

## **Section C**

### **METALS**

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## SECTION C

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## **INTRODUCTION**

The following sections are divided into various topics including:

- 1.0 Sample Preparation
- 2.0 Instrumental Analysis
- 3.0 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 at this time. Future revisions will likely include these methods as well as any updated information available.

## **1.0 SAMPLE PREPARATION**

### **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.

### **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.

### **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.

### **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 appropriate method validation procedure.

### **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**

### **1.1.1 Nitric Acid Digestion For Water Samples**

**Sample Type:** Fresh Water  
Waste Water

**Container:** Polyethylene bottle - 0.5 L or 0.25 L (acid washed)

**Field Preparation:** 02 Unfiltered: field adds 4 mL conc HNO<sub>3</sub> per litre.  
03 Unfiltered: lab adds 4 mL conc HNO<sub>3</sub> per litre.

**Principle of Method:** The water sample is digested with nitric acid to solubilize the solid matter and to remove the organics by oxidation and volatilization. The sample is then introduced into the ICP or the graphite furnace atomic absorption spectrophotometer. The atomic emission or absorption (depending on method) corresponding to each element is measured.

- Heavy Metals Analysis:** The digested samples may be analyzed by one of the following procedures:
- Flame Atomic Absorption (Flame - AA) is used for high level screening. This method yields adequate quantitative results for some elements, e.g. K, Cd, and Pb.
  - Inductively Coupled Argon Plasma Spectrograph (variously ICP or ICAP) is a broad scope technique but needs to be backed up by GFAA for low levels.
  - Graphite Furnace AA (GFAA) is used for low concentrations, especially for Cu, Pb and Cd.
  - Hydride Vapour Generation AA (HVGAA) is used as an alternative to GFAA for As and Se.
  - Cold Vapour AA (CVAA) is used for analysis of mercury in view of its volatility.
  - Inductively Coupled Argon Plasma/Mass Spectrometer (ICP/MS) may be used as an alternative to GFAA.

- Apparatus:**
- Hot plate
  - Glassware

- Reagents:**
- conc.  $\text{HNO}_3$  analytical grade.

- Procedure:**
- Measure 100 mL sample with a graduated cylinder into a 125 mL erlenmeyer flask, rinse cylinder with a small amount of deionized water and add to the flask.
  - Add 2 mL conc.  $\text{HNO}_3$  to each sample and heat on hot plate until 5 - 10 mL remains.
  - Remove from heat and wash down sides with deionized water
  - Bulk to 100 mL with deionized water in a 100 mL volumetric flask

Run one duplicate for every 20 samples, two digested blanks and internal quality control standards (spikes or reference materials) with each batch.

This digestion procedure is not to be used for samples with turbidity greater than 70 NTU.

#### 1.1.2 Nitric Acid Digestion For Turbid Water Samples (Turbidity greater than 70 NTU)

**Sample Type:** Fresh Water  
Waste Water

**Container:** Polyethylene bottle - 0.5 L or 0.25 L (acid washed)

**Field Preparation:** 02 Unfiltered: field adds 4 mL conc  $\text{HNO}_3$  per litre.  
03 Unfiltered: lab adds 4 mL conc  $\text{HNO}_3$  per litre

**Principle of Method:** The water sample is digested with nitric and hydrochloric acids to solubilize the solid matter and to remove the organics by oxidation and volatilization. The sample is then introduced into the ICP or the graphite furnace atomic absorption spectrophotometer. The atomic emission or absorption (depending on method) corresponding to each element is measured.

**Interference:** The recoveries of silver are suspect by this method since silver chloride is insoluble.

**Heavy Metals Analysis:** The digested samples may be analyzed by one of the following procedures:

- Flame Atomic Absorption (Flame - AA) is used for high level screening. This method yields adequate quantitative results for some elements, e.g. K, Cd, and Pb.
- Inductively Coupled Argon Plasma Spectrograph (variously ICP or ICAP) is a broad scope technique but needs to be backed up by GFAA for low levels.
- Graphite Furnace AA (GFAA) is used for low concentrations, especially for Cu, Pb and Cd.
- Hydride Vapour Generation AA (HVGAA) is used as an alternative to GFAA for As and Se.
- Cold Vapour AA (CVAA) is used for analysis of mercury in view of its volatility.
- Inductively Coupled Argon Plasma/Mass Spectrometer (ICP/MS) may be used as an alternative to GFAA.

**Apparatus:**

- Hot plate
- Glassware

**Reagents:**

- conc. HNO<sub>3</sub> analytical grade
- 1:1 HCl analytical grade

**Procedure:**

- Measure 100 mL sample with a graduated cylinder into a 125 mL erlenmeyer flask, rinse cylinder with a small amount of deionized water and add to the flask.
- Add 3 mL conc HNO<sub>3</sub> to each sample and heat on hot plate to almost dryness.
- Add another 3 mL conc. HNO<sub>3</sub> and again heat to almost dryness.
- Add 2 mL 1:1 HCl to each sample. Remove from hotplate and wash down sides with deionized water.
- Bulk to 100 mL with deionized water in a 100 mL volumetric flask.

Run one duplicate for every 20 samples, two digested blanks and internal quality control standards (spikes or reference materials) with each batch.

### 1.1.3 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 <sub>3</sub> (see section 2.1.6) per litre or 20% (w/v) K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> in 1:1 HNO <sub>3</sub> , 2mL/L
Unfiltered-lab:	add 4 mL HNO <sub>3</sub> (see section 2.1.6) per litre or 20% (w/v) K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> in 1:1 HNO <sub>3</sub> , 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 ( $\text{H}_2\text{SO}_4$ ), concentrated, reagent grade
- c) Nitric acid ( $\text{HNO}_3$ ), concentrated, reagent grade
- d) Potassium permanganate ( $\text{KMnO}_4$ ), 5% w/v, mercury-free
- e) Potassium persulfate ( $\text{K}_2\text{S}_2\text{O}_8$ ), 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  $\text{H}_2\text{SO}_4$ , 2.5 mL of concentrated  $\text{HNO}_3$ , and 15 mL 5%  $\text{KMnO}_4$  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%  $\text{KMnO}_4$  solution, mixing well after each addition, until the purple color persists for longer than 15 minutes.
  1. Add 8 mL 5%  $\text{K}_2\text{S}_2\text{O}_8$  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  $\text{KMnO}_4$ .
  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

### 1.2.1 Strong Acid Leachable Metals (SALM) in Soil – Performance Based Method (PBM)

**Analytical Method:** Nitric – Hydrochloric digestion, Instrumental analysis

**Introduction and Explanatory Notes:**

This method was prepared for the B.C. Ministry of Environment (B.C.MOE), specifically for analyses dealing with metals in soils for use under the Waste Management Act, Contaminated Sites Regulation (CSR). It has been suggested that it could be used as an appropriate method for other B.C.MOE regulatory purposes, and for similar initiatives in other jurisdictions. However it may not be suitable for certain study or project requirements.

The Contaminated Sites Regulation includes “Water” and “Soil” as “Matrix Types” but “Soil” is only broadly defined (CSR, section 1). After consultation with B.C.MOE representatives it was decided that Carter’s definition of “Soil” (reference 16), as being “minus 10 mesh” material, would be used for this method. Due to concerns with sub-sampling variance, it was decided that the minimum representative “minus 10 mesh” sample size taken for digestion be one gram of dry sample.

It was noted that a variety of digestion apparatus and digestion procedures were being used. After review, it was decided to use an “open-beaker digestion”, a mixture of nitric acid and hydrochloric acid, and standardized digestion time and temperature. Laboratories are allowed some flexibility regarding apparatus and heating methods while limited variations in acid mixture composition, digestion time and temperature are permitted if method equivalency is proven. The inclusion of all undigested material in the final diluted extract was permitted to accommodate the use of calibrated digestion tubes.

Results of analyses of Certified Reference Materials using the common mixed acid digestion procedures indicate that barium, chromium, nickel, and vanadium are often incompletely recovered. For example barium typically yields recoveries ranging from 5% to 25%. Other “heavy metals: (e.g. copper, cadmium, lead, zinc, etc.) yield recoveries generally between 90 and 100% for most samples. The toxicological significance of the low recoveries seen using this method for barium, chromium, nickel, and vanadium obtained using “open beaker mixed acid digestion” is relatively inconsequential. The aim of this method is not necessarily to achieve “better recoveries” but rather to ensure consistent results between laboratories over the long term.

Regarding pressurized closed vessel microwave digestion, this technology has been specifically excluded from the Version 1.0 method for two reasons. First, recoveries for barium, chromium, nickel, and vanadium are consistently and significantly higher than those seen using “open beaker mixed acid digestion” procedures. Second, the use of the minimum one gram sample size may not be technically feasible for many closed vessel microwave systems.

**Method Summary:**

Samples are dried at 60°C and sieved using a 2 mm (10 mesh) sieve. Solid samples are digested with the combination of nitric and hydrochloric acids with a 1:1 ratio of acids. For environmental purposes, strong acid leaches are used routinely since they have the advantage of speed, low cost, and superior reproducibility. All metals trapped within the refractory matrix are

unlikely to have environmental consequences. Instrumental analysis of extracts produced using this digestion method can be performed by a variety of techniques.

**Scope and Application:** This method is written in a performance based method (PBM) format. A PBM includes both mandatory and non-mandatory elements. Provided that the mandatory elements are met, laboratories have the flexibility to select analytical methods, procedures and instrumentation of their preference. The most important of the mandatory elements are the data quality objectives (DQO's) specified by the ministry and the criteria set out in this methodology. Laboratories using this method have two key responsibilities. The first is to have a detailed written operating procedure documenting how the method is carried out in their laboratory. **This must include the mandatory elements.** The second responsibility is to audit annually their method performance to ensure that the data quality objectives are met. Laboratories should use a documented quality system conforming to ISO 17025 [2].

**NOTE: The mandatory elements of this performance based method are specified in bold text.**

PBM Strong Acid Leachable Metals in Soils provides the sample preparation and digestion methodology for analysis of metals, including mercury, and other elements such as barium, phosphorus and sulphur. The selection of analytical methods for a client or program specification includes: availability of accepted or standard methods, required method detection limits (MDL), turn around time, sample type, available technology, operator expertise and economy. Additional analytical issues include the analytes to be measured, expected concentrations and potential interferences using this method. Metals can be detected and quantified from parts per million ( $\mu\text{g/g}$ ) to parts per trillion ( $\text{pg/g}$ ) levels depending on the method and instrumentation used for analysis. The strong acid leach results in a partial to complete extraction of target elements. **All results must be reported on a dry weight basis.**

**Where laboratories use modifications to this method, they must prove equivalency (as described in the Method Equivalency Section).**

**Method Limitation:**

- a) Aluminum, barium, chromium, iron, manganese, nickel, vanadium and other refractory elements, are known to have low recovery by the this procedure [14].
- b) Preliminary studies have shown that antimony (Sb) and tin (Sn) may degrade over time once the extract has been diluted in the presence of the soil. Once the soil has been removed from the digestate, Sb and Sn appear to be more stable.
- c) This method is not applicable to hexavalent chromium.
- d) Samples high in organic matter (e.g. humus, peat) may yield lower recoveries of Strong Acid Leachable Metals.
- e) Samples with high petroleum or non-petroleum hydrocarbon content ("Oil & Grease") may require specialized sample pre-treatment or different digestion procedures.
- f) Sulphur determination by this test method is not 'elemental sulphur' analyzed by acetone extraction followed by colorimetric analysis.

**Significance and Use:** The impacts of metals in soils range from beneficial, to troublesome, to dangerously toxic in the environment. This method allows for the determination of metals in soils so as to monitor contamination in the environment. Laboratories throughout the country use different methods for the chemical analysis of soils. These differences include analysing different grain size fractions, and using different acid digestion methods. As a result, the heavy metal data produced in different laboratories may be incomparable and unverifiable [9]. This PBM specifies mandatory sample preparation steps, drying temperature, sieve size and digestion procedures, so that laboratories will have comparable and verifiable results, specifically for those dealing with metals in soils under the Province of British Columbia's Waste Management Act, Contaminated Sites Regulations (CSR) [12].

**Definitions:** *Certified Reference Material (CRM)* - A reference material, one or more of whose property values are certified by a technically valid procedure, accompanied by or traceable to a certificate or other documentation which is issued by a certifying body.

*Reference Material (RM)* - A material or substance, one or more properties of which are sufficiently well established to be used for the calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials.

*Duplicate* - a quality control sample, often chosen randomly, from a batch of samples and undergoing separate, but identical sample preparation and analysis whose purpose is to monitor method precision and sample homogeneity.

*Method Blank* - a quality control sample that is free of the target parameter or analyte and contains only the reagents used and undergoes the same analysis procedure as the unknown sample. The method blank is used to monitor possible contamination sources.

*Soils* – the minus 10 mesh fraction and as defined by the Contaminated Sites Regulation

*Strong Acid Leachable Metals (SALM)* - dissolves nearly all the "heavy metal" in solids including arsenic, cadmium, cobalt, copper, lead, mercury, selenium, silver and zinc, but does not dissolve all silicate minerals. Elements that are not recovered completely by this strong acid leachable digestion may include: antimony, barium, beryllium, chromium, iron, manganese, molybdenum, nickel, silver, thallium, tin, titanium and vanadium.

*Refractory Elements* – Substances that resist attack by ordinary laboratory acids; brought into solution by high temperature processes such as: fusion with a flux, acid digestion under pressure greater than one atmosphere, acid digestion with hydrofluoric and/perchloric acids or any combination of these techniques.

*Total Acid Digestable Metals (TADM)* - completely dissolves the silicate minerals, so that recoveries are complete. Acids used in TADM digestion include perchloric and hydrofluoric acid. TADM analyses are not part of this procedure.

*Total Metals* - the phrase "Total Metals" as used by the British Columbia Ministry of Environment, Lands and Parks (B.C.MOE) CSR refers to this procedure and not the TADM procedure.

**Sample Collection and Preservation:**

- a) Sampling should be done by qualified personnel, experienced in sampling procedures and working under standard documented operating conditions. It is important that the sample be properly taken in a quality-controlled manner for submission to a laboratory and that the sample be representative of the area being sampled [7].
- b) **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. It is recommended that glass containers be used, particularly if mercury analysis is required on the samples. Samples can be frozen or stored at 4°C. **The holding time prior to digestion must not exceed 28 days for mercury and 6 months for all other metals (from the time of sampling prior to digestion). Results reported for samples digested beyond holding times must be flagged.**
- c) Samples must be clearly labeled with the date and time of sampling, location or source of the sample, type of sample (grab or composite), analysis required and the identity of the individual who collected the sample. Labels must be filled out in indelible ink and fixed to the sample container such that they will not fall off when wet or during transport.

**Interferences:**

- a) The interferences encountered will differ depending on the instrumental method used to analyze the extracts. These interferences should be clearly outlined in the analysis procedure. Analysts should be aware of the limitations to the instrumentation and methodologies used for the analysis of metals in solids.
- b) High concentrations of acids may cause physical interferences in instrumental analyses.

**Method Performance:**

- a) **Method detection limits (MDL) must be determined statistically using the formulas outlined in Appendix 2.**
- b) **Method Blanks must be analyzed with each batch to monitor contamination and background interferences.**
- c) **Method Accuracy: Certified Reference Materials (CRM) or Reference Materials (RM) must be analyzed with every batch to check validity of test results, and the recovery of metals measured against the certified or accepted values.**
- d) **Method Precision: Duplicates must be analyzed with every batch.** Precision is determined using Relative Percent Difference (RPD). See Appendix 2 for formulas.
- e) Laboratory MDL should be at least five times lower than the applicable regulatory limits, (where possible, given the most economical and best technology currently available). For example, if the regulatory limit is 100 micrograms per gram (ug/g), the laboratory MDL must be not be greater than 20 ug/g; current technology may only allow laboratories

to achieve a 50 ug/g MDL. Current Province of British Columbia CSR Regulatory Limits are listed in Appendix 3, Table 1.

**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.

**Apparatus:**

- a) Apparatus required for the preparation and digestion of samples and analysis will vary depending on the method and instrumentation of choice.
- b) **It is mandatory to use a 2 mm (or a “10 mesh”) sieve.** It is recommended that a stainless steel screen/sieve with all tin solder be used. **Sieves must not be constructed of brass or contain tin lead solder.** Polypropylene or nylon sieves may also be used.
- c) **The heat for digestion must be supplied by a heat source capable of maintaining a temperature of  $90 \pm 5^{\circ}\text{C}$ .**
- d) **Digestion vessels must be capable of supporting reflux action. The vessel design must be such that the sample must be completely covered by the digestion acid mixture at all times.**

**Reagents:**

- a) **Nitric acid,  $\text{HNO}_3$  (concentrated).**
- b) **Hydrochloric acid,  $\text{HCl}$  (concentrated).**

Note 1: The laboratory is responsible for using the appropriate grade of acid; reagent grade as a minimum.

Note 2: **Hydrofluoric, perchloric and sulphuric acids must not be used.**

- c) **Laboratory grade water : Water free of substances that interfere with the analytical method; equivalent to Type 1 water as set out in the current edition of Standard Methods (APHA).**

**Procedure:** The samples are digested and prepared using the following procedures. The mandatory elements of this method are specified in bold text.

- a) Sample Homogenization and Sub-Sampling
  1. **Inspect the sample and record any unusual or significant characteristics (e.g. lead shot pellets, metal turnings, screws, etc).**
  2. **Remove any obviously foreign material such as vegetation.**
  3. **If the sample has separated into visually obvious layers (e.g., water/marine water, 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. **When**

**these non-standard procedures have deviated from the prescribed method, the results must be clearly flagged.**

- 4. Homogenize the entire sample** by vigorous stirring using a non-contaminated 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 non-contaminating 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;** otherwise proceed to Procedure Section 2.

b) **Sample Preparation - Drying**

1. Dry sample to be analyzed at a temperature of  $60 \pm 5^{\circ}\text{C}$  to a constant weight. For drying temperatures other than  $60 \pm 5^{\circ}\text{C}$ , a note should accompany the results. Freeze drying of samples is acceptable.

**Note: Sample drying temperature must not exceed  $60^{\circ}\text{C}$  to minimize volatilization of certain analytes such as mercury [14].**

2. Drying may not be necessary, as sample may be dry, and in some instances, the laboratory may wish to (and be able to) sieve a “moist” undried sample. Results must be reported on a dry weight basis.

c) **Sample Preparation - Sieving**

1. **Sieve each sample through a 2 mm (“10 mesh”) sieve. DO NOT grind samples to pass through this sieve/screen size.** It is suggested that “easily friable materials” (dried clay clods, disintegrating rock, etc.) should be included “by being subjected to some sort of gentle mechanical action (rolling, etc.)” prior to screening. Dis-aggregation of sample is permissible prior to sieving.
2. Where available, it is recommended that a minimum of 25 grams of sieved sample be obtained for analysis.
3. Discard the “greater than 2 mm” fraction.
4. Field sampling personnel may pre-screen the samples in the field.

d) Sample Digestion Procedure

1. Weigh a minimum of 1.00 grams of dry sample, into a vessel capable of refluxing, such as a covered beaker or digestion tube. Include method blanks, duplicates and at least one reference material per batch of samples. Weight must be recorded to  $\pm 0.05$  grams.

Note 1: In cases where one gram of sieved sample is not available it is permissible to perform the analysis as described but **a note must accompany the results.**

Note 2: It is permissible to use more than one gram of sample for digestion but the acid to sample ratio must be maintained as stated in 2 (below), and the sample must be covered by the acid mixture at all times.

2. Add equal volumes of concentrated nitric and concentrated hydrochloric acid. The minimum acid volumes required are 2.5 mL of concentrated nitric acid and 2.5 mL of concentrated hydrochloric acid. The acid ratio (by volume) should be one part nitric acid to one part hydrochloric acid. In addition the minimum acid to sample ratio must be a minimum of 5 mL of acid for every gram of dry sample. **Sample must be fully covered by the acid mixture.**

Note: It is permissible to use more than 5 mL of acid mixture per one gram of dry sample.

3. **Swirl acid and sample to mix gently. Allow the sample to sit at room temperature for at least one hour before heating.**
4. Digest samples for two hours  $\pm 15$  minutes at a temperature of  $90 \pm 5^\circ\text{C}$  **at atmospheric pressure.** A hotblock or waterbath are the preferred methods of heating. **The heat for digestion must be supplied by a heat source capable of maintaining a temperature of  $90 \pm 5^\circ\text{C}$ .**
5. 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 elements being analysed. 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, the sample extracts must be centrifuged or filtered within 4 hours of dilution to separate the digestate from the particulates.** This must be done to minimize tin and antimony losses. **The decanted or filtered digestates must be analyzed within 7 days.**
7. Analyze the final extract using appropriate analytical techniques and report the results on a dry weight basis.

8. Report any anomalies observed during the digestion and analysis.

**Quality Control:**

- a) **Before analyzing any samples, the laboratory must demonstrate that the selected analytical methods can provide valid data under practical conditions in the laboratory. The laboratory should have in place a method validation process and data to demonstrate that validation has occurred and that the methods chosen can meet the data quality objectives.**
- b) Quality control procedures are essential to ensure data quality and to monitor the accuracy and precision of the instrument.
- c) Detail and document any non-conformances.
- d) The uncertainty of the results, detection limits, selectivity of the analysis, and its robustness in the hands of different staff should be tested and documented. Techniques used for validation include results obtained on certified or other reference materials, comparison of results with data obtained using other methods, interlaboratory comparison data, systematic assessment of factors which could influence the results, and assessment of uncertainty based on accuracy and precision. The influence of instrumental, human and environmental factors should be considered.
- e) **Assess whether the method shows statistical control by considering:**
  1. **the range of duplicate results, to monitor precision**
  2. **the measured check standards, reference materials, and control standards ( to monitor bias).**

**If any parameter lies outside of the established ( $2\sigma$ ) *control limits* for the CSR Regulated elements, or ( $3\sigma$ ) *control limits* for the non CSR Regulated elements OR if two consecutive data points for a parameter lie outside of the ( $1\sigma$ ) *warning limits*, for the CSR Regulated elements and ( $2\sigma$ ) *warning limits* for the non CSR Regulated elements, then re-calibration and/or an instrument check may be necessary. Document any non-conformance and the action taken.**

**Calculation and Reporting:**

*Report results on a dry weight basis*

$$\text{Concentration of analyte in sample } (\mu\text{g/g}) = \frac{\text{A } (\mu\text{g/mL}) \times \text{sample volume (mL)} \times \text{dilution factor}}{\text{dry weight of sample used (g)}}$$

where A = analyte concentration as determined by the instrument of choice



## Method Equivalency Procedure

### 1. Use of Alternative Methods

This method contains several prescribed and required elements that may not be modified.

Modification or omission is not permitted to anything described within the method text as “required” or preceded by the word “must”. In this procedure, as noted above, all mandatory elements are specified in bold text.

All of the prescribed requirements of the method are summarized in section 1.1 below.

#### 1.1 Prescribed Elements

Laboratories that report data for regulatory purposes may not alter any method conditions listed in this section without prior written permission by B.C.MOE:

- 1.1.1 Every laboratory that uses this method, whether modified or not, must validate the method to meet Appendix 5 Data Quality Objectives (DQO's).
- 1.1.2 Maximum holding time for samples prior to digestion is 6 months for all metals except mercury, which is 28 days. Where holding times are exceeded, data must be flagged.
- 1.1.3 The Sample Homogenization and Sub-Sampling procedure must be followed as described in PROCEDURE - Section (a).
- 1.1.4 Certain elements of Sample Preparation - Drying must be followed as described in PROCEDURE - Section (b).
- 1.1.5 Certain elements of Sample Preparation - Sieving Steps must be followed as described in PROCEDURE - Section (c).
- 1.1.6 Certain elements of Sample Digestion Procedure must be followed as described in PROCEDURE - Section (d) as follows:
  - 1.1.6.1 The amount of sample digested must not be less than 1 gram dry weight, except in special cases as described in section (d)1 Note 1.
  - 1.1.6.2 Only nitric & hydrochloric acids can be used for the sample digestion (hydrofluoric, perchloric and sulphuric acids are not allowed).
  - 1.1.6.3 The minimum acid to sample ratio must be 5:1. Use a minimum of 5 mL of concentrated acid for every 1 gram of dry sample. The sample to be digested must be fully covered by the total volume of acid mixture added.
  - 1.1.6.4 Sample heating/digestion must be carried out at atmospheric pressure.
- 1.1.7 Certain elements of the Calculations and Reporting Procedure must be followed:
  - 1.1.7.1 Final data must be reported on a dry weight basis.

### 2. Performance Based Method Changes

This is a Performance Based Method. Unless prohibited in section 1.1 (above) or elsewhere, modifications to this method are permitted, provided that the laboratory possesses adequate documentation to demonstrate an equivalent level of performance. **Laboratories that modify this method must achieve all specified Quality Control requirements, and must maintain**

**on file the Standard Operating Procedures which thoroughly describe any revised or alternate methods which are used at any time following the initial adoption of this method by B.C.MOE. This information must be available in the event of audit by B.C.MOE.**

## 2.1 Modifications Where Equivalence-Testing is Required

Except where expressly disallowed in section 1.1 or elsewhere, changes to the following components of this method are permitted, but only if the laboratory has conducted and documented a rigorous test for equivalence to this reference method:

### 2.1.1 PROCEDURE - Section (d) - Sample Digestion Procedure

- 2.1.1.1 The acid ratio may be changed from the 1:1 nitric acid/hydrochloric acid ratio as stated in the procedure. However, the acid ratio must not exceed a 3:1 ratio of either acid (i.e. 3:1 nitric acid/hydrochloric acid or 3:1 hydrochloric acid/nitric acid).
- 2.1.1.2 The use of concentrated nitric and hydrochloric acids may be changed to allow the use of diluted acids. A minimum of 5 mL concentrated acid per one gram of sample must be used.
- 2.1.1.3 The digestion time may be changed.
- 2.1.1.4 The digestion temperature may be changed.
- 2.1.1.5 Digestion procedures may be changed due to advances in technology (e.g. open vessel microwave assisted digestion).

An equivalence test for modifications to Section (d) of the PROCEDURE, involves a comparison of results from the modified method with results from the reference method for several appropriately selected samples, with all B.C. CSR-listed metals analyzed.

## 3. Evaluation Procedure

### 3.1 Two evaluations must be performed, an Accuracy Evaluation, using Certified Reference Materials, and a Precision Evaluation using both Certified Reference Materials and Authentic Field Samples.

#### 3.1.1 Accuracy Evaluation:

**Analyze at least two soil/sediment Certified Reference Materials (CRM). Each CRM must be digested and analyzed in triplicate (at minimum) by both this reference method and by the modified method. Samples must include the following:**

- **NIST 2711.**
- **CANMET TILL -1**

Other CRM's that may be used for equivalency testing in the future may include:

- NIST 2704 (terrestrial soil)
- NRC MESS-3 (marine sediment)
- NRC PACS-2 (contaminated marine sediment)

Note: Required QC Acceptance Criteria have not been developed for these CRM's.

**The mean results of each element of each sample must meet the Appendix 5, Table 1 and Table 2 "Required QC Acceptance Criteria".**

Note1: Failure of an individual element or elements under this stage of the equivalency test would not disqualify the Modified Procedure, but it would disqualify the individual element(s). Those elements not meeting this criteria are not to be reported if the Modified Procedure is used for client sample analysis. Failure under this section would disqualify the element even though the evaluation under "Precision Evaluation" might pass.

Note2: Laboratories may wish to validate and use a modified test method that includes only some, but not all elements in the CSR list. For example, projects requiring only the analysis of copper might use a validated modified procedure that uses only a one hour digestion time; other elements in the CSR list may not show equivalence using the modified procedure. Under these circumstances, the laboratory must ensure that the modified test method is used only for the validated elements.

3.1.2. **Precision Evaluation:**

**Prepare (sieve), digest and analyze at least five unspiked field samples. Each sample must be digested and analyzed in triplicate (at minimum) by both this reference method and the modified method. Samples must include:**

- **One or more clay samples.**
- **Two or more heavy metal contaminated soil or sediment samples.**
- **One or more hydrocarbon contaminated soils**
- **All CSR-listed metals must be present in at least one of the five samples at greater than five times the lab's reported detection limit (where possible).**

For the "Precision Evaluation", use the data generated from both CRM and authentic samples as described in sections 3.1.1 and 3.1.2. **Compare the mean results for each element in each sample generated by the two methods. For each element, except where both means are less than 5 times the lab's commonly reported method detection limit for the analyte, one of the following must be satisfied:**

3.1.2.1 **The means for each element in each method must differ by less than 20% relative percent difference (RPD) at greater than five times the MDL, where relative percent difference of  $X_1$  and  $X_2$  is defined as:**

$$RPD = \frac{X_1 - X_2}{\text{Mean}(X_1, X_2)} \times 100\%$$

or,

3.1.2.2 **The difference between the means for each method must not be statistically significant at the 95% confidence level, using a test for significance of the difference of two means, as described by John Keenan Taylor [13]. This test is summarized in Appendix 6.**

3.1.2.3 **The precision validation will typically generate seven data pairs for each element. The maximum number of precision validation failures per element is limited to two.**

3.2.1 If results for one or more samples do not meet one of the above criteria, additional replicates of the same samples may be analyzed, with the tests applied to the larger populations. If necessary, either the Dixon or Grubbs outlier tests may be used to discard outlier data points [13].

3.2.2 If elements are not detected in authentic samples or certified reference materials, then these elements would be considered a conditional pass.

**3.2.3 For all methods that include modifications that require equivalence testing, a detailed report that demonstrates equivalence to the reference method using the above procedure must be available to clients or to B.C.MOE on request.**

**References**

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## **Revision History**

February 2001  
November 2002

Method Introduction  
Method Incorporated into main Laboratory Manual; formatted to match style of  
Lab manual

## Appendix 1

**Table 1: EMS Codes for Inductive Coupled Plasma Atomic Emission Spectrometry (ICP-AES)**

<b>Parameter</b>	<b>Parameter Code</b>	<b>Method Code Using a Sieve Size of 10 (&lt;2 mm)</b>
Aluminium	AL-T	FS01
Antimony	SB-T	FS01
Arsenic	AS-T	FS01
Boron	B—T	FS01
Barium	BA-T	FS01
Beryllium	BE-T	FS01
Cadmium	CD-T	FS01
Calcium	CA-T	FS01
Chromium	CR-T	FS01
Cobalt	CO-T	FS01
Copper	CU-T	FS01
Iron	FE-T	FS01
Lead	PB-T	FS01
Magnesium	MG-T	FS01
Manganese	MN-T	FS01
Molybdenum	MO-T	FS01
Nickel	NI-T	FS01
Phosphorus	P—T	FS01
Potassium	K—T	FS01
Selenium	SE-T	FS01
Silicon	SI-T	FS01
Silver	AG-T	FS01
Sodium	NA-T	FS01
Strontium	SR-T	FS01
Sulphur	S—T	FS01
Thallium	TL-T	FS01
Tin	SN-T	FS01
Titanium	TI-T	FS01
Uranium	U—T	FS01
Vanadium	V—T	FS01
Zinc	ZN-T	FS01

## Appendix 2

1. The Method Detection Limit (MDL) is set at the 95% confidence level above zero (or the blank) and is calculated as follows:

$$\text{MDL} = 2 * t_{1, 0.05} * \text{St Dev}_{\text{near zero}}$$

$$t_{1, 0.05} * = \text{the one tailed "t" statistic at } p=0.05$$

where, t = Student's t value for a 95% confidence level and a standard deviation estimate with n-1 degrees of freedom. t = 1.943 for seven replicates.

Std. Dev.<sub>near zero</sub> = Standard deviation of the replicate analyses.

2. Percent Recovery is calculated as follows:

$$\% \text{ Recovery} = \frac{\text{measured value}}{\text{certified value}} \times 100\%$$

3. Percent Relative Standard Deviation is calculated as follows:

$$\% \text{ Relative Standard Deviation (\%RSD)} = \frac{\text{Standard Deviation}}{\text{Obtained Value}} \times 100\%$$

4. Relative Percent Difference (RPD) is calculated as follows:

$$\text{RPD} = \frac{X_1 - X_2}{\text{Mean}(X_1, X_2)} \times 100\%$$

### Appendix 3

**Table 1: Range of Soil Standards For B.C. Contaminated Sites Regulations (CSR)**

<b>Parameter</b>	<b>Agriculture (AL) in (ug/g)</b>	<b>Urban Park (PL) in (ug/g)</b>	<b>Residential (RL) in (ug/g)</b>	<b>Commercial (CL) in (ug/g)</b>	<b>Industrial (IL) in (ug/g)</b>
Antimony	20	20	20	40	40
Arsenic	15 - 100	15 - 100	15 - 100	15 - 300	15 - 150
Barium	750	500	500	2,000	2,000
Beryllium	4	4	4	8	8
Boron	2				
Cadmium	1.5 - 4,500	1.5 - 4,000	1.5 - 4,000	1.5 - 4,000	1.5 - 4,000
Chromium	9 - 750	60 - 250	60 - 250	60 - 800	60 - 800
Cobalt	40	50	50	300	300
Copper	40 - 350,000	90 - 350,000	90 - 350,000	90 - 350,000	90 - 350,000
Lead	100 - 100,000	100 - 100,000	100 - 100,000	100 - 100,000	100 - 100,000
Mercury	0.8	2	2	10	10
Molybdenum	5	10	10	40	40
Nickel	150	100	100	500	500
Selenium	2	3	3	10	10
Silver	20	20	20	40	40
Sulphur	500				
Thallium	2				
Tin	5	50	50	300	300
Vanadium	200	200	200		
Zinc	150 - 150,000	150 - 15,000	150 - 15,000	150 - 15,000	150 - 15,000



## Appendix 4

**Table 1: Certified and Non-certified Values for NIST 2711**

Parameter	Element	Certified	Value (ug/g)
Aluminum	Al	Yes	6.53 ± 0.09 wt. %
Antimony	Sb	Yes	19.4 ± 1.8
Arsenic	As	Yes	105 ± 8
Barium	Ba	Yes	726 ± 38
Cadmium	Cd	Yes	41.70 ± 0.25
Calcium	Ca	Yes	2.88 ± 0.08 wt. %
Chromium	Cr	No	47
Cobalt	Co	No	10
Copper	Cu	Yes	114 ± 2
Iron	Fe	Yes	2.89 ± 0.06 wt. %
Lead	Pb	Yes	1162 ± 31
Magnesium	Mg	Yes	1.05 ± 0.03 wt. %
Manganese	Mn	Yes	638 ± 28
Mercury	Hg	Yes	6.25 ± 0.19
Molybdenum	Mo	No	1.6
Nickel	Ni	Yes	20.6 ± 1.1
Phosphorus	P	Yes	0.086 ± 0.007 wt. %
Potassium	K	Yes	2.45 ± 0.08 wt. %
Selenium	Se	Yes	1.52 ± 0.14
Silicon	Si	Yes	30.44 ± 0.19 wt. %
Silver	Ag	Yes	4.63 ± 0.39
Sodium	Na	Yes	1.14 ± 0.03 wt. %
Strontium	Sr	Yes	245.3 ± 0.7
Sulphur	S	Yes	0.042 ± 0.001 wt. %
Thallium	Tl	Yes	2.47 ± 0.15
Titanium	Ti	Yes	0.306 ± 0.023 wt. %
Uranium	U	No	2.6
Vanadium	V	Yes	81.6 ± 2.9
Zinc	Zn	Yes	350.4 ± 4.8

## Appendix 4 (Continued)

**Table 2: Certified and Non-certified Values for CANMET TILL -1**

Parameter	Element	Total (ug/g)	Conc Acid (ug/g)	Dilute Acid (ug/g)	EPA 3050 (ug/g)	EPA 3051 (ug/g)
Aluminum	Al	7.25%	-		18,883	18,050
Antimony	Sb	7.8	-			
Arsenic	As	18	13			
Barium	Ba	702	84		84.3	77.8
Beryllium	Be	2.4	-		1.1	<0.2
Cadmium	Cd		<0.2		<0.33	<0.35
Calcium	Ca	1.94%	-		4145	3817
Chromium	Cr	65	30		29.3	29.3
Cobalt	Co	18	12	12	11.7	12.3
Copper	Cu	47	48	49	44.0	44.8
Iron	Fe	4.81%	3.1%	3.4%	29167	37,900
Lead	Pb	22	12	14	24.0	<10.0
Magnesium	Mg	1.30%	-		6,250	6,990
Manganese	Mn	1,420	950	1,020	1,060	1,060
Mercury	Hg	-	92 ppb			
Molybdenum	Mo	2	<2	1	8.7	<2.5
Nickel	Ni	24	18	17	14.0	18.7
Phosphorus	P	930	-		914	834
Potassium	K	1.84%	-		1,188	640
Silver	Ag	-	0.2	<0.2		
Sodium	Na	2.01%	-		530	575
Strontium	Sr	291	-			
Sulphur	S	<0.05%	-			
Titanium	Ti	5,990	-			
Uranium	U	2.2	-			
Vanadium	V	99	48		89	70
Zinc	Zn	98	70	71	65.2	69.8

Total - Total metals

Conc Acid - concentrated HNO<sub>3</sub> and HCl

Dilute Acid - dilute HNO<sub>3</sub> and HCl

USEPA 3050 - Method digestion - ICP-AES Analysis

USEPA 3051 - Method digestion (microwave) - ICP-AES Analysis

## Appendix 5

**Table 1: Required QC Acceptance Criteria (DQO's) for NIST 2711**

Parameter	Element	CSR Regulated	Minimum (ug/g)	Maximum (ug/g)
Aluminum	Al	No	11,000	23,000
Antimony	Sb	Yes	15*	23*
Arsenic	As	Yes	83	110
Boron	B	Yes		
Barium	Ba	Yes	170	220
Beryllium	Be	Yes	0.61	1.35
Cadmium	Cd	Yes	32	47
Calcium	Ca	No	16,000	26,000
Chromium	Cr	Yes	16	27
Cobalt	Co	Yes	6.3	10.1
Copper	Cu	Yes	89	130
Iron	Fe	No	16,000	28,000
Lead	Pb	Yes	890	1,400
Magnesium	Mg	No	6,076	9,114
Manganese	Mn	No	410	614
Mercury	Hg	Yes	5.3	7.2
Molybdenum	Mo	Yes	0.5	2.7
Nickel	Ni	Yes	8.4	24
Phosphorus	P	No	510	860
Potassium	K	No		
Selenium	Se	Yes	1.2*	1.8*
Silicon	Si	No		
Silver	Ag	Yes	2.4	5.6
Sodium	Na	No		
Strontium	Sr	No	33	49
Sulphur	S	No	203	655
Tin	Sn	Yes	2.0*	3.0*
Titanium	Ti	No	238	356
Uranium	U	No		
Vanadium	V	Yes	32	55
Zinc	Zn	Yes	290	350

\* Certified values for NIST and recommended tolerances ( $\pm 20\%$ ), values in  $\mu\text{g/g}$

## Appendix 5 (continued)

**Table 2: Required QC Acceptance Criteria(DQO's)for CANMET TILL-1**

Parameter	Element	CSR Regulated	Minimum (ug/g)	Maximum (ug/g)
Aluminum	Al	No	14,000	21,000
Antimony	Sb	Yes	6.2*	9.4*
Arsenic	As	Yes	10	19
Boron	B	Yes		
Barium	Ba	Yes	62	101
Beryllium	Be	Yes	0.25	0.73
Cadmium	Cd	Yes	0.01	0.65
Calcium	Ca	No	2,100	4,400
Chromium	Cr	Yes	22	34
Cobalt	Co	Yes	8.4	17
Copper	Cu	Yes	36	54
Iron	Fe	No	23,000	43,000
Lead	Pb	Yes	7.8	20.5
Magnesium	Mg	No	4,629	6,943
Manganese	Mn	No	870	1,310
Mercury	Hg	Yes	0.03	0.16
Molybdenum	Mo	Yes	0.1	1.8
Nickel	Ni	Yes	8.9	26.9
Phosphorus	P	No	600	990
Potassium	K	No	321	873
Selenium	Se	Yes		
Silicon	Si	No		
Silver	Ag	Yes	0.01	0.43
Sodium	Na	No	143	527
Strontium	Sr	No	8	12
Sulphur	S	No	96	292
Tin	Sn	Yes		
Titanium	Ti	No	570	860
Uranium	U	No		
Vanadium	V	Yes	33	73
Zinc	Zn	Yes	55	80

**\*Provisional Values for Till-1 and recommended tolerances ( $\pm 20\%$ ), values in  $\mu\text{g/g}$**

## Appendix 6

### Test for Determining the Significance of the Difference of Two Means

The following is a summary of a two-tailed test for determining whether two means are significantly different (at the 95% confidence level). Two cases are described in John Keenan Taylor's Statistical Techniques for Data Analysis [13]. The case where the standard deviations of the two populations differ is summarized below. An alternative test, for where the standard deviations of the two populations do not significantly differ, is summarized in the reference text and may also be used.

This test is one of two options given in Method Equivalency section 1.2.1.(e)(ii) for determining the equivalence of any two data sets produced by the reference method and a modified method.

**Step 1:** Calculate the variances ( $V$ ) for the respective means for data sets A and B:

$$V_A = s_A^2 / n_A \qquad V_B = s_B^2 / n_B$$

where:  $s$  = the estimate of the standard deviation (in units of sample concentration, not %RSD)  
 $n$  = the number of independent data points

**Step 2:** Calculate the *effective number of degrees of freedom*,  $f$ , to be used for selecting  $t$  when calculating  $U$ :

$$f = \frac{(V_A + V_B)^2}{\frac{V_A^2}{(n-1)} + \frac{V_B^2}{(n-1)}}$$

Round the calculated value for  $f$  to the nearest integer. Values below 10 are typical for smaller data sets.

**Step 3:** Calculate  $U$ , the uncertainty in the difference of the means:

$$U_{\Delta} = t \sqrt{V_A + V_B}$$

where:  $t$  = the student's  $t$ -variate for a 2-tailed data set, at 95% confidence and  $f$  degrees of freedom.

**Step 4:** If the difference between the means is less than  $U$  the uncertainty in the difference of the means, then there is no evidence that the two data sets are significantly different at the 95% confidence level.

#### 1.2.2 Digestion Of Solids For Metals Analysis: Aqua Regia Digestion

**Application:** The methods summarized here apply to the analysis of sediments, soils, sludges and similar materials. **This method is not appropriate for Contaminated Sites (CSR) soil analysis.**

**Method Principle:** For "Heavy Metal" parameters a sample must be thoroughly mixed prior to acid digestion and analysis.

**Matrix:** Soils  
Solids  
(Marine) Sediment

**Heavy Metals Analysis:** An aqua regia (nitric/hydrochloric acid) digestion is performed either on an undried "as received" sample (results reported as ug/g - wet) or on a dried sample (results reported as ug/g). The digested samples may be analyzed by one of the following procedures:

- a) Flame Atomic Absorption (Flame AA) is used for high level screening. This method yields adequate quantitative results for some elements, e.g. K, Cd, and Pb.
- b) Inductively Coupled Argon Plasma Spectrograph (variously ICP or ICAP) is a broad scope technique but needs to be backed up by GFAA for low levels.
- c) Graphite Furnace AA (GFAA) is used for low concentrations, especially for Cu, Pb and Cd.
- d) Hydride Vapour Generation AA (HVGAA) is used as an alternative to GFAA for As and Se.
- e) Cold Vapour AA (CVAA) is used for analysis of mercury in view of its volatility.
- f) Inductively Coupled Argon Plasma/Mass Spectrometer (ICP/MS) may be used as an alternative to GFAA.

**Quality Control:** Multiple digestion blanks a minimum of two are prepared with each batch of samples. Some or all samples, depending upon project requirements, are digested and analyzed in duplicate. Marine Sediment Certified Reference Materials are digested and analyzed concurrently, other geological reference materials are available and can be used as alternatives. It should be noted that certain elements (i.e. barium, chromium and molybdenum) are often associated with the silicate matrix of sediment samples. Due to this circumstance the recoveries are often low when compared to the certified values using the described "nitric/hydrochloric" digestion scheme. From an environmental stand point, this generally is not a major issue since the more readily available metals (ie arsenic, cadmium, copper, lead, mercury and zinc) are typically those of most concern. These available elements also generally show a 90+ percent recovery in all reference materials analysed. Note that no correction values are applied where specific elements have shown low recoveries.

**Sample Containers:** Plastic or glass containers with tight fitting lids. Special cleaning is generally not necessary if new containers are used.

**Reagents:**

- a) "Trace Metal" grade nitric acid.
- b) "Trace Metal" grade hydrochloric acid.
- c) Ultrapure water.

**Apparatus:**

- a) 250 or 400 mL pyrex beakers with watchglass cover (note 1)
- b) Analytical balance (0.0001 g accuracy)
- c) Hot plate
- d) 50, 100, 200 mL volumetric flasks (note 2)
- e) Polypropylene bottles

Note 1 - All glass should be acid washed with "trace metal" nitric acid  
Note 2 - Class A and acid washed

**Sample Preparation Digestion Procedures:** Sample material can consist of relatively uniform fine granular material or material that can be described as non-homogeneous. The non-

homogeneous material can include slimes, fines, sand, gravel, rocks, wood chips, paint chips, organic material, shell fragments, and other material.

A specific referenced procedure for sample preparation has not been identified. The guideline is that thorough mixing to provide a homogenous sample is required. Most digestions require an undried sample size of at least five grams.

A tentative homogenation procedure is as follows:

- remove all sample material from container.
- place all material into a clean large glass plate or mixing bowl
- hand mix with the aid of an inert mixing device (i.e. wooden or plastic spoon).
- store mixed material in original sample bottle.

**Digestion Procedure:**

- a) Sample preparation
- b) Moisture Determination  
A moisture value calculated gravimetrically after drying an aliquot at 105°C is performed on a representative portion of the sample. This value is used for calculations of results from a wet to dry weight basis.
- c) Digestion
  1. Weigh mixed sample into an acid washed 250 mL beaker. Generally a 15g undried aliquot of material is used, but in cases of limited sample size a lower weight may be used. Record all weights to the nearest 3rd decimal (i.e. 16.025g).
  2. Add 10 mL nitric acid and 20 mL hydrochloric acid. Cover with watch glass. Allow any reaction to subside.
  3. Place on hot plate and heat gently until brown fumes disappear and volume is reduced to approximately 10 mL. If heavy brown fumes are still being produced a further 5 mL nitric acid may be added and digested further, until complete. NOTE: If samples "hop or bump" reduce the heat of the hot plate or move the samples to a cooler position on the plate and continue digestion.
  4. Cool solutions and bulk to volume in volumetric flasks (100 mL for most samples). Transfer to plastic bottles to proceed with instrumental analysis.

**Instrument Analysis:**

Analysis is performed by Flame AA, ICP, GFAA, HVGAA, CVAA or ICP/MS. Conditions and procedures are described in the respective methods.

**Calculations:**

Final results for all elements are calculated as follows:

Final Results (mg/g) = Conc. of Element in digest sol'n (mg/mL) x vol. of digest sol'n (mL) / Dry Weight (g)

**Quality Control:**

- a) Blanks: A minimum of two reagent blanks are run with each batch.
- b) Duplicates: Frequency depends on contract/client requirements. Unless otherwise specified a 10% duplication rate (minimum of one) is used for each batch.
- c) Certified Reference Materials: At least one per batch, preferably two per set. Choose reference materials which match the sample matrix as closely as possible.

**Safety Notes:** a) Care should be taken in handling the samples as some may be from heavily contaminated sites and thus may contain toxic compounds or be biologically active.

**References:**

- a) "Manual on Soil Sampling and Methods of Analysis", Canadian Society of Soil Science, 2nd Edition, 1978.
- b) "Procedures for Handling and Chemical Analysis of Sediment and Water Samples", U.S. EPA/Corps of Engineers, May 1981. This manual provides information on digestion and analysis procedures. Digestion procedures include HCl-HNO<sub>3</sub>, HNO<sub>3</sub>-H<sub>2</sub>O<sub>2</sub>, HF-HClO<sub>4</sub>-HNO<sub>3</sub> digestions. The focus is on environmental analysis.
- c) "Test Methods for Evaluating Solids Waste, Volume 1A", U.S. EPA, Third Edition, Nov. 1986. The focus is on environmental analysis). The main method #3050 includes Nitric Acid-Hydrogen Peroxide-Hydrochloric Acid Digestion and a variety of analysis methods.
- d) ASTM Methods, various sections.
- e) "A Manual on Analytical Methods Used by the Canadian Mining Industry", Canadian Mineral Analysts, (two volumes).

### 1.2.3 Digestion Of Solids For Metals Analysis: Perchloric Digestion

**Application:** The methods summarized here apply to the analysis of sediments, soils, sludges and similar materials. **This method is not appropriate for Contaminated Sites (CSR) soil analysis.**

**Container:** Glass or plastic container, wide mouth preferred.

**Principle of Method:** The sample is dried, ground to pass 100 mesh, and digested with a nitric-perchloric acid mixture to solubilize the solid matter and to remove the organic material by oxidation and volatilization. The sample is then analysed for the element(s) of interest.

**Matrix:** Soils  
Solids  
(Marine) Sediment

**Heavy Metals Analysis** The digested samples may be analyzed by one of the following procedures:

- a) Flame Atomic Absorption (Flame - AA) is used for high level screening. This method yields adequate quantitative results for some elements, e.g. K, Cd, and Pb.
- b) Inductively Coupled Argon Plasma Spectrograph (variously ICP or ICAP) is a broad scope technique but needs to be backed up by GFAA for low levels.
- c) Graphite Furnace AA (GFAA) is used for low concentrations, especially for Cu, Pb and Cd.
- d) Hydride Vapour Generation AA (HVGAA) is used as an alternative to GFAA for As and Se.
- e) Cold Vapour AA (CVAA) is used for analysis of mercury in view of its volatility.
- f) Inductively Coupled Argon Plasma/Mass Spectrometer (ICP/MS) may be used as an alternative to GFAA.

**Interferences:** Not available

**Apparatus:**

- a) Glassware
- b) Digest block



- Reagents:**
- a) Nitric Acid (HNO<sub>3</sub>), concentrated, analytical grade.
  - b) Perchloric Acid (HClO<sub>4</sub>), 70%, analytical grade.

- Procedure:**
- Notes:
- a) Soil and Sediment - All samples are dried at 60°C (maximum) and ground to pass 0.15 mm sieve (100 mesh).
  - b) Digestion should be carried out in a fumehood designed for use with perchloric acid.
  - c) Weights and volumes are specified for a 75 mL digestion tube. If using a smaller tube, eg. 40 or 50 mL, reduce sample size and reagent volumes proportionally.
1. Weigh 0.75 g of sample to the nearest 0.1 mg into a 75 mL digestion tube.
  2. Add 2 mL conc. HNO<sub>3</sub>. More acid may be needed for some samples.
  3. Heat in block digester at 100 - 150°C until brown fumes are eliminated. Remove and cool.
  4. Add 3.75 mL HClO<sub>4</sub>, 70%.
  5. Heat in block at 220 - 250°C until dense white fumes are present. Remove and cool. Digestate should be light yellow to colourless.
  6. Dilute to 75 mL mark with deionized water. Filter soils and sediments through Whatman #42 filter paper and plant tissue through Whatman #41 filter paper. Store filtered digestate in 250 mL polyethylene bottles.

- Quality Control:**
- a) Blanks: A minimum of two reagent blanks are run with each batch.
  - b) Duplicates: Frequency depends on contract/client requirements. Unless otherwise specified a 10% duplication rate (minimum of one) is used for each batch.
  - d) Certified Reference Materials: At least one per batch, preferably two per set. Choose reference materials which match the sample matrix as closely as possible.

#### 1.2.4 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; ie, 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  $\text{Hg}^{+2}$ ,  $\text{Sb}^{+3}$  and  $\text{Se}^{+4}$  tend to be lost from HCl solutions; in contrast,  $\text{Cr}^{+3}$  tends to be lost from perchloric acid solutions at temperatures above 150°C through the formation of chromyl chloride ( $\text{CrO}_2\text{Cl}_2$ ).  $\text{As}^{+3}$ ,  $\text{Sn}^{+2}$ , 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.

## **2.0 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<sup>(1)</sup>**

<b>Metal</b>	<b><u>Direct Aspiration</u></b>				<b><u>Furnace Procedure (4,5)</u></b>		
	<b>Detection Limit mg/L</b>	<b>Sensitivity* mg/L</b>	<b>Optimum Concentration Range mg/L</b>		<b>Detection Limit mg/L</b>	<b>Optimum Concentration Range mg/L</b>	
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-1 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  $\pm 10\%$ ) 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. The 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  $\text{HNO}_3$  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 ( $\text{HNO}_3$ ): 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 Fig. 1.

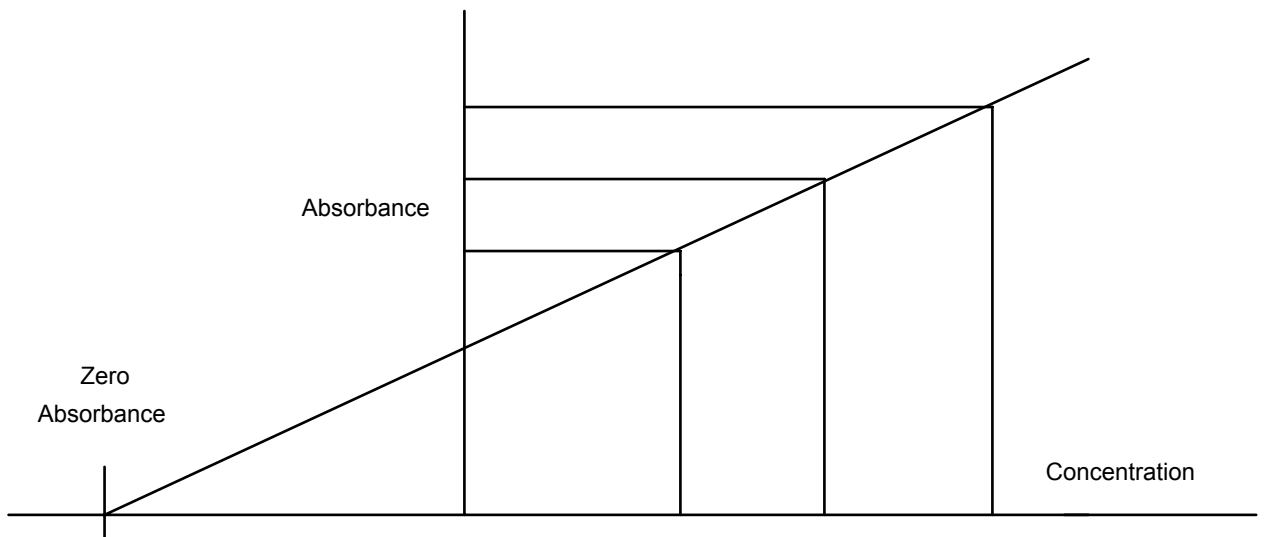


Figure 1. Standard Addition Plot

Conc. of sample	Addn 0 No Addn	Addn 1 Addn of 50% of Expected Amount	Addn 2 Addn of 100% of Expected Amount	Addn 3 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. **If dilution of sample was required:**

$$\text{mg metal/L in sample} = \frac{A (C+B)}{C}$$

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. **For samples containing particulates:**

$$\text{mg metal/L in sample} = \frac{A (V / C)}$$

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. **For solid samples:** 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  $\mu\text{g/L}$  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:**

$$\mu\text{g metal/L of sample} = Z ( S/U )$$

where: Z =  $\mu\text{g/L}$  of metal read from calibration curve or readout system  
S =  $\mu\text{L}$  of standard injected into furnace for calibration curve  
U =  $\mu\text{L}$  of sample injected for analysis

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

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

where: Z =  $\mu\text{g/L}$  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:**

$$\mu\text{g metal/L of sample} = Z ( V / C )$$

where: Z =  $\mu\text{g/L}$  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:**

$$\text{mg metal /kg sample} = ( Z \times V / 1000 ) / D$$

where: Z =  $\mu\text{g/L}$  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:**

$$\text{mg metal/kg sample} = ( Z \times V / 1000 ) / (W \times P)$$

where: Z =  $\mu\text{g/L}$  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  $\pm 10$  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  $\pm 10$  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.

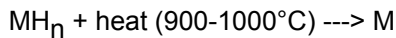
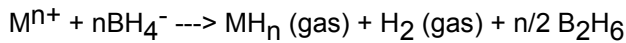
### **2.2.3 Interferences**

The following metals, compounds and conditions may interfere:

- easily reduced metals; ie, copper, silver, mercury, etc.
- high concentrations of transition metals (>200 mg/L)
- oxidizing agents remaining following sample digestion; ie, 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 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]

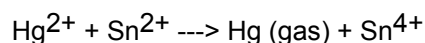
### 2.3.3 Interferences and Precautions

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:



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 includes:

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 ultra violet, 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  $\pm 5\%$  [2, 3] although Millward and Kluckner [4] found that  $\pm 2.5\%$  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	30-100
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 monochromator 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  $10^6$ .
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:  
December 31, 2000:

Publication in 1994 Laboratory Manual.  
SEAM codes removed. Minor editing.

### 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.

<b>MDL</b>	<b>Target Element</b>	<b>Detection Limit (ug/g)</b>
	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 dependant on the specific instrument configuration.

<b>Matrix</b>	Soil Solids (Marine) Sediments
<b>Interferences and Precautions</b>	Not available
<b>Sample Handling and Preservation</b>	Container - Acid Washed Polyethylene Bottle Digested soils are already in an acid medium and require no extra preservation chemicals.
<b>Stability</b>	Metallic elements in acid digested soil samples have a holding time of six months.
<b>Instrumentation/ Calibration and Analysis Procedures</b>	Refer to Specific Instrument Operations Manuals, EPA Method 6010A
<b>Precision</b>	Refer to EPA Method 6010A and Section 2.5.6 of the ICP-AES method in the B.C. Laboratory Manual for further explanations.
<b>Accuracy</b>	Refer to EPA Method 6010A and Section 2.5.7 of the ICP-AES method in the B.C. Laboratory Manual for further explanations.
<b>Quality Control</b>	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
<b>References</b>	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.

**3.0 SPECIFIC ELEMENTAL CONDITIONS**

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

## ALUMINUM (Atomic Absorption - Direct Aspiration)

<b>Parameter</b>	Aluminum, total Aluminum, dissolved
<b>Sample Preparation</b>	See section 1.0, the sample preparation section.
<b>Analytical Method</b>	See section 2.1, the AA methods section.
<b>EMS Code</b>	FA: HNO <sub>3</sub> : AA (total) <b>AI-T X073</b> LA: HNO <sub>3</sub> : AA (total) <b>AI-T X351</b> FF, FA: HNO <sub>3</sub> : AA (dissolved) <b>AI-D X203</b> LF, LA: HNO <sub>3</sub> : AA (dissolved) <b>AI-D X085</b>
<b>Method Summary</b>	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.
<b>MDL</b>	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.
<b>Matrix</b>	Water, wastewater, marine water
<b>Interferences and Precautions</b>	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.
<b>Sample Handling and Preservation</b>	See section 1.0, the sample preparation section of this manual.
<b>Stability</b>	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
<b>Instrument Parameters</b>	Source: Al Hollow cathode Lamp Wavelength: 309.3 nm (primary); 396.2 nm (alternate) Type of Flame: nitrous oxide-acetylene Background Correction: recommended
<b>Apparatus, Materials and Reagents</b>	See sections 2.1.5 and 2.1.6 of this manual.
<b>Precision</b>	None listed.
<b>Accuracy</b>	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)

<b>Parameter</b>	Antimony, total Antimony, dissolved
<b>Sample Preparation</b>	See section 1.0, the sample preparation section.
<b>Analytical Method</b>	See section 2.1, the AA methods section.
<b>EMS Code</b>	FA: HNO <sub>3</sub> : AA (total) <b>Sb-T X073</b> LA: HNO <sub>3</sub> : AA (total) <b>Sb-T X351</b> FF, FA: HNO <sub>3</sub> : AA (dissolved) <b>Sb-D X203</b> LF, LA: HNO <sub>3</sub> :AA (dissolved) <b>Sb-D X085</b>
<b>Introduction</b>	Antimony and its compounds have been reported to cause dermatitis, keratitis, conjunctivitis and nasal septal ulceration by contact, fumes, or dust.
<b>Method Summary</b>	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.
<b>MDL</b>	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.
<b>Matrix</b>	Water, waste water and marine water.
<b>Interferences and Precautions</b>	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.
<b>Sample Handling and Preservation</b>	See section 1.0, the sample preparation section of this manual.
<b>Stability</b>	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
<b>Instrument Parameters</b>	Source: Sb EDL or hollow cathode lamp Wavelength: 217.6 nm (primary) Type of Flame: air/acetylene Background Correction: recommended
<b>Apparatus, Materials and Reagents</b>	See section 2.1.5 and 2.1.6 of this manual.
<b>Precision</b>	None listed.

<b>Accuracy</b>	None listed.	
<b>Quality Control</b>	See section 2.1.9, QA/QC Guidelines in this manual.	
<b>References</b>	<ul style="list-style-type: none"> <li>a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992, Method 3111 B/D.</li> <li>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.</li> </ul>	
<b>Revision History</b>	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)

<b>Parameter</b>	Antimony, total Antimony, dissolved																
<b>Sample Preparation</b>	See section 1.0, the sample preparation section.																
<b>Analytical Method</b>	See section 2.1, the AA methods section, and section 2.2 the hydride AA method section.																
<b>EMS Code</b>	<table border="0"> <tr> <td>FA: HNO<sub>3</sub>: HVAAS (total)</td> <td><b>Sb-T X289</b></td> </tr> <tr> <td>LA: HNO<sub>3</sub>: HVAAS (total)</td> <td><b>Sb-T X354</b></td> </tr> <tr> <td>FA: HCl: HVAAS (total)</td> <td><b>Sb-T X345</b></td> </tr> <tr> <td>LA: HCl: HVAAS (total)</td> <td><b>Sb-T X355</b></td> </tr> <tr> <td>FF, FA: HNO<sub>3</sub>: HVAAS (dissolved)</td> <td><b>Sb-D X202</b></td> </tr> <tr> <td>LF, LA: HNO<sub>3</sub>: HVAAS (dissolved)</td> <td><b>Sb-D X359</b></td> </tr> <tr> <td>FF, FA: HCl: HVAAS (dissolved)</td> <td><b>Sb-D X348</b></td> </tr> <tr> <td>LF, LA: HCl: HVAAS (dissolved)</td> <td><b>Sb-D X360</b></td> </tr> </table>	FA: HNO <sub>3</sub> : HVAAS (total)	<b>Sb-T X289</b>	LA: HNO <sub>3</sub> : HVAAS (total)	<b>Sb-T X354</b>	FA: HCl: HVAAS (total)	<b>Sb-T X345</b>	LA: HCl: HVAAS (total)	<b>Sb-T X355</b>	FF, FA: HNO <sub>3</sub> : HVAAS (dissolved)	<b>Sb-D X202</b>	LF, LA: HNO <sub>3</sub> : HVAAS (dissolved)	<b>Sb-D X359</b>	FF, FA: HCl: HVAAS (dissolved)	<b>Sb-D X348</b>	LF, LA: HCl: HVAAS (dissolved)	<b>Sb-D X360</b>
FA: HNO <sub>3</sub> : HVAAS (total)	<b>Sb-T X289</b>																
LA: HNO <sub>3</sub> : HVAAS (total)	<b>Sb-T X354</b>																
FA: HCl: HVAAS (total)	<b>Sb-T X345</b>																
LA: HCl: HVAAS (total)	<b>Sb-T X355</b>																
FF, FA: HNO <sub>3</sub> : HVAAS (dissolved)	<b>Sb-D X202</b>																
LF, LA: HNO <sub>3</sub> : HVAAS (dissolved)	<b>Sb-D X359</b>																
FF, FA: HCl: HVAAS (dissolved)	<b>Sb-D X348</b>																
LF, LA: HCl: HVAAS (dissolved)	<b>Sb-D X360</b>																
<b>Introduction</b>	Antimony and its compounds have been reported to cause dermatitis, keratitis, conjunctivitis, and nasal septal ulceration by contact, fumes, or dust.																
<b>Method Summary</b>	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.																
<b>MDL</b>	<p>Given an aqueous sample free of interferences, the instrumental performance characteristics are:</p> <p>MDL: 0.0001 mg/L</p> <p>Range: 0.0001-0.010 mg/L</p> <p>See Table C-1 in section 2.1, the AA methods section, for additional information.</p>																
<b>Matrix</b>	Water, wastewater, marine water.																
<b>Interferences and Precautions</b>	See section 2.2.3 in the hydride AA section of this manual.																
<b>Sample Handling and Preservation</b>	See section 1.0, the sample preparation section of this manual.																
<b>Stability</b>	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.																
<b>Instrument Parameters</b>	<p>Source: Sb EDL or hollow cathode lamp</p> <p>Wavelength: 217.6 nm</p> <p>Background Correction: not required</p>																
<b>Apparatus, Materials and Reagents</b>	See section 2.2 and section 2.1.5 and 2.1.6 of this manual.																
<b>Precision</b>	None listed.																

<b>Accuracy</b>	None listed.				
<b>Quality Control</b>	See section 2.1.9, QA/QC Guidelines in this manual.				
<b>References</b>	<ul style="list-style-type: none"> <li>a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 18th edition, 1992.</li> <li>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.</li> </ul>				
<b>Revision History</b>	<table> <tr> <td>February 14, 1994:</td> <td>Publication in 1994 Laboratory Manual.</td> </tr> <tr> <td>December 31, 2000:</td> <td>SEAM codes replaced by EMS codes. Sample matrix added.</td> </tr> </table>	February 14, 1994:	Publication in 1994 Laboratory Manual.	December 31, 2000:	SEAM codes replaced by EMS codes. Sample matrix added.
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)

<b>Parameter</b>	Antimony, total Antimony, dissolved
<b>Sample Preparation</b>	See section 1.0, the sample preparation section.
<b>Analytical Method</b>	See section 2.1, the AA methods section.
<b>EMS Code</b>	FA: HNO <sub>3</sub> : GFAA (total) <b>Sb-T X072</b> LA: HNO <sub>3</sub> : GFAA (total) <b>Sb-T X179</b> FF, FA: HNO <sub>3</sub> : GFAA (dissolved) <b>Sb-D X116</b> LF, LA: HNO <sub>3</sub> : GFAA (dissolved) <b>Sb-D X357</b>
<b>Introduction</b>	Antimony and its compounds have been reported to cause dermatitis, keratitis, conjunctivitis and nasal septal ulceration by contact, fumes, or dust.
<b>Method Summary</b>	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.
<b>MDL</b>	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.
<b>Matrix</b>	Water, wastewater, marine water.
<b>Interferences and Precautions</b>	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.
<b>Sample Handling and Preservation</b>	See section 1.0, the sample preparation section of this manual.
<b>Stability</b>	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
<b>Instrument Parameters</b>	Source: Sb EDL or hollow cathode lamp Wavelength: 217.6 nm Background Correction: recommended
<b>Apparatus, Materials and Reagents</b>	See sections 2.1.5 and 2.1.6 of this manual.

<b>Precision</b>	None listed.	
<b>Accuracy</b>	None listed.	
<b>Quality Control</b>	See section 2.1.9, QA/QC Guidelines in this manual.	
<b>References</b>	<ul style="list-style-type: none"> <li>a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992, Method 3111 B.</li> <li>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.</li> </ul>	
<b>Revision History</b>	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})

<b>Parameter</b>	Antimony, total Antimony, dissolved
<b>Sample Preparation</b>	See section 1.0, the sample preparation section.
<b>Analytical Method</b>	See section 2.4, the ICP-AES method section.
<b>EMS Code</b>	FA: HNO <sub>3</sub> : ICAP (total) <b>Sb-T X349</b> LA: HNO <sub>3</sub> : ICAP (total) <b>Sb-T X352</b> FF, FA: HNO <sub>3</sub> : ICAP (dissolved) <b>Sb-D X350</b> LF, LA: HNO <sub>3</sub> : ICAP (dissolved) <b>Sb-D X356</b>
<b>Introduction</b>	Antimony and its compounds have been reported to cause dermatitis, keratitis, conjunctivitis, and nasal septal ulceration by contact, fumes, or dust.
<b>Method Summary</b>	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.
<b>MDL</b>	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.
<b>Matrix</b>	Water, wastewater, marine water.
<b>Interferences and Precautions</b>	See section 2.4.4, the ICP-AES section of this manual.
<b>Sample Handling and Preservation</b>	See section 1.0, the sample preparation section of this manual.
<b>Stability</b>	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
<b>Instrument Parameters</b>	Wavelength: 206.8 nm Background Correction: recommended
<b>Apparatus, Materials and Reagents</b>	See section 2.4, the ICP-AES methods section in this manual.
<b>Precision</b>	None listed.
<b>Accuracy</b>	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)

<b>Parameter</b>	Arsenic, total Arsenic, dissolved								
<b>Sample Preparation</b>	See section 1.0, the sample preparation section.								
<b>Analytical Method</b>	See section 2.1, the AA methods section.								
<b>EMS Code</b>	<table border="0"> <tr> <td>FA: HNO<sub>3</sub>: AA (total)</td> <td><b>As-T X073</b></td> </tr> <tr> <td>LA: HNO<sub>3</sub>: AA (total)</td> <td><b>As-T X351</b></td> </tr> <tr> <td>FF, FA: HNO<sub>3</sub>: AA (dissolved)</td> <td><b>As-D X203</b></td> </tr> <tr> <td>LF, LA: HNO<sub>3</sub>: AA (dissolved)</td> <td><b>As-D X085</b></td> </tr> </table>	FA: HNO <sub>3</sub> : AA (total)	<b>As-T X073</b>	LA: HNO <sub>3</sub> : AA (total)	<b>As-T X351</b>	FF, FA: HNO <sub>3</sub> : AA (dissolved)	<b>As-D X203</b>	LF, LA: HNO <sub>3</sub> : AA (dissolved)	<b>As-D X085</b>
FA: HNO <sub>3</sub> : AA (total)	<b>As-T X073</b>								
LA: HNO <sub>3</sub> : AA (total)	<b>As-T X351</b>								
FF, FA: HNO <sub>3</sub> : AA (dissolved)	<b>As-D X203</b>								
LF, LA: HNO <sub>3</sub> : AA (dissolved)	<b>As-D X085</b>								
<b>Introduction</b>	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.								
<b>Method Summary</b>	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.								
<b>MDL</b>	<p>Given an aqueous sample free of interferences, the instrumental performance characteristics are:</p> <p>MDL: 0.20 mg/L</p> <p>Range: 0.2-100mg/L</p> <p>See Table C-1 in section 2.1, the AA methods section, for additional information.</p>								
<b>Matrix</b>	Water, wastewater, marine water.								
<b>Interferences and Precautions</b>	<p>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.</p> <p>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.</p>								
<b>Sample Handling and Preservation</b>	See section 1.0, the sample preparation section of this manual.								
<b>Stability</b>	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.								

<b>Instrument Parameters</b>	Source: As EDL or hollow cathode lamp Wavelength: 193.7 nm Type of flame: air/acetylene Background correction: recommended	
<b>Apparatus, Materials and Reagents</b>	See section 2.1.5 and 2.1.6 of this manual.	
<b>Precision</b>	None listed.	
<b>Accuracy</b>	None listed.	
<b>Quality Control</b>	See section 2.1.9, QA/QC Guidelines in this manual.	
<b>References</b>	<ul style="list-style-type: none"> <li>a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992, Method 3111 B/D.</li> <li>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.</li> </ul>	
<b>Revision History</b>	February 14, 1994:	Publication in 1994 Laboratory Manual.
	December 31, 2000:	SEAM codes replaced by EMS codes.

## ARSENIC (Atomic Absorption - Gaseous Hydride)

<b>Parameter</b>	Arsenic, total Arsenic, dissolved	
<b>Sample Preparation</b>	See section 1.0, the sample preparation section.	
<b>Analytical Method</b>	See section 2.1, the AA methods section, and section 2.2, the hydride AA method section.	
<b>EMS Code</b>	FA: HNO <sub>3</sub> : HVAAS (total)	<b>As-T X289</b>
	LA: HNO <sub>3</sub> : HVAAS (total)	<b>As-T X354</b>
	FA: HCl: HVAAS (total)	<b>As-T X345</b>
	LA: HCl: HVAAS (total)	<b>As-T X355</b>
	FF, FA: HNO <sub>3</sub> : HVAAS (dissolved)	<b>As-D X202</b>
	LF, LA: HNO <sub>3</sub> : HVAAS (dissolved)	<b>As-D X359</b>
	FF, FA: HCl: HVAAS (dissolved)	<b>As-D X348</b>
	LF, LA: HCl: HVAAS (dissolved)	<b>As-D X360</b>
<b>Introduction</b>	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.	
<b>Method Summary</b>	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.	
<b>MDL</b>	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.	
<b>Matrix</b>	Water, wastewater, marine water.	
<b>Interferences and Precautions</b>	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.	
<b>Stability</b>	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.	
<b>Instrument</b>	Source: As EDL or hollow cathode lamp	

<b>Parameters</b>	Wavelength: 193.7 nm Background Correction: not required	
<b>Apparatus, Materials and Reagents</b>	See section 2.2.3 and section 2.1.5 and 2.1.6 of this manual.	
<b>Precision</b>	None listed.	
<b>Accuracy</b>	None listed.	
<b>Quality Control</b>	See section 2.1.9, QA/QC Guidelines in this manual.	
<b>References</b>	<ul style="list-style-type: none"> <li>a) B.C. Ministry of Environment, Laboratory Manual p. 97, 1989.</li> <li>b) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 18th edition, 1992.</li> <li>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.</li> </ul>	
<b>Revision History</b>	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})**

<b>Parameter</b>	Arsenic, total Arsenic, dissolved
<b>Sample Preparation</b>	See section 1.0, the sample preparation section.
<b>Analytical Method</b>	See section 2.4, the ICP-AES method section.
<b>EMS Code</b>	FA: HNO <sub>3</sub> : ICAP (total) <b>As-T X349</b> LA: HNO <sub>3</sub> : ICAP (total) <b>As-T X352</b> FF, FA: HNO <sub>3</sub> : ICAP (dissolved) <b>As-D X350</b> LF, LA: HNO <sub>3</sub> : ICAP (dissolved) <b>As-D X356</b>
<b>Introduction</b>	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.
<b>Method Summary</b>	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.
<b>MDL</b>	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.
<b>Matrix</b>	Water, wastewater, marine water.
<b>Interferences and Precautions</b>	See section 2.4.4 of the ICP-AES section of this manual.
<b>Sample Handling and Preservation</b>	See section 1.0, the sample preparation section of this manual.
<b>Stability</b>	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
<b>Instrument Parameters</b>	Wavelength: 193.8 nm (primary) Background Correction: recommended
<b>Apparatus, Materials and Reagents</b>	See section 2.4 of this manual.
<b>Precision</b>	None listed.

<b>Accuracy</b>	None listed.	
<b>Quality Control</b>	See section 2.1.9, QA/QC Guidelines in this manual.	
<b>References</b>	<ul style="list-style-type: none"> <li>a) Standard Method for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992, Method 3120 B.</li> <li>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.</li> </ul>	
<b>Revision History</b>	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

<b>Parameter</b>	As-T - Arsenic Total
<b>Sample Preparation</b>	Nitric-perchloric acid digestion
<b>Analytical Method</b>	N/P Digestion: Hydride Generation Atomic Absorption Spectrophotometry
<b>EMS Codes</b>	AS-T      1194                      HYDRIDE ATOM. ABSORPTION SPEC
<b>Method Summary</b>	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 the aqueous solution and introduced to a flame heated quartz absorption cell. Atomic absorption is measured at 193.77 nm.
<b>MDL</b>	0.2 µg/g
<b>Matrix</b>	Soil Solids (Marine) Sediments
<b>Stability</b>	Digested samples are stable for 6 months.
<b>Procedure Apparatus</b>	a) Digest Block b) Glassware
<b>Instrumentation</b>	A system consisting of: a) peristaltic pump b) hydride generator, (mixing coils and phase separator) c) Quartz absorption cell d) Atomic absorption spectrophotometer
<b>Reagents</b>	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.
<b>Standards</b>	a) Stock Arsenic Calibration standards, 1000 mg/L; available commercially, or: 1) 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.

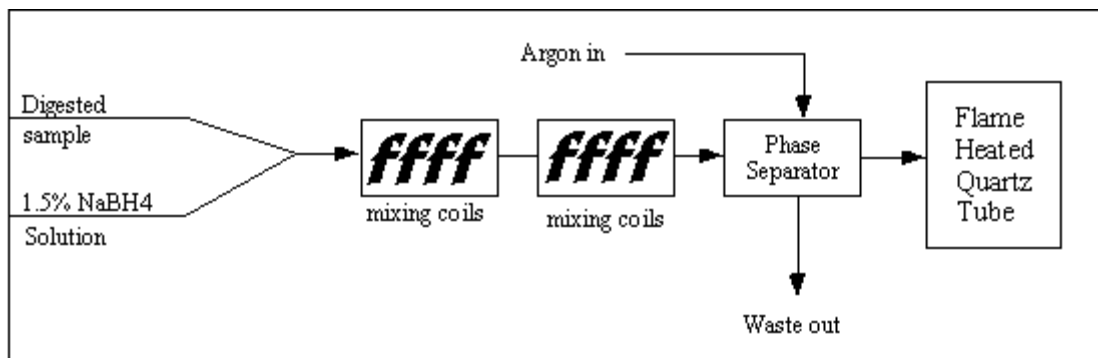
**Procedure** See "Digestion of Soils for metals Analysis".

- 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) NaBH<sub>4</sub> 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 solutions 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:  
November 2002:

Published in Supplement Manual #1  
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.

<b>Compounds Determined and Detection Limits</b>	<b>Element</b>	<b>Detection Limit (µg/g)</b>
	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 tips  
1000 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 Certified Reference Materials include: Environmental Sediments: 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 atomizer 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 Sources

- 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)  
Varian Instruments at Work (Various Issues)

## Revision History:

March 1997;  
November 2002.

Published in Manual Supplement #1  
Method adopted from Supplement #1



## BARIUM (Atomic Absorption - Direct Aspiration)

<b>Parameter</b>	Barium, total Barium, dissolved								
<b>Sample Preparation</b>	See section 1.0, the sample preparation section.								
<b>Analytical Method</b>	See section 2.1, the AA methods section.								
<b>EMS Code</b>	<table> <tr> <td>FA: HNO<sub>3</sub>: AA (total)</td> <td><b>Ba-T X073</b></td> </tr> <tr> <td>LA: HNO<sub>3</sub>: AA (total)</td> <td><b>Ba-T X351</b></td> </tr> <tr> <td>FF, FA: HNO<sub>3</sub>: AA (dissolved)</td> <td><b>Ba-D X203</b></td> </tr> <tr> <td>LF, LA: HNO<sub>3</sub>: AA (dissolved)</td> <td><b>Ba-D X085</b></td> </tr> </table>	FA: HNO <sub>3</sub> : AA (total)	<b>Ba-T X073</b>	LA: HNO <sub>3</sub> : AA (total)	<b>Ba-T X351</b>	FF, FA: HNO <sub>3</sub> : AA (dissolved)	<b>Ba-D X203</b>	LF, LA: HNO <sub>3</sub> : AA (dissolved)	<b>Ba-D X085</b>
FA: HNO <sub>3</sub> : AA (total)	<b>Ba-T X073</b>								
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FF, FA: HNO <sub>3</sub> : AA (dissolved)	<b>Ba-D X203</b>								
LF, LA: HNO <sub>3</sub> : AA (dissolved)	<b>Ba-D X085</b>								
<b>Introduction</b>	<p>Barium is found mainly as barite, BaSO<sub>4</sub>, and witherite, BaCO<sub>3</sub>, both of which are highly insoluble salts.</p> <p>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.</p> <p>Canadian Drinking Water Guidelines stipulates 1mg/L as the IMAC (interim maximum acceptable concentration).</p>								
<b>Method Summary</b>	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.								
<b>MDL</b>	<p>Given an aqueous sample free of interferences, the instrumental performance characteristics are:</p> <p>MDL: 0.1 mg/L</p> <p>Range: 0.1-20.0 mg/L</p> <p>See Table C-1 in section 2.1, the AA methods section, for additional information.</p>								
<b>Matrix</b>	Water, wastewater, marine water.								
<b>Interferences and Precautions</b>	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 using the 553.6 nm line.								
<b>Sample Handling and Preservation</b>	See section 1.0, the sample preparation section.								
<b>Stability</b>	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.								

<b>Instrument Parameters</b>	Source: Ba hollow cathode lamp Wavelength: 553.6 nm Type of Flame: nitrous oxide/acetylene Background Correction: recommended	
<b>Apparatus, Materials and Reagents</b>	See section 2.1.5 and 2.1.6 of this manual.	
<b>Precision</b>	None listed.	
<b>Accuracy</b>	None listed.	
<b>Quality Control</b>	See section 2.1.9, QA/QC Guidelines in this manual.	
<b>References</b>	<ul style="list-style-type: none"> <li>a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 18th edition, 1992.</li> <li>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.</li> </ul>	
<b>Revision History</b>	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)

<b>Parameter</b>	Barium, total Barium, dissolved								
<b>Sample Preparation</b>	See section 1.0, the sample preparation section.								
<b>Analytical Method</b>	See section 2.1, the AA methods section.								
<b>EMS Code</b>	<table border="0"> <tr> <td>X072 FA: HNO<sub>3</sub>: GFAA (total)</td> <td><b>Ba-T X072</b></td> </tr> <tr> <td>X179 LA: HNO<sub>3</sub>: GFAA (total)</td> <td><b>Ba-T X179</b></td> </tr> <tr> <td>X116 FF, FA: HNO<sub>3</sub>: GFAA (dissolved)</td> <td><b>Ba-D X116</b></td> </tr> <tr> <td>X357 LF, LA: HNO<sub>3</sub>: GFAA (dissolved)</td> <td><b>Ba-D X357</b></td> </tr> </table>	X072 FA: HNO <sub>3</sub> : GFAA (total)	<b>Ba-T X072</b>	X179 LA: HNO <sub>3</sub> : GFAA (total)	<b>Ba-T X179</b>	X116 FF, FA: HNO <sub>3</sub> : GFAA (dissolved)	<b>Ba-D X116</b>	X357 LF, LA: HNO <sub>3</sub> : GFAA (dissolved)	<b>Ba-D X357</b>
X072 FA: HNO <sub>3</sub> : GFAA (total)	<b>Ba-T X072</b>								
X179 LA: HNO <sub>3</sub> : GFAA (total)	<b>Ba-T X179</b>								
X116 FF, FA: HNO <sub>3</sub> : GFAA (dissolved)	<b>Ba-D X116</b>								
X357 LF, LA: HNO <sub>3</sub> : GFAA (dissolved)	<b>Ba-D X357</b>								
<b>Introduction</b>	<p>Barium is found mainly as barite, BaSO<sub>4</sub>, and witherite, BaCO<sub>3</sub>, 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.</p> <p>Canadian Drinking Water Guidelines stipulates 1 mg/L as the IMAC (interim maximum acceptable concentration).</p>								
<b>Method Summary</b>	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.								
<b>MDL</b>	<p>Given an aqueous sample free of interferences, the instrumental performance characteristics are:</p> <p>MDL: 0.002 mg/L Range: 0.002-0.200 mg/L</p> <p>See Table C-1 in section 2.1, the AA methods section, for additional information.</p>								
<b>Matrix</b>	Water, wastewater, marine water.								
<b>Interferences and Precautions</b>	<p>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.</p> <p>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.</p>								

<b>Sample Handling and Preservation</b>	See section 1.0, the sample preparation section.				
<b>Stability</b>	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.				
<b>Instrument Parameters</b>	Source: Ba hollow cathode lamp Wavelength: 553.6 nm Background Correction: recommended				
<b>Apparatus, Materials and Reagents</b>	See section 2.1.5 and 2.1.6 of this manual.				
<b>Precision</b>	None listed.				
<b>Accuracy</b>	None listed.				
<b>Quality Control</b>	See section 2.1.9, QA/QC Guidelines in this manual.				
<b>References</b>	<ul style="list-style-type: none"> <li>a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 18th edition, 1992.</li> <li>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.</li> </ul>				
<b>Revision History</b>	<table> <tr> <td>February 14, 1994:</td> <td>Publication in 1994 Laboratory Manual.</td> </tr> <tr> <td>December 31, 2000:</td> <td>SEAM codes replaced by EMS codes. Sample matrix added.</td> </tr> </table>	February 14, 1994:	Publication in 1994 Laboratory Manual.	December 31, 2000:	SEAM codes replaced by EMS codes. Sample matrix added.
February 14, 1994:	Publication in 1994 Laboratory Manual.				
December 31, 2000:	SEAM codes replaced by EMS codes. Sample matrix added.				

## CADMIUM (Atomic Absorption - Direct Aspiration)

<b>Parameter</b>	Cadmium, total Cadmium, dissolved								
<b>Sample Preparation</b>	See section 1.0, the sample preparation section.								
<b>Analytical Method</b>	See section 2.1, the AA methods section.								
<b>EMS Code</b>	<table border="0"> <tr> <td>FA: HNO<sub>3</sub>: AA (total)</td> <td><b>Cd-T X073</b></td> </tr> <tr> <td>LA: HNO<sub>3</sub>: AA (total)</td> <td><b>Cd-T X351</b></td> </tr> <tr> <td>FF, FA: HNO<sub>3</sub>: AA (dissolved)</td> <td><b>Cd-D X203</b></td> </tr> <tr> <td>LF, LA: HNO<sub>3</sub>: AA (dissolved)</td> <td><b>Cd-D X085</b></td> </tr> </table>	FA: HNO <sub>3</sub> : AA (total)	<b>Cd-T X073</b>	LA: HNO <sub>3</sub> : AA (total)	<b>Cd-T X351</b>	FF, FA: HNO <sub>3</sub> : AA (dissolved)	<b>Cd-D X203</b>	LF, LA: HNO <sub>3</sub> : AA (dissolved)	<b>Cd-D X085</b>
FA: HNO <sub>3</sub> : AA (total)	<b>Cd-T X073</b>								
LA: HNO <sub>3</sub> : AA (total)	<b>Cd-T X351</b>								
FF, FA: HNO <sub>3</sub> : AA (dissolved)	<b>Cd-D X203</b>								
LF, LA: HNO <sub>3</sub> : AA (dissolved)	<b>Cd-D X085</b>								
<b>Introduction</b>	<p>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.</p> <p>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.</p>								
<b>Method Summary</b>	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.								
<b>MDL</b>	<p>Given an aqueous sample free of interferences, the instrumental performance characteristics are:</p> <p>MDL: 0.005 mg/L Range: 0.005-2.00 mg/L</p> <p>See Table C-1 in section 2.1, the AA methods section, for additional information.</p>								
<b>Matrix</b>	Water, wastewater, marine water.								
<b>Interferences and Precautions</b>	See section 2.1.4 of the AA methods section of this manual. Coexisting elements causing relatively large interferences are Ca, Si, and Ti.								
<b>Sample Handling and Preservation</b>	See section 1.0 the sample preparation section of this manual.								
<b>Stability</b>	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.								
<b>Instrument Parameters</b>	<p>Source: Cd hollow cathode lamp Wavelength: 228.8 nm Type of Flame: air/acetylene Background Correction: recommended</p>								

<b>Apparatus, Materials and Reagents</b>	See section 2.1.5 and 2.1.6 of the AA methods section of this manual.	
<b>Precision</b>	None listed.	
<b>Accuracy</b>	None listed.	
<b>Quality Control</b>	See section 2.1.9 QA/QC Guidelines in this manual.	
<b>References</b>	<ul style="list-style-type: none"> <li>a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 17th edition, 1989 Method 3500-Cd.</li> <li>b) Methods for Chemical Analysis of Water and Wastes, EPA-600 4-79-020, March 1983, Method 213.1.</li> <li>c) Trace Elements in Human and Animal Nutrition, Eric J. Underwood, 4th edition, Academic Press, 1977.</li> <li>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.</li> </ul>	
<b>Revision History</b>	February 14, 1994:	Publication in 1994 Laboratory Manual.
	December 31, 2000:	SEAM codes replaced by EMS codes. Sample matrix added.

## **BORON, HOT WATER SOLUBLE**

<b>Parameter</b>	Boron, Hot Water Soluble
<b>Sample Preparation</b>	Soil air dried, soil – water mix water extracted
<b>Analytical Method</b>	Hot Water Extraction followed by ICP-AES or colorimetric determination
<b>EMS Codes</b>	To be assigned on request
<b>Introduction</b>	Boron is a plant micronutrient essential for healthy growth and crop yield. Small amounts are required while concentrations of available Boron above 2 u/g may begin to affect sensitive crops. Typically, Boron becomes less available with increasing soil pH and is easily leached from soils at low pH.
<b>Method Summary</b>	Hot water soluble Boron is an operationally defined technique used to estimate the concentration of Boron available for plant uptake. Boron is extracted from air-dried soil by boiling a 2:1 water:soil mixture for 5 minutes, the extract is filtered and Boron determined using ICP-AES or a colorimetric method.
<b>MDL</b>	MDL is dependent on the method of determination. An MDL of 0.1 ug/g should be attainable by ICP-AES.
<b>Matrix</b>	Although designed for soils the method may also be applicable to solids and sludges.
<b>Interferences</b>	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 reagent water from glass distillation equipment or picked up from borosilicate glassware.
<b>Sample Handling</b>	Samples should be collected in glass or plastic containers. Samples should be air-dried and screened to 2mm (10 mesh) prior to extraction.
<b>Stability</b>	Although no reference specific to hot water soluble Boron was found holding time is nominally 6 months as for metals.
<b>Apparatus</b>	Refer to method references
<b>Reagents</b>	Refer to method references
<b>Extraction</b>	Extraction procedure is described in “Soil Sampling and Methods of Analysis” Carter. 1993. (Procedure 12.2.2) Weigh 25 grams of air-dried sub 2mm sample into a beaker. If a colourimetric finish is to be used, add 0.4 grams of charcoal or just enough to produce a colourless filtrate. Add 50 ml. of Boron free reagent water, cover with a watchglass and bring to a boil for 5 minutes on a hot plate. After cooling adjust volume with reagent water to compensate for loss of water during boiling. Filter extract and store in plastic containers prior to determination of Boron. Please note that glassware should be washed with 1:1 HCl prior to use.

<b>Determination</b>	Boron may be determined in the filtered extract by any of the methods described in Carter or other soil testing manuals providing they meet the following performance requirements.
<b>Performance Requirements</b>	The following performance requirements are to be demonstrated during validation of the method. These do not constitute acceptance requirements for routine Quality Control samples. Accuracy: The method must recover 80-120% of a clean matrix (ie clean sand) spike at above 10 times the MDL. Precision: The method must produce a Relative Standard Deviation of 15% or less on replicate clean matrix spikes at 20 times the MDL. Sensitivity: An MDL of 0.4 ug/g is required for CSR work,
<b>Quality Control</b>	<ul style="list-style-type: none"> <li>a) Method Blank, carry at least on method blank through the procedure.</li> <li>b) Replicates, analyze at between 5-10% of the samples in duplicate.(minimum of 1 duplicate per batch)</li> <li>c) Matrix Spikes, analyze at least one clean matrix spike per batch.</li> </ul>
<b>References</b>	<ul style="list-style-type: none"> <li>a) <u>Soil Sampling and Methods of Analysis</u>. 1993. Canadian Society of Soil Science. Martin Carter, Editor.</li> <li>b) <u>Manual on Soil Sampling and methods of Analysis</u>. 1978. Canada Soil Survey Committee. J.A. McKeague, Editor.</li> </ul>
<b>Revision History</b>	December 2002                      Method developed by BCLQAAC Technical Committee

## CADMIUM (Atomic Absorption - Graphite Furnace)

<b>Parameter</b>	Cadmium, total Cadmium, dissolved	
<b>Sample Preparation</b>	See section 1.0, the sample preparation section.	
<b>Analytical Method</b>	See section 2.1, the AA methods section.	
<b>EMS Code</b>	FA: HNO <sub>3</sub> : GFAA (total)	<b>Cd-T X072</b>
	LA: HNO <sub>3</sub> : GFAA (total)	<b>Cd-T X179</b>
	FF, FA: HNO <sub>3</sub> : GFAA (dissolved)	<b>Cd-D X116</b>
	LF, LA: HNO <sub>3</sub> : GFAA (dissolved)	<b>Cd-D X357</b>

**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<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> & Mg(NO<sub>3</sub>)<sub>2</sub>  
(NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> & Mg(NO<sub>3</sub>)<sub>2</sub>  
(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>  
Mg(NO<sub>3</sub>)<sub>2</sub>

<b>Sample Handling and Preservation Stability</b>	See section 1.0, the sample preparation section of this manual.  An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.				
<b>Instrument Parameters</b>	Source: Cd hollow cathode lamp Wavelength: 228.8 nm Background Correction: recommended				
<b>Apparatus, Materials and Reagents</b>	See section 2.1.5 and 2.1.6 of the AA methods section of this manual.				
<b>Precision</b>	None listed.				
<b>Accuracy</b>	None listed.				
<b>Quality Control</b>	See section 2.1.9, QA/QC Guidelines in this manual.				
<b>References</b>	<ul style="list-style-type: none"> <li>a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 17th edition, 1989 Section 3113.</li> <li>b) Methods for Chemical Analysis of Water and Wastes, EPA-600 4-79-020, March 1983, Method 213.2.</li> <li>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.</li> </ul>				
<b>Revision History</b>	<table border="0" style="width: 100%;"> <tr> <td style="width: 50%;">February 14, 1994:</td> <td>Publication in 1994 Laboratory Manual.</td> </tr> <tr> <td>December 31, 2000:</td> <td>SEAM codes replaced by EMS codes. Sample matrix added.</td> </tr> </table>	February 14, 1994:	Publication in 1994 Laboratory Manual.	December 31, 2000:	SEAM codes replaced by EMS codes. Sample matrix added.
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})**

<b>Parameter</b>	Cadmium, total Cadmium, dissolved
<b>Sample Preparation</b>	See section 1.0, the sample preparation section.
<b>Analytical Method</b>	See section 2.4, the ICP-AES method section.
<b>EMS Code</b>	FA: HNO <sub>3</sub> : ICAP (total) <b>Cd-T X349</b> LA: HNO <sub>3</sub> : ICAP (total) <b>Cd-T X352</b> FF, FA: HNO <sub>3</sub> : ICAP (dissolved) <b>Cd-D X350</b> LF, LA: HNO <sub>3</sub> : ICAP (dissolved) <b>Cd-D X356</b>
<b>Introduction</b>	<p>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.</p> <p>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.</p>
<b>Method Summary</b>	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.
<b>MDL</b>	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.
<b>Matrix</b>	Water, wastewater, marine water.
<b>Interferences and Precautions</b>	See section 2.4.4 of the ICP-AES method section of this manual.
<b>Sample Handling and Preservation</b>	See section 1.0, the sample preparation section of this manual.
<b>Stability</b>	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
<b>Instrument Parameters</b>	Wavelength: 228.8 nm Background Correction: recommended

<b>Apparatus, Materials and Reagents</b>	See section 2.4, the ICP-AES methods section of this manual.	
<b>Precision</b>	None listed.	
<b>Accuracy</b>	None listed.	
<b>Quality Control</b>	See section 2.1.9, QA/QC Guidelines in this manual.	
<b>References</b>	<ul style="list-style-type: none"> <li>a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 17th edition, 1989 Section 3120 B.</li> <li>b) Methods for Chemical Analysis of Water and Wastes, EPA-600 4-79-020, March 1983, Method 200.7.</li> <li>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.</li> </ul>	
<b>Revision History</b>	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)

<b>Parameter</b>	Calcium, total Calcium, dissolved
<b>Sample Preparation</b>	See section 1.0, the sample preparation section.
<b>Analytical Method</b>	See section 2.1, the AA methods section.
<b>EMS Code</b>	FA: HNO <sub>3</sub> : AA (total) <b>Ca-T X073</b> LA: HNO <sub>3</sub> : AA (total) <b>Ca-T X351</b> FF, FA: HNO <sub>3</sub> : AA (dissolved) <b>Ca-D X203</b> LF, LA: HNO <sub>3</sub> : AA (dissolved) <b>Ca-D X085</b>
<b>Method Summary</b>	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.
<b>MDL</b>	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.
<b>Matrix</b>	Water, wastewater, marine water.
<b>Interferences and Precautions</b>	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.
<b>Sample Handling and Preservation</b>	See section 1.0, the sample preparation section of this manual.
<b>Stability</b>	An aqueous solution preserved with nitric acid to pH <2 has a hold time of 6 months.
<b>Instrument Parameters</b>	Source: Ca Hollow cathode Lamp Wavelength: 422.7 nm (primary); 239.9 nm (alternate) Type of Flame: air/acetylene Background Correction: recommended
<b>Apparatus, Materials and Reagents</b>	See sections 2.1.5 and 2.1.6 of this manual.
<b>Precision</b>	None listed.
<b>Accuracy</b>	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)

<b>Parameter</b>	Chromium, total Chromium, dissolved
<b>Sample Preparation</b>	See section 1.0, the sample preparation section.
<b>Analytical Method</b>	See section 2.1, the AA methods section.
<b>EMS Code</b>	X073 FA: HNO <sub>3</sub> : AA (total) <b>Cr-T X073</b> X351 LA: HNO <sub>3</sub> : AA (total) <b>Cr-T X351</b> X203 FF, FA: HNO <sub>3</sub> : AA (dissolved) <b>Cr-D X203</b> X085 LF, LA: HNO <sub>3</sub> : AA (dissolved) <b>Cr-D X085</b>
<b>Introduction</b>	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.
<b>Method Summary</b>	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.
<b>MDL</b>	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.
<b>Matrix</b>	Water, wastewater, marine water.
<b>Interferences and Precautions</b>	See section 2.1.4 of the AA methods section of this manual. Coexisting elements causing relatively large interferences are Fe and Ni.
<b>Sample Handling and Preservation</b>	See section 1.0, the sample preparation section of this manual.
<b>Stability</b>	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
<b>Instrument Parameters</b>	Source: Cr hollow cathode lamp Wavelength: 357.9 nm Type of Flame: air/acetylene Background Correction: recommended

<b>Apparatus, Materials and Reagents</b>	See section 2.1.5 and 2.1.6 of the AA methods section of this manual.	
<b>Precision</b>	None listed.	
<b>Accuracy</b>	None listed.	
<b>Quality Control</b>	See section 2.1.9, QA/QC Guidelines in this manual.	
<b>References</b>	<ul style="list-style-type: none"> <li>a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 17th edition, 1989 Method 3111 B, 3111C.</li> <li>b) Methods for Chemical Analysis of Water and Wastes, EPA-600 4-79-020, March 1983, Method 218.1.</li> <li>c) Trace Elements in Human and Animal Nutrition, Eric J. Underwood, 4th edition, Academic Press, 1977.</li> <li>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.</li> </ul>	
<b>Revision History</b>	February 14, 1994:	Publication in 1994 Laboratory Manual.
	December 31, 2000:	SEAM codes replaced by EMS codes. Sample matrix added.

## CHROMIUM (Atomic Absorption - Graphite Furnace)

<b>Parameter</b>	Chromium, total Chromium, dissolved								
<b>Sample Preparation</b>	See section 1.0, the sample preparation section.								
<b>Analytical Method</b>	See section 2.1, the AA methods section.								
<b>EMS Code</b>	<table border="0"> <tr> <td>FA: HNO<sub>3</sub>: GFAA (total)</td> <td><b>Cr-T X072</b></td> </tr> <tr> <td>LA: HNO<sub>3</sub>: GFAA (total)</td> <td><b>Cr-T X179</b></td> </tr> <tr> <td>FF, FA: HNO<sub>3</sub>: GFAA (dissolved)</td> <td><b>Cr-D X116</b></td> </tr> <tr> <td>LF, LA: HNO<sub>3</sub>: GFAA (dissolved)</td> <td><b>Cr-D X357</b></td> </tr> </table>	FA: HNO <sub>3</sub> : GFAA (total)	<b>Cr-T X072</b>	LA: HNO <sub>3</sub> : GFAA (total)	<b>Cr-T X179</b>	FF, FA: HNO <sub>3</sub> : GFAA (dissolved)	<b>Cr-D X116</b>	LF, LA: HNO <sub>3</sub> : GFAA (dissolved)	<b>Cr-D X357</b>
FA: HNO <sub>3</sub> : GFAA (total)	<b>Cr-T X072</b>								
LA: HNO <sub>3</sub> : GFAA (total)	<b>Cr-T X179</b>								
FF, FA: HNO <sub>3</sub> : GFAA (dissolved)	<b>Cr-D X116</b>								
LF, LA: HNO <sub>3</sub> : GFAA (dissolved)	<b>Cr-D X357</b>								
<b>Introduction</b>	<p>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.</p> <p>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.</p>								
<b>Method Summary</b>	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.								
<b>MDL</b>	<p>Given an aqueous sample free of interferences, the instrumental performance characteristics are:</p> <p>MDL: 0.001 mg/L Range: 0.001-0.100 mg/L</p> <p>See Table C-1 in section 2.1, the AA methods section, for additional information.</p>								
<b>Matrix</b>	Water, wastewater, marine water.								
<b>Interferences and Precautions</b>	<p>See section 2.1.4 of the AA methods section of this manual. Matrix modifiers for interference removal are given by Standard Methods as:</p> <p style="text-align: center;">Mg(NO<sub>3</sub>)<sub>2</sub></p>								
<b>Sample Handling and Preservation</b>	See section 1.0, the sample preparation section of this manual.								
<b>Stability</b>	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.								

<b>Instrument Parameters</b>	Source: Cr hollow cathode lamp Wavelength: 357.9 nm Background Correction: recommended	
<b>Apparatus, Materials and Reagents</b>	See section 2.1.5 and 2.1.6 of the AA methods section of this manual.	
<b>Precision</b>	None listed.	
<b>Accuracy</b>	None listed.	
<b>Quality Control</b>	See section 2.1.9, QA/QC Guidelines in this manual.	
<b>References</b>	<ul style="list-style-type: none"> <li>a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 17th edition, 1989 Section 3113.</li> <li>b) Methods for Chemical Analysis of Water and Wastes, EPA-600 4-79-020, March 1983, Method 218.2.</li> <li>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.</li> </ul>	
<b>Revision History</b>	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})**

<b>Parameter</b>	Chromium, total Chromium, dissolved
<b>Sample Preparation</b>	See section 1.0, the sample preparation section.
<b>Analytical Method</b>	See section 2.4, the ICP-AES method section.
<b>EMS Code</b>	FA: HNO <sub>3</sub> : ICAP (total) <b>Cr-T X349</b> LA: HNO <sub>3</sub> : ICAP (total) <b>Cr-T X352</b> FF, FA: HNO <sub>3</sub> : ICAP (dissolved) <b>Cr-D X350</b> LF, LA: HNO <sub>3</sub> : ICAP (dissolved) <b>Cr-D X356</b>

**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 Parameters** Wavelength: 205.5 nm  
Background Correction: recommended

<b>Apparatus, Materials and Reagents</b>	See section 2.4 of the ICP methods section of this manual.	
<b>Precision</b>	None listed.	
<b>Accuracy</b>	None listed.	
<b>Quality Control</b>	See section 2.1.9, QA/QC Guidelines in this manual.	
<b>References</b>	<ul style="list-style-type: none"> <li>a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 17th edition, 1989 Section 3120B.</li> <li>b) Methods for Chemical Analysis of Water and Wastes, EPA-600 4-79-020, March 1983, Method 200.7.</li> <li>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.</li> </ul>	
<b>Revision History</b>	February 14, 1994:	Publication in 1994 Laboratory Manual.
	December 31, 2000:	SEAM codes replaced by EMS codes. Sample matrix added.

## **HEXAVALENT CHROMIUM IN SOLIDS BY ALKALINE DIGESTION, PBM**

<b>Parameter</b>	<b>Hexavalent Chromium, Performance Based (PBM)</b>
<b>Sample Handling Preservation</b>	Samples should be collected in glass or plastic containers. Samples should be collected using devices that do not contain stainless steel. Samples should be stored field-moist at 4° C.
<b>Analytical Method</b>	Alkaline extraction – Colorimetric or IC determination
<b>EMS Codes</b>	To be assigned on request
<b>Introduction</b>	<p>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.</p> <p>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 &gt;4, and do not tend to leach from a soil matrix into groundwaters. At pH &gt; 8.5, Cr(VI) solids are highly soluble and completely mobile, and can readily leach from soils into groundwater systems.</p> <p>The group of Cr(VI) compounds as a whole have been classified as “carcinogenic to humans” by the Government of Canada.</p>
<b>Method Summary</b>	Soluble, adsorbed, and precipitated forms of Cr(VI) are extracted from field-moist solids using a NaOH / Na <sub>2</sub> CO <sub>3</sub> alkaline digestion procedure. Magnesium chloride in phosphate buffer is added to prevent oxidation to Cr(III). 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 analyzed by UV-VIS colorimetry, by Ion Chromatography with colourimetric detection, by ICP-MS coupled with an appropriate separatory technique, or by any analytical speciation technique for Cr(VI) that has been approved by the US EPA.
<b>MDL</b>	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 colorimetry, an MDL of 0.5 mg/kg is achievable.
<b>Matrix</b>	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 sulphate, will cause a loss of Cr(VI).

**Stability**

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

**Apparatus**

Refer to applicable method references.

**Reagents**

Refer to applicable method references.

**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(VI).

Modifications to the chemistry (including temperature) of the digestion procedure are not permitted.

Method 3060A specifies the use of continuous stirring throughout the digestion process. Periodic manual stirring (before heating, and approximately every 20 minutes throughout the digestion process) is deemed to be equivalent (in combination with the natural mixing of convection), and may be substituted without further investigation. Other physical and procedural changes may be adopted only after rigorous demonstration of equivalence.

**Analytical****Options**

Follow the principles described in one of the following analytical methods to quantify Cr(VI) in the digestate and in the extracted sample.

- a) APHA Method 3500-Cr B. Colorimetric Method, 1998 or later.
- b) APHA Method 3500-Cr C. Ion Chromatographic Method, 1998 or later.
- c) EPA Method 1636. Determination of Hexavalent Chromium by Ion Chromatography, January 1996 or later.
- d) EPA SW-846 Method 7195, Chromium, Hexavalent (Coprecipitation), September, 1986 or later.
- e) EPA SW-846 Method 7196A, Chromium, Hexavalent (Colorimetric), July 1992 or later.

- f) EPA SW-846 Method 7197, Chromium, Hexavalent (Chelation / Extraction), September, 1986 or later.
- g) EPA SW-846, Method 7198, Chromium, Hexavalent (Differential Pulse Polarography), September, 1986 or later.

ICP-MS with an appropriate separatory technique (i.e. IC, HPLC, or CE) may also be used. This technique must be validated as equivalent to one of the above techniques prior to use.

Digestates may be screened using an appropriate analytical technique for total chromium, provided that calibration standards are fully matrix-matched, and that all applicable QC samples are successfully analyzed in this way also. Any samples with positive hits on the screen technique must then be analyzed for hexavalent chromium by one of the above speciation techniques.

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

**Performance Requirements**

Any analytical method selected for this analysis must meet or exceed the performance requirements specified below. Achievement of these requirements is to be demonstrated during method validation. These requirements are not to be confused with acceptance criteria for routine Quality Control samples:

**Accuracy Requirement**

The method must recover CrVI at between 75-125%, on average, for method spikes on a clean sediment or clean soil matrix, at concentrations above twenty times the method detection limit.

**Precision Requirement**

The method must generate precision equal to or better than 15% relative standard deviation for homogeneous reference materials and/or for method spikes on a clean sediment or clean soil matrix, at concentrations above twenty times the method detection limit.

**Selectivity Requirement**

Except where screening of digestates for total chromium is acceptable, one of the speciation techniques specified under the Analytical Options section of this method must be used.

**Sensitivity Requirement**

The method must be capable of achieving an MDL of 0.5 mg/kg, or must meet appropriate guideline or criteria levels.

**Quality Control**

- a) Analyze at least one Method Blank with each sample batch.
- b) Approximately 5 to 10% of samples, with a minimum of one per extraction batch, should be split by the laboratory and analyzed as laboratory duplicates.
- c) At least one Reference Material (if available) or one pre-digestion Method Spike into a clean solid matrix (i.e. clean sand) must be analyzed with each batch. Spike preparation instructions are provided in EPA Method 3060A. Prepare the Method Spike with a 1:1 mixture of soluble and insoluble Cr(VI) salts (e.g. PbCrO<sub>4</sub> and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>). If recovery problems are experienced, perform separate Method Spikes

with soluble and insoluble Cr(VI) salts to help identify the cause of the problem.

- d) 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.

**Note:** The Quality Control acceptance criteria specified within Method 3060A are recommended as general guidelines, but are not requirements of this method. Laboratories should establish internal QC acceptance criteria that maintain statistical control of the method, and which are consistent with Data Quality Objectives.

## References

- a) 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.
- b) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 20th edition, 1998. Method 3500 - Cr B, Colorimetric Method.
- c) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 20th edition, 1998. Method 3500 - Cr C, Ion Chromatographic Method.
- d) Test Methods for Evaluating Solid Wastes – Physical / Chemical Methods, SW-846, 3rd Edition, Method 7195, Chromium, Hexavalent (Coprecipitation), September 1986, Final Update III. United States Environmental Protection Agency, Washington, D.C.
- e) 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.
- f) Test Methods for Evaluating Solid Wastes – Physical / Chemical Methods, SW-846, 3rd Edition, Method 7197, Chromium, Hexavalent (Chelation / Extraction), September 1986, Final Update III. United States Environmental Protection Agency, Washington, D.C.
- g) Test Methods for Evaluating Solid Wastes – Physical / Chemical Methods, SW-846, 3rd Edition, Method 7198, Chromium, Hexavalent (Differential Pulse Polarography), September 1986, Final Update III. United States Environmental Protection Agency, Washington, D.C.
- h) Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health, Chromium, 1999, Canadian Council of Ministers of the Environment.

## Revision History

December 2002;	method developed by BCLQAAC Technical Sub-Committee, superceding the method published in Supplement #1.
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## TRIVALENT CHROMIUM IN SOLIDS BY CALCULATION

<b>Parameter</b>	Trivalent Chromium
<b>Sample Handling Preservation</b>	Refer to individual techniques for total and hexavalent chromium
<b>Analytical Method</b>	Calculation: SALM-digestable total chromium minus chromium (VI)
<b>EMS Codes</b>	To be assigned on request
<b>Introduction</b>	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 B.C. 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”.

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

<b>Matrix</b>	Soil Sediment Sludges Solid wastes
<b>Interferences and Precautions</b>	<p>Refer to individual analytical techniques for total and hexavalent chromium.</p> <p>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.</p>
<b>Stability</b>	Refer to individual analytical techniques for total and hexavalent chromium.
<b>Calculation</b>	Analyze the sample for total chromium using the B.C. Strong Acid Leachable
<b>Procedure</b>	<p>Metals (SALM) digestion procedure and an appropriate analytical technique for chromium (e.g. ICP-OES or AAS).</p> <p>Analyze the sample for hexavalent chromium using the B.C. Method for Hexavalent Chromium in Solids by Alkaline Digestion.</p> <p>Subtract the hexavalent chromium result from the total chromium result to approximate the concentration of trivalent chromium.</p> <p>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.</p> <p>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:</p> $MDL_{Cr(III)} = \sqrt{[ (U_{T-Cr})^2 + (U_{Cr(VI)})^2 ]}$ <p><math>U_{T-Cr}</math> and <math>U_{Cr(VI)}</math> 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.</p> <p>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.</p> <p>Report results as mg/kg on a dry weight basis.</p>
<b>Precision and Accuracy</b>	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)

<b>Parameter</b>	Cobalt, total Cobalt, dissolved
<b>Sample Preparation</b>	See section 1.0, the sample preparation section.
<b>Analytical Method</b>	See section 2.1, the AA methods section.
<b>EMS Code</b>	FA: HNO <sub>3</sub> : AA (total) <b>Co-T X073</b> LA: HNO <sub>3</sub> : AA (total) <b>Co-T X351</b> FF, FA: HNO <sub>3</sub> : AA (dissolved) <b>Co-D X203</b> LF, LA: HNO <sub>3</sub> : AA (dissolved) <b>Co-D X085</b>
<b>Introduction</b>	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.
<b>Method Summary</b>	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.
<b>MDL</b>	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.
<b>Matrix</b>	Water, wastewater, marine water.
<b>Interferences and Precautions</b>	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.
<b>Sample Handling and Preservation</b>	See section 1.0, the sample preparation section of this manual.
<b>Stability</b>	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
<b>Instrument Parameters</b>	Source: Co hollow cathode lamp Wavelength: 240.7 nm Type of flame: air/acetylene Background correction: recommended
<b>Apparatus, Materials and Reagents</b>	See section 2.1.5 and 2.1.6 of this manual.
<b>Precision</b>	None listed.

<b>Accuracy</b>	None listed.	
<b>Quality Control</b>	See section 2.1.9, QA/QC Guidelines in this manual.	
<b>References</b>	<ul style="list-style-type: none"> <li>a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992 Method 3111 B/D.</li> <li>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.</li> </ul>	
<b>Revision History</b>	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)

<b>Parameter</b>	Cobalt, total Cobalt, dissolved
<b>Sample Preparation</b>	See section 1.0, the sample preparation section.
<b>Analytical Method</b>	See section 2.1, the AA methods section.
<b>EMS Code</b>	FA: HNO <sub>3</sub> : GFAA (total) <b>Co-T X072</b> LA: HNO <sub>3</sub> : GFAA (total) <b>Co-T X179</b> FF, FA: HNO <sub>3</sub> : GFAA (dissolved) <b>Co-D X116</b> LF, LA: HNO <sub>3</sub> : GFAA (dissolved) <b>Co-D X357</b>
<b>Introduction</b>	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.
<b>Method Summary</b>	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.
<b>MDL</b>	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.
<b>Matrix</b>	Water, wastewater, marine water.
<b>Interferences and Precautions</b>	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.
<b>Sample Handling and Preservation</b>	See section 1.0, the sample preparation section of the manual.
<b>Stability</b>	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
<b>Instrument Parameters</b>	Source: Co hollow cathode lamp Wavelength: 240.7 nm Background Correction: recommended
<b>Apparatus, Materials and Reagents</b>	See section 2.1.5 and 2.1.6 of the AA methods section of this manual.

<b>Precision</b>	None listed.				
<b>Accuracy</b>	None listed.				
<b>Quality Control</b>	See section 2.1.9, QA/QC Guidelines in this manual.				
<b>References</b>	<ul style="list-style-type: none"> <li>a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992, Method 3113B.</li> <li>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.</li> </ul>				
<b>Revision History</b>	<table> <tr> <td>February 14, 1994:</td> <td>Publication in 1994 Laboratory Manual.</td> </tr> <tr> <td>December 31, 2000:</td> <td>SEAM codes replaced by EMS codes. Sample matrix added.</td> </tr> </table>	February 14, 1994:	Publication in 1994 Laboratory Manual.	December 31, 2000:	SEAM codes replaced by EMS codes. Sample matrix added.
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)

<b>Parameter</b>	Copper, total Copper, dissolved
<b>Sample Preparation</b>	See section 1.0, the sample preparation section.
<b>Analytical Method</b>	See section 2.1, the AA methods section.
<b>EMS Code</b>	FA: HNO <sub>3</sub> : AA (total) <b>Cu-T X073</b> LA: HNO <sub>3</sub> : AA (total) <b>Cu-T X351</b> FF, FA: HNO <sub>3</sub> : AA (dissolved) <b>Cu-D X203</b> LF, LA: HNO <sub>3</sub> : AA (dissolved) <b>Cu-D X085</b>
<b>Introduction</b>	<p>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.</p> <p>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.</p>
<b>Method Summary</b>	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.
<b>MDL</b>	<p>Given an aqueous sample free of interferences, the instrumental performance characteristics are:</p> <p>MDL: 0.020 mg/L Range: 0.020-5.0 mg/L</p> <p>See Table C-1 in section 2.1, the AA methods section, for additional information.</p>
<b>Matrix</b>	Water, wastewater, marine water.
<b>Interferences and Precautions</b>	See section 2.1.4 of the AA methods section of this manual. Coexisting elements causing relatively large interferences are Al, Si, and Ti.
<b>Sample Handling and Preservation</b>	See section 1.0, the sample preparation section of this manual.
<b>Stability</b>	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
<b>Instrument Parameters</b>	<p>Source: Cu hollow cathode lamp Wavelength: 324.7 nm Type of Flame: air/acetylene Background Correction: recommended</p>
<b>Apparatus, Materials and Reagents</b>	See section 2.1.5 and 2.1.6 of the AA methods section of this manual.

<b>Precision</b>	None listed.	
<b>Accuracy</b>	None listed.	
<b>Quality Control</b>	See section 2.1.9, QA/QC Guidelines in this manual.	
<b>References</b>	<ul style="list-style-type: none"> <li>a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 17th edition, 1989 Method 3500-Cu.</li> <li>b) Methods for Chemical Analysis of Water and Wastes, EPA-600 4-79-020, March 1983 Method 220.1.</li> <li>c) Trace Elements in Human and Animal Nutrition, Eric J. Underwood, 4th edition, Academic Press, 1977.</li> <li>d) (Revised). Publication #SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd Edition 1990.</li> </ul>	
<b>Revision History</b>	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)

<b>Parameter</b>	Copper, total Copper, dissolved
<b>Sample Preparation</b>	See section 1.0, the sample preparation section.
<b>Analytical Method</b>	See section 2.1, the AA methods section.
<b>EMS Code</b>	FA: HNO <sub>3</sub> : GFAA (total) <b>Cu-T X072</b> LA: HNO <sub>3</sub> : GFAA (total) <b>Cu-T X179</b> FF, FA: HNO <sub>3</sub> : GFAA (dissolved) <b>Cu-D X116</b> LF, LA: HNO <sub>3</sub> : GFAA (dissolved) <b>Cu-D X357</b>
<b>Introduction</b>	<p>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.</p> <p>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.</p>
<b>Method Summary</b>	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.
<b>MDL</b>	<p>Given an aqueous sample free of interferences, the instrumental performance characteristics are:</p> <p>MDL: 0.001 mg/L Range: 0.001-0.100 mg/L</p> <p>See Table C-1 in section 2.1, the AA methods section, for additional information.</p>
<b>Matrix</b>	Water, wastewater, marine water.
<b>Interferences and Precautions</b>	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 <sub>4</sub> NO <sub>3</sub> , ascorbic acid.
<b>Sample Handling and Preservation</b>	See section 1.0, the sample preparation section of this manual.
<b>Stability</b>	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
<b>Instrument Parameter</b>	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})**

<b>Parameter</b>	Copper, total Copper, dissolved
<b>Sample Preparation</b>	See section 1.0, the sample preparation section.
<b>Analytical Method</b>	See section 2.4, the ICP-AES method section.
<b>EMS Code</b>	FA: HNO <sub>3</sub> : ICAP (total) <b>Cu-T X349</b> LA: HNO <sub>3</sub> : ICAP (total) <b>Cu-T X352</b> FF, FA: HNO <sub>3</sub> : ICAP (dissolved) <b>Cu-D X350</b> LF, LA: HNO <sub>3</sub> : ICAP (dissolved) <b>Cu-D X356</b>
<b>Introduction</b>	<p>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.</p> <p>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.</p>
<b>Method Summary</b>	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.
<b>MDL</b>	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.
<b>Matrix</b>	Water, wastewater, marine water.
<b>Interferences and Precautions</b>	See section 2.4.4 of the ICP methods section of this manual.
<b>Sample Handling and Preservation</b>	See section 1.0, the sample preparation section of this manual.
<b>Stability</b>	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
<b>Instrument Parameter</b>	Wavelength: 324.7 nm Background Correction: recommended
<b>Apparatus, Materials and Reagents</b>	See section 2.4 of the ICP-AES methods section of this manual.
<b>Precision</b>	None listed.

<b>Accuracy</b>	None listed.	
<b>Quality Control</b>	See section 2.1.9, QA/QC Guidelines in this manual.	
<b>References</b>	<ul style="list-style-type: none"> <li>a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 17th edition, 1989 Section 3120 B.</li> <li>b) Methods for Chemical Analysis of Water and Wastes, EPA-600 4-79-020, March 1983, Method 200.7.</li> <li>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.</li> </ul>	
<b>Revision History</b>	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)

<b>Parameter</b>	Iron, total Iron, dissolved								
<b>Sample Preparation</b>	See section 1.0, the sample preparation section.								
<b>Analytical Method</b>	See section 2.1, the AA methods section.								
<b>EMS Code</b>	<table border="0"> <tr> <td>FA: HNO<sub>3</sub>: AA (total)</td> <td><b>Fe-T X073</b></td> </tr> <tr> <td>LA: HNO<sub>3</sub>: AA (total)</td> <td><b>Fe-T X351</b></td> </tr> <tr> <td>FF, FA: HNO<sub>3</sub>: AA (dissolved)</td> <td><b>Fe-D X203</b></td> </tr> <tr> <td>LF, LA: HNO<sub>3</sub>: AA (dissolved)</td> <td><b>Fe-D X085</b></td> </tr> </table>	FA: HNO <sub>3</sub> : AA (total)	<b>Fe-T X073</b>	LA: HNO <sub>3</sub> : AA (total)	<b>Fe-T X351</b>	FF, FA: HNO <sub>3</sub> : AA (dissolved)	<b>Fe-D X203</b>	LF, LA: HNO <sub>3</sub> : AA (dissolved)	<b>Fe-D X085</b>
FA: HNO <sub>3</sub> : AA (total)	<b>Fe-T X073</b>								
LA: HNO <sub>3</sub> : AA (total)	<b>Fe-T X351</b>								
FF, FA: HNO <sub>3</sub> : AA (dissolved)	<b>Fe-D X203</b>								
LF, LA: HNO <sub>3</sub> : AA (dissolved)	<b>Fe-D X085</b>								
<b>Introduction</b>	<p>Iron is an essential trace element for plants and animals, but is an undesirable constituent of water supplies if present at appreciable concentrations.</p> <p>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.</p>								
<b>Method Summary</b>	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.								
<b>MDL</b>	<p>Given an aqueous sample free of interferences, the instrumental performance characteristics are:</p> <p>MDL: 0.03 mg/L</p> <p>Range: 0.03-5.0 mg/L</p> <p>See Table C-1 in section 2.1, the AA methods section, for additional information.</p>								
<b>Matrix</b>	Water, wastewater, marine water.								
<b>Interferences and Precautions</b>	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.								
<b>Sample Handling and Preservation</b>	See section 1.0, the sample preparation section.								
<b>Stability</b>	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.								

<b>Instrument Parameters</b>	Source: Fe hollow cathode lamp Wavelength: 248.3 nm Type of Flame: air/acetylene Background Correction: recommended	
<b>Apparatus, Materials and Reagents</b>	See sections 2.1.5 and 2.1.6 of this manual.	
<b>Precision</b>	None listed.	
<b>Accuracy</b>	None listed.	
<b>Quality Control</b>	See section 2.1.9, QA/AC Guidelines in this manual.	
<b>References</b>	<ul style="list-style-type: none"> <li>a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992, Method 3111 B/D.</li> <li>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.</li> </ul>	
<b>Revision History</b>	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)

<b>Parameter</b>	Iron, total Iron, dissolved
<b>Sample Preparation</b>	See section 1.0, the sample preparation section.
<b>Analytical Method</b>	See section 2.1, the AA methods section.
<b>EMS Code</b>	FA: HNO <sub>3</sub> : GFAA (total) <b>Fe-T X072</b> LA: HNO <sub>3</sub> : GFAA (total) <b>Fe-T X179</b> FF, FA: HNO <sub>3</sub> : GFAA (dissolved) <b>Fe-D X116</b> LF, LA: HNO <sub>3</sub> : GFAA (dissolved) <b>Fe-D X357</b>
<b>Introduction</b>	<p>Iron is an essential trace element for plants and animals, but is an undesirable constituent of water supplies if present in appreciable concentrations.</p> <p>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.</p>
<b>Method Summary</b>	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.
<b>MDL</b>	<p>Given an aqueous sample free of interferences, the instrumental performance characteristics are:</p> <p>MDL: 0.001 mg/L Range: 0.001-0.10 mg/L</p> <p>See Table C-1 in section 2.1, the AA methods section, for additional information.</p>
<b>Matrix</b>	Water, wastewater, marine water.
<b>Interferences and Precautions</b>	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.
<b>Sample Handling and Preservation</b>	See section 1.0, the sample preparation section of this manual.

<b>Stability</b>	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.	
<b>Instrument Parameters</b>	Source: Fe hollow cathode lamp Wavelength: 248.3 nm Background Correction: recommended	
<b>Apparatus, Materials and Reagents</b>	See section 2.1.5 and 2.1.6 of this manual.	
<b>Precision</b>	None listed.	
<b>Accuracy</b>	None listed.	
<b>Quality Control</b>	See section 2.1.9, QA/QC Guidelines in this manual.	
<b>References</b>	<ul style="list-style-type: none"> <li>a) Standard Method for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992, Method 3113B.</li> <li>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.</li> </ul>	
<b>Revision History</b>	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)

<b>Parameter</b>	Lead, total Lead, dissolved								
<b>Sample Preparation</b>	See section 1.0, the sample preparation section.								
<b>Analytical Method</b>	See section 2.1, the AA methods section.								
<b>EMS Code</b>	<table border="0"> <tr> <td>FA: HNO<sub>3</sub>: AA (total)</td> <td><b>Pb-T X073</b></td> </tr> <tr> <td>LA: HNO<sub>3</sub>: AA (total)</td> <td><b>Pb-T X351</b></td> </tr> <tr> <td>FF, FA: HNO<sub>3</sub>: AA (dissolved)</td> <td><b>Pb-D X203</b></td> </tr> <tr> <td>LF, LA: HNO<sub>3</sub>: AA (dissolved)</td> <td><b>Pb-D X085</b></td> </tr> </table>	FA: HNO <sub>3</sub> : AA (total)	<b>Pb-T X073</b>	LA: HNO <sub>3</sub> : AA (total)	<b>Pb-T X351</b>	FF, FA: HNO <sub>3</sub> : AA (dissolved)	<b>Pb-D X203</b>	LF, LA: HNO <sub>3</sub> : AA (dissolved)	<b>Pb-D X085</b>
FA: HNO <sub>3</sub> : AA (total)	<b>Pb-T X073</b>								
LA: HNO <sub>3</sub> : AA (total)	<b>Pb-T X351</b>								
FF, FA: HNO <sub>3</sub> : AA (dissolved)	<b>Pb-D X203</b>								
LF, LA: HNO <sub>3</sub> : AA (dissolved)	<b>Pb-D X085</b>								
<b>Introduction</b>	<p>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.</p> <p>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.</p>								
<b>Method Summary</b>	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.								
<b>MDL</b>	<p>Given an aqueous sample free of interferences, the instrumental performance characteristics are:</p> <p>MDL: 0.10 mg/L</p> <p>Range: 0.10-20.0 mg/L</p> <p>See Table C-1 in section 2.1, the AA methods section, for additional information.</p>								
<b>Matrix</b>	Water, wastewater, marine water.								
<b>Interferences and Precautions</b>	<p>See section 2.1.4 of the AA methods section of this manual.</p> <p>Coexisting elements causing relatively large interferences are Fe and Ti.</p>								
<b>Sample Handling and Preservation</b>	See section 1.0, the sample preparation section of this manual.								
<b>Stability</b>	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.								
<b>Instrument Parameters</b>	<p>Source: Pb hollow cathode lamp</p> <p>Wavelength: 283.3 nm</p> <p>Type of Flame: air/acetylene</p> <p>Background Correction: recommended</p>								



<b>Apparatus, Materials and Reagents</b>	See section 2.1.5 and 2.1.6 of the AA methods section of this manual.	
<b>Precision</b>	None listed.	
<b>Accuracy</b>	None listed.	
<b>Quality Control</b>	See section 2.1.9, QA/QC Guidelines in this manual.	
<b>References</b>	<ul style="list-style-type: none"> <li>a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 17th edition, 1989 Method 3500-Pb.</li> <li>b) Method for Chemical Analysis of Water and Wastes EPA-600 4-79-020, March 1983, Method 239.1.</li> <li>c) Trace Elements in Human and Animal Nutrition, Eric J. Underwood, 4th edition, Academic Press, 1977.</li> <li>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.</li> </ul>	
<b>Revision History</b>	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)

<b>Parameter</b>	Lead, total Lead, dissolved								
<b>Sample Preparation</b>	See section 1.0, the sample preparation section.								
<b>Analytical Method</b>	See section 2.1, the AA methods section.								
<b>EMS Code</b>	<table border="0"> <tr> <td>FA: HNO<sub>3</sub>: GFAA (total)</td> <td><b>Pb-T X072</b></td> </tr> <tr> <td>LA: HNO<sub>3</sub>: GFAA (total)</td> <td><b>Pb-T X179</b></td> </tr> <tr> <td>FF, FA: HNO<sub>3</sub>: GFAA (dissolved)</td> <td><b>Pb-D X116</b></td> </tr> <tr> <td>LF, LA: HNO<sub>3</sub>: GFAA (dissolved)</td> <td><b>Pb-D X357</b></td> </tr> </table>	FA: HNO <sub>3</sub> : GFAA (total)	<b>Pb-T X072</b>	LA: HNO <sub>3</sub> : GFAA (total)	<b>Pb-T X179</b>	FF, FA: HNO <sub>3</sub> : GFAA (dissolved)	<b>Pb-D X116</b>	LF, LA: HNO <sub>3</sub> : GFAA (dissolved)	<b>Pb-D X357</b>
FA: HNO <sub>3</sub> : GFAA (total)	<b>Pb-T X072</b>								
LA: HNO <sub>3</sub> : GFAA (total)	<b>Pb-T X179</b>								
FF, FA: HNO <sub>3</sub> : GFAA (dissolved)	<b>Pb-D X116</b>								
LF, LA: HNO <sub>3</sub> : GFAA (dissolved)	<b>Pb-D X357</b>								
<b>Introduction</b>	<p>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.</p> <p>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.</p>								
<b>Method Summary</b>	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.								
<b>MDL</b>	<p>Given an aqueous sample free of interferences, the instrumental performance characteristics are:</p> <p>MDL: 0.001 mg/L Range: 0.001-0.100 mg/L</p> <p>See Table C-1 in section 2.1, the AA methods section, for additional information.</p>								
<b>Matrix</b>	Water, wastewater, marine water.								
<b>Interferences and Precautions</b>	<p>See section 2.1.4 of the AA methods section of this manual. Matrix modifiers for interference removal are given by Standard Methods as:</p> <p>NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> Mg(NO<sub>3</sub>)<sub>2</sub>, NH<sub>4</sub>NO<sub>3</sub> ascorbic acid, oxalic acid phosphoric acid, HNO<sub>3</sub>, LaCl, (NH<sub>4</sub>)EDTA</p>								
<b>Sample Handling and Preservation</b>	See section 1.0, the sample preparation section of this manual.								

<b>Stability</b>	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.	
<b>Instrument Parameters</b>	Source: Pb hollow cathode lamp Wavelength: 283.3 nm Background Correction: recommended	
<b>Apparatus, Materials and Reagents</b>	See section 2.1.5 and 2.1.6 of the AA methods section of this manual.	
<b>Precision</b>	None listed.	
<b>Accuracy</b>	None listed.	
<b>Quality Control</b>	See section 2.1.9, QA/QC Guidelines in this manual.	
<b>References</b>	<ul style="list-style-type: none"> <li>a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 17th edition, 1989 Section 3113.</li> <li>b) Methods for Chemical Analysis of Water and Wastes, EPA-600 4-79-020, March 1983, Method 239.2.</li> <li>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.</li> </ul>	
<b>Revision History</b>	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

## LEAD

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

<b>Parameter</b>	Lead, total Lead, dissolved
<b>Sample Preparation</b>	See section 1.0, the sample preparation section.
<b>Analytical Method</b>	See section 2.4, the ICP-AES methods section.
<b>EMS Code</b>	FA: HNO <sub>3</sub> : ICAP (total) <b>Pb-T X349</b> LA: HNO <sub>3</sub> : ICAP (total) <b>Pb-T X352</b> FF, FA: HNO <sub>3</sub> : ICAP (dissolved) <b>Pb-D X350</b> LF, LA: HNO <sub>3</sub> : ICAP (dissolved) <b>Pb-D X356</b>
<b>Introduction</b>	<p>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.</p> <p>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.</p>
<b>Method Summary</b>	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.
<b>MDL</b>	<p>Given an aqueous sample free of interferences, the instrumental performance characteristics are:</p> <p>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.</p>
<b>Matrix</b>	Water, wastewater, marine water.
<b>Interferences and Precautions</b>	See section 2.4.4 of the ICP methods section of this manual.
<b>Sample Handling and Preservation</b>	See section 1.0, the sample preparation section of this manual.
<b>Stability</b>	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
<b>Instrument Parameters</b>	Wavelength: 220.3 nm Background Correction: recommended

<b>Apparatus, Materials and Reagents</b>	See section 2.4 of the ICP methods section of this manual.	
<b>Precision</b>	None listed.	
<b>Accuracy</b>	None listed.	
<b>Quality Control</b>	See section 2.1.9, QA/QC Guidelines in this manual.	
<b>References</b>	<ul style="list-style-type: none"> <li>a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 17th edition, 1989 Section 3120 B.</li> <li>b) Methods for Chemical Analysis of Water and Wastes, EPA-600 4-79-020, March 1983, Method 200.7.</li> <li>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.</li> </ul>	
<b>Revision History</b>	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**

<b>Parameter</b>	Lead (Pb)												
<b>Sample Preparation</b>	See Section 1.2 for sample preparation												
<b>EMS CODES</b>	<b>EMS CODES ASSIGNED ON REQUEST</b>												
<b>Analytical Method</b>	US EPA Method 7420 Atomic Absorption, Direct Aspiration												
<b>Introduction</b>	Lead is a highly toxic, cumulative poison in man and animals. Chronic lead poisoning is often characterized by central nervous system disorders.												
<b>Method Summary</b>	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.												
<b>General Operating Conditions / Detection Limits</b>	<table><thead><tr><th>Element</th><th>Wavelength</th><th>Slit</th><th>Lamp</th><th>Current</th><th>Detection Limit</th></tr></thead><tbody><tr><td>Lead</td><td>283.3 nm *</td><td>0.7 nm</td><td></td><td>8 mA</td><td>1.0 µg/g</td></tr></tbody></table> <p>* The wavelength provided is the primary one used, alternatively the 217.0 nm line may be used.</p>	Element	Wavelength	Slit	Lamp	Current	Detection Limit	Lead	283.3 nm *	0.7 nm		8 mA	1.0 µg/g
Element	Wavelength	Slit	Lamp	Current	Detection Limit								
Lead	283.3 nm *	0.7 nm		8 mA	1.0 µg/g								
<b>Matrix</b>	Soil Solids (Marine) Sediments												
<b>Source</b>	Lead Hollow Cathode Lamp												
<b>Type of Flame</b>	Air / Acetylene												
<b>Background Correction</b>	Required												
<b>Interferences</b>	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.												
<b>Sample Handling and Preservation</b>	Container - acid washed polyethylene bottle Digested soils are already in an acid medium and require no extra preservation chemicals.												

<b>Stability</b>	Lead in digested soil samples have a holding time of six month.		
<b>Instrument</b>	Direct flame atomic absorption spectrophotometer with background correct system.		
<b>Calibration / Analysis Procedures</b>	Refer to instrument operations manual for set-up and analysis techniques.		
<b>Precision</b>	Refer to EPA Method 7420.		
<b>Accuracy</b>	Refer to EPA Method 7420.		
<b>Quality Control</b>	<ul style="list-style-type: none"> <li>a) Confirm calibration by analyzing a separate sourced calibration verification standard.</li> <li>b) Blanks, Reference Materials and Duplicates prepared with each digestion batch must meet predetermined QA/QC requirements</li> </ul>		
<b>References</b>	<ul style="list-style-type: none"> <li>a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 17th edition, 1989 Method 3500-Pb.</li> <li>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.</li> </ul>		
<b>Revision History</b>	<table border="0" style="width: 100%;"> <tr> <td style="width: 50%;">December 2002</td> <td>Method adopted from Supplement #1 Manual, EMS Codes assigned</td> </tr> </table>	December 2002	Method adopted from Supplement #1 Manual, EMS Codes assigned
December 2002	Method adopted from Supplement #1 Manual, EMS Codes assigned		

## MAGNESIUM (Atomic Absorption - Direct Aspiration)

<b>Parameter</b>	Magnesium, total Magnesium, dissolved
<b>Sample Preparation</b>	See section 1.0, the sample preparation section.
<b>Analytical Method</b>	See section 2.1, the AA methods section.
<b>EMS Code</b>	FA: HNO <sub>3</sub> : AA (total) <b>Mg-T X073</b> LA: HNO <sub>3</sub> : AA (total) <b>Mg-T X351</b> FF, FA: HNO <sub>3</sub> : AA (dissolved) <b>Mg-D X203</b> LF, LA: HNO <sub>3</sub> : AA (dissolved) <b>Mg-D X085</b>
<b>Method Summary</b>	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.
<b>MDL</b>	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.
<b>Matrix</b>	Water, wastewater, marine water.
<b>Interferences and Precautions</b>	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.
<b>Sample Handling and Preservation</b>	See section 1.0, the sample preparation section of this manual.
<b>Stability</b>	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
<b>Instrument Parameters</b>	Source: Mg Hollow cathode Lamp Wavelength: 285.2 nm (primary); 202.6 nm (alternate) Type of Flame: air/acetylene Background Correction: recommended
<b>Apparatus, Materials and Reagents</b>	See sections 2.1.5 and 2.1.6 of this manual.
<b>Precision</b>	None listed.
<b>Accuracy</b>	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)

<b>Parameter</b>	Manganese, total Manganese, dissolved	
<b>Sample Preparation</b>	See section 1.0, the sample preparation section.	
<b>Analytical Method</b>	See section 2.1, the AA methods section.	
<b>EMS Code</b>	FA: HNO <sub>3</sub> : AA (total)	<b>Mn-T X073</b>
	LA: HNO <sub>3</sub> : AA (total)	<b>Mn-T X351</b>
	FF, FA: HNO <sub>3</sub> : AA (dissolved)	<b>Mn-D X203</b>
	LF, LA: HNO <sub>3</sub> : AA (dissolved)	<b>Mn-D X085</b>
<b>Introduction</b>	<p>Manganese occurs naturally as salts and minerals in nature. Major manganese containing substances are pyrolusite (MnO<sub>2</sub>), rhodochrosite (MnCO<sub>3</sub>) and rhodonite.</p> <p>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 &lt;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.</p>	
<b>Method Summary</b>	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.	
<b>MDL</b>	<p>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.</p>	
<b>Matrix</b>	Water, wastewater, marine water.	
<b>Interferences and Precautions</b>	<p>Silicon has a suppressing effect on the manganese signal. This interference can be controlled by the addition of 2000 ppm CaCl<sub>2</sub>.  See also section 2.1.4 of the AA methods section of this manual.</p>	
<b>Sample Handling and Preservation</b>	See section 1.0, the sample preparation section of this manual.	
<b>Stability</b>	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.	

<b>Instrument Parameters</b>	Source: Mn hollow cathode lamp Wavelength: 279.5 nm Type of flame: Air/Acetylene Background Correction: recommended	
<b>Apparatus, Materials and Reagents</b>	See section 2.1.5 and 2.1.6 of this manual.	
<b>Precision</b>	None listed.	
<b>Accuracy</b>	None listed.	
<b>Quality Control</b>	See section 2.1.9, QA/QC Guidelines in this manual.	
<b>References</b>	<ol style="list-style-type: none"> <li>1. Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992, Method 3111 B/D.</li> <li>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.</li> </ol>	
<b>Revision History</b>	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)

<b>Parameter</b>	Manganese, total Manganese, dissolved								
<b>Sample Preparation</b>	See section 1.0, the sample preparation section.								
<b>Analytical Method</b>	See section 2.1, the AA methods section.								
<b>EMS Code</b>	<table border="0"> <tr> <td>FA: HNO<sub>3</sub>: GFAA (total)</td> <td><b>Mn-T X072</b></td> </tr> <tr> <td>LA: HNO<sub>3</sub>: GFAA (total)</td> <td><b>Mn-T X179</b></td> </tr> <tr> <td>FF, FA: HNO<sub>3</sub>: GFAA (dissolved)</td> <td><b>Mn-D X116</b></td> </tr> <tr> <td>LF, LA: HNO<sub>3</sub>: GFAA (dissolved)</td> <td><b>Mn-D X357</b></td> </tr> </table>	FA: HNO <sub>3</sub> : GFAA (total)	<b>Mn-T X072</b>	LA: HNO <sub>3</sub> : GFAA (total)	<b>Mn-T X179</b>	FF, FA: HNO <sub>3</sub> : GFAA (dissolved)	<b>Mn-D X116</b>	LF, LA: HNO <sub>3</sub> : GFAA (dissolved)	<b>Mn-D X357</b>
FA: HNO <sub>3</sub> : GFAA (total)	<b>Mn-T X072</b>								
LA: HNO <sub>3</sub> : GFAA (total)	<b>Mn-T X179</b>								
FF, FA: HNO <sub>3</sub> : GFAA (dissolved)	<b>Mn-D X116</b>								
LF, LA: HNO <sub>3</sub> : GFAA (dissolved)	<b>Mn-D X357</b>								
<b>Introduction</b>	<p>Manganese occurs naturally as salts and minerals. Major manganese containing substances are pyrolusite (MnO<sub>2</sub>), rhodochrosite (MnCO<sub>3</sub>) and rhodonite.</p> <p>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 &lt;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.</p>								
<b>Method Summary</b>	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.								
<b>MDL</b>	<p>Given an aqueous sample free of interferences, the instrumental performance characteristics are:</p> <p>MDL: 0.0002 mg/L</p> <p>Range: 0.0002-0.030 mg/L</p> <p>See Table C-1 in section 2.1, the AA methods section, for additional information.</p>								
<b>Matrix</b>	Water, wastewater, marine water.								
<b>Interferences and Precautions</b>	See section 2.1.4 of the AA methods section of this manual.								
<b>Sample Handling and Preservation</b>	See section 1.0, the sample preparation section of this manual.								
<b>Stability</b>	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.								

<b>Instrument Parameters</b>	Source: Mn hollow cathode lamp Wavelength: 279.5 nm Background Correction: recommended	
<b>Apparatus, Materials and Reagents</b>	See section 2.1.5 and 2.1.6 of this manual.	
<b>Precision</b>	None listed.	
<b>Accuracy</b>	None listed.	
<b>Quality Control</b>	See section 2.1.9 QA/QC Guidelines in this manual.	
<b>References</b>	<ul style="list-style-type: none"> <li>a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992, Method 3113B.</li> <li>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.</li> </ul>	
<b>Revision History</b>	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)

<b>Parameter</b>	Mercury, total Mercury, dissolved
<b>Sample Preparation</b>	See section 1.0 the sample preparation section.
<b>Analytical Method</b>	See section 2.1, the AA methods section, and section 2.3, the cold vapour methods section.
<b>EMS Code</b>	FA: HNO <sub>3</sub> /K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> : CVAA (total) <b>Hg-T X346</b> LA: HNO <sub>3</sub> /K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> : CVAA (total) <b>Hg-T X353</b> FF, FA: HNO <sub>3</sub> /K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> : CVAA (dissolved) <b>Hg-D X347</b> LF, LA: HNO <sub>3</sub> /K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> : CVAA (dissolved) <b>Hg-D X358</b>
<b>Introduction</b>	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.
<b>Method Summary</b>	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.
<b>MDL</b>	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.
<b>Matrix</b>	Water, wastewater, marine water.
<b>Interferences and Precautions</b>	a) specific volatile material which absorbs at 253.7 nm, b) sulfide c) copper d) chlorides and free chlorine.
<b>Sample Handling and Preservation</b>	See Section 1.0, the sample preparation section of this manual.
<b>Stability</b>	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.
<b>Instrument Parameters</b>	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)**

<b>Parameter</b>	Hg-T - Mercury Total
<b>Sample Handling and Preservation</b>	Not available
<b>Analytical Method</b>	Aqua Regia digestion; CVAA
<b>EMS Codes</b>	
<b>Introduction</b>	This method is applicable to the quantitative determination of mercury in soil.
<b>Summary</b>	Organomercury compounds are oxidized via Aqua regia/KMnO <sub>4</sub> 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.
<b>MDL</b>	0.05 µg/g
<b>Matrix</b>	Soil Sediments Solids
<b>Interferences and Precautions</b>	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 253.7nm will also interfere. If this is suspected, run the sample without the addition of reagents to determine if this type of interference is present.
<b>Stability</b>	Not available
<b>Procedure Apparatus</b>	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<sub>3</sub>) - Concentrated (Non-detectable Mercury Content).
- c) Potassium Permanganate (KMnO<sub>4</sub>), 1.2% Dissolve 23.1g KMnO<sub>4</sub> into DI and adjust volume to 2L.
- d) Aqua Regia, 50% - To 100mL DI, add 25mL conc. HCl and 75mL HNO<sub>3</sub>.
- 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<sub>2</sub> 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<sub>3</sub> to 2L DI.
- h) Potassium Dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>), 10% - 100g K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> to 1L DI.
- i) Stock Mercury Solution, 100mg/L Hg - Dissolve 0.1678g of phenyl mercuric acetate in 1L flask of 1% H<sub>2</sub>SO<sub>4</sub>. 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<sub>2</sub>SO<sub>4</sub>, 5mL 10% K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> 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<sub>2</sub>SO<sub>4</sub>, 0.5mL 10% K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> 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<sub>4</sub>. Cap and gently mix. If sample fails to maintain a permanganate colour after the addition of the digestion solution, add 5% KMnO<sub>4</sub> 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<sub>4</sub> 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 cell 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 $\pm$ 10%, QCB $\pm$ 15%, duplicate $\pm$ 20%, and blank spikes $\pm$ 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

## MOLYBDENUM (Atomic Absorption - Direct Aspiration)

<b>Parameter</b>	Molybdenum, total Molybdenum, dissolved
<b>Sample Preparation</b>	See section 1.0, the sample preparation section.
<b>Analytical Method</b>	See section 2.1, the AA methods section.
<b>EMS Code</b>	FA: HNO <sub>3</sub> : AA (total) <b>Mo-T X073</b> LA: HNO <sub>3</sub> : AA (total) <b>Mo-T X351</b> FF, FA: HNO <sub>3</sub> : AA (dissolved) <b>Mo-D X203</b> LF, LA: HNO <sub>3</sub> : AA (dissolved) <b>Mo-D X085</b>
<b>Introduction</b>	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.
<b>Method Summary</b>	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.
<b>MDL</b>	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.
<b>Matrix</b>	Water, wastewater, marine water.
<b>Interferences and Precautions</b>	See section 2.1.4 of the AA methods section of this manual. Interferences in an air/acetylene flame from Ca, Sr, SO <sub>4</sub> , 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.
<b>Sample Handling and Preservation</b>	See section 1.0, the sample preparation section of this manual.
<b>Stability</b>	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
<b>Instrument Parameters</b>	Source: Mo Hollow cathode Lamp. Wavelength: 313.3 nm Type of flame: nitrous oxide/Acetylene Background correction: recommended

<b>Apparatus, Materials and Reagents</b>	See sections 2.1.5 and 2.1.6 of this manual.	
<b>Precision</b>	None listed.	
<b>Accuracy</b>	None listed.	
<b>Quality Control</b>	See section 2.1.9, QA/QC Guidelines in this manual.	
<b>References</b>	<ul style="list-style-type: none"> <li>a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992, Method 3111 B/D.</li> <li>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.</li> </ul>	
<b>Revision History</b>	February 14, 1994:	Publication in 1994 Laboratory Manual.
	December 31, 2000:	SEAM codes replaced by EMS codes. Sample matrix added.

## MOLYBDENUM (Atomic Absorption - Graphite Furnace)

<b>Parameter</b>	Molybdenum, total Molybdenum, dissolved
<b>Sample Preparation</b>	See section 1.0, the sample preparation section.
<b>Analytical Method</b>	See section 2.1, the AA methods section.
<b>EMS Code</b>	FA: HNO <sub>3</sub> : GFAA (total) <b>Mo-T X072</b> LA: HNO <sub>3</sub> : GFAA (total) <b>Mo-T X179</b> FF, FA: HNO <sub>3</sub> : GFAA (dissolved) <b>Mo-D X116</b> LF, LA: HNO <sub>3</sub> : GFAA (dissolved) <b>Mo-D X357</b>
<b>Introduction</b>	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.
<b>Method Summary</b>	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.
<b>MDL</b>	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.
<b>Matrix</b>	Water, wastewater, marine water.
<b>Interferences and Precautions</b>	See section 2.1.4 of the AA methods section of this manual.
<b>Sample Handling and Preservation</b>	See section 1.0, the sample preparation section of this manual.
<b>Stability</b>	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
<b>Instrument</b>	Source: Mo Hollow cathode Lamp.
<b>Parameters</b>	Wavelength: 313.3 nm Background correction: recommended
<b>Apparatus, Materials and Reagents</b>	See sections 2.1.5 and 2.1.6 of this manual.

<b>Precision</b>	None listed.	
<b>Accuracy</b>	None listed.	
<b>Quality Control</b>	See section 2.1.9, QA/QC Guidelines in this manual.	
<b>References</b>	<ul style="list-style-type: none"> <li>a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992, Method 3111 B/D.</li> <li>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.</li> </ul>	
<b>Revision History</b>	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)

<b>Parameter</b>	Nickel, total Nickel, dissolved								
<b>Sample Preparation</b>	See section 1.0, the sample preparation section.								
<b>Analytical Method</b>	See section 2.1, the AA methods section.								
<b>EMS Code</b>	<table border="0"> <tr> <td>FA: HNO<sub>3</sub>: AA (total)</td> <td><b>Ni-T X073</b></td> </tr> <tr> <td>LA: HNO<sub>3</sub>: AA (total)</td> <td><b>Ni-T X351</b></td> </tr> <tr> <td>FF, FA: HNO<sub>3</sub>: AA (dissolved)</td> <td><b>Ni-D X203</b></td> </tr> <tr> <td>LF, LA: HNO<sub>3</sub>: AA (dissolved)</td> <td><b>Ni-D X085</b></td> </tr> </table>	FA: HNO <sub>3</sub> : AA (total)	<b>Ni-T X073</b>	LA: HNO <sub>3</sub> : AA (total)	<b>Ni-T X351</b>	FF, FA: HNO <sub>3</sub> : AA (dissolved)	<b>Ni-D X203</b>	LF, LA: HNO <sub>3</sub> : AA (dissolved)	<b>Ni-D X085</b>
FA: HNO <sub>3</sub> : AA (total)	<b>Ni-T X073</b>								
LA: HNO <sub>3</sub> : AA (total)	<b>Ni-T X351</b>								
FF, FA: HNO <sub>3</sub> : AA (dissolved)	<b>Ni-D X203</b>								
LF, LA: HNO <sub>3</sub> : AA (dissolved)	<b>Ni-D X085</b>								
<b>Introduction</b>	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.								
<b>Method Summary</b>	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.								
<b>MDL</b>	<p>Given an aqueous sample free of interferences, the instrumental performance characteristics are:</p> <p>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.</p>								
<b>Matrix</b>	Water, wastewater, marine water.								
<b>Interferences and Precautions</b>	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 nitrous oxide-acetylene flame.								
<b>Sample Handling and Preservation</b>	See section 1.0, the sample preparation section of this manual.								
<b>Stability</b>	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.								
<b>Instrument Parameters</b>	<p>Source: Ni Hollow cathode Lamp  Wavelength: 232.0 nm (primary); 352.4 nm (alternate)  Type of Flame: air/acetylene  Background Correction: recommended</p>								
<b>Apparatus, Materials and Reagents</b>	See sections 2.1.5 and 2.1.6 of this manual.								

<b>Precision</b>	None listed.	
<b>Accuracy</b>	None listed.	
<b>Quality Control</b>	See section 2.1.9, QA/QC Guidelines in this manual.	
<b>References</b>	<ul style="list-style-type: none"> <li>a) Standard Methods for the Examination of Water and Wastewater APHA, AWWA, WEF, 18th edition, 1992, Method 3111 B/D.</li> <li>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.</li> </ul>	
<b>Revision History</b>	February 14, 1994:	Publication in 1994 Laboratory Manual.
	December 31, 2000:	SEAM codes replaced by EMS codes. Sample matrix added.



## NICKEL (Atomic Absorption - Graphite Furnace)

<b>Parameter</b>	Nickel, total Nickel, dissolved
<b>Sample Preparation</b>	See section 1.0, the sample preparation section.
<b>Analytical Method</b>	See section 2.1, the AA methods section.
<b>EMS Code</b>	FA: HNO <sub>3</sub> : GFAA (total) <b>Ni-T X072</b> LA: HNO <sub>3</sub> : GFAA (total) <b>Ni-T X179</b> FF, FA: HNO <sub>3</sub> : GFAA (dissolved) <b>Ni-D X116</b> LF, LA: HNO <sub>3</sub> : GFAA (dissolved) <b>Ni-D X357</b>
<b>Introduction</b>	Nickel's principle 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.
<b>Method Summary</b>	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.
<b>MDL</b>	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.
<b>Matrix</b>	Water, wastewater, marine water.
<b>Interferences and Precautions</b>	See section 2.1.4 of the AA methods section of this manual.
<b>Sample Handling and Preservation</b>	See section 1.0, the sample preparation section of this manual.
<b>Stability</b>	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
<b>Instrument Parameters</b>	Source: Ni hollow cathode lamp Wavelength: 232.0 nm Background Correction: recommended
<b>Apparatus, Materials and Reagents</b>	See section 2.1.5 and 2.1.6 of this manual.

<b>Precision</b>	None listed.	
<b>Accuracy</b>	None listed.	
<b>Quality Control</b>	See section 2.1.9, QA/QC Guidelines in this manual.	
<b>References</b>	<ul style="list-style-type: none"> <li>a) Standard Method for the Examination of Water and Wastewater APHA, AWWA, WEF, 18th edition, 1992, Method 3113B.</li> <li>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.</li> </ul>	
<b>Revision History</b>	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)

<b>Parameter</b>	Potassium, total Potassium, dissolved
<b>Sample Preparation</b>	See section 1.0, the sample preparation section.
<b>Analytical Method</b>	See section 2.1, the AA methods section.
<b>EMS Code</b>	FA: HNO <sub>3</sub> : AA (total) <b>K-TX073</b> LA: HNO <sub>3</sub> : AA (total) <b>K-TX351</b> FF, FA: HNO <sub>3</sub> : AA (dissolved) <b>K-DX203</b> LF, LA: HNO <sub>3</sub> : AA (dissolved) <b>K-DX085</b>
<b>Method Summary</b>	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.
<b>MDL</b>	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.
<b>Matrix</b>	Water, wastewater, marine water.
<b>Interferences and Precautions</b>	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%.
<b>Sample Handling and Preservation</b>	See section 1.0, the sample preparation section of this manual.
<b>Stability</b>	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
<b>Instrument Parameters</b>	Source: K hollow cathode lamp Wavelength: 766.5 nm (primary); 404.4 nm (alternate) Type of Flame: air/acetylene Background Correction: recommended
<b>Apparatus, Materials and Reagents</b>	See sections 2.1.5 and 2.1.6 of this manual.
<b>Precision</b>	None listed.
<b>Accuracy</b>	None listed.
<b>Quality Control</b>	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.

## SELENIUM (Atomic Absorption - Direct Aspiration)

<b>Parameter</b>	Selenium, total Selenium, dissolved
<b>Sample Preparation</b>	See section 1.0, the sample preparation section.
<b>Analytical Method</b>	See section 2.1, the AA methods section.
<b>EMS Code</b>	FA: HNO <sub>3</sub> : AA (total) <b>Se-TX073</b> LA: HNO <sub>3</sub> : AA (total) <b>Se-TX351</b> FF, FA: HNO <sub>3</sub> : AA (dissolved) <b>Se-DX203</b> LF, LA: HNO <sub>3</sub> : AA (dissolved) <b>Se-DX085</b>
<b>Introduction</b>	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.
<b>Method Summary</b>	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.
<b>MDL</b>	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.
<b>Matrix</b>	Water, wastewater, marine water.
<b>Interferences and Precautions</b>	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.
<b>Sample Handling and Preservation</b>	See section 1.0, the sample preparation section of this manual.
<b>Stability</b>	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
<b>Instrument Parameters</b>	Source: Se EDL or hollow cathode lamp Wavelength: 196.0 nm Type of Flame: air/acetylene Background Correction: recommended

<b>Apparatus, Materials and Reagents</b>	See section 2.1.5 and 2.1.6 of this manual.	
<b>Precision</b>	None listed.	
<b>Accuracy</b>	None listed.	
<b>Quality Control</b>	See section 2.1.9, QA/QC Guidelines in this manual.	
<b>References</b>	<ul style="list-style-type: none"> <li>a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 18th edition, 1992.</li> <li>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.</li> </ul>	
<b>Revision History</b>	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)

<b>Parameter</b>	Selenium, total Selenium, dissolved	
<b>Sample Preparation</b>	See section 1.0, the sample preparation section.	
<b>Analytical Method</b>	See section 2.1, the AA methods section.	
<b>EMS Code</b>	FA: HNO <sub>3</sub> : GFAA (total)	<b>Se-T X072</b>
	LA: HNO <sub>3</sub> : GFAA (total)	<b>Se-T X179</b>
	FF, FA: HNO <sub>3</sub> : GFAA (dissolved)	<b>Se-D X116</b>
	LF, LA: HNO <sub>3</sub> : GFAA (dissolved)	<b>Se-D X357</b>
<b>Introduction</b>	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.	
<b>Method Summary</b>	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.	
<b>MDL</b>	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.	
<b>Matrix</b>	Water, wastewater, marine water.	
<b>Interferences and Precautions</b>	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)

<b>Parameter</b>	Selenium, total Selenium, dissolved																
<b>Sample Preparation</b>	See section 1.0, the sample preparation section.																
<b>Analytical Method</b>	See section 2.1, the AA methods section, and section 2.2 the hydride AA method section.																
<b>EMS Code</b>	<table> <tr> <td>FA: HNO<sub>3</sub>: HVAAS (total)</td> <td><b>Se-T X289</b></td> </tr> <tr> <td>LA: HNO<sub>3</sub>: HVAAS (total)</td> <td><b>Se-T X354</b></td> </tr> <tr> <td>FA: HCl: HVAAS (total)</td> <td><b>Se-T X345</b></td> </tr> <tr> <td>LA: HCl: HVAAS (total)</td> <td><b>Se-T X355</b></td> </tr> <tr> <td>FF, FA: HNO<sub>3</sub>: HVAAS (dissolved)</td> <td><b>Se-D X202</b></td> </tr> <tr> <td>LF, LA: HNO<sub>3</sub>: HVAAS (dissolved)</td> <td><b>Se-D X359</b></td> </tr> <tr> <td>FF, FA: HCl: HVAAS (dissolved)</td> <td><b>Se-D X348</b></td> </tr> <tr> <td>LF, LA: HCl: HVAAS (dissolved)</td> <td><b>Se-D X360</b></td> </tr> </table>	FA: HNO <sub>3</sub> : HVAAS (total)	<b>Se-T X289</b>	LA: HNO <sub>3</sub> : HVAAS (total)	<b>Se-T X354</b>	FA: HCl: HVAAS (total)	<b>Se-T X345</b>	LA: HCl: HVAAS (total)	<b>Se-T X355</b>	FF, FA: HNO <sub>3</sub> : HVAAS (dissolved)	<b>Se-D X202</b>	LF, LA: HNO <sub>3</sub> : HVAAS (dissolved)	<b>Se-D X359</b>	FF, FA: HCl: HVAAS (dissolved)	<b>Se-D X348</b>	LF, LA: HCl: HVAAS (dissolved)	<b>Se-D X360</b>
FA: HNO <sub>3</sub> : HVAAS (total)	<b>Se-T X289</b>																
LA: HNO <sub>3</sub> : HVAAS (total)	<b>Se-T X354</b>																
FA: HCl: HVAAS (total)	<b>Se-T X345</b>																
LA: HCl: HVAAS (total)	<b>Se-T X355</b>																
FF, FA: HNO <sub>3</sub> : HVAAS (dissolved)	<b>Se-D X202</b>																
LF, LA: HNO <sub>3</sub> : HVAAS (dissolved)	<b>Se-D X359</b>																
FF, FA: HCl: HVAAS (dissolved)	<b>Se-D X348</b>																
LF, LA: HCl: HVAAS (dissolved)	<b>Se-D X360</b>																
<b>Introduction</b>	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.																
<b>Method Summary</b>	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.																
<b>MDL</b>	<p>Given an aqueous sample free of interferences, the instrumental performance characteristics are:</p> <p>MDL: 0.0005 mg/L</p> <p>Range: 0.0005-0.020 mg/L</p> <p>See Table C-1 in section 2.1, the AA methods section, for additional information.</p>																
<b>Matrix</b>	Water, wastewater, marine water.																
<b>Interferences and Precautions</b>	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.																
<b>Sample Handling and Preservation</b>	See section 1.0, the sample preparation section of this manual.																
<b>Stability</b>	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.																

<b>Instrument Parameters</b>	Source: Se EDL or hollow cathode lamp Wavelength: 196.0 nm Background Correction: not required
<b>Apparatus, Materials and Reagents</b>	See section 2.2, the hydride AA methods section in this manual.
<b>Precision</b>	None listed.
<b>Accuracy</b>	None listed.
<b>Quality Control</b>	See section 2.1.9, QA/QC Guidelines in this manual.
<b>References</b>	<ul style="list-style-type: none"> <li>a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 18th edition, 1992.</li> <li>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.</li> </ul>
<b>Revision History</b>	<p>February 14, 1994: Publication in 1994 Laboratory Manual.</p> <p>December 31, 2000: SEAM codes replaced by EMS codes. Sample matrix added.</p>

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

<b>Parameter</b>	Selenium, total Selenium, dissolved
<b>Sample Preparation</b>	See section 1.0, the sample preparation section.
<b>Analytical Method</b>	See section 2.4, the ICP-AES method section.
<b>EMS Code</b>	FA: HNO <sub>3</sub> : ICAP (total) <b>Se-T X349</b> LA: HNO <sub>3</sub> : ICAP (total) <b>Se-T X352</b> FF, FA: HNO <sub>3</sub> : ICAP (dissolved) <b>Se-D X350</b> LF, LA: HNO <sub>3</sub> : ICAP (dissolved) <b>Se-D X356</b>
<b>Introduction</b>	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.
<b>Method Summary</b>	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.
<b>MDL</b>	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.
<b>Matrix</b>	Water, wastewater, marine water.
<b>Interferences and Precautions</b>	See section 2.4, the ICP-AES section of this manual.
<b>Sample Handling and Preservation</b>	See section 1.0, the sample preparation section of this manual.
<b>Stability</b>	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
<b>Instrument Parameters</b>	Wavelength: 196.0 nm (primary) Background Correction: recommended
<b>Apparatus, Materials and Reagents</b>	See section 2.4, of the ICP-AES methods section in this manual.
<b>Precision</b>	None listed.

<b>Accuracy</b>	None listed.
<b>Quality Control</b>	See section 2.1.9, QA/QC Guidelines in this manual.
<b>References</b>	<ul style="list-style-type: none"> <li>a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 18th edition, 1992.</li> <li>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.</li> </ul>
<b>Revision History</b>	<p>February 14, 1994: Publication in 1994 Laboratory Manual.</p> <p>December 31, 2000: SEAM codes replaced by EMS codes. Sample matrix added.</p>

## **SILVER (Atomic Absorption - Direct Aspiration)**

<b>Parameter</b>	Silver, total Silver, dissolved
<b>Sample Preparation</b>	See section 1.0, the sample preparation section.
<b>Analytical Method</b>	See section 2.1, the AA methods section.
<b>EMS Code</b>	FA: HNO <sub>3</sub> : AA (total) <b>Ag-T X073</b> LA: HNO <sub>3</sub> : AA (total) <b>Ag-T X351</b> FF, FA: HNO <sub>3</sub> : AA (dissolved) <b>Ag-D X203</b> LF, LA: HNO <sub>3</sub> : AA (dissolved) <b>Ag-D X085</b>

**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.

<b>Stability</b>	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months. Silver nitrate (AgNO <sub>3</sub> ) 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.	
<b>Instrument Parameters</b>	Source: Ag hollow cathode lamp Wavelength: 328.1 nm Type of Flame: air/acetylene Background Correction: recommended	
<b>Apparatus, Materials and Reagents</b>	See section 2.1.5 and 2.1.6 of this manual.	
<b>Precision</b>	None listed.	
<b>Accuracy</b>	None listed.	
<b>Quality Control</b>	See section 2.1.9, QA/QC Guidelines in this manual.	
<b>References</b>	<ul style="list-style-type: none"> <li>a) Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 272.1.</li> <li>b) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 18th edition, 1992.</li> <li>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.</li> </ul>	
<b>Revision History</b>	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)

<b>Parameter</b>	Silver, total Silver, dissolved								
<b>Sample Preparation</b>	See section 1.0, the sample preparation section.								
<b>Analytical Method</b>	See section 2.1, the AA methods section.								
<b>EMS Code</b>	<table border="0"> <tr> <td>FA: HNO<sub>3</sub>: GFAA (total)</td> <td><b>Ag-T X072</b></td> </tr> <tr> <td>LA: HNO<sub>3</sub>: GFAA (total)</td> <td><b>Ag-T X179</b></td> </tr> <tr> <td>FF, FA: HNO<sub>3</sub>: GFAA (dissolved)</td> <td><b>Ag-D X116</b></td> </tr> <tr> <td>LF, LA: HNO<sub>3</sub>: GFAA (dissolved)</td> <td><b>Ag-D X357</b></td> </tr> </table>	FA: HNO <sub>3</sub> : GFAA (total)	<b>Ag-T X072</b>	LA: HNO <sub>3</sub> : GFAA (total)	<b>Ag-T X179</b>	FF, FA: HNO <sub>3</sub> : GFAA (dissolved)	<b>Ag-D X116</b>	LF, LA: HNO <sub>3</sub> : GFAA (dissolved)	<b>Ag-D X357</b>
FA: HNO <sub>3</sub> : GFAA (total)	<b>Ag-T X072</b>								
LA: HNO <sub>3</sub> : GFAA (total)	<b>Ag-T X179</b>								
FF, FA: HNO <sub>3</sub> : GFAA (dissolved)	<b>Ag-D X116</b>								
LF, LA: HNO <sub>3</sub> : GFAA (dissolved)	<b>Ag-D X357</b>								
<b>Introduction</b>	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.								
<b>Method Summary</b>	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.								
<b>MDL</b>	<p>Given an aqueous sample free of interferences, the instrumental performance characteristics are:</p> <p>MDL: 0.0002 mg/L</p> <p>Range: 0.0002-0.005 mg/L</p> <p>See Table C-1 in section 2.1, the AA methods section, for additional information.</p>								
<b>Matrix</b>	Water, wastewater, marine water.								
<b>Interferences and Precautions</b>	<p>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.</p> <p>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.</p> <p>Silver chloride is insoluble; therefore, hydrochloric acid should be avoided unless the silver is already in solution as a chloride complex.</p>								
<b>Sample Handling and Preservation</b>	See section 1.0, the sample preparation section of this manual.								

<b>Stability</b>	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.	
	Silver nitrate (AgNO <sub>3</sub> ) 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.	
<b>Instrument Parameters</b>	Source: Ag hollow cathode lamp Wavelength: 328.1 nm Background Correction: recommended	
<b>Apparatus, Materials and Reagents</b>	See section 2.1.5 and 2.1.6 of this manual.	
<b>Precision</b>	None listed.	
<b>Accuracy</b>	None listed.	
<b>Quality Control</b>	See section 2.1.9, QA/QC Guidelines in this manual.	
<b>References</b>	<ul style="list-style-type: none"> <li>a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992, Method 3113B.</li> <li>b) Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 272.2.</li> <li>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.</li> </ul>	
<b>Revision History</b>	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)

<b>Parameter</b>	Sodium, total Sodium, dissolved
<b>Sample Preparation</b>	See section 1.0, the sample preparation section.
<b>Analytical Method</b>	See section 2.1, the AA methods section.
<b>EMS Code</b>	FA: HNO <sub>3</sub> : AA (total) <b>Na-T X073</b> LA: HNO <sub>3</sub> : AA (total) <b>Na-T X351</b> FF, FA: HNO <sub>3</sub> : AA (dissolved) <b>Na-D X203</b> LF, LA: HNO <sub>3</sub> : AA (dissolved) <b>Na-D X085</b>
<b>Method Summary</b>	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.
<b>MDL</b>	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.
<b>Matrix</b>	Water, wastewater, marine water.
<b>Interferences and Precautions</b>	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%.
<b>Sample Handling and Preservation</b>	See section 1.0, the sample preparation section of this manual.
<b>Stability</b>	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
<b>Instrument Parameters</b>	Source: Na Hollow cathode Lamp Wavelength: 589.0 nm (primary); 330.2 nm (alternate) Type of Flame: air/acetylene Background Correction: recommended
<b>Apparatus, Materials and Reagents</b>	See sections 2.1.5 and 2.1.6 of this manual.
<b>Precision</b>	None listed.
<b>Accuracy</b>	None listed.
<b>Quality Control</b>	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)

<b>Parameter</b>	Tin, total Tin, dissolved
<b>Sample Preparation</b>	See section 1.0, the Sample Preparation section.
<b>Analytical Method</b>	See section 2.1, the AA methods section.
<b>EMS Code</b>	FA: HNO <sub>3</sub> : AA (total) <b>Sn-T X073</b> LA: HNO <sub>3</sub> : AA (total) <b>Sn-T X351</b> FF, FA: HNO <sub>3</sub> : AA (dissolved) <b>Sn-D X203</b> LF, LA: HNO <sub>3</sub> : AA (dissolved) <b>Sn-D X085</b>
<b>Introduction</b>	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.
<b>Method Summary</b>	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.
<b>MDL</b>	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.
<b>Matrix</b>	Water, wastewater, marine water.
<b>Interferences and Precautions</b>	See section 2.1.4 of the AAS methods section of this manual.
<b>Sample Handling and Preservation</b>	See section 1.0, the sample preparation section of this manual.
<b>Stability</b>	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
<b>Instrument Parameters</b>	Source: Sn EDL or hollow cathode lamp Wavelength: 286.3 nm Type of Flame: Nitrous oxide/Acetylene Background Correction: recommended
<b>Apparatus, Material and Reagents</b>	See section 2.1.5 and 2.1.6 of this manual.
<b>Precision</b>	None listed.

<b>Accuracy</b>	None listed.				
<b>Quality Control</b>	See Section 2.1.9, QA/QC Guidelines in this manual.				
<b>References</b>	<ul style="list-style-type: none"> <li>a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 18th edition, 1992.</li> <li>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.</li> <li>c) Analytical Methods For Atomic Absorption Spectrophotometry, Published by The Perkin-Elmer Corporation. Norwalk, Connecticut, U.S.A.. January 1982.</li> </ul>				
<b>Revision History</b>	<table> <tr> <td>February 14, 1994:</td> <td>Publication in 1994 Laboratory Manual.</td> </tr> <tr> <td>December 31, 2000:</td> <td>SEAM codes replaced by EMS codes. Sample matrix added.</td> </tr> </table>	February 14, 1994:	Publication in 1994 Laboratory Manual.	December 31, 2000:	SEAM codes replaced by EMS codes. Sample matrix added.
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)

<b>Parameter</b>	Tin, total Tin, dissolved																
<b>Sample Preparation</b>	See section 1.0, the sample preparation section.																
<b>Analytical Method</b>	See section 2.1, the AA methods section and 2.2, the hydride AA method section of this manual.																
<b>EMS Code</b>	<table border="0"> <tr> <td>FA: HNO<sub>3</sub>: HVAAS (total)</td> <td><b>Sn-T X289</b></td> </tr> <tr> <td>LA: HNO<sub>3</sub>: HVAAS (total)</td> <td><b>Sn-T X354</b></td> </tr> <tr> <td>FA: HCl: HVAAS (total)</td> <td><b>Sn-T X345</b></td> </tr> <tr> <td>LA: HCl: HVAAS (total)</td> <td><b>Sn-T X355</b></td> </tr> <tr> <td>FF, FA: HNO<sub>3</sub>: HVAAS (dissolved)</td> <td><b>Sn-D X202</b></td> </tr> <tr> <td>LF, LA: HNO<sub>3</sub>: HVAAS (dissolved)</td> <td><b>Sn-D X359</b></td> </tr> <tr> <td>FF, FA: HCl: HVAAS (dissolved)</td> <td><b>Sn-D X348</b></td> </tr> <tr> <td>LF, LA: HCl: HVAAS (dissolved)</td> <td><b>Sn-D X360</b></td> </tr> </table>	FA: HNO <sub>3</sub> : HVAAS (total)	<b>Sn-T X289</b>	LA: HNO <sub>3</sub> : HVAAS (total)	<b>Sn-T X354</b>	FA: HCl: HVAAS (total)	<b>Sn-T X345</b>	LA: HCl: HVAAS (total)	<b>Sn-T X355</b>	FF, FA: HNO <sub>3</sub> : HVAAS (dissolved)	<b>Sn-D X202</b>	LF, LA: HNO <sub>3</sub> : HVAAS (dissolved)	<b>Sn-D X359</b>	FF, FA: HCl: HVAAS (dissolved)	<b>Sn-D X348</b>	LF, LA: HCl: HVAAS (dissolved)	<b>Sn-D X360</b>
FA: HNO <sub>3</sub> : HVAAS (total)	<b>Sn-T X289</b>																
LA: HNO <sub>3</sub> : HVAAS (total)	<b>Sn-T X354</b>																
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FF, FA: HNO <sub>3</sub> : HVAAS (dissolved)	<b>Sn-D X202</b>																
LF, LA: HNO <sub>3</sub> : HVAAS (dissolved)	<b>Sn-D X359</b>																
FF, FA: HCl: HVAAS (dissolved)	<b>Sn-D X348</b>																
LF, LA: HCl: HVAAS (dissolved)	<b>Sn-D X360</b>																
<b>Introduction</b>	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.																
<b>Method Summary</b>	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.																
<b>MDL</b>	<p>Given an aqueous sample free of interferences, the instrumental performance characteristics are:</p> <p>MDL: 0.0005 mg/L</p> <p>Range: 0.0005 - 0.200 mg/L</p> <p>See Table C-1 in section 2.1, the AA methods section, for additional information.</p>																
<b>Matrix</b>	Water, wastewater, marine water.																
<b>Interferences and Precautions</b>	<ul style="list-style-type: none"> <li>• easily reduced metals - i.e., copper, silver, mercury, etc.</li> <li>• high concentrations of transition metals (&gt;200 mg/L),</li> <li>• oxidizing agents remaining following sample digestion - i.e., oxides of nitrogen. (USEPA, 1986)</li> </ul>																
<b>Sample Handling and Preservation</b>	See section 1.0, the sample preparation section of this manual.																
<b>Stability</b>	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.																

<b>Instrument Parameters</b>	Source: Sn EDL or hollow cathode lamp Wavelength: 286.3 nm Background Correction: not required				
<b>Apparatus, Material and Reagents</b>	See section 2.1.5 and 2.1.6 of this manual.				
<b>Precision</b>	None listed.				
<b>Accuracy</b>	None listed.				
<b>Quality Control</b>	See Section 2.1.9, QA/QC Guidelines in this manual.				
<b>References</b>	<ul style="list-style-type: none"> <li>a) Instructions - MHS-20 Mercury/Hydride System, Publication 338-A2-M 294/12.79. Bodenseewerk Perkin-Elmer &amp; Co. GMBH/UBERLINGEN. 1979.</li> <li>b) Analytical Methods For Atomic Absorption Spectrophotometry, Published The Perkin-Elmer Corporation. Norwalk, Connecticut, U.S.A.. January 1982.</li> <li>c) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 18th edition, 1992.</li> <li>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.</li> </ul>				
<b>Revision History</b>	<table border="0" style="width: 100%;"> <tr> <td style="width: 50%;">February 14, 1994:</td> <td>Publication in 1994 Laboratory Manual.</td> </tr> <tr> <td>December 31, 2000:</td> <td>SEAM codes replaced by EMS codes. Sample matrix added.</td> </tr> </table>	February 14, 1994:	Publication in 1994 Laboratory Manual.	December 31, 2000:	SEAM codes replaced by EMS codes. Sample matrix added.
February 14, 1994:	Publication in 1994 Laboratory Manual.				
December 31, 2000:	SEAM codes replaced by EMS codes. Sample matrix added.				

## URANIUM, TOTAL OR DISSOLVED

<b>Parameter</b>	Uranium, total Uranium, dissolved
<b>Analytical Method</b>	Laser-induced fluorescence HNO <sub>3</sub> digestion, laser-induced fluorescence
<b>EMS Code</b>	a) Dissolved <b>U--D X343</b> b) Total <b>U--T X344</b>
<b>Introduction</b>	Most sources of drinking water, especially groundwaters, contain dissolved carbonates and bicarbonates that are capable of complexing with uranium and keeping it in solution.
<b>Method Summary</b>	Uranyl ion (UO <sub>2</sub> <sup>2+</sup> ), 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.
<b>MDL</b>	Typical: 0.0002 mg/L for uranium, total 0.0001 mg/L for uranium, dissolved
<b>Matrix</b>	Fresh water
<b>Interferences and Precautions</b>	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.
<b>Sample Handling and Preservation</b>	Plastic or glass bottle, sample acidified in the field with 4mL concentrated HNO <sub>3</sub> /L
<b>Stability</b>	M. H. T.: 14 days
<b>Principle or Procedure</b>	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.
<b>Precision</b>	Authentic samples at concentrations of 3.9 and 30.4 µg/L gave coefficients of variation of 5.5% and 4.0% respectively.
<b>Accuracy</b>	±3% at 30 µg/L level
<b>Quality Control</b>	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:  
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Publication in 1994 Laboratory Manual.  
SEAM codes replaced by EMS codes. Out of  
print reference deleted. Sample matrix added.



## ZINC (Atomic Absorption - Direct Aspiration)

<b>Parameter</b>	Zinc, total Zinc, dissolved
<b>Sample Preparation</b>	See section 1.0, the sample preparation section.
<b>Analytical Method</b>	See section 2.1, the AA methods section.
<b>EMS Code</b>	FA: HNO <sub>3</sub> : AA (total) <b>Zn-T X073</b> LA: HNO <sub>3</sub> : AA (total) <b>Zn-T X351</b> FF, FA, HNO <sub>3</sub> : AA (dissolved) <b>Zn-D X203</b> LF, LA: HNO <sub>3</sub> : AA (dissolved) <b>Zn-D X085</b>
<b>Introduction</b>	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.
<b>Method Summary</b>	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.
<b>MDL</b>	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.
<b>Matrix</b>	Water, wastewater, marine water.
<b>Interferences and Precautions</b>	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.
<b>Sample Handling and Preservation</b>	See section 1.0, the sample preparation section.
<b>Stability</b>	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.
<b>Instrument Parameters</b>	Source: Zn hollow cathode lamp Wavelength: 213.9 nm Type of Flame: air/acetylene Background Correction: recommended

<b>Apparatus, Materials and Reagents</b>	See section 2.1.5 and 2.1.6 of this manual.	
<b>Precision</b>	None listed.	
<b>Accuracy</b>	None listed.	
<b>Quality Control</b>	See section 2.1.9, QA/QC Guidelines in this manual.	
<b>References</b>	<ul style="list-style-type: none"> <li>a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992, Method 3111 B/D.</li> <li>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.</li> </ul>	
<b>Revision History</b>	February 14, 1994:	Publication in 1994 Laboratory Manual.
	December 31, 2000:	SEAM codes replaced by EMS codes. Sample matrix added.

## ZINC (Atomic Absorption - Graphite Furnace)

<b>Parameter</b>	Zinc, total Zinc, dissolved								
<b>Sample Preparation</b>	See section 1.0, the sample preparation section.								
<b>Analytical Method</b>	See section 2.1, the AA methods section.								
<b>EMS Code</b>	<table border="0"> <tr> <td>FA: HNO<sub>3</sub>: GFAA (total)</td> <td><b>Zn-T X072</b></td> </tr> <tr> <td>LA: HNO<sub>3</sub>: GFAA (total)</td> <td><b>Zn-T X179</b></td> </tr> <tr> <td>FF, FA: HNO<sub>3</sub>: GFAA (dissolved)</td> <td><b>Zn-D X116</b></td> </tr> <tr> <td>LF, LA: HNO<sub>3</sub>: GFAA (dissolved)</td> <td><b>Zn-D X357</b></td> </tr> </table>	FA: HNO <sub>3</sub> : GFAA (total)	<b>Zn-T X072</b>	LA: HNO <sub>3</sub> : GFAA (total)	<b>Zn-T X179</b>	FF, FA: HNO <sub>3</sub> : GFAA (dissolved)	<b>Zn-D X116</b>	LF, LA: HNO <sub>3</sub> : GFAA (dissolved)	<b>Zn-D X357</b>
FA: HNO <sub>3</sub> : GFAA (total)	<b>Zn-T X072</b>								
LA: HNO <sub>3</sub> : GFAA (total)	<b>Zn-T X179</b>								
FF, FA: HNO <sub>3</sub> : GFAA (dissolved)	<b>Zn-D X116</b>								
LF, LA: HNO <sub>3</sub> : GFAA (dissolved)	<b>Zn-D X357</b>								
<b>Introduction</b>	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.								
<b>Method Summary</b>	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.								
<b>MDL</b>	<p>Given an aqueous sample free of interferences, the instrumental performance characteristics are:</p> <p>MDL: 0.0002 mg/L</p> <p>Range: 0.0002-0.004 mg/L</p> <p>See Table C-1 in section 2.1, the AA methods section, for additional information.</p>								
<b>Matrix</b>	Water, wastewater, marine water.								
<b>Interferences and Precautions</b>	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.								
<b>Sample Handling and Preservation</b>	See section 1.0, the sample preparation section of this manual.								
<b>Stability</b>	An aqueous solution preserved with nitric acid to pH <2, has a hold time of 6 months.								

<b>Instrument Parameters</b>	Source: Zn hollow cathode lamp Wavelength: 213.9 nm Background Correction: recommended
<b>Apparatus, Materials and Reagents</b>	See section 2.1.5 and 2.1.6 of this manual.
<b>Precision</b>	None listed.
<b>Accuracy</b>	None listed.
<b>Quality Control</b>	See section 2.1.9, QA/QC Guidelines in this manual.
<b>References</b>	<ul style="list-style-type: none"> <li>a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992, Method 3113B.</li> <li>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.</li> </ul>
<b>Revision History</b>	<p>February 14, 1994: Publication in 1994 Laboratory Manual.</p> <p>December 31, 2000: SEAM codes replaced by EMS codes. Sample matrix added.</p>