless otherwise indicated.

1. Reagents

    1.1. 1.0 M $CaCl_2$. Volumetrically prepare the extraction solution by dissolving 147.0 g $CaCl_2 \cdot 2\ H_20$ per 1L of laboratory grade water. Test new lots or supplies or calcium chloride for barium background before use.

    1.2. Laboratory Grade Water: Water free of substances that interfere with the analytical method.

2. Sample Preparation
    - 2.1. Inspect the sample and record any unusual or significant characteristics (i.e., foreign material, metals etc.).
    - 2.2. Remove any obvious foreign material such as vegetation.
    - 2.3. Homogenize the entire sample and subsample a sufficient quantity for drying and analysis. Use appropriate subsampling techniques and quantities to ensure that the sample has been sufficiently represented.
    - 2.4. Dry sub-samples to constant weight at a temperature of <60°C. If no other metals or temperature-sensitive analytes are to be determined using the same sub-sample, a drying temperature of up to 105°C may be used.
    - 2.5. Disaggregate the dried sample by manual or gentle mechanical action.
    - 2.6. Sieve each sample through a 2 mm (10 mesh) sieve. Discard the "greater than 2 mm" fraction.
3. Sample Extraction Procedure
    - 3.1. Accurately weigh 5.0 ± 0.5 g of dry sample into a vessel appropriate for mechanical mixing (e.g., 250 mL glass Erlenmeyer). Include method blanks, duplicates and at least one reference material per batch of samples. Record sample weights to ± 0.01 g.
    - 3.2. Add 50 ± 0.5 mL of 1.0 M $CaCl_2$ extraction solution.
    - 3.3. Extract the mixture for 2 hours ± 15 minutes using a mechanical agitation method such as a shaker table or rotary mixer.
    - 3.4. Filter the extract under gravity or suction, using a filter paper fine enough to yield a clear filtrate. Alternatively, extracts can be centrifuged to remove suspended particles.
    - 3.5. Accurately dilute the entire sample with laboratory grade water to the volume required for the analysis. The dilution volume will depend on the analysis technique, the detection limit, and the sample concentration.
4. Sample Analysisfor Barium
    - 4.1. Analyze the appropriately diluted extract of samples and QC samples using an appropriate technique for barium, such as ICP-AES or ICP-MS. Report results for soluble barium on a dry weight basis.
    - 4.2. Report any anomalies during extraction and analysis.

Performance Requirements

All laboratories performing this analytical method must conduct validation to confirm that the requirements below are met.

Accuracy and Precision requirements apply to measures of long-term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method re-validation studies. They do not constitute acceptance criteria or Data Quality Objectives for individual Quality Control samples. For Initial Validations, averages of at least 8 spikes or CRMs must be assessed (preferably taken from multiple analytical batches). Ongoing Re-validations (performance reviews) should assess QC data encompassing longer timeframes (e.g., 6 months to 1 year). A minimum frequency of 2 years is recommended for Ongoing Re-validations.

Accuracy Requirement: Laboratories must demonstrate method accuracy (measured as average recovery) of 80% or better for a minimum of 8 clean matrix spikes of barium chloride in clean sand, at concentrations above ten times the MDL.

Precision Requirement: Laboratories must demonstrate method precision equal to or better than 15% relative standard deviation for a minimum of 8 clean matrix spikes of barium chloride in clean sand, at concentrations above ten times the MDL.

Sensitivity Requirement: Where possible, the method should generate Method Detection Limits that are less than 1/5 of applicable numerical standards. The method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

Quality Control

Summary of QC Requirements		
QC Component	Minimum Frequency	Minimum Data Quality Objectives*
Method Blank	One per batch	Less than reported DL
Method Spike or Ref. Material	One per batch	70 – 130% recovery
Lab Duplicates	Approximately 5-10%	40% RPD

* Minimum DQOs apply to individual QC samples, not averages, and only at levels above 10x MDL. If any DQOs are exceeded at a frequency of more than ~5%, the laboratory's method should be reviewed in an attempt to improve its performance. Laboratories should report qualified data when DQOs are not met, unless other evidence demonstrates that the quality of associated sample data has not been adversely affected.

Method Blank: Required. Minimum one per batch or as necessary to ensure contamination control.

Lab Duplicates: Required. Replicate all components of the test from start to finish. Random duplicate selection at an approximate frequency of 5-10% is recommended.

Reference Material or Method Spike: Required. Use of a Clean Matrix Spike of Barium Chloride in sand is strongly recommended. In-house prepared RMs are permitted.

Revision History

June 10, 2007:	Prepared for BCMOE by the BCLQAAC Barite Task Group (Mark Hugdahl, Darlene Lintott, John Ashworth and Miles Tindal).
Aug 16, 2007:	BCLQAAC final approved version 1.0, submitted for Director's approval. Approved Sept 20, 2007; Effective Date: Oct 15, 2007.

Barium (Atomic Absorption - Direct Aspiration)

Parameter	Barium, total Barium, dissolved
Sample Preparation	See section 1.0, the sample preparation section.
Analytical Method	See section 2.1, the AA methods section.
EMS Code	FA: HNO_3: AA (total) Ba-T X073 LA: HNO_3: AA (total) Ba-T X351 FF, FA: HNO_3: AA (dissolved) Ba-D X203 LF, LA: HNO_3: AA (dissolved) Ba-D X085
Introduction	Barium is found mainly as barite, $BaSO_4$, and witherite, $BaCO_3$, both of which are highly insoluble salts. Barium therefore, usually occurs only in trace amounts in water. Appreciable levels in water supplies are indicative of undesirable industrial waste pollution. Ingestion of high doses of barium can be fatal. Canadian Drinking Water Guidelines stipulates 1mg/L as the IMAC (interim maximum acceptable concentration).
Method Summary	Aqueous solutions of metals are aspirated into a flame and atomized. The absorption of light, at a wavelength specific to the element being analyzed, is measured and the concentration of the analyte is determined by comparison with standards.
MDL	Given an aqueous sample free of interferences, the instrumental performance characteristics are: MDL: 0.1 mg/L Range: 0.1-20.0 mg/L See Table C-1 in section 2.1, the AA methods section, for additional information.
Matrix	Water, wastewater, marine water.
Interferences and Precautions	See section 2.1.4 of the AA methods section of this manual. Control ionization by addition of 0.1% or more potassium chloride to standards and samples. Use nitrous oxide-acetylene to eliminate or reduce interferences and increase sensitivity. Potential background absorption from calcium is possible when sing the 553.6 nm line.
Sample Handling and Preservation	See section 1.0, the sample preparation section.
Stability	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
Instrument Parameters	Source: Ba hollow cathode lamp Wavelength: 553.6 nm Type of Flame: nitrous oxide/acetylene Background Correction: recommended
Apparatus, Materials and Reagents	See section 2.1.5 and 2.1.6 of this manual.
Precision	None listed.
Accuracy	None listed.
Quality Control	See section 2.1.9, QA/QC Guidelines in this manual.

References	a)	Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 18th edition, 1992.
	b)	Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods (Revised). Publication #SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd Edition 1990.

Revision History	February 14, 1994:	Publication in 1994 Laboratory Manual.
	December 31, 2000:	SEAM codes replaced by EMS codes. Sample matrix added.

Barium (Atomic Absorption - Graphite Furnace)

Parameter	Barium, total Barium, dissolved
Sample Preparation	See section 1.0, the sample preparation section.
Analytical Method	See section 2.1, the AA methods section.
EMS Code	X072 FA: HNO_3: GFAA (total) Ba-T X072 X179 LA: HNO_3: GFAA (total) Ba-T X179 X116 FF, FA: HNO_3: GFAA (dissolved) Ba-D X116 X357 LF, LA: HNO_3: GFAA (dissolved) Ba-D X357
Introduction	Barium is found mainly as barite, $BaSO_4$, and witherite, $BaCO_3$, both of which are highly insoluble salts. Barium, therefore, usually occurs only in trace amounts in water. Appreciable levels in water supplies are indicative of undesirable industrial waste pollution. Ingestion of high doses of barium can be fatal. Canadian Drinking Water Guidelines stipulates 1 mg/L as the IMAC (interim maximum acceptable concentration).
Method Summary	A discrete sample volume is introduced into the graphite sample boat which is heated in stages to accommodate drying of the solution, charring and volatilization of organics and other matrix components, and finally, atomization of the analyte into the light path of the spectrometer. The concentration of the analyte is determined by comparison with standards.
MDL	Given an aqueous sample free of interferences, the instrumental performance characteristics are: MDL: 0.002 mg/L Range: 0.002-0.200 mg/L See Table C-1 in section 2.1, the AA methods section, for additional information.
Matrix	Water, wastewater, marine water.
Interferences and Precautions	Interferences in electrothermal analysis will be more pronounced than those in flame atomic absorption, and are due mainly to molecular absorption, chemical and matrix effects. Control of interferences can be achieved by the use of deuterium, tungsten halide or Zeeman effect background correction. In some cases matrix modifiers are used to minimize or eliminate interferences. Off the wall atomization is recommended for Barium analysis. Memory effect problems are frequently encountered with this analysis. See also section 2.1.4 of the AA methods section of this manual.
Sample Handling and Preservation	See section 1.0, the sample preparation section.
Stability	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
Instrument Parameters	Source: Ba hollow cathode lamp Wavelength: 553.6 nm Background Correction: recommended
Apparatus, Materials and Reagents	See section 2.1.5 and 2.1.6 of this manual.

Precision	None listed.
Accuracy	None listed.
Quality Control	See section 2.1.9, QA/QC Guidelines in this manual.
References	a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 18th edition, 1992. b) Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods (Revised). Publication #SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd Edition 1990.
Revision History	February 14, 1994: Publication in 1994 Laboratory Manual. December 31, 2000: SEAM codes replaced by EMS codes. Sample matrix added.

Boron, Hot Water Soluble (Prescriptive)

Parameter

Boron, Hot Water Soluble

Analytical Method

Hot aqueous 0.01 M $CaCl_2$ extraction followed by ICPOES, colourimetric determination, or other appropriate instrumental analysis.

Introduction

Boron is a plant micronutrient essential for healthy growth and crop yield. Small amounts are required for normal growth, while higher concentrations of available Boron can cause toxic effects and yield reductions to plants and crops. Irrigation water ranging from 0.3 to 2.0 mg/L Boron can cause toxic effects or yield reductions to crops. However, Boron availability to plants is only related to the activity of Boron in the soil solutions. Boron adsorbs to soils and especially to clay minerals, with maximum adsorption occurring at alkaline pH. Leaching of Boron from soils is greatest at low pH. The Hot Water Soluble Boron procedure is the most commonly used method for predicting the concentration of Boron that will be available to plants in a soil solution.

Method Summary

Hot Water Soluble Boron is an operationally defined technique used to estimate the concentration of Boron available for plant uptake. Soil samples are extracted by boiling a 2:1 mixture of aqueous 0.01 M $CaCl_2$ to soil for 5-15 minutes, prior to filtration of the extract and Boron determination using ICPOES, colourimetry, or another suitable instrumental technique. The presence of $CaCl_2$ in the extracting solution does not alter the amount of Boron (compared with hot water alone), and after filtration, results in extracts that are clear, colourless, and free of colloidal matter (References: SSSA, Carter).

This method is prescriptive and may not be modified.

Parameters and Parameter Codes

Parameter	Approx. MDL
Hot Water Soluble Boron	0.1 mg/kg

MDL is dependent on method of determination. An MDL of 0.1 mg/kg is achievable by ICPOES.

Matrix

Although designed for soils the method may also be applicable to solids and sludges.

Interferences and Precautions

If a colourimetric determination is used charcoal may be added to the sample prior to boiling to produce a colourless extract. Boron may be present in deionized water from glass distillation equipment or may be introduced from borosilicate glassware.

Sample Handling and Preservation

Samples should be collected in glass or plastic containers.

Samples should be dried and screened to 2 mm (10 mesh) prior to extraction.

Stability

Holding Time: 6 months from sampling (field moist), indefinite when dried.

Storage: No storage temperature requirement.

Equipment and Supplies

1. Heating source (e.g., block digester, hotplate, water bath)
2. Balance, minimum 3 place
3. Drying oven (not required)
4. Sieve, 2 mm (ASTM-E11 Sieve No. 10, US Sieve No. 10, Tyler 9 Mesh)
5. Digestion Vessels (e.g., block digester tube, beaker, flask, etc.)
6. Cover to fit digestion vessel (e.g., watch glass etc.)
7. Gloves
8. Spatula
9. Apparatus for filtering

Reagents

1. Water, de-ionized (ASTM Type I or equivalent recommended)
2. Calcium chloride
3. Activated charcoal

Safety

Wear appropriate PPE (Personal Protective Equipment) including lab coat, gloves, and safety glasses. Add acid to samples and perform digestions under a fume hood.

Procedure

<u>Sample Homogenization and Sub-Sampling</u>

1. Inspect the sample and record any unusual or significant characteristics.
2. Remove any obviously foreign material such as vegetation.
3. If the sample has separated into visually discrete layers (e.g., aqueous, organic, and sediment phases), the entire sample must be homogenized prior to sub-sampling.
4. The aqueous phase must not be decanted.
5. Homogenize the entire sample by vigorous stirring using a spatula. If it is not possible to homogenize the sample in the container it was received in, the sample may be transferred to a larger container prior to homogenization.

<u>Sample Preparation – Drying and Sieving</u>

1. Dry the sample to a constant weight at a temperature of ≤ 60°C. Air drying to constant weight is acceptable. Freeze drying is acceptable.
2. Sieve each sample through a 2 mm sieve. DO NOT pulverize samples to pass through either sieve type. Easily friable materials (dried clay clods, disintegrating rock, etc.) should be disaggregated prior to screening. Where necessary, non-pulverizing disaggregating tools like rolling mills, mortar and pestle, or flail grinders may be used.

<u>Sample Preparation - Extraction</u>

1. Extraction procedure is described in “Soil Sampling and Methods of Analysis” Carter, 2008 Procedure 9.2.2.
2. Weigh a minimum of 5 grams of dried sub 2 mm sample into a hotblock tube, beaker, or flask.
3. If a colourimetric finish is to be used, activated charcoal may be added if necessary to produce a colourless filtrate (0.1 grams of activated charcoal per 5 grams sample is recommended).
4. For each 5 grams of dried sample, dispense 10 mL of 0.01 M $CaCl_2$, cover with a watch glass and bring to a boil for at least 5 minutes (but no longer than 15 minutes) on a hot plate, hot block, or water bath. After cooling, adjust volume with deionized water to compensate for loss of water during boiling.
5. Filter extract (Whatman No. 42 or equivalent filter paper is recommended) and store in plastic containers prior to the determination of Boron.

Performance Requirements

Any analytical method options selected for this analysis must meet or exceed the performance requirements specified below.

Accuracy and Precision requirements apply to measures of long term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method re-validation studies. They do not constitute acceptance criteria or Data Quality Objectives for individual Quality Control samples. For Initial Validations, averages of at least 8 spikes or CRMs must be assessed (preferably taken from multiple analytical batches). Ongoing re-validations (performance reviews) should assess QC data encompassing longer timeframes (e.g., 6 months to 1 year). A minimum frequency of 2 years is recommended for ongoing re-validations.

Accuracy Requirement: Laboratories must demonstrate method accuracy (measured as average recovery) of 80 – 120% or better for clean matrix spikes or certified reference materials at concentrations above ten times the MDL.

Precision Requirement: Laboratories must demonstrate method precision equal to or better than 15% relative standard deviation for clean matrix spikes at concentrations above ten times the MDL.

Sensitivity Requirement: Where possible, the method should generate Method Detection Limits that are less than 1/5 of applicable numerical standards. The method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

Quality Control

Summary of QC Requirements

Method QC Component	Minimum Frequency	Minimum Data Quality Objectives*
Method Blank	1 per batch (max 20 samples)	Less than reported DL
Laboratory Control Sample or Reference Material	1 per batch (max 20 samples)	60 – 140%
Lab Duplicate	1 per batch (max 20 samples)	≤ 40% RPD
Field Duplicate	Recommended	None Specified

* Minimum DQOs apply to individual QC samples, not averages, and only at levels above 10x MDL. Laboratories must report qualified data when DQOs are not met.

References

1. Soil Sampling and Methods of Analysis. 2008. Canadian Society of Soil Science, Chapter 9, “Boron, Molybdenum, and Selenium”. Carter and Gregorich, Editors.
2. Manual on Soil Sampling and methods of Analysis. 1978. Canada Soil Survey Committee. J.A. McKeague, Editor.
3. Methods of Soil Analysis, Part 3, Chemical Methods, Chapter 21, “Boron”. Soil Science Society of America, 1996.

Revision History	Dec 2002:	Method initially developed by BCLQAAC Technical Committee.
	July 26, 2013:	Method revision. Format updated. Changed extraction solution from hot water to 0.01 M $CaCl_2$ extraction for consistency with proposed CCME method guidelines, and to improve method performance. DQOs were revised. Infinite hold time added for dried soils. Effective date for this version is October 1, 2013.
	October 1, 2013:	Boron, Hot Water Soluble method updated.

Cadmium (Atomic Absorption - Direct Aspiration)

Parameter	Cadmium, total Cadmium, dissolved
Sample Preparation	See section 1.0, the sample preparation section.
Analytical Method	See section 2.1, the AA methods section.
EMS Code	FA: HNO_3: AA (total) Cd-T X073 LA: HNO_3: AA (total) Cd-T X351 FF, FA: HNO_3: AA (dissolved) Cd-D X203 LF, LA: HNO_3: AA (dissolved) Cd-D X085
Introduction	Cadmium is toxic to virtually every system in the animal body, whether ingested, injected, or inhaled. Histological changes have been observed in the kidneys, liver, gastrointestinal tract, heart, testes, pancreas, bones and blood vessels. Cadmium in man has a tenacious retention time in the body with a long half-life estimated at 16-33 years. The Canadian drinking water guideline for cadmium is 0.005 mg/L. The limit indicated in Water Criteria for Salmonid Hatcheries is 0.0003 mg/L.
Method Summary	Aqueous solutions of metals are aspirated into a flame and atomized. The absorption of light, at a wavelength specific to the element being analyzed, is measured and the concentration of the analyte is determined by comparison with standards.
MDL	Given an aqueous sample free of interferences, the instrumental performance characteristics are: MDL: 0.005 mg/L Range: 0.005-2.00 mg/L See Table C-1 in section 2.1, the AA methods section, for additional information.
Matrix	Water, wastewater, marine water.
Interferences and Precautions	See section 2.1.4 of the AA methods section of this manual. Coexisting elements causing relatively large interferences are Ca, Si, and Ti.
Sample Handling and Preservation	See section 1.0 the sample preparation section of this manual.
Stability	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
Instrument Parameters	Source: Cd hollow cathode lamp Wavelength: 228.8 nm Type of Flame: air/acetylene Background Correction: recommended
Apparatus, Materials and Reagents	See section 2.1.5 and 2.1.6 of the AA methods section of this manual.
Precision	None listed.
Accuracy	None listed.
Quality Control	See section 2.1.9 QA/QC Guidelines in this manual.

References

a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 17th edition, 1989 Method 3500-Cd.

b) Methods for Chemical Analysis of Water and Wastes, EPA-600 4-79-020, March 1983, Method 213.1.

c) Trace Elements in Human and Animal Nutrition, Eric J. Underwood, 4th edition, Academic Press, 1977.

d) Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods (Revised). Publication #SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd Edition 1990.

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes. Sample matrix added.

Cadmium (Atomic Absorption - Graphite Furnace)

Parameter	Cadmium, total Cadmium, dissolved
Sample Preparation	See section 1.0, the sample preparation section.
Analytical Method	See section 2.1, the AA methods section.
EMS Code	FA: HNO_3: GFAA (total) Cd-T X072 LA: HNO_3: GFAA (total) Cd-T X179 FF, FA: HNO_3: GFAA (dissolved) Cd-D X116 LF, LA: HNO_3: GFAA (dissolved) Cd-D X357
Introduction	Cadmium is toxic to virtually every system in the animal body, whether ingested, injected, or inhaled. Histological changes have been observed in the kidneys, liver, gastrointestinal tract, heart, testes, pancreas, bones and blood vessels. Cadmium in man has a tenacious retention time in the body with a long half-life estimated at 16-33 years. The Canadian drinking water guideline for cadmium is 0.005 mg/L. The limit indicated in Water Criteria for Salmonid Hatcheries is 0.0003 mg/L.
Method Summary	A discrete sample volume is introduced into the graphite sample boat which is heated in stages to accommodate drying of the solution, charring and volatilization of organics and other matrix components, and finally, atomization of the analyte into the light path of the spectrometer. The absorption of light, at a wavelength specific to the element being analyzed, is measured and the concentration of the analyte is determined by comparison with standards.
MDL	Given an aqueous sample free of interferences, the instrumental performance characteristics are: MDL: 0.0001 mg/L Range: 0.0001-0.010 mg/L See Table C-1 in section 2.1, the AA methods section, for additional information.
Matrix	Water, wastewater, marine water.
Interferences and Precautions	See section 2.1.4 of the AA methods section of this manual. Matrix modifiers for interference removal are given by Standard Methods as: $NH_4H_2PO_4$ & $Mg(NO_3)_2$ $(NH_4)_2HPO_4$ & $Mg(NO_3)_2$ $(NH_4)_2SO_4$, HNO_3, $(NH_4)_2S_2O_8$ $Mg(NO_3)_2$
Sample Handling and Preservation	See section 1.0, the sample preparation section of this manual.
Stability	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
Instrument Parameters	Source: Cd hollow cathode lamp Wavelength: 228.8 nm Background Correction: recommended
Apparatus, Materials, and Reagents	See section 2.1.5 and 2.1.6 of the AA methods section of this manual.

Precision	None listed.
Accuracy	None listed.
Quality Control	See section 2.1.9, QA/QC Guidelines in this manual.
References	a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 17th edition, 1989 Section 3113. b) Methods for Chemical Analysis of Water and Wastes, EPA-600 4-79-020, March 1983, Method 213.2. c) Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods (Revised). Publication #SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd Edition 1990.
Revision History	February 14, 1994: Publication in 1994 Laboratory Manual. December 31, 2000: SEAM codes replaced by EMS codes. Sample matrix added.

Cadmium (Atomic Emission - Inductively Coupled Argon Plasma {ICAP})

Parameter	Cadmium, total Cadmium, dissolved
Sample Preparation	See section 1.0, the sample preparation section.
Analytical Method	See section 2.4, the ICP-AES method section.
EMS Code	FA: HNO_3: ICAP (total) Cd-T X349 LA: HNO_3: ICAP (total) Cd-T X352 FF, FA: HNO_3: ICAP (dissolved) Cd-D X350 LF, LA: HNO_3: ICAP (dissolved) Cd-D X356
Introduction	Cadmium is toxic to virtually every system in the animal body, whether ingested, injected, or inhaled. Histological changes have been observed in the kidneys, liver, gastrointestinal tract, heart, testes, pancreas, bones and blood vessels. Cadmium in man has a tenacious retention time in the body with a half-life estimated at 16-33 years. The Canadian drinking water guideline for cadmium is 0.005 mg/L. The limit indicated in Water Criteria for Salmonid Hatcheries is 0.0003 mg/L.
Method Summary	Aqueous solutions of metals are converted to aerosols in the nebulizer of the ICP and injected directly into a high temperature plasma (6000 to 8000°K). The highly efficient ionization produces ionic emission spectra and wavelengths specific to the elements of interest it can be monitored either simultaneously or sequentially.
MDL	Given an aqueous sample free of interferences, the instrumental performance characteristics are: MDL: 0.010 mg/L Range: 0.010-100 mg/L See Table C-2 in section 2.4, the ICP-AES method section, for additional information.
Matrix	Water, wastewater, marine water.
Interferences and Precautions	See section 2.4.4 of the ICP-AES method section of this manual.
Sample Handling and Preservation	See section 1.0, the sample preparation section of this manual.
Stability	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
Instrument Parameters	Wavelength: 228.8 nm Background Correction: recommended
Apparatus, Materials, and Reagents	See section 2.4, the ICP-AES methods section of this manual.
Precision	None listed.
Accuracy	None listed.
Quality Control	See section 2.1.9, QA/QC Guidelines in this manual.

References	a)	Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 17th edition, 1989 Section 3120 B.
	b)	Methods for Chemical Analysis of Water and Wastes, EPA-600 4-79-020, March 1983, Method 200.7.
	c)	Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods (Revised). Publication #SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd Edition 1990.

Revision History	February 14, 1994:	Publication in 1994 Laboratory Manual.
	December 31, 2000:	SEAM codes replaced by EMS codes. Sample matrix added.

Calcium (Atomic Absorption - Direct Aspiration)

Parameter	Calcium, total Calcium, dissolved
Sample Preparation	See section 1.0, the sample preparation section.
Analytical Method	See section 2.1, the AA methods section.
EMS Code	FA: HNO_3: AA (total) Ca-T X073 LA: HNO_3: AA (total) Ca-T X351 FF, FA: HNO_3: AA (dissolved) Ca-D X203 LF, LA: HNO_3: AA (dissolved) Ca-D X085
Method Summary	Aqueous solutions of metals are aspirated into a flame and atomized. The absorption of light, at a wavelength specific to the element being analyzed, is measured and the concentration of the analyte is determined by comparison with standards.
MDL	Given an aqueous sample free of interferences, the instrumental performance characteristics are: MDL: 0.01 mg/L Range: 0.01-5.0 mg/L See Table C-1 in section 2.1, the AA methods section, for additional information.
Matrix	Water, wastewater, marine water.
Interferences and Precautions	See section 2.1.4 of the AA methods section of this manual. Ionization can occur in an air-acetylene flame and can be controlled by the addition of potassium chloride to a level of 0.1%. Elements that form stable oxides (Al, Be, P, Si, Ti, V, Zr) will reduce calcium sensitivity. These can be controlled by the addition 0.1-1.0% lanthanum or strontium.
Sample Handling and Preservation	See section 1.0, the sample preparation section of this manual.
Stability	An aqueous solution preserved with nitric acid to pH <2 has a hold time of 6 months.
Instrument Parameters	Source: Ca hollow cathode lamp Wavelength: 422.7 nm (primary); 239.9 nm (alternate) Type of Flame: air/acetylene Background Correction: recommended
Apparatus, Materials and Reagents	See sections 2.1.5 and 2.1.6 of this manual.
Precision	None listed.
Accuracy	None listed.
Quality Control	See section 2.1.9, QA/QC Guidelines in this manual.

References	a)	Standard Methods for the Examination of Water and Wastewater APHA, AWWA, WEF, 18th edition, 1992, Method 3111 B/D.
	b)	Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods (Revised). Publication #SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd Edition 1990.
Revision History	February 14, 1994:	Publication in 1994 Laboratory Manual.
	December 31, 2000:	SEAM codes replaced by EMS codes. Sample matrix added.

Chromium (Atomic Absorption - Direct Aspiration)

Parameter	Chromium, total Chromium, dissolved
Sample Preparation	See section 1.0, the sample preparation section.
Analytical Method	See section 2.1, the AA methods section.
EMS Code	X073 FA: HNO_3: AA (total) Cr-T X073 X351 LA: HNO_3: AA (total) Cr-T X351 X203 FF, FA: HNO_3: AA (dissolved) Cr-D X203 X085 LF, LA: HNO_3: AA (dissolved) Cr-D X085
Introduction	Chromium is an essential element and is necessary for glucose metabolism, lipid metabolism, protein synthesis, growth and longevity. Simple chromium salts are poorly absorbed in animals and man, to the extent of 1-3%. Hexavalent chromium is much more toxic than the trivalent form. The Canadian drinking water guideline for chromium is 0.05mg/L. The limit indicated in Water Criteria for Salmonid Hatcheries is 0.04 mg/L.
Method Summary	Aqueous solution of metals are aspirated into a flame and atomized. The absorption of light, at a wavelength specific to the element being analyzed, is measured and the concentration of the analyte is determined by comparison with standards.
MDL	Given an aqueous sample free of interferences, the instrumental performance characteristics are: MDL: 0.050 mg/L Range: 0.050-10.0 mg/L See Table C-1 in section 2.1, the AA methods section, for additional information.
Matrix	Water, wastewater, marine water.
Interferences and Precautions	See section 2.1.4 of the AA methods section of this manual. Coexisting elements causing relatively large interferences are Fe and Ni.
Sample Handling and Preservation	See section 1.0, the sample preparation section of this manual.
Stability	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
Instrument Parameters	Source: Cr hollow cathode lamp Wavelength: 357.9 nm Type of Flame: air/acetylene Background Correction: recommended
Apparatus, Materials and Reagents	See section 2.1.5 and 2.1.6 of the AA methods section of this manual.
Precision	None listed.
Accuracy	None listed.
Quality Control	See section 2.1.9, QA/QC Guidelines in this manual.

References

a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 17th edition, 1989 Method 3111 B, 3111C.

b) Methods for Chemical Analysis of Water and Wastes, EPA-600 4-79-020, March 1983, Method 218.1.

c) Trace Elements in Human and Animal Nutrition, Eric J. Underwood, 4th edition, Academic Press, 1977.

d) Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods (Revised). Publication #SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd Edition 1990.

Revision History

February 14, 1994: Publication in 1994 Laboratory Manual.

December 31, 2000: SEAM codes replaced by EMS codes. Sample matrix added.

Revision Date: December 31, 2000

Chromium (Atomic Absorption - Graphite Furnace)

Parameter	Chromium, total Chromium, dissolved
Sample Preparation	See section 1.0, the sample preparation section.
Analytical Method	See section 2.1, the AA methods section.
EMS Code	FA: HNO_3: GFAA (total) Cr-T X072 LA: HNO_3: GFAA (total) Cr-T X179 FF, FA: HNO_3: GFAA (dissolved) Cr-D X116 LF, LA: HNO_3: GFAA (dissolved) Cr-D X357
Introduction	Chromium is an essential element and is necessary for glucose metabolism, lipid metabolism, protein synthesis, growth and longevity. Simple chromium salts are poorly absorbed in animal and man, to the extent of 1-3%. Hexavalent chromium is much more toxic than the trivalent form. The Canadian drinking water guideline for chromium is 0.05 mg/L. The limit indicated in Water Criteria for Salmonid Hatcheries is 0.04 mg/L.
Method Summary	A discrete sample volume is introduced into the graphite sample boat which is heated in stages to accommodate drying of the solution, charring and volatilization of organics and other matrix components, and finally, atomization of the analyte into the light path of the spectrometer. The absorption of light, at a wavelength specific to the element being analyzed, is measured and the concentration of the analyte is determined by comparison with standards.
MDL	Given an aqueous sample free of interferences, the instrumental performance characteristics are: MDL: 0.001 mg/L Range: 0.001-0.100 mg/L See Table C-1 in section 2.1, the AA methods section, for additional information.
Matrix	Water, wastewater, marine water.
Interferences and Precautions	See section 2.1.4 of the AA methods section of this manual. Matrix modifiers for interference removal are given by Standard Methods as: $Mg(NO_3)_2$
Sample Handling and Preservation	See section 1.0, the sample preparation section of this manual.
Stability	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
Instrument Parameters	Source: Cr hollow cathode lamp Wavelength: 357.9 nm Background Correction: recommended
Apparatus, Materials, and Reagents	See section 2.1.5 and 2.1.6 of the AA methods section of this manual.
Precision	None listed.
Accuracy	None listed.
Quality Control	See section 2.1.9, QA/QC Guidelines in this manual.

References	a)	Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 17th edition, 1989 Section 3113.
	b)	Methods for Chemical Analysis of Water and Wastes, EPA-600 4-79-020, March 1983, Method 218.2.
	c)	Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods (Revised). Publication #SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd Edition 1990.
Revision History	February 14, 1994:	Publication in 1994 Laboratory Manual.
	December 31, 2000:	SEAM codes replaced by EMS codes. Sample matrix added.

Chromium (Atomic Emission - Inductively Coupled Argon Plasma {ICAP})

Parameter	Chromium, total Chromium, dissolved
Sample Preparation	See section 1.0, the sample preparation section.
Analytical Method	See section 2.4, the ICP-AES method section.
EMS Code	FA: HNO$_3$: ICAP (total) Cr-T X349 LA: HNO$_3$: ICAP (total) Cr-T X352 FF, FA: HNO$_3$: ICAP (dissolved) Cr-D X350 LF, LA: HNO$_3$: ICAP (dissolved) Cr-D X356
Introduction	Chromium is an essential element and is necessary for glucose metabolism, lipid metabolism, protein synthesis, growth and longevity, Simple chromium salts are poorly absorbed in animals and man, to the extent of 1-3%. Hexavalent chromium is much more toxic than the trivalent form. The Canadian drinking water guideline for chromium is 0.05 mg/L. The limit indicated in Water Criteria for Salmonid Hatcheries is 0.04 mg/L.
Method Summary	Aqueous solutions of metals are converted to aerosols in the nebulizer of the ICP and injected directly into a high temperature plasma (6000 to 8000°K). The highly efficient ionization produces ionic emission spectra and wavelengths specific to the elements of interest can be monitored either simultaneously or sequentially.
MDL	Given an aqueous sample free of interferences, the instrumental performance characteristics are: MDL: 0.010 mg/L Range: 0.010-100.0 mg/L See Table C-2 in section 2.4, the ICP method section, for additional information.
Matrix	Water, wastewater, marine water.
Interferences and Precautions	See section 2.4.4 of the ICP section of this manual.
Sample Handling and Preservation	See section 1.0, the sample preparation section of this manual.
Stability	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
Instrument	Wavelength: 205.5 nm
Parameters	Background Correction: recommended
Apparatus, Materials, and Reagents	See section 2.4 of the ICP methods section of this manual.
Precision	None listed.
Accuracy	None listed.
Quality Control	See section 2.1.9, QA/QC Guidelines in this manual.

References

a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 17th edition, 1989 Section 3120B.

b) Methods for Chemical Analysis of Water and Wastes, EPA-600 4-79-020, March 1983, Method 200.7.

c) Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods (Revised). Publication #SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd Edition 1990.

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes. Sample matrix added.

Chromium, Hexavalent in Water – PBM

Parameter

Chromium, Hexavalent

Analytical Method

Colourimetric Method - Ion Chromatographic Method

Introduction

This procedure is applicable to the determination of hexavalent chromium in water samples. Multiple analytical techniques are possible and as such, the determinative portion of this method is performance based.

Hexavalent chromium (Cr(VI)) compounds are those which contain the element chromium in the +6 oxidation state. Industrial uses of hexavalent chromium compounds include chromate pigments in dyes, paints, inks, and plastics; chromates added as anticorrosive agents to paints, primers, and other surface coatings; and chromic acid electroplated onto metal parts to provide a decorative or protective coating.

Reduction of Cr(VI) to Cr(III) can occur in the presence of reducing species in an acidic medium. At pH 6.5 or greater, however, CrO_4^{2-}, which is less reactive than $HCrO_4^{-}$, is the predominant species. Therefore, preservation with NaOH is used to prevent species conversion (EPA 1636).

The group of hexavalent chromium compounds as a whole have been classified as “carcinogenic to humans” by the Government of Canada.

Method Summary

Various techniques are available for the determination of hexavalent chromium in water:

Colourimetric Method – Involves the reaction of hexavalent chromium with diphenylcarbazide in acid solution to produce a red-violet complex that is measured at 530 or 540 nm.

Ion Chromatographic Method – Involves sample pH adjustment to 9.0-9.5 to reduce the solubility of trivalent chromium and to preserve the oxidative state of hexavalent chromium. The sample is introduced into an ion chromatography system where the hexavalent chromium is separated from trivalent chromium. The hexavalent chromium reacts with a diphenylcarbazide dye and is measured colourimetrically at 530 or 540 nm.

MDL and EMS Codes

MDL is dependent on analytical technique and instrumental parameters. The following values provide general guidance:

- Typical MDL: 1 – 5 ug/L depending on technique
- Typical Range: up to 1,000 ug/L depending on technique

Matrix

Natural and treated waters.

Interferences and Precautions

Colourimetric Method – The colourimetric method is nearly specific to chromium, and for practical purposes, chemical interferences are minimal. Sample color may affect absorbance readings, and measures should be taken to mitigate this effect.

Ion Chromatographic Method – Chemical interferences are minimal. High ionic concentrations my cause column overload, and/or result in changes in peak geometry.

Sample Handling and Preservation

Container: Plastic or glass, metals free.

Preservation: No preservation is required if analysis will be complete within 24 hours. Preserve as soon as possible after collection (but within 24 hours of collection) with 1mL of 50% NaOH per 125mL sample (EPA 1669), to extend holding time to 30 days.

Filtration: Field filter through 0.45um filter when dissolved analysis is required.

Stability

Holding Time: Preserved samples are stable for 30 days (EPA 1669). Unpreserved samples must be analyzed within 24 hours of collection.

Storage: Cool temperatures (≤6ºC).

Procedure

As this is a performance-based method, and because multiple analytical approaches are possible, detailed analysis steps are not provided in this method. Refer to the methods cited in the References section for specific details, and ensure that Performance Requirements are achieved.

Performance Requirements

Any analytical method options selected for this analysis must meet or exceed the method validation performance requirements specified below:

Accuracy and Precision requirements apply to measures of long term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method re-validation studies. They do not constitute acceptance criteria or Data Quality Objectives for individual Quality Control samples.

For Initial Validations, averages of at least 8 spikes must be assessed (preferably taken from multiple analytical batches).

Ongoing Re-validations (performance reviews) should assess QC data encompassing longer timeframes (e.g., 6 months to 1 year). A minimum frequency of 2 years is recommended for Ongoing Re-validations.

Accuracy Requirement: Laboratories must demonstrate method accuracy (measured as average recovery) through repeat analysis of clean matrix spikes. Average recovery must be between 85-115%.

Precision Requirement: Laboratories must demonstrate method precision through repeat analysis. Precision measured as percent relative standard deviation (%RSD) must be <15%.

Sensitivity Requirement: Where possible, the method should generate Method Detection Limits that are less than 1/5 of applicable numerical standards. The method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

Quality Control

Summary of QC Requirements		
QC Component	Minimum Frequency	Minimum Data Quality Objectives*
Method Blank	1 per batch	Less than reported DL
Method Spike	1 per batch	80 – 120% recovery
Duplicates	1 per batch	20% RPD

* Minimum DQOs apply to individual QC samples, not averages, and only at levels above 10x MDL. If any DQOs are exceeded at a frequency of more than ~5%, the laboratory's method should be reviewed in an attempt to improve its performance. Laboratories should report qualified data when DQOs are not met, unless other evidence demonstrates that the quality of associated sample data has not been adversely affected.

Prescribed Elements	1. Determinative analysis must be by ion chromatography, or by the diphenyl carbazide colourimetric method. 2. Ensure that Sample Handling and Preservation requirements are achieved. 3. All Performance Requirements and Quality Control requirements must be met.
References	Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 21st Edition 2005, Method 3500-Cr B, Colorimetric Method. Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 21st Edition 2005, Method 3500-Cr C, Ion Chromatographic Method. EPA Method 1636, US Environmental Protection Agency, Determination of Hexavalent Chromium by Ion Chromatography, January 1996. EPA Method 1669, US Environmental Protection Agency, Sampling Ambient Water for the Determination of Metals at EPA Water Quality Criteria Levels, July 1996 (Reference for preservation technique). EPA 40CFR Part 136, March 12, 2007 (Reference for storage temperature).
Revision History	January 25, 2008: Initial BCLQAAC endorsed version.

Hexavalent Chromium in Solids by Alkaline Digestion - PBM

Parameter	Hexavalent Chromium
Analytical Method	Alkaline extraction – Colorimetric or IC Determination

Introduction

This procedure is applicable to the determination of hexavalent chromium in solid samples (soils, sediments, sludges, etc.). The analysis portion of this method is performance based.

Chromium can exist in nine different oxidation states, but trivalent (III) and hexavalent (VI) are the most common in the environment. Cr(III) is the most thermodynamically stable species under ambient redox conditions. Complexed Cr(III) occurs naturally and is ubiquitous in the environment. The principal source of Cr(VI) in the environment is anthropogenic pollution. Cr(VI) has an affinity to react with organic matter and other reducing substances. Cr(III) solids are practically insoluble in water at pH >4, and do not tend to leach from a soil matrix into groundwaters. At pH > 8.5, Cr(VI) solids are highly soluble and completely mobile, and can readily leach from soils into groundwater systems.

The group of Cr(VI) compounds as a whole have been classified as “carcinogenic to humans” by the Government of Canada.

Method Summary

Soluble, adsorbed, and precipitated forms of Cr(VI) are extracted from field-moist solids using a NaOH / Na_2CO_3 alkaline digestion procedure. Magnesium chloride in phosphate buffer is added to prevent oxidation of Cr(III) to Cr(VI). The digestate is filtered through a 0.45µm membrane filter prior to acidification to a target pH range (dependent upon the analytical method used). The filtered digestate is normally analyzed by UV-VIS colourimetry or by Ion Chromatography with colourimetric detection. Other published reference methods may also be appropriate for analysis of Cr(VI) in alkaline digests.

This method is performance-based. Laboratories may adopt alternative options to improve performance or efficiency provided that all stated performance requirements and prescribed (mandatory) elements are met.

MDL

MDL is dependent on analytical technique and on instrument parameters. For a 2.5 g dry weight sample free from interference digested into 50 mL and analyzed by UV-VIS colourimetry, an MDL of 0.5 mg/kg is achievable.

Matrix

Soil, sediment, sludges, solid wastes.

Interferences and Precautions

Concentrations of hexavalent molybdenum or mercury of >200 mg/L in the leachate can interfere with the UV-VIS colourimetric determination, as can Vanadium when present at levels above ten times the Cr(VI) concentration.

Reduction of Cr(VI) to Cr(III) can occur in the presence of reducing species in an acidic medium. Laboratories are not normally expected to determine the reducing or oxidizing tendency of samples except by special request (see Method 3060A, section 3.1, Interferences).[a]

For Ion Chromatography determinations, overloading the analytical column with high concentrations of anionic species, especially chloride and sulfate, will cause a loss of Cr(VI).

Sample Handling and Preservation

Collect samples in plastic or glass containers. No chemical preservative techniques are applicable.

Stability

Holding Time: Digest samples within 30 days of sample collection. Analyze digestate within 7 days of preparation.

Storage: Store field moist at ≤ 6°C.

Digestion Procedure

Follow the procedure described in US EPA SW846 Method 3060A (Dec, 1996 or newer). Add magnesium chloride in phosphate buffer to all samples to prevent oxidation of Cr(III).

Modifications to the chemistry of the 3060A digestion procedure (including temperature, reagent compositions or ratios, and the continuous stirring requirement) are not permitted. Minor physical and procedural changes may be adopted if performance criteria are met.

Adjustment of the digest pH is generally required for compatibility with standard analytical methods – consult EPA Method 3060A for details of pH adjustment and consult the chosen analytical method references for acceptable pH.

Analysis Procedure

Detailed analysis procedures are not provided in this method. The published reference methods below are recommended for general guidance:

APHA Method 3500-Cr B. Colorimetric Method, 2009 or later.

APHA Method 3500-Cr C. Ion Chromatographic Method, 2009 or later.

EPA Method 1636. Determination of Hexavalent Chromium by Ion Chromatography, January 1996 or later.

EPA SW-846 Method 7196A, Chromium, Hexavalent (Colorimetric), July 1992 or later.

Other reference methods not listed here may also be employed if performance requirements can be met.

Performance Requirements

Any analytical method options selected for this analysis must meet or exceed the performance requirements specified below.

Accuracy and Precision requirements apply to measures of long term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method re-validation studies. They do not constitute acceptance criteria or Data Quality Objectives for individual Quality Control samples. For Initial Validations, averages of at least 8 spikes or CRMs must be assessed (preferably taken from multiple analytical batches). Ongoing Re-validations (performance reviews) should assess QC data encompassing longer timeframes (e.g., 6 months to 1 year). A minimum frequency of 2 years is recommended for Ongoing Re-validations.

Accuracy Requirement: Laboratories must demonstrate method accuracy (measured as average recovery) of 80-120% for Laboratory Control Samples or Certified Reference Materials at concentrations above ten times the MDL.

Precision Requirement: Laboratories must demonstrate method precision equal to or better than 15% relative standard deviation for clean matrix spikes at concentrations above ten times the MDL.

Sensitivity Requirement: Where possible, the method should generate Method Detection Limits that are less than 1/5 of applicable numerical standards. The method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

Quality Control

Summary of QC Requirements		
QC Component	Minimum Frequency	Minimum Data Quality Objectives*
Method Blank	One per 20 samples	Less than reported DL
Laboratory Control Sample (LCS) or Reference Material	One per 20 samples	70 – 130%
Matrix Spikes	Not Required	n/a
Lab Duplicates	One per 20 samples	35% RPD

* Minimum DQOs apply to individual QC samples, not averages, and only at levels above 10x MDL. Laboratories should report qualified data when DQOs are not met, unless other evidence demonstrates that the quality of associated sample data has not been adversely affected.

Prepare the LCS using a 1:1 mixture of soluble (e.g., $K_2Cr_2O_7$) and insoluble (e.g., $PbCrO_4$) Cr(VI) salts. If recovery problems are experienced, perform separate Method Spikes with soluble and insoluble Cr(VI) salts to help identify the cause of the problem.

Sample Matrix Spikes, as described in Method 3060A, are recommended for specific projects where it is desirable to know whether a sample matrix can support Cr(VI) species. Reducing sample matrices (e.g., anoxic sediments, clays) tend to reduce Cr(VI) species to Cr(III), causing low spike recoveries. Method 3060A provides advice for interpreting low Sample Matrix Spike recoveries.

Prescribed Elements

The following components of this method are mandatory:

1. All primary elements of the alkaline digestion procedure from US EPA SW846 3060A (Dec 1996 or newer) must be followed as described. No significant modifications to the digestion procedure are permitted.
2. The digestion solution and phosphate buffer must be of the same strengths and relative amounts as prescribed in EPA 3060A.
3. The ratio of sample to digestion solution and phosphate buffer must be the same as prescribed by EPA 3060A.
4. Magnesium chloride in phosphate buffer must be added to all samples to prevent oxidation of Cr(III) to Cr(VI).
5. Soils must not be dried prior to digestion.
6. A minimum of 1.5 grams of soil (wet weight) must be digested, except if limited by available sample.

   The pH ranges specified in Method 3060A and the chosen analytical method must be adhered to.
7. Digestion temperature (solution temperature, not hotblock temperature) must be 90-95˚C.
8. Digestion time must be at least 1 hour.
9. Samples must be stirred continuously during digestion as prescribed by 3060A.
10. Sample digests must be filtered or centrifuged prior to analysis.

11. All QC Requirements and Performance Elements must be met as indicated.

Apart from the limitations above, and provided performance requirements are met, laboratories may introduce minor physical and procedural modifications to the method in order to improve quality and/or efficiency.

Reference

Test Methods for Evaluating Solid Wastes – Physical / Chemical Methods, SW-846, 3rd Edition, Method 3060A, Alkaline Digestion for Hexavalent Chromium, December 1996, Final Update III, US EPA, Washington, D.C.

Revision History

Dec, 2002:	Method developed by BCLQAAC Technical Sub-Committee, superceding the method published in Supplement #1.
July 26, 2013:	Method was modified such that continuous stirring as per EPA 3060A is required, Other key elements of the method became prescribed, including minimum sample weight, minimum digestion time, and requirement for filtration or centrifugation of digest solution. QC requirements and DQOs were revised. Effective date for this method is October 1, 2013.
October 1, 2013:	Hexavalent Chromium in Solids by Alkaline Digestion – PBM method updated.

Revision History: May 9, 2003

Trivalent Chromium in Solids by Calculation

Parameter Trivalent Chromium

Sample Handling Preservation Refer to individual techniques for total and hexavalent chromium.

Analytical Method Calculation: SALM-digestable total chromium minus chromium (VI).

EMS Codes To be assigned on request.

Introduction This procedure is applicable to the determination of trivalent chromium in solid samples (soils, sediments, sludges, etc.).

Chromium can exist in nine different oxidation states, but trivalent (III) and hexavalent (VI) are the most common in the environment. Cr(III) is the most thermodynamically stable species under ambient redox conditions. Complexed Cr(III) occurs naturally and is ubiquitous in the environment. The principal source of Cr(VI) in the environment is anthropogenic pollution. Cr(VI) has an affinity to react with organic matter and other reducing substances. Cr(III) solids are practically insoluble in water at pH > 4, and do not tend to leach from a soil matrix into groundwaters. At pH > 8.5, Cr(VI) solids are highly soluble and completely mobile and can readily leach from soils into groundwater systems.

Direct determination of Cr(III) requires complex speciation work. However, Cr(III) concentrations can be conservatively approximated by subtracting measured Cr(VI) concentrations from measured total chromium concentrations in the same sample. Note that this method requires the use of the BC Strong Acid Leachable Metals (SALM) method for determination of total chromium, so the resulting Cr(III) concentration reflects only those species liberated by this digestion procedure.

Cr(III) is considered to be an essential trace element in animal and human nutrition. The Government of Canada has determined that Cr(III) compounds are “unclassifiable with respect to carcinogenicity in humans”.

Method Summary Chrome(III) is determined by difference of Total Chromium (Cr-T) and hexavalent chromium (Total Chromium by SALM method minus Hexavalent Chromium by Alkaline Digestion).

MDL When the Cr(VI) concentration in a sample is less than or equal to one-third of the Total Chromium concentration, the MDL for calculated Cr(III) is equal to the MDL for the Cr-T result.

However, as the relative proportion of Cr(VI) in the sample increases, the uncertainty (and therefore the MDL) in the calculated Cr(III) concentration increases exponentially with the relative proportion of Cr(VI) in the sample. Refer to the Calculation Procedure for guidance on how to determine the MDL for situations where the Cr(VI) value exceeds one-third of the Cr-T value.

Matrix Soil, sediment, sludges, solid wastes.

Interferences and Precautions Refer to individual analytical techniques for total and hexavalent chromium.

In samples where chromium (VI) species dominate, the calculated result for Cr(III) is subject to high uncertainty (and therefore high detection limits) due to the propagation of the uncertainties of the total chromium and Cr(VI) analytical results. This is not normally problematic from a regulatory point of view because guidelines for Cr(VI) will be exceeded before the variability of the Cr(III) result becomes an issue.

Stability

Refer to individual analytical techniques for total and hexavalent chromium.

Calculation Procedure

Analyze the sample for total chromium using the BC Strong Acid Leachable Metals (SALM) digestion procedure and an appropriate analytical technique for chromium (e.g., ICP-OES or AAS).

Analyze the sample for hexavalent chromium using the BC Method for Hexavalent Chromium in Solids by Alkaline Digestion.

Subtract the hexavalent chromium result from the total chromium result to approximate the concentration of trivalent chromium.

If the Cr(VI) concentration is less than or equal to one-third of the Cr-T concentration, then the MDL for the Cr-T result may be used as the MDL for the Cr(III) result.

If the Cr(VI) concentration exceeds one-third of the Cr-T concentration, then the MDL for the Cr(III) result is calculated as follows:

$$MDL_{Cr(III)} = \sqrt{[\,(U_{T\text{-}Cr})^2 + (U_{Cr(VI)})^2\,]}$$

$U_{T\text{-}Cr}$ and $U_{Cr(VI)}$ represent the analytical uncertainties (at the 95% confidence level) of the results for Cr-T and Cr(VI). Laboratories are referred to the Eurachem/CITAC Guide "Quantifying Uncertainty in Analytical Measurement," and to CAEAL's "Policy on Uncertainty of Measurement in Environmental Testing" for more information on the estimation of analytical uncertainty.

Reported detection limits should be no less than the appropriate MDL. If the MDL exceeds the relevant action limit, then this method is inappropriate, and a direct determination of Cr(III) may be necessary.

Report results as mg/kg on a dry weight basis.

Precision and Accuracy

Precision and accuracy for Cr(III) by calculation is a function of the precision and accuracy of the Cr-T and Cr(VI) results for a given sample, and a function of the relative magnitude of the Cr(VI) result versus the total chromium result.

Quality Control

Perform calculations to determine Cr(III) concentration on all relevant QC samples for which total and hexavalent chromium data is available.

References

1. Test Methods for Evaluating Solid Wastes – Physical / Chemical Methods, SW-846, 3rd Edition, Method 3060A, Alkaline Digestion for Hexavalent Chromium, December 1996, Final Update III. United States Environmental Protection Agency, Washington, D.C.
2. Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 20th edition, 1998. Method 3500 - Cr B, Colorimetric Method.
3. Test Methods for Evaluating Solid Wastes – Physical / Chemical Methods, SW-846, 3rd Edition, Method 7196A, Chromium, Hexavalent (Colorimetric), July 1992, Final Update III. United States Environmental Protection Agency, Washington, D.C.
4. Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 20th edition, 1998. Method 3500 - Cr C, Ion Chromatographic Method.
5. Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health, Chromium, 1999, Canadian Council of Ministers of the Environment.
6. CSR Analytical Method 8, “Strong Acid Leachable Metals (SALM) in Soil”, Version 1.0, February, 2001, British Columbia Ministry of Environment, Lands and Parks.
7. “Hexavalent Chromium in Solids by Alkaline Digestion”, Version 1.0, December 2, 2001, British Columbia Ministry of Water, Land and Air Protection.
8. Eurachem / CITAC Guide, "Quantifying Uncertainty in Analytical Measurement," Second Edition (QUAM:2000.P1). Editors SLR Ellison, M Rosslein, A Williams.
9. “CAEAL Policy on Uncertainty of Measurement in Environmental Testing,” Revision 1.4.

Cobalt (Atomic Absorption - Direct Aspiration)

Parameter	Cobalt, total Cobalt, dissolved
Sample Preparation	See section 1.0, the sample preparation section.
Analytical Method	See section 2.1, the AA methods section.
EMS Code	FA: HNO_3: AA (total) Co-T X073 LA: HNO_3: AA (total) Co-T X351 FF, FA: HNO_3: AA (dissolved) Co-D X203 LF, LA: HNO_3: AA (dissolved) Co-D X085
Introduction	Cobalt appears to be essential to life and plays an important part in vegetation and animal nutrition. Natural waters usually contain less than 0.010 mg/L of cobalt.
Method Summary	Aqueous solutions of metals are aspirated into a flame and atomized. The absorption of light, at a wavelength specific to the element being analyzed, is measured and the concentration of the analyte is determined by comparison with standards.
MDL	Given an aqueous sample free of interferences, the instrumental performance characteristics are: MDL: 0.05 mg/L Range: 0.05-5.0 mg/L See Table C-1 in section 2.1, the AA methods section, for additional information.
Matrix	Water, wastewater, marine water.
Interferences and Precautions	See section 2.1.4 of the AA methods section of this manual. Excesses of other transition metals may slightly depress the response of cobalt. Matrix matching or the method of standard additions is recommended.
Sample Handling and Preservation	See section 1.0, the sample preparation section of this manual.
Stability	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
Instrument Parameters	Source: Co hollow cathode lamp Wavelength: 240.7 nm Type of flame: air/acetylene Background correction: recommended
Apparatus, Materials, and Reagents	See section 2.1.5 and 2.1.6 of this manual.
Precision	None listed.
Accuracy	None listed.
Quality Control	See section 2.1.9, QA/QC Guidelines in this manual.

References	a)	Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992 Method 3111 B/D.
	b)	Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods (Revised). Publication #SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd Edition 1990.

Revision History	February 14, 1994:	Publication in 1994 Laboratory Manual.
	December 31, 2000:	SEAM codes replaced by EMS codes. Sample matrix added.

Cobalt (Atomic Absorption - Graphite Furnace)

Parameter	Cobalt, total Cobalt, dissolved
Sample Preparation	See section 1.0, the sample preparation section.
Analytical Method	See section 2.1, the AA methods section.
EMS Code	FA: HNO_3: GFAA (total) Co-T X072 LA: HNO_3: GFAA (total) Co-T X179 FF, FA: HNO_3: GFAA (dissolved) Co-D X116 LF, LA: HNO_3: GFAA (dissolved) Co-D X357
Introduction	Cobalt appears to be essential to life, and plays an important part in vegetation and animal nutrition. Natural waters usually contain less than 0.010 mg/L of cobalt.
Method Summary	A discrete sample volume is introduced into the graphite sample boat which is heated in stages to accommodate drying of the solution, charring and volatilization of organics and other matrix components, and finally, atomization of the analyte into the light path of the spectrometer. The absorption of light, at a wavelength specific to the element being analyzed, is measured and the concentration of the analyte is determined by comparison with standards.
MDL	Given an aqueous sample free of interferences, the instrumental performance characteristics are: MDL: 0.001 mg/L Range: 0.001-0.100 mg/L See Table C-1 in section 2.1, the AA methods section, for additional information.
Matrix	Water, wastewater, marine water.
Interferences and Precautions	See section 2.1.4 of the AA methods section of this manual. Excess chloride may interfere. Verification by standard additions may be necessary to ensure that this interference is absent.
Sample Handling and Preservation	See section 1.0, the sample preparation section of the manual.
Stability	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
Instrument Parameters	Source: Co hollow cathode lamp Wavelength: 240.7 nm Background Correction: recommended
Apparatus, Materials and Reagents	See section 2.1.5 and 2.1.6 of the AA methods section of this manual.
Precision	None listed.
Accuracy	None listed.
Quality Control	See section 2.1.9, QA/QC Guidelines in this manual.

References	a)	Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992, Method 3113B.
	b)	Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods (Revised). Publication #SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd Edition 1990.
Revision History	February 14, 1994:	Publication in 1994 Laboratory Manual.
	December 31, 2000:	SEAM codes replaced by EMS codes. Sample matrix added.

Copper (Atomic Absorption - Direct Aspiration)

Parameter	Copper, total Copper, dissolved
Sample Preparation	See section 1.0, the sample preparation section.
Analytical Method	See section 2.1, the AA methods section.
EMS Code	FA: HNO_3: AA (total) Cu-T X073 LA: HNO_3: AA (total) Cu-T X351 FF, FA: HNO_3: AA (dissolved) Cu-D X203 LF, LA: HNO_3: AA (dissolved) Cu-D X085
Introduction	Copper is an essential element in man and animal. Both excesses and deficiencies of this metal can occur. In soft water areas, corrosion of copper water pipes can increase the daily intake of copper. The Canadian drinking water guideline for copper is 1 mg/L. The limit indicated in Water Criteria for Salmonid Hatcheries is 0.002 mg/L.
Method Summary	Aqueous solutions of metals are aspirated into a flame and atomized. The absorption of light at a wavelength specific to the element being analyzed, is measured and the concentration of the analyte is determined by comparison with standards.
MDL	Given an aqueous sample free of interferences, the instrumental performance characteristics are: MDL: 0.020 mg/L Range: 0.020-5.0 mg/L See Table C-1 in section 2.1, the AA methods section, for additional information.
Matrix	Water, wastewater, marine water.
Interferences and Precautions	See section 2.1.4 of the AA methods section of this manual. Coexisting elements causing relatively large interferences are Al, Si, and Ti.
Sample Handling and Preservation	See section 1.0, the sample preparation section of this manual.
Stability	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
Instrument Parameters	Source: Cu hollow cathode lamp Wavelength: 324.7 nm Type of Flame: air/acetylene Background Correction: recommended
Apparatus, Materials, and Reagents	See section 2.1.5 and 2.1.6 of the AA methods section of this manual.
Precision	None listed.
Accuracy	None listed.
Quality Control	See section 2.1.9, QA/QC Guidelines in this manual.

References

a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 17th edition, 1989 Method 3500-Cu.

b) Methods for Chemical Analysis of Water and Wastes, EPA-600 4-79-020, March 1983 Method 220.1.

c) Trace Elements in Human and Animal Nutrition, Eric J. Underwood, 4th edition, Academic Press, 1977.

d) (Revised). Publication #SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd Edition 1990.

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes. Sample matrix added.

Copper (Atomic Absorption - Graphite Furnace)

Parameter	Copper, total Copper, dissolved
Sample Preparation	See section 1.0, the sample preparation section.
Analytical Method	See section 2.1, the AA methods section.
EMS Code	FA: HNO_3: GFAA (total) Cu-T X072 LA: HNO_3: GFAA (total) Cu-T X179 FF, FA: HNO_3: GFAA (dissolved) Cu-D X116 LF, LA: HNO_3: GFAA (dissolved) Cu-D X357
Introduction	Copper is an essential element in man and animal. Both excesses and deficiencies of this metal can occur. In soft water areas, corrosion of copper water pipes can increase the daily intake of copper. The Canadian drinking water guideline for copper is 1 mg/L. The limit indicated in Water Criteria for Salmonid Hatcheries is 0.002 mg/L.
Method Summary	A discrete sample volume is introduced into the graphite sample boat which is heated in stages to accommodate drying of the solution, charring and colatilization of organics and other matrix components, and finally, atomization of the analyte into the light path of the spectrometer. The absorption of light at a wavelength specific to the element being analyzed, is measured and the concentration of the analyte is determined by comparison with standards.
MDL	Given an aqueous sample free of interferences, the instrumental performance characteristics are: MDL: 0.001 mg/L Range: 0.001-0.100 mg/L See Table C-1 in section 2.1, the AA methods section, for additional information.
Matrix	Water, wastewater, marine water.
Interferences and Precautions	See section 2.1.4 of the AA methods section of this manual. Matrix modifiers for interference removal are given by Standard Methods as: NH_4NO_3, ascorbic acid.
Sample Handling and Preservation	See section 1.0, the sample preparation section of this manual.
Stability	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
Instrument Parameters	Source: Cu hollow cathode lamp Wavelength: 324.7 nm Background Correction: recommended
Apparatus, Materials and Reagents	See section 2.1 of the AA methods section of this manual.
Precision	None listed.
Accuracy	None listed.
Quality Control	See section 2.1.9, QA/QC Guidelines in this manual.

References

a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 17th edition, 1989 Section 3113.

b) Methods for Chemical Analysis of Water and Wastes, EPA-600 4-79-020, March 1983, Method 220.2.

c) Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods (Revised). Publication #SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd Edition 1990.

Revision History

February 14, 1994: Publication in 1994 Laboratory Manual.

December 31, 2000: SEAM codes replaced by EMS codes. Sample matrix added.

Copper (Atomic Emission - Inductively Coupled Plasma {ICAP})

Parameter	Copper, total Copper, dissolved
Sample Preparation	See section 1.0, the sample preparation section.
Analytical Method	See section 2.4, the ICP-AES method section.
EMS Code	FA: HNO_3: ICAP (total) Cu-T X349 LA: HNO_3: ICAP (total) Cu-T X352 FF, FA: HNO_3: ICAP (dissolved) Cu-D X350 LF, LA: HNO_3: ICAP (dissolved) Cu-D X356
Introduction	Copper is an essential element in man and animal. Both excesses and deficiencies of this metal can occur. In soft water areas, corrosion of copper water pipes can increase the daily intake of copper. The Canadian drinking water guideline for copper is 1 mg/L. The limit indicated in Water Criteria for Salmonid Hatcheries is 0.002 mg/L.
Method Summary	Aqueous solutions of metals are converted to aerosols in the nebulizer of the ICP and injected directly into a high temperature plasma (6000 to 8000°K). The highly efficient ionization produces ionic emission spectra and wavelengths specific to the elements of interest can be monitored either simultaneously or sequentially.
MDL	Given an aqueous sample free of interferences, the instrumental performance characteristics are: MDL: 0.005 mg/L Range: 0.005-1000.0 mg/L See Table C-2 in section 2.4, the ICP method section, for additional information.
Matrix	Water, wastewater, marine water.
Interferences and Precautions	See section 2.4.4 of the ICP methods section of this manual.
Sample Handling and Preservation	See section 1.0, the sample preparation section of this manual.
Stability	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
Instrument Parameters	Wavelength: 324.7 nm Background Correction: recommended
Apparatus, Materials, and Reagents	See section 2.4 of the ICP-AES methods section of this manual.
Precision	None listed.
Accuracy	None listed.
Quality Control	See section 2.1.9, QA/QC Guidelines in this manual.

References	a)	Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 17th edition, 1989 Section 3120 B.
	b)	Methods for Chemical Analysis of Water and Wastes, EPA-600 4-79-020, March 1983, Method 200.7.
	c)	Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods (Revised). Publication #SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd Edition 1990.
Revision History	February 14, 1994:	Publication in 1994 Laboratory Manual.
	December 31, 2000:	SEAM codes replaced by EMS codes. Sample matrix added.

Iron (Atomic Absorption - Direct Aspiration)

Parameter	Iron, total Iron, dissolved
Sample Preparation	See section 1.0, the sample preparation section.
Analytical Method	See section 2.1, the AA methods section.
EMS Code	FA: HNO_3: AA (total) Fe-T X073 LA: HNO_3: AA (total) Fe-T X351 FF, FA: HNO_3: AA (dissolved) Fe-D X203 LF, LA: HNO_3: AA (dissolved) Fe-D X085
Introduction	Iron is an essential trace element for plants and animals, but is an undesirable constituent of water supplies if present at appreciable concentrations. Iron has a deleterious effect on the taste of potable water and produces objectionable stains, therefore the Canadian drinking water guideline is set at a maximum limit of 0.3 mg iron/L. (aesthetic objective - not health related). Major sources of pollution include mine drainage and industrial waste.
Method Summary	Aqueous solutions of metals are aspirated into a flame and atomized. The absorption of light, at a wavelength specific to the element being analyzed, is measured and the concentration of the analyte is determined by comparison with standards.
MDL	Given an aqueous sample free of interferences, the instrumental performance characteristics are: MDL: 0.03 mg/L Range: 0.03-5.0 mg/L See Table C-1 in section 2.1, the AA methods section, for additional information.
Matrix	Water, wastewater, marine water.
Interferences and Precautions	See section 2.1.4 of the AA methods section of this manual. Cobalt, copper and nickel can cause a reduction in sensitivity. A very lean, hot flame can aid in minimizing these interferences. Treat standards and samples with 0.2% calcium chloride to eliminate silicon depression of the iron signal. A nitrous oxide-acetylene flame reduces or eliminates most interferences but sensitivity will be markedly reduced.
Sample Handling and Preservation	See section 1.0, the sample preparation section
Stability	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
Instrument Parameters	Source: Fe hollow cathode lamp Wavelength: 248.3 nm Type of Flame: air/acetylene Background Correction: recommended
Apparatus, Materials and Reagents	See sections 2.1.5 and 2.1.6 of this manual.
Precision	None listed.
Accuracy	None listed.
Quality Control	See section 2.1.9, QA/AC Guidelines in this manual.

References	a)	Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992, Method 3111 B/D.
	b)	Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods (Revised). Publication #SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd Edition 1990.
Revision History	February 14, 1994:	Publication in 1994 Laboratory Manual.
	December 31, 2000:	SEAM codes replaced by EMS codes. Sample matrix added.

Iron (Atomic Absorption - Graphite Furnace)

Parameter	Iron, total Iron, dissolved	
Sample Preparation	See section 1.0, the sample preparation section.	
Analytical Method	See section 2.1, the AA methods section.	
EMS Code	FA: HNO_3: GFAA (total) LA: HNO_3: GFAA (total) FF, FA: HNO_3: GFAA (dissolved) LF, LA: HNO_3: GFAA (dissolved)	Fe-T X072 Fe-T X179 Fe-D X116 Fe-D X357
Introduction	Iron is an essential trace element for plants and animals but is an undesirable constituent of water supplies if present in appreciable concentrations. Iron has a deleterious effect on the taste of potable water and produces objectionable stains, therefore the Canadian drinking water guideline is set at a maximum limit of 0.3 mg iron/L. (aesthetic objective - not health related). Major sources of pollution include mine drainage and industrial waste.	
Method Summary	A discrete sample volume is introduced into the graphite sample boat which is heated in stages to accommodate drying of the solution, charring and volatilization of organics and other matrix components, and finally, atomization of the analyte into the light path of the spectrometer. The absorption of light, at a wavelength specific to the element being analyzed, is measured and the concentration of the analyte is determined by comparison with standards.	
MDL	Given an aqueous sample free of interferences, the instrumental performance characteristics are: MDL: 0.001 mg/L Range: 0.001-0.10 mg/L See Table C-1 in section 2.1, the AA methods section, for additional information.	
Matrix	Water, wastewater, marine water.	
Interferences and Precautions	See section 2.1.4 of the AA methods section of this manual. Due to the extreme sensitivity of the method and presence of iron as a trace contaminant in dust, plastics, glassware, acids and other reagents, appropriate blanks must be included to allow for correction of results. Platform atomization is recommended for iron analysis. New platforms and tubes might require repeated firing at high temperature to reduce background signal to acceptable levels.	
Sample Handling and Preservation	See section 1.0, the sample preparation section of this manual.	
Stability	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.	
Instrument Parameters	Source: Fe hollow cathode lamp Wavelength: 248.3 nm Background Correction: recommended	
Apparatus, Materials and Reagents	See section 2.1.5 and 2.1.6 of this manual.	
Precision	None listed.	
Accuracy	None listed.	

Quality Control	See section 2.1.9, QA/QC Guidelines in this manual.

References

a) Standard Method for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992, Method 3113B.

b) Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods (Revised). Publication #SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd Edition 1990.

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes. Sample matrix added.

Lead (Atomic Absorption - Direct Aspiration)

Parameter	Lead, total Lead, dissolved	
Sample Preparation	See section 1.0, the sample preparation section.	
Analytical Method	See section 2.1, the AA methods section.	
EMS Code	FA: HNO_3: AA (total) LA: HNO_3: AA (total) FF, FA: HNO_3: AA (dissolved) LF, LA: HNO_3: AA (dissolved)	Pb-T X073 Pb-T X351 Pb-D X203 Pb-D X085
Introduction	Lead is a highly toxic cumulative poison in man and animals. Chronic lead poisoning is characterized particularly by neurological defects, renal tubular dysfunction and anemia. Children will absorb 50% of ingested lead; adults absorb 10%. In children, even low lead levels have been linked to learning disabilities and behaviour problems. The Canadian drinking water guideline for lead is 0.01 mg/L. The limit indicated in Water Criteria for Salmonid Hatcheries is 0.004 mg/L.	
Method Summary	Aqueous solutions of metals are aspirated into a flame and atomized. The absorption of light, at a wavelength specific to the element being analyzed, is measured and the concentration of the analyte is determined by comparison with standards.	
MDL	Given an aqueous sample free of interferences, the instrumental performance characteristics are: MDL: 0.10 mg/L Range: 0.10-20.0 mg/L See Table C-1 in section 2.1, the AA methods section, for additional information.	
Matrix	Water, wastewater, marine water.	
Interferences and Precautions	See section 2.1.4 of the AA methods section of this manual. Coexisting elements causing relatively large interferences are Fe and Ti.	
Sample Handling and Preservation	See section 1.0, the sample preparation section of this manual.	
Stability	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.	
Instrument Parameters	Source: Pb hollow cathode lamp Wavelength: 283.3 nm Type of Flame: air/acetylene Background Correction: recommended	
Apparatus, Materials and Reagents	See section 2.1.5 and 2.1.6 of the AA methods section of this manual.	
Precision	None listed.	
Accuracy	None listed.	
Quality Control	See section 2.1.9, QA/QC Guidelines in this manual.	

References	a)	Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 17th edition, 1989 Method 3500-Pb.
	b)	Method for Chemical Analysis of Water and Wastes EPA-600 4-79-020, March 1983, Method 239.1.
	c)	Trace Elements in Human and Animal Nutrition, Eric J. Underwood, 4th edition, Academic Press, 1977.
	d)	Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods (Revised). Publication #SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd Edition 1990.

Revision History	February 14, 1994:	Publication in 1994 Laboratory Manual.
	December 31, 2000:	SEAM codes replaced by EMS codes. Sample matrix added.

Lead (Atomic Absorption - Graphite Furnace)

Parameter	Lead, total Lead, dissolved	
Sample Preparation	See section 1.0, the sample preparation section.	
Analytical Method	See section 2.1, the AA methods section.	
EMS Code	FA: HNO_3: GFAA (total)	Pb-T X072
	LA: HNO_3: GFAA (total)	Pb-T X179
	FF, FA: HNO_3: GFAA (dissolved)	Pb-D X116
	LF, LA: HNO_3: GFAA (dissolved)	Pb-D X357
Introduction	Lead is a highly toxic cumulative poison in man and animals. Chronic lead poisoning is characterized particularly by neurological defects, renal tubular dysfunction and anemia. Children will absorb 50% of ingested lead; adults absorb 10%. In children, even low lead levels have been linked to learning disabilities and behaviour problems. The Canadian drinking water guideline for lead is 0.01 mg/L. The limit indicated in Water Criteria for Salmonid Hatcheries is 0.004 mg/L.	
Method Summary	A discrete sample volume is introduced into the graphite sample boat which is heated in stages to accommodate drying of the solution, charring and volatilization of organics and other matrix components, and finally, atomization of the analyte into the light path of the spectrometer. The absorption of light, at a wavelength specific to the element being analyzed, is measured and the concentration of the analyte is determined by comparison with standards.	
MDL	Given an aqueous sample free of interferences, the instrumental performance characteristics are: MDL: 0.001 mg/L Range: 0.001-0.100 mg/L See Table C-1 in section 2.1, the AA methods section, for additional information.	
Matrix	Water, wastewater, marine water.	
Interferences and Precautions	See section 2.1.4 of the AA methods section of this manual. Matrix modifiers for interference removal are given by Standard Methods as: $NH_4H_2PO_4$, $(NH_4)_2HPO_4$ $Mg(NO_3)_2$, NH_4NO_3 ascorbic acid, oxalic acid phosphoric acid, HNO_3, LaCl, (NH_4)EDTA	
Sample Handling and Preservation	See section 1.0, the sample preparation section of this manual.	
Stability	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.	
Instrument Parameters	Source: Pb hollow cathode lamp Wavelength: 283.3 nm Background Correction: recommended	
Apparatus, Materials, and Reagents	See section 2.1.5 and 2.1.6 of the AA methods section of this manual.	

Precision	None listed.
Accuracy	None listed.
Quality Control	See section 2.1.9, QA/QC Guidelines in this manual.
References	a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 17th edition, 1989 Section 3113. b) Methods for Chemical Analysis of Water and Wastes, EPA-600 4-79-020, March 1983, Method 239.2. c) Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods (Revised). Publication #SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd Edition 1990.
Revision History	February 14, 1994: Publication in 1994 Laboratory Manual. December 31, 2000: SEAM codes replaced by EMS codes. Sample matrix added.

Lead (Atomic Emission - Inductively Coupled Argon Plasma {ICAP})

Parameter	Lead, total Lead, dissolved
Sample Preparation	See section 1.0, the sample preparation section.
Analytical Method	See section 2.4, the ICP-AES methods section.
EMS Code	FA: HNO_3: ICAP (total) Pb-T X349 LA: HNO_3: ICAP (total) Pb-T X352 FF, FA: HNO_3: ICAP (dissolved) Pb-D X350 LF, LA: HNO_3: ICAP (dissolved) Pb-D X356
Introduction	Lead is a highly toxic cumulative poison in man and animals. Chronic lead poisoning is characterized particularly by neurological defects, renal tubular dysfunction and anemia. Children will absorb 50% of ingested lead; adults absorb 10%. In children, even low lead levels have been linked to learning disabilities and behaviour problems. The Canadian drinking water guideline for lead is 0.01 mg/L. The limit indicated in Water Criteria for Salmonid Hatcheries is 0.004 mg/L.
Method Summary	Aqueous solutions of metals are converted to aerosols in the nebulizer of the ICP and injected directly into a high temperature plasma (6000 to 8000°K). The highly efficient ionization produces ionic emission spectra and wavelengths specific to the elements of interest can be monitored either simultaneously or sequentially.
MDL	Given an aqueous sample free of interferences, the instrumental performance characteristics are: MDL: 0.050 mg/L Range: 0.050-500.0 mg/L See Table C-2 in section 2.4, the ICP method section, for additional information.
Matrix	Water, wastewater, marine water.
Interferences and Precautions	See section 2.4.4 of the ICP methods section of this manual.
Sample Handling and Preservation	See section 1.0, the sample preparation section of this manual.
Stability	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
Instrument Parameters	Wavelength: 220.3 nm Background Correction: recommended
Apparatus, Materials and Reagents	See section 2.4 of the ICP methods section of this manual.
Precision	None listed.
Accuracy	None listed.
Quality Control	See section 2.1.9, QA/QC Guidelines in this manual.

References	a)	Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 17th edition, 1989 Section 3120 B.
	b)	Methods for Chemical Analysis of Water and Wastes, EPA-600 4-79-020, March 1983, Method 200.7.
	c)	Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods (Revised). Publication #SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd Edition 1990.
Revision History	February 14, 1994:	Publication in 1994 Laboratory Manual.
	December 31, 2000:	SEAM codes replaced by EMS codes. Sample matrix added.

Lead in Solids by Flame AA

Parameter	Lead (Pb)
Sample Preparation	See Section 1.2 for sample preparation.
Ems Codes	EMS Codes assigned on request
Analytical Method	US EPA Method 7420 Atomic Absorption, Direct Aspiration.
Introduction	Lead is a highly toxic, cumulative poison in man and animals. Chronic lead poisoning is often characterized by central nervous system disorders.
Method Summary	The soil or sediment sample is initially homogenized to ensure representative sub-aliquots will be analyzed. An accurate weight of soil is acid digested and the resulting digestate is analyzed for lead content by direct aspiration into a standard atomic absorption spectrophotometer.

General Operating Conditions / Detection Limits

Element	Wavelength	Slit	Lamp Current	Detection Limit
Lead	283.3 nm *	0.7 nm	8 mA	1.0 µg/g

* The wavelength provided is the primary one used, alternatively the 217.0 nm line may be used.

Matrix	Soil, solids, (marine) sediments.
Source	Lead Hollow Cathode Lamp
Type of Flame	Air / Acetylene
Background Correction	Required
Interferences	The most common type of interferences is "chemical" and is caused by lack of absorption of atoms bound in molecular combination in the flame. The addition of chemicals such as lanthanum can reduce this effect. The presence of high dissolved solids (a common case in digested soils) may result in light scattering. Background correction should aid in the elimination of this problem. Refer to instrument operations manual, EPA Method 7420, and B.C. Laboratory Manual Section 2.1.4.1 in the Laboratory Manual for other sources and corrective measures.
Sample Handling and Preservation	Container - acid washed polyethylene bottle. Digested soils are already in an acid medium and require no extra preservation chemicals.
Stability	Lead in digested soil samples have a holding time of six month.
Instrument	Direct flame atomic absorption spectrophotometer with background correct system.
Calibration / Analysis Procedures	Refer to instrument operations manual for set-up and analysis techniques.
Precision	Refer to EPA Method 7420.
Accuracy	Refer to EPA Method 7420.
Quality Control	a) Confirm calibration by analyzing a separate sourced calibration verification standard. b) Blanks, Reference Materials and Duplicates prepared with each digestion batch must meet predetermined QA/QC requirements.

References	a)	Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 17th edition, 1989 Method 3500-Pb.
	b)	Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods (Revised). Publication # SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd Edition, 1990. Method 7420.
Revision History	December 2002:	Method adopted from Supplement #1 Manual, EMS Codes assigned.

Magnesium (Atomic Absorption - Direct Aspiration)

Parameter	Magnesium, total Magnesium, dissolved
Sample Preparation	See section 1.0, the sample preparation section.
Analytical Method	See section 2.1, the AA methods section.
EMS Code	FA: HNO$_3$: AA (total) Mg-T X073 LA: HNO$_3$: AA (total) Mg-T X351 FF, FA: HNO$_3$: AA (dissolved) Mg-D X203 LF, LA: HNO$_3$: AA (dissolved) Mg-D X085
Method Summary	Aqueous solutions of metals are aspirated into a flame and atomized. The absorption of light, at a wavelength specific to the element being analyzed, is measured and the concentration of the analyte is determined by comparison with standards.
MDL	Given an aqueous sample free of interferences, the instrumental performance characteristics are: MDL: 0.001 mg/L Range: 0.001-0.50 mg/L See Table C-1 in section 2.1, the AA methods section, for additional information.
Matrix	Water, wastewater, marine water.
Interferences and Precautions	See section 2.1.4 of the AA methods section of this manual. Ionization can occur in an air-acetylene flame and can be controlled by the addition of potassium chloride to a level of 0.1%. Elements that form stable oxides (Al, Be, P, Si, Ti, V, Zr) will reduce magnesium sensitivity. These can be controlled by the addition 0.1-1.0% lanthanum or strontium.
Sample Handling and Preservation	See section 1.0, the sample preparation section of this manual.
Stability	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
Instrument Parameters	Source: Mg hollow cathode lamp Wavelength: 285.2 nm (primary); 202.6 nm (alternate) Type of Flame: air/acetylene Background Correction: recommended
Apparatus, Materials and Reagents	See sections 2.1.5 and 2.1.6 of this manual.
Precision	None listed.
Accuracy	None listed.
Quality Control	See section 2.1.9, QA/QC Guidelines in this manual.

References	a)	Standard Methods for the Examination of Water and Wastewater APHA, AWWA, WEF, 18th edition, 1992, Method 3111 B/D.
	b)	Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods (Revised). Publication #SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd Edition 1990.

Revision History	February 14, 1994:	Publication in 1994 Laboratory Manual.
	December 31, 2000:	SEAM codes replaced by EMS codes. Sample matrix added.

Manganese (Atomic Absorption - Direct Aspiration)

Parameter	Manganese, total Manganese, dissolved
Sample Preparation	See section 1.0, the sample preparation section.
Analytical Method	See section 2.1, the AA methods section.
EMS Code	FA: HNO_3: AA (total) Mn-T X073 LA: HNO_3: AA (total) Mn-T X351 FF, FA: HNO_3: AA (dissolved) Mn-D X203 LF, LA: HNO_3: AA (dissolved) Mn-D X085
Introduction	Manganese occurs naturally as salts and minerals in nature. Major manganese containing substances are pyrolusite (MnO_2), rhodochrosite ($MnCO_3$) and rhodonite. Manganese is a vital micronutrient for plants and animals, but can be toxic when very large doses are ingested. The objective for drinking water supplies is <0.05 mg/L. This relatively low limit is not due to toxicological consideration but rather due to the staining effect of manganese on laundry and plumbing fixtures. Discharges known to contain manganese are domestic and industrial effluents.
Method Summary	Aqueous solutions of metals are aspirated into a flame and atomized. The absorption of light, at a wavelength specific to the element being analyzed, is measured and the concentration of the analyte is determined by comparison with standards.
MDL	Given an aqueous sample free of interferences, the instrumental performance characteristics are: MDL: 0.01 mg/L Range: 0.01-3.0 mg/L See Table C-1 in section 2.1, the AA methods section, for additional information.
Matrix	Water, wastewater, marine water.
Interferences and Precautions	Silicon has a suppressing effect on the manganese signal. This interference can be controlled by the addition of 2000 ppm $CaCl_2$. See also section 2.1.4 of the AA methods section of this manual.
Sample Handling and Preservation	See section 1.0, the sample preparation section of this manual.
Stability	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
Instrument Parameters	Source: Mn hollow cathode lamp Wavelength: 279.5 nm Type of flame: Air/Acetylene Background Correction: recommended
Apparatus, Materials and Reagents	See section 2.1.5 and 2.1.6 of this manual.
Precision	None listed.
Accuracy	None listed.

Quality Control

See section 2.1.9, QA/QC Guidelines in this manual.

References

1. Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992, Method 3111 B/D.
2. Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods (Revised). Publication #SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd Edition 1990.

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes. Sample matrix added.

Manganese (Atomic Absorption - Graphite Furnace)

Parameter	Manganese, total Manganese, dissolved
Sample Preparation	See section 1.0, the sample preparation section.
Analytical Method	See section 2.1, the AA methods section.
EMS Code	FA: HNO_3: GFAA (total) Mn-T X072 LA: HNO_3: GFAA (total) Mn-T X179 FF, FA: HNO_3: GFAA (dissolved) Mn-D X116 LF, LA: HNO_3: GFAA (dissolved) Mn-D X357
Introduction	Manganese occurs naturally as salts and minerals. Major manganese containing substances are pyrolusite (MnO_2), rhodochrosite ($MnCO_3$) and rhodonite. Manganese is a vital micronutrient for plants and animals, but can be toxic when very large doses are ingested. The objective for drinking water supplies is <0.05 mg/L. This relatively low limit is not due to toxicological consideration but rather due to the staining effect of manganese on laundry and plumbing fixtures. Discharges known to contain manganese are domestic and industrial effluents.
Method Summary	A discrete sample volume is introduced into the graphite sample boat which is heated in stages to accommodate drying of the solution, charring and volatilization of organics and other matrix components, and finally, atomization of the analyte into the light path of the spectrometer. The absorption of light, at a wavelength specific to the element being analyzed, is measured and the concentration of the analyte is determined by comparison with standards.
MDL	Given an aqueous sample free of interferences, the instrumental performance characteristics are: MDL: 0.0002 mg/L Range: 0.0002-0.030 mg/L See Table C-1 in section 2.1, the AA methods section, for additional information.
Matrix	Water, wastewater, marine water.
Interferences and Precautions	See section 2.1.4 of the AA methods section of this manual
Sample Handling and Preservation	See section 1.0, the sample preparation section of this manual.
Stability	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
Instrument Parameters	Source: Mn hollow cathode lamp Wavelength: 279.5 nm Background Correction: recommended
Apparatus, Materials and Reagents	See section 2.1.5 and 2.1.6 of this manual.
Precision	None listed.
Accuracy	None listed.
Quality Control	See section 2.1.9 QA/QC Guidelines in this manual.

References	a)	Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992, Method 3113B.
	b)	Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods (Revised). Publication #SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd Edition 1990.
Revision History	February 14, 1994:	Publication in 1994 Laboratory Manual.
	December 31, 2000:	SEAM codes replaced by EMS codes. Sample matrix added.

Mercury (Atomic Absorption - Cold Vapour)

Parameter	Mercury, total Mercury, dissolved
Sample Preparation	See section 1.0 the sample preparation section.
Analytical Method	See section 2.1, the AA methods section, and section 2.3, the cold vapour methods section.
EMS Code	FA: $HNO_3/K_2Cr_2O_7$: CVAA (total) Hg-T X346 LA: $HNO_3/K_2Cr_2O_7$: CVAA (total) Hg-T X353 FF, FA: $HNO_3/K_2Cr_2O_7$: CVAA (dissolved) Hg-D X347 LF, LA: $HNO_3/K_2Cr_2O_7$: CVAA (dissolved) Hg-D X358
Introduction	The determination of small traces of mercury has been of importance in toxicology for many years. In geochemistry, metallurgy and many industries, the trace determination of this element is also of importance. Because of its simplicity and specificity, atomic absorption spectroscopy, with a cold vapour generation sample introduction system, best meets the requirements for the economical determination of trace concentrations of mercury.
Method Summary	Mercury is converted to its ionic form in solution. This ionic mercury is reduced to its elemental state and swept from solution into a cell positioned in the light path of a standard AAS. The concentration of mercury in solution is determined using conventional AAS techniques.
MDL	Given an aqueous sample free of interferences, the instrumental performance characteristics are: MDL: 0.00005 mg/L Range: 0.00005 - 0.001 mg/L See Table C-1 in section 2.1, the AA methods section, for additional information.
Matrix	Water, wastewater, marine water.
Interferences and Precautions	a) specific volatile material which absorbs at 253.7 nm, b) sulfide, c) copper, d) chlorides, and free chlorine.
Sample Handling and Preservation	See Section 1.0, the sample preparation section of this manual.
Stability	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 28 days. Preservation using a solution of nitric acid and potassium dichromate has been reported to increase mercury stability in some instances.
Instrument Parameters	Source: Hg vapour lamp or electrodeless discharge lamp (EDL) Wavelength: 253.7 nm Background Correction: not required
Apparatus, Materials and Reagents	See sections 2.1.5 and 2.1.6 of this manual.
Accuracy	None listed.
Precision	None listed.
Quality Control	See Section 2.1.9, QA/QC Guidelines in this manual.

References

a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992.

b) Instructions - MHS-20 Mercury/Hydride System, Publication 338-A2-M 294/12.79. Bodenseewerk Perkin-Elmer & Co. GMBH/Uberlingen. 1979.

c) Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods (Revised). Publication #SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd Edition 1990.

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes. Sample matrix added.

Mercury in Solids by Semi-automated Cold Vapour Atomic Absorption (CVAA)

Parameter	Hg-T - Mercury Total
Sample Handling and Preservation	Not available.
Analytical Method	Aqua Regia digestion; CVAA
EMS Codes	
Introduction	This method is applicable to the quantitative determination of mercury in soil.
Summary	Organomercury compounds are oxidized via Aqua regia/$KMnO_4$ digestion. The mercury compounds are then reduced to elemental mercury. A stream of synthetic air introduced into the system passes through a reference cell and then, after sparging the elemental mercury, passes through the sample cell. Absorbance is measured at 253.7nm against the reference as a function of the mercury concentration.
MDL	0.05 µg/g
Matrix	Soil, sediments, solids.
Interferences and Precautions	a) Samples containing high chloride may interfere due to the liberation of free chlorine which absorbs at 253.7nm. Additional permanganate must be compensated by excess hydroxylamine sulphate-sodium chloride to avoid this positive interference. b) Certain volatile organic material which absorbs at 253.7 nm will also interfere. If this is suspected, run the sample without the addition of reagents to determine if this type of interference is present.
Stability	Not available.
Procedure	
Apparatus	a) Water Bath with alcohol thermometer able to read to 100°C. b) Compressed Air with a 2-stage regulator and an adjustable valve able to deliver between 50 and 500cc/min. c) An automated system consisting of: 1) sampler, 2) proportioning pump, 3) manifold, 4) phase separating reaction tube, 5) UV monitor equipped with 30cm flow cell and 253.7 nm lamp and 6) data collection.
Reagents	a) Hydrochloric Acid (HCl) - Concentrated (Nondetectable Mercury Content). b) Nitric Acid (HNO_3) - Concentrated (Non-detectable Mercury Content). c) Potassium Permanganate ($KMnO_4$), 1.2% Dissolve 23.1g $KMnO_4$ into DI and adjust volume to 2L. d) Aqua Regia, 50% - to 100mL DI, add 25mL conc. HCl and 75mL HNO_3.

e) Hydroxylamine Sulphate-Sodium Chloride, 12% - Dissolve 120g Hydroxylamine Sulphate and 120g Sodium Chloride (NaCl) into DI and adjust volume to 1L.

f) Stannous Chloride, 10% - Dissolve 100g $SnCl_2$ into 100mL concentrated HCl. Warm to dissolve and add to a 1L flask containing approximately 800mL DI and adjust volume to 1L.

g) Instrument Background Solution - 60mL concentrated HNO_3 to 2L DI.

h) Potassium Dichromate ($K_2Cr_2O_7$), 10% - 100g $K_2Cr_2O_7$ to 1L DI.

i) Stock Mercury Solution, 100mg/L Hg - Dissolve 0.1678g of phenyl mercuric acetate in 1L flask of 1% H_2SO_4. Store at 4°C in an amber glass bottle.

j) Intermediate Mercury Solution, 500µg/L Hg - Pipet 5mL of the stock Mercury solution in a 1L flask of 5mL H_2SO_4, 5mL 10% $K_2Cr_2O_7$ and adjust volume to 1L with DI. Store at 4°C in an amber glass bottle.

k) Working Mercury Standards, 1.0mg/L, 0.50mg/L, 0.25mg/L, 0.05mg/L, and 0.00mg/L Hg - Pipet 5.0, 3.0, 2.0, 1.0, and 0.5mL of the Intermediate Mercury solution in a 100mL flask of 0.5mL H_2SO_4, 0.5mL 10% $K_2Cr_2O_7$ and adjust volume to 100mL with DI.

Procedure

Digestion Procedure:

a) Accurately weigh and record 0.1g of air dried (60°C) and ground soil into a 50mL falcon tube. For standards, accurately pipet 100µL of standards into each tube for the 5 standards.

b) Add 5mL of 50% Aqua Regia and mix.

c) Place in a water bath preheated @ 95°C for 2 minutes.

d) Remove samples, allow to cool for 5-10 minutes and add 32mL of 1.2% $KMnO_4$. Cap and gently mix. If sample fails to maintain a permanganate colour after the addition of the digestion solution, add 5% $KMnO_4$ in 3mL increments until the colour remains constant.

e) Place in a water bath preheated @ 95°C for 30 minutes.

f) Remove samples, allow to cool for 5-10 minutes and add 3mL of 12% hydroxylamine sulphate-sodium chloride. If extra $KMnO_4$ was added, add an appropriate addition of hydroxylamine sulphate-sodium chloride and adjust for this at time of analysis. Cap and gently mix until clear.

g) Allow elemental mercury vapour to enter sample call of AAS.

h) Record absorbance on recording device and calculate mercury concentration by comparison to calibration standards prepared and analyzed concurrently.

Calibration

According to manufacturer's specifications.

Precision

Standard reference material NBS 2704 and NRCC Best1 at concentrations of 1.47 µg/g Hg and 0.092 µg/g gave coefficients of variation of 7% and 8% respectively.

Accuracy

Standard reference material NBS 2704 and NRCC Best1 at concentrations of 1.47 µg/g Hg and 0.092 µg/g gave recoveries of 98% and 100% respectively.

Quality Control

a) Run QCA/QCB daily, run Duplicates 1 in 10, run blanks 1 in 10, run blank spikes 1 in 10. The acceptable levels should be as follows; QCA±10%, QCB±15%, duplicate±20%, and blank spikes±20%. Also run NBS 2704 and NRCC Best1 (see acceptance range from Certificate).

b) Monitor baseline drift, sensitivity drift, and carryover. Automatic correcting of these will be done by the Labtronic Data System.

References

a) Environmental Protection Agency. Method For Determination of Mercury. Cincinnati, Ohio. Method 7471 (1992).

Revision History

March 1997: Method Published in Manual Supplement #1.

December 2002: Method adopted from Supplement #1.

Revision Date: July 10, 2017

Methylmercury in Water - PBM

Parameter

Methylmercury, MeHg

Analytical Method

Distillation, Aqueous Ethylation, Purge & Trap, GC-Pyrolysis-CVAFS

Introduction

This method is applicable to the analysis of total or dissolved mono-methylmercury cation (methylmercury) in waters and seawaters.

Method Summary

This method is based on the procedures published in Method 1630 by the United States Environmental Protection Agency (US EPA).

Acid preserved samples are distilled under an inert gas flow. The pH of the distillate is adjusted to approximately 4.9 using an acetate buffer. The distillate is ethylated in a purge vessel using sodium tetraethylborate ($NaBEt_4$) to convert methylmercury to volatile methylethylmercury, which is then purged and collected on an adsorbent carbon trap. The methylethylmercury is thermally desorbed to a packed GC column for separation from other ethylated mercury species. The GC effluent is pyrolized to convert methylethylmercury to elemental mercury, with detection and quantitation by Cold Vapour Atomic Fluorescence Spectroscopy (CVAFS).

For dissolved analysis, samples are field-filtered through a 0.45 µm filter prior to preservation and distillation.

This method is performance-based. Laboratories may adopt alternative options to improve performance or efficiency provided that all stated performance requirements and prescribed (mandatory) elements are met.

MDL(s) and EMS Analyte Codes*

Analyte	CAS #	Approx. MDL (µg/L)	EMS Analyte Code
Methylmercury (as MeHg) - Total	22967-92-6	0.00006	HgMe
Methylmercury (as MeHg) - Dissolved	22967-92-6	0.00006	

The BC CSR standards for methylmercury use “as MeHg” units. Data users should be aware that test results for methylmercury may sometimes be reported in “as Hg” units. Test results in “as Hg” units may be multiplied by 1.07x to convert to “as MeHg” units.

MDL values indicated above reflect the Method Limit from EPA 1630. Lower detection limit values may be achievable.

Analysis for total mercury may be used to determine compliance with methylmercury standards, if the total mercury concentration is shown to be lower than the methylmercury standard (with consideration of concentration unit differences as described above).

EMS Method Code(s)*

Refer to EMS Parameter Dictionary on the Ministry of Environment and Climate Change Strategy website for all current EMS codes.

Matrix

Freshwater, seawater, groundwater, wastewater.

Interferences and Precautions

Contaminants present in reagents, sample containers, or sample processing equipment may cause interferences or yield artifacts. Test method conditions must be suitably monitored by routine analysis of method blanks.

Nitric acid (HNO_3) will partially decompose methylmercury during the distillation process, therefore samples preserved with nitric acid cannot be analyzed for methylmercury.

The level of hydrochloric acid (HCl) in the sample must be controlled. If too little HCl is present, the distillation will not be quantitative, but too much HCl will result in co-distillation of HCl fumes which may interfere with the ethylation process. EPA 1630 states that freshwater samples should be preserved to 0.3% - 0.5% (v/v) 11.6 M HCl and seawater samples should be preserved to 0.1% - 0.2% (v/v) 9 M H_2SO_4.

High levels of inorganic mercury have been shown to cause positive artifact formation during the distillation process. In natural waters, approximately 0.01% - 0.05% of the ambient inorganic mercury in solution may be methylated by ambient organic matter during the distillation procedure. In most environmental waters, the percent methylmercury ranges from 1% - 30% of the total mercury, so this effect is trivial, and can be ignored in most cases. In extreme cases, this effect can be prevented using solvent extraction.

Sample Handling and Preservation

Sample Containers: Fluoropolymer (FLPE) bottle or borosilicate glass bottle with FLPE cap or FLPE lined cap.

Preservation: Samples should preferably be field preserved or may be preserved at the lab within 48 hours of collection (for lab preservation, preserve within the original sample container, and equilibrate at least 16 hours before proceeding). For dissolved analysis, samples must be filtered prior to preservation. Field filtration is recommended (qualify if lab filtered).

Freshwater samples are preserved to pH < 2 with HCl (e.g., using 2 mL 1:1 HCl / 250 mL sample).

Seawaters are preserved to pH < 2 with H_2SO_4 (e.g., using 0.5 mL 1:1 M H_2SO_4 / 250 mL sample) to avoid interference from excess chloride.

Samples must be preserved within 48 hours of collection.

Stability

Holding Time: 180 days for preserved samples.

Storage: $\leq$6°C (store in an opaque container or in the dark). Freezing is permitted but is not recommended due to the potential for container breakage.

Procedure

This method provides a brief summary of the analytical method conditions for this test but does not include all information necessary to conduct the test. Refer to US EPA Method 1630 for detailed step-by-step guidance on sample preparation and analysis by this method.

This method consists of five main processes conducted in series, for the preparation and analysis of water samples for methylmercury: Distillation, ethylation, purge and trap, Gas Chromatographic (GC) separation, and detection by pyrolysis with Cold Vapour Atomic Fluorescence Spectroscopy (CVAFS).

A 45 mL aliquot of preserved sample is dispensed into a distillation vessel where a complexing agent is added to improve the recovery of methylmercury. EPA 1630 recommends using a small amount (200 µL) of 1% ammonium pyrrolidinedithiocarbamate (APDC) but studies have shown that a dilute solution of L-cysteine instead of APDC can yield slightly better recoveries (Creswell et. al. 2015). The sample and complexing agent are then distilled using a heating block temperature of 125 ± 3°C under an inert gas flow of 60 ± 20 mL/min. The distillation is complete once 40 mL of distillate has been collected. Typically, the distillation will take between 2.5 to 4.0 hours, but the exact time required will vary based on the temperature, gas flow and sample matrix of each sample. Over-distillation may result in poor recoveries due to the co-distillation of HCl fumes, which can interfere with the ethylation procedure. The distillate must be analyzed within 48 hours. If analysis cannot be done immediately after distillation, the distillate can be stored in an opaque vessel or in the dark at >0 - 6°C until analysis.

Before proceeding with the ethylation process, the pH of the distillate must be checked. EPA 1630 states that the optimal pH for the ethylation reaction is pH 4.9. If the pH of the distillate is less than 3.5, over-distillation may have occurred. Although chloride and low pH can interfere with the ethylation reaction recent studies have shown that the reaction shows little to no variation in ethylation efficiency over the pH range of 3.0-5.0 in samples with low salinity and ionic strength as seen in distillates (Mansfield & Black 2015). Therefore it is not necessary to discard distillates that are below pH 3.5 as recommended by EPA 1630. The ethylation reaction is not affected by low initial pH as long as the buffered pH of the distillate is within an optimal pH range of approximately 4.0-5.0 before the addition of the ethylating reagent.

Transfer the distillate to an appropriate reaction vessel for the ethylation step (e.g., purge and trap bubbler or purge and trap vial). Add 0.3 mL of 2 M acetate buffer to each vessel, and check that pH is within 4.0 – 5.0 (additional buffer solution may be added if necessary). Note the exact final volume of the buffered distillate for calculation purposes (in case dilutions are required). Once the buffer and sample are mixed add 0.04 mL of freshly thawed 1% sodium tetraethylborate ($NaBEt_4$) then quickly seal the reaction vessel. The reagent amounts specified are per 45 mL sample volume. Allow a minimum of 17 minutes for the ethylation reaction to complete.

The reaction vessel is attached to a purge and trap system and is purged with mercury-free nitrogen, with volatile ethylated mercury species collected on an adsorptive carbon trap. The trap is then dried to remove moisture using a secondary nitrogen flow. Once dried the ethylated mercury species are thermally desorbed from the carbon trap, and separated using a packed GC column. The separated species are then pyrolized (>700°C) to form elemental mercury, which is detected and quantitated by cold vapour atomic fluorescence spectroscopy. A minimum 5 point linear calibration is recommended.

Performance Requirements

Any analytical method options selected for this analysis must meet or exceed the performance requirements specified below.

Accuracy and Precision performance requirements are distinct from daily QC requirements, and apply to measures of long term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method re-validation studies. For Initial Validations, averages of at least 8 Lab Control Samples or RMs must be assessed. Ongoing Re-validations (performance reviews) should assess QC data encompassing longer timeframes (e.g., 6 months to 1 year). A minimum frequency of 2 years is recommended for Ongoing Re-validations.

Accuracy Requirement: Laboratories must demonstrate method accuracy (measured as average recovery) of 85-115% for Lab Control Samples or Reference Materials at concentrations above ten times the MDL.

Precision Requirement: Laboratories must demonstrate method precision equal to or better than 15% relative standard deviation for clean matrix spikes at concentrations above ten times the MDL.

Sensitivity Requirement: Where possible, the method should support Reporting Limits (and MDLs) that are less than 1/5 of applicable numerical standards. The method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

Quality Control

Summary of QC Requirements		
QC Component	Minimum Frequency	Minimum Data Quality Objectives
Method Blank (MB)	One per batch (max 20 samples)	Less than reported DL
Lab Control Sample (LCS)	One per batch (max 20 samples)	70 – 130%
Lab Duplicates (DUP)	One per batch (max 20 samples)	< 30% RPD [or within 2x reported DL for low level results]
Matrix Spike (MS)	One per batch (max 20 samples)	60 – 140%
Calibration Verification Standard (CVS) – 2nd source	One per initial calibration	85 – 115%
Continuing Calibration Verification (CCV)	One per 20 samples and at the end of each run	85 – 115%
If DQOs are not met, repeat testing or report qualified test results. DQOs do not apply to MS results where sample background exceeds spike amount.		

Prescribed Elements

The following components of this method are mandatory:

1. Samples must be preserved with HCl (freshwaters) or H_2SO_4 (seawaters). Samples preserved with HNO_3 cannot be analyzed by this method.
2. A complexing agent must be added to the sample distillation vessel to ensure distillation efficiency. Either ammonium pyrrolidinedithiocarbamate (APDC) or L-cysteine are recommended. Other complexing agents (e.g., $CuSO_4$) may be used if validated.
3. Distillation is to be carried out using a heating block temperature of 125 ± 3°C at 60 ± 20 mL/min inert gas flow.
4. Samples must be buffered using an acetate buffer (e.g., as per EPA 1630 sec 7.7) prior to the addition of the ethylating reagent.
5. Sodium tetraethylborate must be used as the ethylating reagent.
6. Sample analysis must follow the general principles and processes of the EPA 1630 method, including distillation, ethylation, and purge and trap with detection by GC-pyrolysis-CVAFS.
7. QC requirements from the Quality Control section must be completed as specified, and must pass all specified acceptance criteria, or sample data must be qualified.
8. Sample Handling, Preservation, and Stability guidelines may not be modified.

Apart from these limitations, and provided performance requirements are met, laboratories may introduce modifications to this method in order to improve quality or efficiency. Laboratories must disclose to their clients where modified or alternative methods are employed.

References

1. U.S. Environmental Protection Agency, Office of Water (2001). *Method 1630: Methyl Mercury in Water by Distillation, Aqueous Ethylation, Purge and Trap and CVAFS*. (EPA-821-R-01-020). Washington, DC.
2. Canadian Council of Ministers of the Environment, CCME. (2016). *Guidance Manual for Environmental Site Characterization in Support of Environmental and Human Health Risk Assessment*, Volume 4 Analytical Methods. (ISBN 978-1-77202-032-8).
3. Creswell, J., P. Kilner and C. Davies (2015), *2015 Brooks Rand Instruments Interlaboratory Comparison Study for Total Mercury and Methylmercury (Intercomp 2015)*, Brooks Rand Instruments, Seattle, WA USA. http://www.brooksrandinc.com/content/uploads/2015/10/Interlaboratory-Comparison-Study-for-Total-Mercury-and-Methylmercury-report.pdf
4. Mansfield, C.R., & Black, F. J. (2015). *Quantification of monomethylmercury in natural waters by direct ethylation: Interference characterization and method optimization*. Limnol. Oceanogr.: Methods 13 (2), 81-91. doi: 10.1002/lom3.10009.

Revision History

July 10, 2017 New BC Lab Manual method in support of 2017 CSR changes.

Methylmercury in Soil/Sediment - PBM

Parameter	Methylmercury, MeHg
Analytical Method	Acidic Leach, Solvent Extraction, Aqueous Back-Extraction, Aqueous Ethylation, Purge & Trap, GC-Pyrolysis-CVAFS
Introduction	This method is applicable to the analysis of mono-methylmercury cation (methylmercury) in soils and sediments. Soil and sediment samples contain relatively higher concentrations of inorganic mercury compared to water samples, which can form interfering artifacts when preparing samples by distillation. To minimize the risk of these interfering artifacts a solvent extraction is the preferred method for preparing soil/sediment samples for methylmercury analysis.
Method Summary	This method is based on the United States Geological Survey (USGS) procedures published by DeWild *et. al.* (Method 5A – 7). Samples are prepared by leaching the soil/sediment with an acidic potassium bromide and copper sulfate solution to release organo-mercury species from inorganic complexes. Methylmercury is then extracted into dichloromethane. An aliquot of the dichloromethane extract is then back-extracted into ultra-pure deionized water by purging with argon. The water extract is then ethylated in a purge vessel using sodium tetraethylborate ($NaBEt_4$) to convert methylmercury to volatile methylethylmercury, which is then purged and collected on an adsorbent carbon trap. The methylethylmercury is thermally desorbed to a packed GC column for separation from other ethylated mercury species. The GC effluent is pyrolized to convert methylethylmercury to elemental mercury, with detection and quantitation by Cold Vapour Atomic Fluorescence Spectroscopy (CVAFS). Results are reported on a dry weight basis. This method is performance-based. Laboratories may adopt alternative options to improve performance or efficiency provided that all stated performance requirements and prescribed (mandatory) elements are met.

MDL(s) and EMS Analyte Codes*

Analyte	Approx. MDL	CAS #	EMS Analyte Code
Methylmercury (as MeHg)	0.00008 mg/Kg	22967-92-6	HgMe

The BC CSR standards for methylmercury use “as MeHg” units. Data users should be aware that test results for methylmercury may sometimes be reported in “as Hg” units. Test results in “as Hg” units may be multiplied by 1.07x to convert to “as MeHg” units.

Analysis for unspeciated mercury in soils (i.e. sum of all species, using the BC SALM digestion method) may be used to determine compliance with methylmercury standards, if the total (unspeciated) mercury concentration is shown to be lower than the methylmercury standard (with consideration of concentration unit differences as described above).

EMS Method Code(s)*	Refer to EMS Parameter Dictionary on the Ministry of Environment and Climate Change Strategy website for all current EMS codes.
Matrix	Soil, sediment.

Interferences and Precautions

Contaminants present in solvents, reagents, sample containers or sample processing equipment may cause interferences or yield artifacts. Test method conditions must be suitably monitored by routine analysis of method blanks.

Interference (artifact formation) from high levels of inorganic mercury is avoided by preparing soil and sediment samples by solvent extraction instead of distillation.

Sample Handling and Preservation

Sample Containers: glass jar with Teflon™ lined lid, or plastic (e.g., HDPE).

Preservation: None.

Stability

Holding Time: 28 Days.

Storage: ≤ 6°C. Freezing is permitted but is not recommended due to the potential for container breakage.

Procedure

This method provides a brief summary of the analytical method conditions for this test but does not include all information necessary to conduct the test. Refer to USGS Method 5A-7 for detailed step by step guidance on sample preparation, and to US EPA Method 1630 for detail guidance on ethylation and analysis.

Prior to sub-sampling, soil/sediment samples must be well-mixed using a mercury-free spatula to ensure homogeneity prior to sub-sampling. Take a representative sub-sample and analyze for moisture content.

Accurately weigh a second sub-sample of 2.0 ± 0.2 g into a clean Teflon$^{\mathrm{TM}}$ centrifuge tube for extraction. Add 10.0 mL of 18% potassium bromide (KBr) extraction solution and 2.0 mL of 1 M copper sulfate ($CuSO_4$) reagent to the sample. Cap the tube and briefly shake to mix, then let stand at room temperature for at least 1 hour. After the 1 hour leaching period, add 20 mL of dichloromethane (CH_2Cl_2) to each tube, cap and then shake vigorously for 1 additional hour. After shaking, centrifuge the samples at ~2000G (~3000 rpm for a typical benchtop centrifuge) for 20 minutes to break any emulsions. Use a Pasteur pipette to remove and discard the aqueous (top) layer. Prepare the back extraction vial (either Teflon or glass) by addition of 40mL of ultra-pure deionized water. Accurately transfer 2.00 mL of the organic layer into the back-extraction vial, then, in a fumehood, place the vial in a heating block or water bath set to 45°C. Purge the sample with mercury-free nitrogen gas at a flow rate of 100 mL/min until all the dichloromethane has been purged away. The extract is now ready for analysis and can be stored in an opaque container or in the dark at 4°C for up to 48 hours.

Transfer the water extract to an appropriate reaction vessel for the ethylation step (e.g., purge and trap bubbler or purge and trap vial). Add 0.3 mL of 2M acetate buffer to each vessel. Once the buffer and sample are mixed, add 0.05 mL of freshly thawed 1% sodium tetraethylborate ($NaBEt_4$) then quickly seal the reaction vessel. The reagent amounts specified are per 40-50 mL volume of aqueous extract. Allow a minimum of 17 minutes for the ethylation reaction to complete.

The reaction vessel is attached to a purge and trap system and is purged with mercury-free nitrogen, and the volatile ethylated mercury species are collected on a carbon trap. The trap is then dried to remove moisture using a secondary nitrogen flow. Once dried the ethylated mercury species are thermally desorbed from the carbon trap and separated using a packed GC column. The separated species are then pyrolized (>700°C) to elemental mercury, which is detected and quantified by cold vapour atomic fluorescence spectroscopy. A minimum 5 point linear calibration is recommended.

Performance Requirements

Any analytical method options selected for this analysis must meet or exceed the performance requirements specified below.

Accuracy and Precision requirements are distinct from daily QC requirements and apply to measures of long term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method re-validation studies. For Initial Validations, averages of at least 8 Lab Control Samples or RMs must be assessed. Ongoing Re-validations (performance reviews) should assess QC data encompassing longer timeframes (e.g., 6 months to 1 year). A minimum frequency of 2 years is recommended for Ongoing Re-validations.

Accuracy Requirement: Laboratories must demonstrate method accuracy (measured as average recovery) of 85-115% for Lab Control Samples or Certified Reference Materials at concentrations above ten times the MDL.

Precision Requirement: Laboratories must demonstrate method precision equal to or better than 15% relative standard deviation for clean matrix spikes at concentrations above ten times the MDL.

Sensitivity Requirement: Where possible, the method should support Reporting Limits (and MDLs) that are less than 1/5 of applicable numerical standards. The method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

Quality Control

Summary of QC Requirements		
QC Component	Minimum Frequency	Minimum Data Quality Objectives
Method Blank (MB)	One per batch (max 20 samples)	Less than reported DL
Lab Control Sample (LCS)	One per batch (max 20 samples)	70 – 130%
Lab Duplicates (DUP)	One per batch (max 20 samples)	30% RPD [or within 2x reported DL for low level results]
Matrix Spike (MS) or Reference Material (RM)	One per batch (max 20 samples)	60 – 140%
Calibration Verification Standard (CVS) – 2nd source	One per initial calibration	85 – 115%
Continuing Calibration Verification (CCV)	One per 20 samples and at the end of each run	85 – 115%
If DQOs are not met, repeat testing or report qualified test results. DQOs do not apply to MS results where sample background exceeds spike amount.		

Prescribed Elements

The following components of this method are mandatory:

1. A separate sub-sample must be used for moisture content analysis. Samples that have been dried cannot be analyzed by this method.
2. The minimum sample amount used for the extraction is 1.8 g wet weight, based on a nominal weight of 2.0 ± 0.2 g. This amount has been scaled up from the USGS reference method to improve homogeneity of sub-sampling.
3. Soil samples must utilize an aqueous acidic extraction to release methylmercury that may be bound to inorganic complexes, prior to solvent extraction.
4. Analysis of extracts by the EPA 1630 method (aqueous phase ethylation, purge and trap, with detection by GC-pyrolysis-CVAFS) is recommended, but alternate detection techniques may be used if DQOs and other prescribed elements are met.
5. Methods using detection by the EPA 1630 method must use an acetate buffer (see EPA 1630 sec 7.7) prior to ethylation with sodium tetraethylborate.
6. QC requirements from the Quality Control section must be completed as specified, and must pass all specified acceptance criteria, or sample data must be qualified.
7. Sample Handling, Preservation, and Stability section guidelines may not be modified.

Apart from these limitations, and provided performance requirements are met, laboratories may introduce modifications to this method in order to improve quality or efficiency. Laboratories must disclose to their clients where modified or alternative methods are employed.

References

DeWild, J.F., Olund, S. D., Olson, M. L., and Tate, M. T. (2004). *Methods for the Preparation and Analysis of Solids and Suspended Solids for Methylmercury*. Techniques and Methods 5-A7. Reston, VA: U.S. Department of the Interior, U.S. Geological Survey.

U.S. Environmental Protection Agency, Office of Water (2001). *Method 1630: Methyl Mercury in Water by Distillation, Aqueous Ethylation, Purge and Trap and CVAFS*. (EPA-821-R-01-020). Washington, DC.

Canadian Council of Ministers of the Environment, CCME. (2016). *Guidance Manual for Environmental Site Characterization in Support of Environmental and Human Health Risk Assessment*, Volume 4 Analytical Methods. (ISBN 978-1-77202-032-8).

Revision History

July 10, 2017	New BC Lab Manual Method in support of 2017 CSR updates.

Molybdenum (Atomic Absorption - Direct Aspiration)

Parameter	Molybdenum, total Molybdenum, dissolved	
Sample Preparation	See section 1.0, the sample preparation section.	
Analytical Method	See section 2.1, the AA methods section.	
EMS Code	FA: HNO_3: AA (total)	Mo-T X073
	LA: HNO_3: AA (total)	Mo-T X351
	FF, FA: HNO_3: AA (dissolved)	Mo-D X203
	LF, LA: HNO_3: AA (dissolved)	Mo-D X085
Introduction	Molybdenum is found in the soil and is an important trace element for the growth of grasses and vegetables. Its uses include pigments for printing, inks, alloying agent in steels and cast iron, high temperature alloys, tool steels, catalysts, solid lubricants, and special batteries.	
Method Summary	Aqueous solutions of metals are aspirated into a flame and atomized. The absorption of light, at a wavelength specific to the element being analyzed, is measured and the concentration of the analyte is determined by comparison with standards.	
MDL	Given an aqueous sample free of interferences, the instrumental performance characteristics are: MDL: 0.1 mg/L Range: 0.1 - 40.0 mg/L See Table C-1 in section 2.1, the AA methods section, for additional information.	
Matrix	Water, wastewater, marine water.	
Interferences and Precautions	See section 2.1.4 of the AA methods section of this manual. Interferences in an air/acetylene flame from Ca, Sr, SO_4, and Fe are severe. These interferences are greatly reduced in the nitrous oxide flame and by making the samples and standards 1,000 mg/L in aluminum.	
Sample Handling and Preservation	See section 1.0, the sample preparation section of this manual.	
Stability	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.	
Instrument Parameters	Source: Mo hollow cathode lamp Wavelength: 313.3 nm Type of flame: nitrous oxide/acetylene Background correction: recommended	
Apparatus, Materials and Reagents	See sections 2.1.5 and 2.1.6 of this manual.	
Precision	None listed.	
Accuracy	None listed.	
Quality Control	See section 2.1.9, QA/QC Guidelines in this manual.	

References

a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992, Method 3111 B/D.

b) Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods (Revised). Publication #SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd Edition 1990.

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes. Sample matrix added.

Revision Date: December 31, 2000

Molybdenum (Atomic Absorption - Graphite Furnace)

Parameter	Molybdenum, total Molybdenum, dissolved
Sample Preparation	See section 1.0, the sample preparation section.
Analytical Method	See section 2.1, the AA methods section.
EMS Code	FA: HNO_3: GFAA (total) Mo-T X072 LA: HNO_3: GFAA (total) Mo-T X179 FF, FA: HNO_3: GFAA (dissolved) Mo-D X116 LF, LA: HNO_3: GFAA (dissolved) Mo-D X357
Introduction	Molybdenum is found in the soil and is an important trace element for the growth of grasses and vegetables. Its uses include pigments for printing, inks, alloying agent in steels and cast iron, high temperature alloys, tool steels, catalysts, solid lubricants, and special batteries.
Method Summary	A discrete sample volume is introduced into the graphite sample boat which is heated in stages to accommodate drying of the solution, charring and volatilization of organics and other matrix components, and finally, atomization of the analyte into the light path of the spectrometer. The absorption of light, at a wavelength specific to the element being analyzed, is measured and the concentration of the analyte is determined by comparison with standards.
MDL	Given an aqueous sample free of interferences, the instrumental performance characteristics are: MDL: 0.001 mg/L Range: 0.001 - 0.06 mg/L See Table C-1 in section 2.1, the AA methods section, for additional information.
Matrix	Water, wastewater, marine water.
Interferences and Precautions	See section 2.1.4 of the AA methods section of this manual.
Sample Handling and Preservation	See section 1.0, the sample preparation section of this manual.
Stability	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
Instrument Parameters	Source: Mo hollow cathode lamp. Wavelength: 313.3 nm Background correction: recommended
Apparatus, Materials and Reagents	See sections 2.1.5 and 2.1.6 of this manual.
Precision	None listed.
Accuracy	None listed.
Quality Control	See section 2.1.9, QA/QC Guidelines in this manual.

References	a)	Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992, Method 3111 B/D.
	b)	Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods (Revised). Publication #SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd Edition 1990.

Revision History	February 14, 1994:	Publication in 1994 Laboratory Manual.
	December 31, 2000:	SEAM codes replaced by EMS codes. Sample matrix added.

Nickel (Atomic Absorption - Direct Aspiration)

Parameter	Nickel, total Nickel, dissolved
Sample Preparation	See section 1.0, the sample preparation section.
Analytical Method	See section 2.1, the AA methods section.
EMS Code	FA: HNO_3: AA (total) Ni-T X073 LA: HNO_3: AA (total) Ni-T X351 FF, FA: HNO_3: AA (dissolved) Ni-D X203 LF, LA: HNO_3: AA (dissolved) Ni-D X085
Introduction	Nickel's principal ores are of two types; sulfide and oxide. Its uses include electroplated protective coatings, alloys (low-alloy steels, stainless steel, copper and brass, permanent magnets, electrical resistance alloys), electroformed coatings, alkaline storage batteries, fuel cell electrodes, and as a catalyst.
Method Summary	Aqueous solutions of metals are aspirated into a flame and atomized. The absorption of light, at a wavelength specific to the element being analyzed, is measured and the concentration of the analyte is determined by comparison with standards.
MDL	Given an aqueous sample free of interferences, the instrumental performance characteristics are: MDL: 0.04 mg/L Range: 0.04-5.0 mg/L See Table C-1 in section 2.1, the AA methods section, for additional information.
Matrix	Water, wastewater, marine water.
Interferences and Precautions	See section 2.1.4 of the AA methods section of this manual. High concentrations of iron, cobalt, or chromium may interfere, requiring either matrix matching or use of a nitrousoxide-acetylene flame.
Sample Handling and Preservation	See section 1.0, the sample preparation section of this manual.
Stability	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
Instrument Parameters	Source: Ni hollow cathode lamp Wavelength: 232.0 nm (primary); 352.4 nm (alternate) Type of Flame: air/acetylene Background Correction: recommended
Apparatus, Materials and Reagents	See sections 2.1.5 and 2.1.6 of this manual.
Precision	None listed.
Accuracy	None listed.
Quality Control	See section 2.1.9, QA/QC Guidelines in this manual.

References	a)	Standard Methods for the Examination of Water and Wastewater APHA, AWWA, WEF, 18th edition, 1992, Method 3111 B/D.
	b)	Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods (Revised). Publication #SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd Edition 1990.

Revision History	February 14, 1994:	Publication in 1994 Laboratory Manual.
	December 31, 2000:	SEAM codes replaced by EMS codes. Sample matrix added.

Revision Date: December 31, 2000

Nickel (Atomic Absorption - Graphite Furnace)

Parameter	Nickel, total Nickel, dissolved	
Sample Preparation	See section 1.0, the sample preparation section.	
Analytical Method	See section 2.1, the AA methods section.	
EMS Code	FA: HNO_3: GFAA (total)	Ni-T X072
	LA: HNO_3: GFAA (total)	Ni-T X179
	FF, FA: HNO_3: GFAA (dissolved)	Ni-D X116
	LF, LA: HNO_3: GFAA (dissolved)	Ni-D X357
Introduction	Nickel's principal ores are of two types: sulfide and oxide. Its uses include electroplated protective coatings, alloys (low-alloy steels, stainless steel, copper and brass, permanent magnets, electrical resistance alloys), electroformed coatings, alkaline storage batteries, fuel cell electrodes and as a catalyst.	
Method Summary	A discrete sample volume is introduced into the graphite sample boat which is heated in stages to accommodate drying of the solution, charring and volatilization of organics and other matrix components, and finally, atomization of the analyte into the light path of the spectrometer. The absorption of light, at a wavelength specific to the element being analyzed, is measured and the concentration of the analyte is determined by comparison with standards.	
MDL	Given an aqueous sample free of interferences, the instrumental performance characteristics are: MDL: 0.001 mg/L Range: 0.001-0.100 mg/L See Table C-1 in section 2.1, the AA methods section, for additional information.	
Matrix	Water, wastewater, marine water.	
Interferences and Precautions	See section 2.1.4 of the AA methods section of this manual.	
Sample Handling and Preservation	See section 1.0, the sample preparation section of this manual.	
Stability	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.	
Instrument Parameters	Source: Ni hollow cathode lamp Wavelength: 232.0 nm Background Correction: recommended	
Apparatus, Materials and Reagents	See section 2.1.5 and 2.1.6 of this manual.	
Precision	None listed.	
Accuracy	None listed.	
Quality Control	See section 2.1.9, QA/QC Guidelines in this manual.	

References

a) Standard Method for the Examination of Water and Wastewater APHA, AWWA, WEF, 18th edition, 1992, Method 3113B.

b) Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods (Revised). Publication #SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd Edition 1990.

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes. Sample matrix added.

Potassium (Atomic Absorption - Direct Aspiration)

Parameter	Potassium, total Potassium, dissolved	
Sample Preparation	See section 1.0, the sample preparation section.	
Analytical Method	See section 2.1, the AA methods section.	
EMS Code	FA: HNO_3: AA (total)	K-TX073
	LA: HNO_3: AA (total)	K-TX351
	FF, FA: HNO_3: AA (dissolved)	K-DX203
	LF, LA: HNO_3: AA (dissolved)	K-DX085
Method Summary	Aqueous solutions of metals are aspirated into a flame and atomized. The absorption of light, at a wavelength specific to the element being analyzed, is measured and the concentration of the analyte is determined by comparison with standards.	
MDL	Given an aqueous sample free of interferences, the instrumental performance characteristics are: MDL: 0.01 mg/L Range: 0.01-2.0 mg/L See Table C-1 in section 2.1, the AA methods section, for additional information.	
Matrix	Water, wastewater, marine water.	
Interferences and Precautions	See section 2.1.4 of the AA methods section of this manual. Ionization should be controlled by the addition of lanthanum chloride to a level of 0.1%.	
Sample Handling and Preservation	See section 1.0, the sample preparation section of this manual.	
Stability	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.	
Instrument Parameters	Source: K hollow cathode lamp Wavelength: 766.5 nm (primary); 404.4 nm (alternate) Type of Flame: air/acetylene Background Correction: recommended	
Apparatus, Materials and Reagents	See sections 2.1.5 and 2.1.6 of this manual.	
Precision	None listed.	
Accuracy	None listed.	
Quality Control	See section 2.1.9, QA/QC Guidelines in this manual.	

References	a)	Standard Methods for the Examination of Water and Wastewater APHA, AWWA, WEF, 18th edition, 1992, Method 3111 B/D.
	b)	Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods (Revised). Publication #SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd Edition 1990.
Revision History	February 14, 1994:	Publication in 1994 Laboratory Manual.
	December 31, 2000:	SEAM codes replaced by EMS codes. Sample matrix added. Sample matrix added.

Revision Date: December 31, 2000

Selenium (Atomic Absorption - Direct Aspiration)

Parameter	Selenium, total Selenium, dissolved	
Sample Preparation	See section 1.0, the sample preparation section.	
Analytical Method	See section 2.1, the AA methods section.	
EMS Code	FA: HNO_3: AA (total)	Se-TX073
	LA: HNO_3: AA (total)	Se-TX351
	FF, FA: HNO_3: AA (dissolved)	Se-DX203
	LF, LA: HNO_3: AA (dissolved)	Se-DX085
Introduction	The toxicity of selenium is similar to that of arsenic. It has also been cited as a potential carcinogen. The presence of selenium in water usually indicates industrial pollution.	
Method Summary	Aqueous solutions of metals are aspirated into a flame and atomized. The absorption of light, at a wavelength specific to the element being analyzed, is measured and the concentration of the analyte is determined by comparison with standards.	
MDL	Given an aqueous sample free of interferences, the instrumental performance characteristics are: MDL: 0.20 mg/L Range: 0.20-20 mg/L See Table C-1 in section 2.1, the AA methods section, for additional information.	
Matrix	Water, wastewater, marine water.	
Interferences and Precautions	See section 2.1.4 of the AA methods section of this manual. The air-acetylene flame absorbs or scatters more than 50% of the radiation from the light source at the 196.0 nm selenium line. Due to this effect, a background corrector should be used to improve the signal-to-noise ratio. Flame absorption is reduced with the use of the nitrous oxide-acetylene flame, although sensitivity is reduced.	
Sample Handling and Preservation	See section 1.0, the sample preparation section of this manual.	
Stability	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.	
Instrument Parameters	Source: Se EDL or hollow cathode lamp Wavelength: 196.0 nm Type of Flame: air/acetylene Background Correction: recommended	
Apparatus, Materials and Reagents	See section 2.1.5 and 2.1.6 of this manual.	
Precision	None listed.	
Accuracy	None listed.	
Quality Control	See section 2.1.9, QA/QC Guidelines in this manual.	

References

a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 18th edition, 1992.

b) Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods (Revised). Publication #SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd Edition 1990.

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes. Sample matrix added. Sample matrix added.

Selenium (Atomic Absorption - Graphite Furnace)

Parameter	Selenium, total Selenium, dissolved
Sample Preparation	See section 1.0, the sample preparation section.
Analytical Method	See section 2.1, the AA methods section.
EMS Code	FA: HNO_3: GFAA (total) Se-T X072 LA: HNO_3: GFAA (total) Se-T X179 FF, FA: HNO_3: GFAA (dissolved) Se-D X116 LF, LA: HNO_3: GFAA (dissolved) Se-D X357
Introduction	The toxicity of selenium is similar to that of arsenic. It has also been cited as a potential carcinogen. The presence of selenium in water usually indicates industrial pollution.
Method Summary	A discrete sample volume is introduced into the graphite sample boat which is heated in stages to accommodate drying of the solution, charring and volatilization of organics and other matrix components, and finally, atomization of the analyte into the light path of the spectrometer. The absorption of light, at a wavelength specific to the element being analyzed, is measured and the concentration of the analyte is determined by comparison with standards.
MDL	Given an aqueous sample free of interferences, the instrumental performance characteristics are: MDL: 0.002 mg/L Range: 0.002-0.100 mg/L See Table C-1 in section 2.1, the AA methods section, for additional information.
Matrix	Water, wastewater, marine water.
Interferences and Precautions	See section 2.1.4 of the AA methods section of this manual. Elemental selenium and many of its compounds are volatile; therefore, samples may be subject to losses of selenium during sample preparation. Spike samples and relevant standard reference materials should be processed to determine if the chosen dissolution method is appropriate. Likewise, caution must be employed during the selection of temperatures and times for the dry and char (ash) cycles. A nickel nitrate solution must be added to all digestates prior to analysis to minimize volatilization losses during drying and ashing. In addition to the normal interferences experienced during graphite furnace analysis, selenium analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Selenium analysis is particularly susceptible to these problems because of its low analytical wavelength (196.0 nm). Simultaneous background correction is required to avoid erroneously high results. High iron levels can give overcorrection with deuterium background. Zeeman background correction can be useful in this situation. If the analyte is not completely volatilized and removed from the furnace during atomization, memory effects will occur. If this situation is detected, the tube should be cleaned by operating the furnace at full power at regular intervals in the analytical scheme. Selenium analysis suffers interference from chlorides (>800 mg/L) and sulfate (>200 mg/L). The addition of nickel nitrate, such that the final concentration is 1% nickel, will lessen this interference.

Sample Handling and Preservation	See section 1.0, the sample preparation section of this manual.
Stability	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
Instrument Parameters	Source: Se EDL or hollow cathode lamp Wavelength: 196.0 nm Background Correction: recommended
Apparatus, Materials and Reagents	See section 2.1.5 and 2.1.6 of this manual.
Precision	None listed.
Accuracy	None listed.
Quality Control	See section 2.1.9, QA/QC Guidelines in this manual.
References	a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 18th edition 1992. b) Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods (Revised). Publication #SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd Edition 1990.
Revision History	February 14, 1994: Publication in 1994 Laboratory Manual. December 31, 2000: SEAM codes replaced by EMS codes. Sample matrix added.

Selenium (Atomic Absorption - Gaseous Hydride)

Parameter	Selenium, total Selenium, dissolved	
Sample Preparation	See section 1.0, the sample preparation section.	
Analytical Method	See section 2.1, the AA methods section, and section 2.2 the hydride AA method section.	
EMS Code	FA: HNO_3: HVAAS (total)	Se-T X289
	LA: HNO_3: HVAAS (total)	Se-T X354
	FA: HCl: HVAAS (total)	Se-T X345
	LA: HCl: HVAAS (total)	Se-T X355
	FF, FA: HNO_3: HVAAS (dissolved)	Se-D X202
	LF, LA: HNO_3: HVAAS (dissolved)	Se-D X359
	FF, FA: HCl: HVAAS (dissolved)	Se-D X348
	LF, LA: HCl: HVAAS (dissolved)	Se-D X360
Introduction	The toxicity of selenium is similar to that of arsenic. It has also been cited as a potential carcinogen. The presence of selenium in water usually indicates industrial pollution.	
Method Summary	Selenium is converted to a gaseous hydride and analyzed by atomization in a heated quartz tube. Conversion to hydride allows selenium to be detected with greater sensitivity.	
MDL	Given an aqueous sample free of interferences, the instrumental performance characteristics are: MDL: 0.0005 mg/L Range: 0.0005-0.020 mg/L See Table C-1 in section 2.1, the AA methods section, for additional information.	
Matrix	Water, wastewater, marine water.	
Interferences and Precautions	See section 2.2, the hydride AA methods section of this manual. High concentrations of chromium, cobalt, copper, mercury, molybdenum, nickel, and silver can cause analytical interferences. Traces of nitric acid left following the sample work-up can result in analytical interferences. Elemental selenium and many of its compounds are volatile; therefore, certain samples may be subject to losses of selenium during sample preparation.	
Sample Handling and Preservation	See section 1.0, the sample preparation section of this manual.	
Stability	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.	
Instrument Parameters	Source: Se EDL or hollow cathode lamp Wavelength: 196.0 nm Background Correction: not required	
Apparatus, Materials and Reagents	See section 2.2, the hydride AA methods section in this manual.	
Precision	None listed.	
Accuracy	None listed.	
Quality Control	See section 2.1.9, QA/QC Guidelines in this manual.	

References

a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 18th edition, 1992.

b) Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods (Revised). Publication #SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd Edition 1990.

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes. Sample matrix added.

Selenium (Atomic Emission - Inductively Coupled Argon Plasma {ICAP})

Parameter	Selenium, total Selenium, dissolved
Sample Preparation	See section 1.0, the sample preparation section.
Analytical Method	See section 2.4, the ICP-AES method section.
EMS Code	FA: HNO_3: ICAP (total) Se-T X349 LA: HNO_3: ICAP (total) Se-T X352 FF, FA: HNO_3: ICAP (dissolved) Se-D X350 LF, LA: HNO_3: ICAP (dissolved) Se-D X356
Introduction	The toxicity of selenium is similar to that of arsenic. It has also been cited as a potential carcinogen. The presence of selenium in water usually indicates industrial pollution.
Method Summary	Aqueous solutions of metals are converted to aerosols in the nebulizer of the ICP and injected directly into a high temperature plasma (6000 to 8000°K). This highly efficient ionization produces ionic emission spectra and wavelengths specific to the elements of interest can be monitored either simultaneously or sequentially.
MDL	Given an aqueous sample free of interferences, the instrumental performance characteristics are: MDL: 0.050 mg/L Range: 0.05-1000 mg/L See Table C-2 in section 2.4, the ICP-AES method section, for additional information.
Matrix	Water, wastewater, marine water.
Interferences and Precautions	See section 2.4, the ICP-AES section of this manual.
Sample Handling and Preservation	See section 1.0, the sample preparation section of this manual.
Stability	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
Instrument Parameters	Wavelength: 196.0 nm (primary) Background Correction: recommended
Apparatus, Materials and Reagents	See section 2.4, of the ICP-AES methods section in this manual.
Precision	None listed.
Accuracy	None listed.
Quality Control	See section 2.1.9, QA/QC Guidelines in this manual.

References	a)	Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 18th edition, 1992.
	b)	Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods (Revised). Publication #SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd Edition 1990.
Revision History	February 14, 1994:	Publication in 1994 Laboratory Manual.
	December 31, 2000:	SEAM codes replaced by EMS codes. Sample matrix added.

Silver (Atomic Absorption - Direct Aspiration)

Parameter	Silver, total Silver, dissolved	
Sample Preparation	See section 1.0, the sample preparation section.	
Analytical Method	See section 2.1, the AA methods section.	
EMS Code	FA: HNO_3: AA (total) LA: HNO_3: AA (total) FF, FA: HNO_3: AA (dissolved) LF, LA: HNO_3: AA (dissolved)	Ag-T X073 Ag-T X351 Ag-D X203 Ag-D X085
Introduction	Uses of silver include photographic chemicals, lining vats and other equipment for chemical reaction vessels, water distillation, mirrors, electric conductors, sterilants, water purification, special batteries, solar cells, table cutlery, jewellery and dental amalgams.	
Method Summary	Aqueous solutions of metals are aspirated into a flame and atomized. The absorption of light, at a wavelength specific to the element being analyzed, is measured and the concentration of the analyte is determined by comparison with standards.	
MDL	Given an aqueous sample free of interferences, the instrumental performance characteristics are: MDL: 0.01 mg/L Range: 0.01 - 4 mg/L See Table C-1 in section 2.1, the AA methods section, for additional information.	
Matrix	Water, wastewater, marine water.	
Interferences and Precautions	See section 2.1.4 of the AA methods section of this manual. Background correction is required because nonspecific absorption and light scattering may occur at the analytical wavelength. Silver nitrate solutions are light-sensitive and have a tendency to plate out on container walls. Therefore, silver standards should be stored in brown bottles. Dilutions of the stock/standard should be discarded after use, as concentrations below 10 mg/L are not stable over a long period of time. Silver chloride is insoluble; therefore, hydrochloric acid should be avoided unless the silver is already in solution as a chloride complex.	
Sample Handling and Preservation	See section 1.0, the sample preparation section of this manual.	
Stability	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months. Silver nitrate ($AgNO_3$) is light sensitive and known to plate out on container walls. Therefore, minimize the sample exposure to light or store the samples in brown bottles.	
Instrument Parameters	Source: Ag hollow cathode lamp Wavelength: 328.1 nm Type of Flame: air/acetylene Background Correction: recommended	

Apparatus, Materials and Reagents	See section 2.1.5 and 2.1.6 of this manual.	
Precision	None listed.	
Accuracy	None listed.	
Quality Control	See section 2.1.9, QA/QC Guidelines in this manual.	
References	a) Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 272.1. b) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 18th edition, 1992. c) Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods (Revised). Publication #SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd Edition 1990.	
Revision History	February 14, 1994:	Publication in 1994 Laboratory Manual.
	December 31, 2000:	SEAM codes replaced by EMS codes. Sample matrix added.

Silver (Atomic Absorption - Graphite Furnace)

Parameter

Silver, total
Silver, dissolved

Sample Preparation

See section 1.0, the sample preparation section.

Analytical Method

See section 2.1, the AA methods section.

EMS Code

FA: HNO_3: GFAA (total)	Ag-T X072
LA: HNO_3: GFAA (total)	Ag-T X179
FF, FA: HNO_3: GFAA (dissolved)	Ag-D X116
LF, LA: HNO_3: GFAA (dissolved)	Ag-D X357

Introduction

Uses of silver include photographic chemicals, lining vats and other equipment for chemical reaction vessels, water distillation, mirrors, electric conductors, sterilants, water purification, special batteries, solar cells, table cutlery, jewellery and dental amalgams.

Method Summary

A discrete sample volume is introduced into the graphite sample boat which is heated in stages to accommodate drying of the solution, charring and volatilization of organics and other matrix components, and finally, atomization of the analyte into the light path of the spectrometer. The absorption of light, at a wavelength specific to the element being analyzed, is measured and the concentration of the analyte is determined by comparison with standards.

MDL

Given an aqueous sample free of interferences, the instrumental performance characteristics are:

MDL: 0.0002 mg/L

Range: 0.0002-0.005 mg/L

See Table C-1 in section 2.1, the AA methods section, for additional information.

Matrix

Water, wastewater, marine water.

Interferences and Precautions

See section 2.1.4 of the AA methods section of this manual. Background correction is required because nonspecific absorption and light scattering may occur at the analytical wavelength.

Silver nitrate solutions are light-sensitive and have a tendency to plate out on container walls. Therefore, silver standards should be stored in brown bottles. Dilutions of the stock/standard should be discarded after use, as concentrations below 10 mg/L are not stable over a long period of time.

Silver chloride is insoluble; therefore, hydrochloric acid should be avoided unless the silver is already in solution as a chloride complex.

Sample Handling and Preservation

See section 1.0, the sample preparation section of this manual.

Stability

An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.

Silver nitrate ($AgNO_3$) is light sensitive and known to plate out on container walls. Therefore, minimize the sample exposure to light or store the samples in brown bottles.

Instrument Parameters

Source: Ag hollow cathode lamp

Wavelength: 328.1 nm

Background Correction: recommended

Apparatus, Materials and Reagents	See section 2.1.5 and 2.1.6 of this manual.
Precision	None listed.
Accuracy	None listed.
Quality Control	See section 2.1.9, QA/QC Guidelines in this manual.
References	a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992, Method 3113B. b) Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055,December 1982, Method 272.2. c) Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods (Revised). Publication #SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd Edition 1990.
Revision History	February 14, 1994: Publication in 1994 Laboratory Manual. December 31, 2000: SEAM codes replaced by EMS codes. Sample matrix added.

Sodium (Atomic Absorption - Direct Aspiration)

Parameter	Sodium, total Sodium, dissolved
Sample Preparation	See section 1.0, the sample preparation section.
Analytical Method	See section 2.1, the AA methods section.
EMS Code	FA: HNO_3: AA (total) Na-T X073 LA: HNO_3: AA (total) Na-T X351 FF, FA: HNO_3: AA (dissolved) Na-D X203 LF, LA: HNO_3: AA (dissolved) Na-D X085
Method Summary	Aqueous solutions of metals are aspirated into a flame and atomized. The absorption of light, at a wavelength specific to the element being analyzed, is measured and the concentration of the analyte is determined by comparison with standards.
MDL	Given an aqueous sample free of interferences, the instrumental performance characteristics are: MDL: 0.002 mg/L Range: 0.002-1.0 mg/L See Table C-1 in section 2.1, the AA methods section, for additional information.
Matrix	Water, wastewater, marine water.
Interferences and Precautions	See section 2.1.4 of the AA methods section of this manual. Ionization should be controlled by the addition of potassium chloride to a level of 0.1%.
Sample Handling and Preservation	See section 1.0, the sample preparation section of this manual.
Stability	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
Instrument Parameters	Source: Na hollow cathode lamp Wavelength: 589.0 nm (primary); 330.2 nm (alternate) Type of Flame: air/acetylene Background Correction: recommended
Apparatus, Materials and Reagents	See sections 2.1.5 and 2.1.6 of this manual.
Precision	None listed.
Accuracy	None listed.
Quality Control	See section 2.1.9, QA/QC Guidelines in this manual.
References	a) Standard Methods for the Examination of Water and Wastewater APHA, AWWA, WEF, 18th edition, 1992, Method 3111 B/D. b) Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods (Revised). Publication #SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd Edition 1990.
Revision History	February 14, 1994: Publication in 1994 Laboratory Manual. December 31, 2000: SEAM codes replaced by EMS codes. Sample matrix added.

Tin (Atomic Absorption - Direct Aspiration)

Parameter	Tin, total Tin, dissolved
Sample Preparation	See section 1.0, the Sample Preparation section.
Analytical Method	See section 2.1, the AA methods section.
EMS Code	FA: HNO_3: AA (total) Sn-T X073 LA: HNO_3: AA (total) Sn-T X351 FF, FA: HNO_3: AA (dissolved) Sn-D X203 LF, LA: HNO_3: AA (dissolved) Sn-D X085
Introduction	Tin is usually present in trace levels in natural waters. The pure metal is relatively non-toxic; however some organo-tin complexes (i.e., tributyltin) are known to be acutely toxic. Tributyltin is commonly used as an antifouling agent for marine paints.
Method Summary	Aqueous sample solutions and calibration standards are aspirated into a flame and atomized. The absorption of light, at a wavelength specific to tin, is measured and the concentration of the analyte is determined by comparison to the calibration standards.
MDL	Given an aqueous sample free of interferences, the instrumental performance characteristics are: MDL: 0.5 mg/L Range: 0.5 mg/L - 300 mg/L See Table C-1 in section 2.1, the AA methods section, for additional information.
Matrix	Water, wastewater, marine water.
Interferences and Precautions	See section 2.1.4 of the AAS methods section of this manual.
Sample Handling and Preservation	See section 1.0, the sample preparation section of this manual.
Stability	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
Instrument Parameters	Source: Sn EDL or hollow cathode lamp Wavelength: 286.3 nm Type of Flame: Nitrous oxide/Acetylene Background Correction: recommended
Apparatus, Materials and Reagents	See section 2.1.5 and 2.1.6 of this manual.
Precision	None listed.
Accuracy	None listed.
Quality Control	See Section 2.1.9, QA/QC Guidelines in this manual.

References	a)	Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 18th edition, 1992.
	b)	Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods (Revised). Publication #SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd edition 1990.
	c)	Analytical Methods For Atomic Absorption Spectrophotometry. Published by The Perkin-Elmer Corporation. Norwalk, Connecticut, U.S.A. January 1982.

Revision History	February 14, 1994:	Publication in 1994 Laboratory Manual.
	December 31, 2000:	SEAM codes replaced by EMS codes. Sample matrix added.

Tin (Atomic Absorption - Gaseous Hydride)

Parameter	Tin, total Tin, dissolved	
Sample Preparation	See section 1.0, the sample preparation section.	
Analytical Method	See section 2.1, the AA methods section and 2.2, the hydride AA method section of this manual.	
EMS Code	FA: HNO_3: HVAAS (total) LA: HNO_3: HVAAS (total) FA: HCl: HVAAS (total) LA: HCl: HVAAS (total) FF, FA: HNO_3: HVAAS (dissolved) LF, LA: HNO_3: HVAAS (dissolved) FF, FA: HCl: HVAAS (dissolved) LF, LA: HCl: HVAAS (dissolved)	Sn-T X289 Sn-T X354 Sn-T X345 Sn-T X355 Sn-D X202 Sn-D X359 Sn-D X348 Sn-D X360
Introduction	Tin is usually present in trace levels in natural waters. The pure metal is relatively non-toxic; however some organo-tin complexes (i.e., tributyltin) are known to be acutely toxic. Tributyltin is commonly used as an antifouling agent for marine paints.	
Method Summary	Hydride vapour generation sample introduction systems utilize a chemical reduction to reduce and form a volatile hydride with tin. This volatile hydride is then swept into a heated quartz cell where the tin is freed from the hydride. Standard AAS (heated reaction cell) is then carried out on the volatile metallic species.	
MDL	Given an aqueous sample free of interferences, the instrumental performance characteristics are: MDL: 0.0005 mg/L Range: 0.0005 - 0.200 mg/L See Table C-1 in section 2.1, the AA methods section, for additional information.	
Matrix	Water, wastewater, marine water.	
Interferences and Precautions	• easily reduced metals - i.e., copper, silver, mercury, etc., • high concentrations of transition metals (>200 mg/L), and • oxidizing agents remaining following sample digestion - i.e., oxides of nitrogen. (USEPA, 1986)	
Sample Handling and Preservation	See section 1.0, the sample preparation section of this manual.	
Stability	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.	
Instrument Parameters	Source: Sn EDL or hollow cathode lamp Wavelength: 286.3 nm Background Correction: not required	
Apparatus, Material and Reagents	See section 2.1.5 and 2.1.6 of this manual.	
Precision	None listed.	
Accuracy	None listed.	
Quality Control	See Section 2.1.9, QA/QC Guidelines in this manual.	

References

a) Instructions - MHS-20 Mercury/Hydride System, Publication 338-A2-M 294/12.79. Bodenseewerk Perkin-Elmer & Co. GMBH/UBERLINGEN. 1979.

b) Analytical Methods For Atomic Absorption Spectrophotometry. Published by the Perkin-Elmer Corporation. Norwalk, Connecticut, U.S.A. January 1982.

c) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 18th edition, 1992.

d) Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods (Revised). Publication #SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd edition 1990.

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
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Revision Date: December 31, 2000

Uranium, Total or Dissolved

Parameter	Uranium, total Uranium, dissolved
Analytical Method	Laser-induced fluorescence HNO_3 digestion, laser-induced fluorescence
EMS Code	Uranium, dissolved U--D X343 Uranium, total U--T X344
Introduction	Most sources of drinking water, especially groundwaters, contain dissolved carbonates and bicarbonates that are capable of complexing with uranium and keeping it in solution.
Method Summary	Uranyl ion (UO_2^{2+}), complexed with pyrophosphate, is excited at 337 nm with a pulsed nitrogen laser and the resulting fluorescence at 494, 516 or 540 nm is monitored. The method of standard additions is used to minimize interferences from matrix effects.
MDL	Typical: 0.0002 mg/L for uranium, total 0.0001 mg/L for uranium, dissolved
Matrix	Fresh water.
Interferences and Precautions	Many of the common cations (Ca, Na, K etc.) interfere at normal concentration levels; however, the interference is minimized by the standard addition technique. Interference from fluorescing organic material is avoided by instituting a delay in measurement to allow the short-lived organic fluorescence to subside.
Sample Handling and Preservation	Plastic or glass bottle, sample acidified in the field with 4mL concentrated HNO_3/L.
Stability	M. H. T.: 14 days
Principle or Procedure	The uranyl ion, when excited at 337 nm, releases energy at 494, 516 and 540 nm. The Scintrex® laser fluorescence analyzer provides a convenient means of analysis.
Precision	Authentic samples at concentrations of 3.9 and 30.4 µg/L gave coefficients of variation of 5.5% and 4.0% respectively.
Accuracy	±3% at 30 µg/L level.
Quality Control	The laser intensity (without a cuvette installed) should be recorded each time a set of analyses is run to monitor laser performance. The slope of the standard addition plot for the sample should be within 20% of the slope attained for the standards and blanks; failure indicates excessive interference and necessitates re-analysis after dilution of the sample.
References	None listed.
Revision History	February 14, 1994: Publication in 1994 Laboratory Manual. December 31, 2000: SEAM codes replaced by EMS codes. Out of print reference deleted. Sample matrix added.

Revision Date: December 31, 2000

Zinc (Atomic Absorption - Direct Aspiration)

Parameter	Zinc, total Zinc, dissolved
Sample Preparation	See section 1.0, the sample preparation section.
Analytical Method	See section 2.1, the AA methods section.
EMS Code	FA: HNO_3: AA (total) Zn-T X073 LA: HNO_3: AA (total) Zn-T X351 FF, FA, HNO_3: AA (dissolved) Zn-D X203 LF, LA: HNO_3: AA (dissolved) Zn-D X085
Introduction	Zinc is an essential trace element for human growth. It imparts a bitter taste to drinking water at concentrations above 5 mg/L. Zinc occurs in nature as the sulfide and is often associated with sulfides of other heavy metals. Common sources of zinc are contaminated industrial waste and deteriorated galvanized steel. It is toxic to aquatic life at a relatively low concentration, depending on water hardness.
Method Summary	Aqueous solutions of metals are aspirated into a flame and atomized. The absorption of light, at a wavelength specific to the element being analyzed, is measured and the concentration of the analyte is determined by comparison with standards.
MDL	Given an aqueous sample free of interferences, the instrumental performance characteristics are: MDL: 0.005 mg/L Range: 0.005-1.0 mg/L See Table C-1 in section 2.1, the AA methods section, for additional information.
Matrix	Water, wastewater, marine water.
Interferences and Precautions	No significant interferences. Possible enhancement or depression of absorbance signal for samples containing high levels of dissolved solids. Use deuterium background correction if warranted. See also section 2.1.4 of the AA methods section of this manual.
Sample Handling and Preservation	See section 1.0, the sample preparation section.
Stability	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
Instrument Parameters	Source: Zn hollow cathode lamp Wavelength: 213.9 nm Type of Flame: air/acetylene Background Correction: recommended
Apparatus, Materials and Reagents	See section 2.1.5 and 2.1.6 of this manual.
Precision	None listed.
Accuracy	None listed.
Quality Control	See section 2.1.9, QA/QC Guidelines in this manual.

References

a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992, Method 3111 B/D.

b) Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods (Revised). Publication #SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd Edition 1990.

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes. Sample matrix added.

Revision Date: December 31, 2000

Zinc (Atomic Absorption - Graphite Furnace)

Parameter	Zinc, total Zinc, dissolved
Sample Preparation	See section 1.0, the sample preparation section.
Analytical Method	See section 2.1, the AA methods section.
EMS Code	FA: HNO_3: GFAA (total) Zn-T X072 LA: HNO_3: GFAA (total) Zn-T X179 FF, FA: HNO_3: GFAA (dissolved) Zn-D X116 LF, LA: HNO_3: GFAA (dissolved) Zn-D X357
Introduction	Zinc is an essential trace element for human growth. It imparts a bitter taste to drinking water at concentrations above 5 mg/L. Zinc occurs in nature as the sulfide and is often associated with sulfides of other heavy metals. Common sources of zinc are contaminated industrial waste and deteriorated galvanized steel. It is toxic to aquatic life at a relatively low concentration, depending on water hardness.
Method Summary	A discrete sample volume is introduced into the graphite sample boat which is heated in stages to accommodate drying of the solution, charring and volatilization of organics and other matrix components, and finally, atomization of the analyte into the light path of the spectrometer. The absorption of light, at a wavelength specific to the element being analyzed, is measured and the concentration of the analyte is determined by comparison with standards.
MDL	Given an aqueous sample free of interferences, the instrumental performance characteristics are: MDL: 0.0002 mg/L Range: 0.0002-0.004 mg/L See Table C-1 in section 2.1, the AA methods section, for additional information.
Matrix	Water, wastewater, marine water.
Interferences and Precautions	See section 2.1.4, of the AA methods section of this manual. Due to the extreme sensitivity of the method and presence of zinc as a trace contaminant in dust, plastics, glassware, acids and other reagents, any manipulation or treatment of samples must be duplicated in the form of appropriate blanks to allow for correction of results. Platform atomization is recommended for zinc analysis.
Sample Handling and Preservation	See section 1.0, the sample preparation section of this manual.
Stability	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
Instrument Parameters	Source: Zn hollow cathode lamp Wavelength: 213.9 nm Background Correction: recommended
Apparatus, Materials and Reagents	See section 2.1.5 and 2.1.6 of this manual.
Precision	None listed.
Accuracy	None listed.

Quality Control

See section 2.1.9, QA/QC Guidelines in this manual.

References

a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992, Method 3113B.

b) Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods (Revised). Publication #SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd Edition 1990.

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes. Sample matrix added.

APPENDIX C

REVISION HISTORY

Record Date	Revision Record Details	Method Name	BC ELM Section
1-Apr-2020	New or revised methods	Digestion for Total Metals in Water – Prescriptive	Section C
1-Apr-2020	New or revised methods	Dissolved Metals or Mercury in Water Method	Section C
1-Apr-2020	approved for publication	In Vitro Bioaccessibility (IVBA) for AS and Pb in Soil - Prescriptive (PDF)	Section C
1-Apr-2020	New or revised methods	Methylmercury in Soil or Sediment	Section C
1-Apr-2020	New or revised methods	Methylmercury in Water	Section C
1-Apr-2020	New or revised methods	Strong Acid Leachable Metals (SALM) in Soil	Section C
1-Apr-2020	New or revised methods	Trace Metals Analysis by ICP-MS	Section C