Method 200.12

Determination of Trace Elements in Marine Waters by Stabilized Temperature Graphite Furnace Atomic Absorption

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1.0 Scope and Application

1.1 This method provides procedures for the determination of total recoverable elements by graphite furnace atomic absorption (GFAA) in marine waters, including estuarine, ocean and brines with salinities of up to 35 ppt. This method is applicable to the following analytes:

Analyte		Chemical Abstracts Service Registry Numbers (CASRN)
Arsenic	(As)	7440-38-2
Cadmium	(Cd)	7440-43-9
Chromium	(Cr)	7440-47-3
Copper	(Cu)	7440-50-8
Lead	(Pb)	7439-92-1
Nickel	(Ni)	7440-02-0
Selenium	(Se)	7782-49-2

1.2 For determination of total recoverable analytes in marine waters, a digestion/extraction is required prior to analysis.

1.3 Method detection limit and instrumental operating conditions for the applicable elements are listed in Tables 1 and 2. These are intended as a guide and are typical of a commercial instrument optimized for the element. However, actual method detection limits and linear working ranges will be dependent on the sample matrix, instrumentation and selected operating conditions.

1.4 Users of the method data should state the data quality objectives prior to analysis. The ultra-trace metal concentrations typically associated with marine water may preclude the use of this method based on its sensitivity. Users of the method must document and have on file the required initial demonstration performance data described in Section 9.2 prior to using the method for analysis.

2.0 Summary of Method

2.1 Nitric acid is dispensed into a beaker containing an accurately weighed or measured, well-mixed, homogeneous aqueous sample. Then, for samples with undissolved material, the beaker is covered with a watch glass and heated, made up to volume, centrifuged or allowed to settle, and the sample is then analyzed.

2.2 The analytes listed in this method are determined by stabilized temperature platform graphite furnace atomic absorption (STPGFAA). In STPGFAA, the sample and the matrix modifier are first pipetted onto the platform or a device which provides delayed atomization.

The furnace chamber is then purged with a continuous flow of a premixed gas (95% argon - 5% hydrogen) and the sample is dried at a relatively low temperature (about 120°C) to avoid spattering. Once dried, the sample is pretreated in a char or ashing step which is designed to minimize the interference effects caused by the concomitant sample matrix. After the char step, the furnace is allowed to cool prior to atomization. The atomization cycle is characterized by rapid heating of the furnace to a temperature where the metal (analyte) is atomized from the pyrolytic graphite surface into a stopped gas flow atmosphere of argon containing 5% hydrogen. (Only selenium is determined in an atmosphere of high purity argon.) The resulting atomic cloud absorbs the element-specific atomic emission produced by a hollow cathode lamp (HCL) or an electrodeless discharge lamp (EDL). Following analysis, the furnace is subjected to a cleanout period of high temperature and continuous argon flow. Because the resulting absorbance usually has a nonspecific component associated with the actual analyte absorbance, Zeeman background correction is required to subtract from the total signal the component which is nonspecific to the analyte. In the absence of interferences, the background-corrected, absorbance is directly related to the concentration of the analyte. Interferences relating to STPGFAA (Section 4.0) must be recognized and corrected. Suppressions or enhancements of instrument response caused by the sample matrix must be corrected for by the method of standard addition (Section 11.3).

3.0 Definitions

3.1 Calibration Blank (CB) -- A volume of reagent water fortified with the same matrix as the calibration standards, but without the analytes, internal standards, or surrogate analytes.

3.2 Calibration Standard (CAL) -- A solution prepared from the primary dilution standard solution or stock standard solutions and the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.3 Field Reagent Blank (FRB) -- An aliquot of reagent water or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the FRB is to determine it method analytes or other interferences are present in the field environment.

3.4 Instrument Detection Limit (IDL) -- The minimum quantity of analyte or the concentration equivalent which gives an analyte signal equal to three times the standard deviation of the background signal at the selected wavelength, mass, retention time, absorbance line, etc.

3.5 Instrument Performance Check Solution (IPC) -- A solution of one or more method analytes, surrogates, internal standards, or other test substances used to evaluate the performance of the instrument system with respect to a defined set of criteria.

3.6 Laboratory Duplicates (LD1 and LD2) -- Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 indicate precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.7 Laboratory Fortified Blank (LFB) -- An aliquot of reagent water or other blank matrices to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

3.8 Laboratory Fortified Sample Matrix (LFM) -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.9 Laboratory Reagent Blank (LRB) -- An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.10 Linear Dynamic Range (LDR) -- The absolute quantity or concentration range over which the instrument response to an analyte is linear.

3.11 Material Safety Data Sheet (MSDS) -- Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties, fire, and reactivity data including storage, spill, and handling precautions.

3.12 Matrix Modifier (MM) -- A substance added to the instrument along with the sample in order to minimize the interference effects by selective volatilization of either analyte or matrix components.

3.13 Matrix Performance Check (MPC) -- A solution of method analytes used to evaluate the laboratory's ongoing capabilities in analyzing high salinity samples. The reference material NASS-3 or its equivalent is fortified with the same analytes at the same concentration as the LFB. This provides an ongoing check of furnace operating conditions to assure the analyte false positives are not being introduced via elevated backgrounds.

3.14 Method Detection Limit (MDL) -- The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero.

3.15 Quality Control Sample (QCS) -- A solution of method analytes of known concentrations which is used to fortify an aliquot of LRB or sample matrix. The QCS is obtained from a source external to the laboratory and

different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

3.16 Standard Addition -- The addition of a known amount of analyte to the sample in order to determine the relative response of the detector to an analyte within the sample matrix. The relative response is then used to assess either an operative matrix effect or the sample analyte concentration.

3.17 Stock Standard Solution (SSS) -- A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

3.18 Total Recoverable Analyte (TRA) -- The concentration of analyte determined to be in either a solid sample or an unfiltered aqueous sample following treatment by refluxing with hot dilute mineral acid(s) as specified in the method.

4.0 Interferences

4.1 Several interference sources may cause inaccuracies in the determination of trace elements by GFAA. These interferences can be classified into three major subdivisions: spectral, matrix, and memory.

4.2 Spectral interferences are caused by absorbance of light by a molecule or atom which is not the analyte of interest or emission from black body radiation.

4.2.1 Spectral interferences caused by an element only occur if there is a spectral overlap between the wavelength of the interfering element and the analyte of interest. Fortunately, this type of interference is relatively uncommon in STPGFAA because of the narrow atomic line widths associated with STPGFAA. In addition, the use of appropriate furnace temperature programs and high spectral purity lamps as light sources can minimize the possibility of this type of interference. However, molecular absorbances can span several hundred nanometers producing broadband spectral interferences. This type of interference is far more common in STPGFAA. The use of matrix modifiers, selective volatilization, and background correctors are all attempts to eliminate unwanted nonspecific absorbance. Table 2 contains typical background absorbances associated with the analysis of the MPC solution (NASS-3) which has a salinity of 35 ppt. These background absorbances were obtained using the suggested matrix modifiers and the appropriate furnace charring conditions. Figure 1 is a plot of integrated background absorbance vs. char temperature for Ni, Cd, Pb, and Se. Figure 1 indicates that the background absorbance in a saline matrix is strongly affected by the char temperature. Therefore, char temperature optimization is a critical part of the successful analysis of metals in saline water by GFAA. The elevated backgrounds associated with ocean water can produce false positives. For this reason, the char temperature profiles shown in Figure 1 should be constructed for each analyte prior to using this method for saline water analysis.

Note: False analyte positives can be generated by large backgrounds. Figure 2 is an atomization profile for Pb using a 800°C char temperature. The background shown in the figure has exceeded the capabilities of the Zeeman corrector. This profile can be used as a guide in screening other analyses which may have background absorbances which exceed the Zeeman capability. The background profile is characterized by a smooth baseline in the beginning of the atomization cycle followed by a sharp increase. During this sharp increase the background peak profile may remain relatively smooth, but when the background exceeds the Zeeman correction capability, the background profile will appear extremely erratic. The atomic profile is also erratic during this part of the atomization cycle. These types of background/atomic profiles obtained during atomization result in false positives.

Since the nonspecific component of the total absorbance can vary considerably from sample type to sample type, to provide effective background correction and eliminate the elemental spectral interference of palladium on copper and iron on selenium, the exclusive use of Zeeman background correction is specified in this method.

4.2.2 Spectral interferences are also caused by black body radiation produced during the atomization furnace cycle. This black body emission reaches the photomultiplier tube, producing erroneous results. The magnitude of this interference can be minimized by proper furnace tube alignment and monochromator design. In addition, atomization temperatures which adequately volatilize the analyte of interest without producing unnecessary black body radiation can help reduce unwanted background emission produced during atomization.

4.3 Matrix interferences are caused by sample components which inhibit the formation of free atomic analyte atoms during atomization. In this method the use of a delayed atomization device which provides a warmer gas

phase environment during atomization is required. These devices provide an environment which is more conducive to the formation of free analyte atoms and thereby minimize this type of interference. This type of interference can be detected by analyzing the sample plus a sample aliquot fortified with a known concentration of the analyte. If the determined concentration of the analyte addition is outside a designated range (Section 9.4.3), a possible matrix effect should be suspected. In addition, the matrix can produce analyte complexes which are lost via volatilization during the char. These losses will result in poor recovery of the analyte within the matrix and should be corrected by adjusting the char temperature.

4.4 Memory interferences result from analyzing a sample containing a high concentration of an element (typically a high atomization temperature element) which cannot be removed quantitatively in one complete set of furnace steps. The analyte which remains in the furnace can produce false positive signals on subsequent sample(s). Therefore, the analyst should establish the analyte concentration which can be injected into the furnace and adequately removed in one complete set of furnace cycles. If this concentration is exceeded, the sample should be diluted and a blank analyzed to assure the memory effect has been eliminated before reanalyzing the diluted sample.

4.5 Specific Element Interferences. -- The matrix effects caused by the saline water can be severe. In order to evaluate the extent of the matrix suppression as a function of increasing salinity a plot of normalized integrated absorbance vs. microliters NASS-3 (Reference Material from the National Research Council of Canada) is constructed. Figure 3 is a plot of relative response of As, Se, Cd, Ni, Cu, and Pb in waters containing salinity of 3.5 ppt (1 µL NASS-3) to 35 ppt (10 µL NASS-3). Figure 3 indicates that the matrix effects caused by the increasing salinity are minor for Pb, Cu, and Ni. The relative responses of Pb, Ni, and Cu shown in Figure 3 are within ± 5% of the 1% HNO_3 standard or zero µL of matrix. Figure 3 indicates that the increasing salinity does cause a substantial matrix interference for Se and Cd. This suppression must be compensated for by methods of standard addition or the use of matrix matched standards where applicable.

4.5.1 Cadmium: The background level associated with the direct determination of Cd in NASS-3 exceeds the Zeeman background correction. Therefore, $NH_4 NO_3$ is used as a matrix removing modifier in addition to the Pd/ $Mg(NO_3)_2$.[1] Figure 4 is a plot of the relative Cd response vs. the amount of seawater on the platform. A similar response profile is observed in a solution containing 10,000 ppm NaCl. Therefore, in well-characterized samples of known salinity it is possible to effectively matrix match the standards with NaCl and perform the analysis directly using matrix matched standards, thereby avoiding the time consuming method of standard additions. If the matrix matched standards are going to be used, it is necessary to document that the use of NaCl is indeed compensating for the suppression. This documentation should include a response plot of increasing matrix vs. relative response similar to Figure 4.

4.5.2 Selenium: The background level associated with the direct determination of Se in NASS-3 exceeds the Zeeman correction capability. Therefore, HNO_3 is used as a matrix removing modifier in addition to the Pd/ $Mg(NO_3)_2$ for the determination of Se in saline waters. Figure 5 is a plot of relative response vs. the amount of seawater on the platform. A similar suppression is observed in a solution containing 10,000 ppm NaCI. Therefore, in well-characterized samples of known salinity it is possible to effectively matrix match the standards with NaCl and perform the analysis directly using matrix matched standards, thereby avoiding the time consuming method of standard additions. If the matrix matched standards are going to be used, it is necessary to document that the use of NaCl is indeed compensating for the suppression. This documentation should include a response plot of increasing matrix vs. relative response similar to Figure 5.

4.5.3 Arsenic: The elevated char temperatures possible with the determination of As minimize the interferences produced by the marine water background levels. Figure 3 is a plot of relative response vs. the amount of seawater on the platform. Figure 3 indicates a matrix suppression on As caused by the seawater. Although this suppression does cause a slight bias as shown in the recovery data in Table 3, the suppression does not warrant the method of standard additions (MSA) given the recovery criteria of 75-125% for LFMS.

5.0 Safety

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. Each laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method.[2-5] A reference file of material data handling sheets should also be made available to all personnel

involved in the chemical analysis. Specifically, concentrated nitric and hydrochloric acids present various hazards and are moderately toxic and extremely irritating to skin and mucus membranes. Use these reagents in a fume hood whenever possible and if eye or skin contact occurs, flush with large volumes of water. Always wear safety glasses or a shield for eye protection, protective clothing, and observe proper mixing when working with these reagents.

5.2 The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. Acidification of samples should be done in a fume hood.

5.3 All personnel handling environmental samples known to contain or to have been in contact with human waste should be immunized against known disease causative agents.

5.4 The graphite tube during atomization emits intense UV radiation. Suitable precautions should be taken to protect personnel from such a hazard.

5.5 The use of the argon/hydrogen gas mixture during the dry and char steps may evolve a considerable amount of HCI gas. Therefore, adequate ventilation is required.

5.6 It is the responsibility of the user of this method to comply with relevant disposal and waste regulations. For guidance see Sections 14.0 and 15.0.

6.0 Equipment and Supplies

6.1 Graphite Furnace Atomic Absorption Spectrometer

6.1.1 The GFAA spectrometer must be capable of programmed heating of the graphite tube and the associated delayed atomization device. The instrument must be equipped with Zeeman background correction and the furnace device must be capable of utilizing an alternate gas supply during specified cycles of the analysis. The capability to record relatively fast (< 1 s) transient signals and evaluate data on a peak area basis is preferred. In addition, a recirculating refrigeration unit is recommended for improved reproducibility of furnace temperatures.

6.1.2 Single element hollow cathode lamps or single element electrodeless discharge lamps along with the associated power supplies.

6.1.3 Argon gas supply (high-purity grade, 99.99%) for use during the atomization of selenium, for sheathing the furnace tube when in operation, and during furnace cleanout.

6.1.4 Alternate gas mixture (hydrogen 5%-argon 95%) for use as a continuous gas flow environment during the dry and char furnace cycles.

6.1.5 Autosampler capable of adding matrix modifier solutions to the furnace, a single addition of analyte, and completing methods of standard additions when required.

6.2 Analytical balance, with capability to measure to 0.1 mg, for preparing standards, and for determining dissolved solids in digests or extracts.

6.3 A temperature adjustable hot plate capable of maintaining a temperature of 95°C.

6.4 An air displacement pipetter capable of delivering volumes ranging from 100 to 2500 µL with an assortment of high quality disposable pipet tips.

6.5 Labware -- All reusable labware (glass, quartz, polyethylene, PTFE, FEP, etc.) should be sufficiently clean for the task objectives. Several procedures found to provide clean labware include washing with a detergent solution, rinsing with tap water, soaking for 4 h or more in 20% (v/v) nitric acid or a mixture of HCI and HNO_3, rinsing with reagent water and storing clean. Chromic acid cleaning solutions must be avoided because chromium is an analyte.

Note: Glassware having ground glass stoppers, etc. should be avoided because the ground glass surface is difficult to clean properly and can contain active sites which adsorb metals.

6.5.1 *Glassware* -- Volumetric flasks, graduated cylinders, funnels and centrifuge tubes (glass and/or metal-free plastic).

6.5.2 Assorted calibrated pipettes.

6.5.3 Griffin beakers, 250-mL with 75-mm watch glasses and (optional) 75-mm ribbed watch glasses.

6.5.4 Narrow-mouth storage bottles, FEP (fluorinated ethylene propylene) with screw closure, 125-mL to 1-L capacities.

6.5.5 One-piece stem FEP wash bottle with screw closure, 125-mL capacity.

7.0 Reagents and Standards

7.1 Reagents may contain elemental impurities which might affect analytical data. Only high-purity reagents that conform to the American Chemical Society specifications[6] should be used whenever possible. If the purity of a reagent is in question, analyze for contamination. All acids used for this method must be of ultra high-purity grade or equivalent. Suitable acids are available from a number of manufacturers. Redistilled acids prepared by sub-boiling distillation are acceptable.

7.2 Nitric acid, concentrated (sp.gr. 1.41) HNO_3.

7.2.1 Nitric acid (1+1) -- Add 500 mL concentrated HNO_3 to 400 mL reagent water and dilute to 1 L.

7.2.2 Nitric acid (1+5) -- Add 50 mL concentrated HNO_3 to 250 mL reagent water.

7.2.3 Nitric acid (1+9) -- Add 10 mL concentrated HNO_3 to 90 mL reagent water.

7.3 Reagent water. All references to water in this method refer to ASTM Type I grade water.[7]

7.4 Ammonium hydroxide, concentrated (sp.gr.0.902).

7.5 Matrix Modifier, dissolve 300 mg palladium (Pd) powder in concentrated HNO_3 (1 mL of HNO_3, adding 10 µL of concentrated HCl if necessary). Dissolve 200 mg of $Mg(NO_3)_2 \cdot 6H_2O$ in ASTM Type I water. Pour the two solutions together and dilute to 100 mL with ASTM Type I water.

Note: It is recommended that the matrix modifier be analyzed separately in order to assess the contribution of the modifier to the absorbance of calibration and reagent blank solutions.

7.6 Standard stock solutions may be purchased or prepared from ultra-high purity grade chemicals (99.99 to 99.999% pure). All compounds must be dried for 1 h at 105°C, unless otherwise specified. It is recommended that stock solutions be stored in FEP bottles. Replace stock standards when succeeding dilutions for preparation of calibration standards cannot be verified.

Caution: Many of these chemicals are extremely toxic if inhaled or swallowed (Section 5.1). Wash hands thoroughly after handling.

Typical stock solution preparation procedures follow for 1-L quantities, but for the purpose of pollution prevention, the analyst is encouraged to prepare smaller quantities when possible. Concentrations are calculated based upon the weight of the pure element or upon the weight of the compound multiplied by the fraction of the analyte in the compound.

From pure element,

$$\text{Concentration} = \frac{\text{weight (mg)}}{\text{volume (L)}}$$

From pure compound,

$$\text{Concentration} = \frac{\text{weight (mg)} \times \text{gravimetric factor}}{\text{volume (L)}}$$

where:

gravimetric factor = the weight fraction of the analyte in the compound.

7.6.1 Arsenic solution, stock, 1 mL = 1000 µg As: Dissolve 1.320 g of As_2O_3 (As fraction = 0.7574), weighed accurately to at least four significant figures, in 100 mL of reagent water containing 10.0 mL concentrated NH_4OH. Warm in solution gently to effect dissolution. Acidify the solution with 20.0 mL concentrated HNO_3 and dilute to volume in a 1-L volumetric flask with reagent water.

7.6.2 Cadmium solution, stock, 1 mL = 1000 µg Cd: Dissolve 1.000 g Cd metal, acid cleaned with (1+9) HNO_3, weighed accurately to at least four significant figures, in 50 mL (1+1) HNO_3 with heating to effect dissolution. Let solution cool and dilute with reagent water in a 1-L volumetric flask.

7.6.3 Chromium solution, stock, 1 mL = 1000 µg Cr: Dissolve 1.923 g CrO_3 (Cr fraction = 0.5200), weighed accurately to at least four significant figures, in 120 mL (1+5) HNO_3. When solution is complete, dilute to volume in a 1-L volumetric flask with reagent water.

7.6.4 Copper solution, stock, 1 mL = 1000 µg Cu: Dissolve 1.000 g Cu metal, acid cleaned with (1+9) HNO_3,

weighed accurately to at least four significant figures, in 50.0 mL (1+1) HNO_3 with heating to effect dissolution. Let solution cool and dilute in a 1-L volumetric flask with reagent water.

7.6.5 Lead solution, stock, 1 mL = 1000 µg Pb: Dissolve 1.599 g $Pb(NO_3)_2$ (Pb fraction = 0.6256), weighed accurately to at least four significant figures, in a minimum amount of (1+1) HNO_3. Add 20.0 mL (1+1) HNO_3 and dilute to volume in a 1-L volumetric flask with reagent water.

7.6.6 Nickel solution, stock, 1 mL = 1000 µg Ni: Dissolve 1.000 g of nickel metal, weighed accurately to at least four significant figures, in 20.0 mL hot concentrated HNO_3, cool, and dilute to volume in a 1-L volumetric flask with reagent water.

7.6.7 Selenium solution, stock, 1 mL = 1000 µg Se: Dissolve 1.405 g SeO_2 (Se fraction = 0.7116), weighed accurately to at least four significant figures, in 200 mL reagent water and dilute to volume in a 1-L volumetric flask with reagent water.

7.7 Preparation of Calibration Standards -- Fresh calibration standards (CAL Solution) should be prepared weekly, or as needed. Dilute each of the stock standard solutions to levels appropriate to the operating range of the instrument using the appropriate acid diluent. The element concentrations in each CAL solution should be sufficiently high to produce good measurement precision and to accurately define the slope of the response curve. The instrument calibration should be initially verified using a IPC sample (Section 7.9).

7.8 Blanks -- Four types of blanks are required for this method. A calibration blank is used to establish the analytical calibration curve, the laboratory reagent blank (LRB) is used to assess possible contamination from the sample preparation procedure and to assess spectral background, the laboratory fortified blank is used to assess routine laboratory performance, and a rinse blank is used to flush the instrument autosampler uptake system. All diluent acids should be made from concentrated acids (Section 7.2) and ASTM Type I water.

7.8.1 The calibration blank consists of the appropriate acid diluent in ASTM Type I water. The calibration blank should be stored in a FEP bottle.

7.8.2 The laboratory reagent blanks must contain all the reagents in the same volumes as used in processing the samples. The preparation blank must be carried through the entire sample digestion and preparation scheme.

7.8.3 The laboratory fortified blank (LFB) is prepared by fortifying an aliquot of the laboratory reagent blank with all analytes to provide a final concentration which will produce an absorbance of approximately 0.1 for each analyte. The LFB must be carried through the complete procedure as used for the samples.

7.8.4 The rinse blank is a 0.1% HCI and 0.1% HNO_3 solution used to flush the autosampler tip and is stored in the appropriate plastic containers.

7.9 Instrument Performance Check (IPC) Solution -- The IPC solution is used to periodically verify instrument performance during analysis. It should be prepared in the same acid mixture as the calibration standards by combining method analytes at appropriate concentrations to approximate the midpoint of the calibration curve. The IPC solution should be prepared from the same standard stock solutions used to prepare the calibration standards and stored in a FEP bottle. Agency programs may specify or request that additional instrument performance check solutions be prepared at specified concentrations in order to meet particular program needs.

7.10 Quality Control Sample (QCS) -- For initial and periodic verification of calibration standards and instrument performance, analysis of a QCS is required. The QCS must be obtained from an outside source different from the standard stock solutions and prepared in the same acid mixture as the calibration standards. The concentration of the analytes in the QCS solution should be such that the resulting solution will provide an absorbance reading of approximately 0.1. The QCS solution should be stored in a FEP bottle and analyzed as needed to meet data-quality needs. A fresh solution should be prepared quarterly or as needed.

7.11 Matrix Performance Check (MPC) -- The MPC solution is used to periodically evaluate the laboratory/ instrument performance in saline samples. It should be prepared in the same acid mixture as the calibration standards by combining method analytes at appropriate concentrations in a seawater matrix (NASS-3, or its equivalent) to produce an absorbance of 0.1. The MPC solution should be prepared from the same standard stock solutions used to prepare the calibration standards and stored in a FEP bottle. The MPC sample should be analyzed after every 10 samples to assure saline matrix is not producing false positives.

8.0 Sample Collection, Preservation and Storage

8.1 Prior to collection of an aqueous sample, consideration should be given to the type of data required. Acid preservation should be performed at the time of sample collection or as soon thereafter as practically possible. The pH of all aqueous samples must be tested immediately prior to aliquoting for analysis to ensure the sample has been properly preserved. If properly acid-preserved, the sample can be held up to 6 months before analysis.

8.2 For determination of total recoverable elements in aqueous samples, acidify with (1+1) nitric acid at the time of collection to pH<2. Normally, 3 mL of (1+1) nitric acid (ultra high purity) per liter of sample is sufficient for most ambient water samples. The sample should not be filtered prior to analysis.

Note: Samples that cannot be acid-preserved at the time of collection because of sampling limitations or transport restrictions, or are > pH 2 because of high alkalinity should be acidified with nitric acid to pH < 2 upon receipt in the laboratory. Following acidification, the sample should be held for 16 h and the pH verified to be <2 before withdrawing an aliquot for sample processing.

8.3 For aqueous samples, a field blank should be prepared and analyzed as required by the data user. Use

the same container and acid as used in sample collection.

9.0 Quality Control

9.1 Each laboratory using this method is required to operate a formal quality control (QC) program. The minimum requirements of this program consist of an initial demonstration of laboratory capability, and the periodic analysis of laboratory reagent blanks, fortified blanks and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data thus generated.

9.2 Initial Demonstration of Performance (Mandatory)

9.2.1 The initial demonstration of performance is used to characterize instrument performance (determination of linear dynamic ranges and analysis of quality control samples) and laboratory performance (determination of method detection limits) prior to samples being analyzed by this method.

9.2.2 Linear dynamic range (LDR) -- The upper limit of the LDR must be established for the wavelength utilized for each analyte by determining the signal responses from a minimum of six different concentration standards across the range, two of which are close to the upper limit of the LDR. Determined LDRs must be documented and kept on file. The linear calibration range which may be used for the analysis of samples should be judged by the analyst from the resulting data. The upper LDR limit should be an observed signal no more than 10% below the level extrapolated from the four lower standards. New LDRs should be determined whenever there is a significant change in instrument response, a change in instrument analytical hardware or operating conditions.

Note: Multiple cleanout furnace cycles may be necessary in order to fully define or utilize the LDR for certain elements such as chromium. For this reason, the upper limit of the linear calibration range may not correspond to the upper operational LDR limit.

Measured sample analyte concentrations that exceed the upper limit of the linear calibration range must either be diluted and reanalyzed (with concern for memory effects Section 4.4) or analyzed by another approved method.

9.2.3 Quality control sample (QCS) -- When beginning the use of this method, on a quarterly basis or as required to meet data-quality needs, verify the calibration standards and acceptable instrument performance with the preparation and analyses of a QCS (Section 7.10). If the determined concentrations are not within ± 10% of the stated values, performance of the determinative step of the method is unacceptable. The source of the problem must be identified and corrected before either proceeding on with the initial determination of method detection limits or continuing with ongoing analyses.

9.2.4 Method detection limit (MDL) -- MDLs must be established for all analytes, using reagent water (blank) fortified at a concentration of two to three times the estimated instrument detection limit.[8] To determine MDL values, take seven replicate aliquots of the fortified reagent water and process through the entire analytical method. Perform all calculations defined in the method and report the concentration values in the appropriate units. Calculate the MDL as follows:

MDL = (t) x (S)

where, t = Student's t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom [t = 3.14 for seven replicates].

S = standard deviation of the replicate analyses.

Note: If the percent relative standard deviation (% RSD) from the analyses of the seven aliquots is < 15%, the concentration used to determine the analyte MDL may have been inappropriately high for the determination. If so, this could result in calculation of an unrealistically low MDL. If additional confirmation of the MDL is desired, reanalyze the seven replicate aliquots on two more nonconsecutive days and again calculate the MDL values for each day. An average of the three MDL values for each analyte may provide a more appropriate MDL estimate. Concurrently, determination of MDL in reagent water represents a best case situation and does not reflect possible matrix effects of real world samples. However, successful analyses of LFMs (Section 9.4) and the analyte addition test described in Section 9.5.1 can give confidence to the MDL value determined in reagent water. Typical single laboratory MDL values using this method are given in Table 2.

MDLs should be determined every six months, when a new operator begins work or whenever there is a significant change in the background or instrument response.

The MDLs reported in Table 2 were determined in fortified NASS-3 samples. It is recommended that a certified saline matrix such as NASS-3 be used to determine MDLS.

9.3 Assessing Laboratory Performance (Mandatory)

9.3.1 Laboratory reagent blank (LRB) -- The laboratory must analyze at least one LRB (Section 7.8.2) with each batch of 20 or fewer samples. LRB data are used to assess contamination from the laboratory environment. LRB values that exceed the MDL indicate laboratory or reagent contamination should be suspected. Any determined source of contamination must be corrected and the samples reanalyzed for the affected analytes after acceptable LRB values have been obtained.

9.3.2 Laboratory fortified blank (LFB) -- The laboratory must analyze at least one LFB (Section 7.8.3) with each batch of samples. Calculate accuracy as percent recovery (Section 9.4.3). If the recovery of any analyte falls outside the required control limits of 85-115%, that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analyses.

9.3.3 The laboratory must use LFB analyses data to assess laboratory performance against the required control limits of 85-115%. When sufficient internal performance data become available (usually a minimum of 20-30 analyses), optional control limits can be developed from the percent mean recovery (x) and the standard deviation (S) of the mean recovery. These data can be used to establish the upper and lower control limits as follows:

Upper Control Limit = x + 3S

Lower Control Limit = x - 3S

The optional control limits must be equal to or better than the required control limits of 85-115%. After each five to ten new recovery measurements, new control limits can be calculated using only the most recent 20-30 data points. Also, the standard deviation (S) data should be used to establish an ongoing precision statement for the level of concentrations included in the LFB. These data must be kept on file and be available for review.

9.3.4 Instrument performance check (IPC) solution -- For all determinations the laboratory must analyze the IPC solution (Section 7.9) and a calibration blank immediately following daily calibration, after every tenth sample (or more frequently, if required) and after the last sample in the batch is analyzed. Analysis of the I PC solution and calibration blank immediately following calibration must verify that the instrument is within ± 5% of calibration. Subsequent analyses of the IPC solution must verify the calibration within ± 10%. If the calibration cannot be verified within the specified limits, reanalyze the IPC solution. If the second analysis of the IPC solution confirms calibration to be outside the limits, sample analysis must be discontinued, the cause determined and/or, in the case of drift, the instrument recalibrated. All samples following the last acceptable IPC solution must be reanalyzed. Data for the calibration blank and IPC solution must be kept on file with associated sample data.

9.3.5 Matrix performance check (MPC) solution -- For all determinations, the laboratory must analyze the MPC solution (Section 7.11) immediately following daily calibration, after every tenth sample (or more frequently, if required) and after the last sample in the batch is analyzed. Analysis of the MPC must verify that the instrument

is within ± 15% of calibration and confirm that the matrix is not causing matrix/background interferences. If the MPC is not within ± 15%, reanalyze the MPC solution. If the second analysis of the MPC solution is outside the limits, sample analysis must be discontinued the cause determined and/or, in the case of drift, the instrument recalibrated. All samples following the last acceptable MPC solution must be reanalyzed. The analysis data for the calibration blank and MPC solution must be kept on file with the sample analyses data.

9.4 Assessing Analyte Recovery and Data Quality

9.4.1 Sample homogeneity and the chemical nature of the sample matrix can affect analyte recovery and the data quality. Taking separate aliquots from the sample for replicate and fortified analyses can in some cases assess these effects. Unless otherwise specified by the data user, laboratory or program, the following laboratory fortified matrix (LFM) procedure (Section 9.4.2) is required. Also, the analyte addition test (Section 9.5.1) can aid in identifying matrix interferences. However, all samples must have a background absorbance < 1.0 before the test results obtained can be considered reliable.

9.4.2 The laboratory must add a known amount of each analyte to a minimum of 10% of the routine samples. In each case the LFM aliquot must be a duplicate of the aliquot used for sample analysis and for total recoverable determinations added prior to sample preparation. For water samples, the added analyte concentration must be the same as that used in the laboratory fortified blank (Section 9.3.2).

9.4.3 Calculate the percent recovery for each analyte, corrected for concentrations measured in the unfortified sample, and compare these values to the designated LFM recovery range of 75-125%. Recovery calculations are not required if the concentration added is less than 25% of the unfortified sample concentration. Percent recovery may be calculated in units appropriate to the matrix, using the following equation:

$$R = \frac{C_s - C}{s} \times 100$$

where, R = percent recovery.
C_s = fortified sample concentration.
C = sample background concentration.
s = concentration equivalent of analyte added to sample.

9.4.4 If the recovery of any analyte falls outside the designated LFM recovery range (but is still within the range of calibration and the background absorbance is < 1.0 abs.) and the laboratory performance for that analyte is shown to be in control (Section 9.3), the recovery problem encountered with the LFM is judged to be either matrix or solution related, not system related. A flowchart of the remainder of this section can be found in Figure 6. This flowchart may clarify the verbal discussion given below.

If the background absorbance is > 1 abs., the sample and the LFM should be diluted 1:3 and reanalyzed until the background absorbance is < 1, at which point a percent recovery of the LFM should be calculated. If the fortified analyte in the diluted LFM is found to be < 25% of the sample concentration or the diluted LFM produces an atomic signal of <10 times the MDL, the diluted sample should be analyzed by methods of standard addition. If the calculated recovery of the diluted sample is within the designated range, the sample concentration should be calculated from the diluted sample. If the calculated recovery of the diluted sample is outside the designated range, follow the directions given below. If the background is reduced and/or the matrix effect is reduced by dilution, all samples of a similar matrix should be diluted and analyzed in a similar fashion. The result should be flagged indicating the methods sensitivity has been reduced by the dilution. If dilution is unacceptable because of data quality objectives the sample should be flagged indicating the analysis is not possible via this analytical procedure.

If the analyte recovery on the LFM is <75% and the background absorbance is <1, complete the analyte addition test (Section 9.5.1) on the original sample (or its dilution). The results of the test should be evaluated as follows:

1. If recovery of the analyte addition test (≤ 85%) confirms a low recovery for the LFM, a suppressive matrix interference is indicated and the unfortified sample aliquot must be analyzed by method of standard additions (Section 11.3).

2. If the recovery of the analyte addition test is between 85% to 115%, a low recovery of the analyte in the LFM (< 75%) may be related to the heterogeneity of the sample, sample preparation or a poor transfer, etc. Report the sample concentration based on the unfortified sample aliquot.

3. If the recovery of the analyte addition test is less than recovery calculated for the LFM, matrix suppression is confirmed. The unfortified sample should be analyzed by MSA (Section 11.3). Significantly lower recoveries (relative to the LFM) associated with the analyte addition test are unlikely unless the sample is heterogeneous.

4. If the recovery of the analyte addition test is >115%, the dramatic change in analyte response should be verified by fortifying the LFM. The recovery in the sample and the recovery in the LFM should be compared. If the recoveries verify the dramatic response difference, the sample results should be flagged indicating the sample matrix is not homogeneous.

If the analyte recovery in the LFM is > 125% and the background absorbance is < 1, complete the analyte addition test (Section 9.5.1) on the unfortified sample (or its dilution) aliquot.

1 . If the percent recovery of the analyte addition test is > 115% and the LFB does not indicate laboratory contamination, an enhancing matrix interference (albeit rare) is indicated, and the unfortified sample aliquot must be analyzed by method of standard additions (Section 11.3).

2. If the percent recovery of the analyte addition test is between 85% to 115%, either random sample contamination of the LFM, an incorrect analyte concentration was added to the LFM prior to sample preparation, or sample heterogeneity should be suspected. Report analyte data determined from the analysis of the unfortified sample aliquot.

3. If the percent recovery of the analyte addition test is < 85%, a heterogeneous sample with matrix interference is suspected. This dramatic change in response should be verified by performing the analyte addition test to the LFM. The recovery in the sample and the recovery in the LFM should be compared. If the recoveries verify the dramatic response difference the sample results should be flagged indicating the sample matrix is not homogeneous.

9.4.5 If the analysis of a LFM sample(s) and the test routines above indicate an operative interference and the LFMs are typical of the other samples in the batch, those samples that are similar must be analyzed in the same manner as the LFMS. Also, the data user must be informed when a matrix interference is so severe that it prevents successful determination of the analyte or when the heterogeneous nature of the sample precludes the use of duplicate analyses.

9.4.6 Where reference materials are available, they should be analyzed to provide additional performance data. Analysis of reference samples is a valuable tool for demonstrating the ability to perform the method acceptably. It is recommended that NASS-3 or its equivalent be fortified and used as an MPC.

9.5 Matrix interference effects and the need for MSA can be assessed by the following test. Directions for using MSA are given in Section 11.3.

9.5.1 Analyte addition test: An analyte standard added to a portion of a prepared sample or its dilution should be

recovered to within 85-115% of the known value. The analyte addition should occur directly to sample in the furnace and should produce a minimum absorbance of 0.1. The concentration of the analyte addition plus that in the sample should not exceed the linear calibration range of the analyte. If the analyte is not recovered within the specified limits, a matrix effect should be suspected and the sample must be analyzed by MSA.

10.0 Calibration and Standardization

10.1 Specific wavelengths and instrument operating conditions are listed in Table 1. However, because of differences among makes and models of spectrophotometers and electrothermal furnace devices, the actual instrument conditions selected may vary from those listed.

10.2 Prior to the use of this method, the instrument operating conditions must be optimized. The analyst should follow the instructions provided by the manufacturer while using the conditions listed in Table 1 as a guide. The appropriate charring condition for each of the analytes is a critical part of the metal analysis in saline waters; therefore, the char temperature profiles should be determined in a saline water matrix. The appropriate charring temperature should be chosen so as to minimize background absorbance while providing some furnace temperature variation without the loss of analyte. For analytical operation, the charring temperature is usually set at least 100°C below the point at which analyte begins to be lost during the char. Because the background absorbance can be affected by the atomization temperature, care should be taken in the choice of an appropriate atomization temperature. The optimum conditions se-

lected should provide the lowest reliable MDLs and be similar to those listed in Table 2. Once the optimum operating conditions are determined, they should be recorded and available for daily reference. The effectiveness of these operating conditions are continually evaluated by analyzing the MPC.

10.3 Prior to an initial calibration the linear dynamic range of the analyte must be determined (Sect 9.2.2) using the optimized instrument operating conditions. For all determinations allow an instrument and hollow cathode lamp warm-up period of not less than 15 min. If an EDL is to be used, allow 30 min for warm-up.

10.4 Before using the procedure (Section 11.0) to analyze samples, there must be data available documenting initial demonstration of performance. The required data and procedure are described in Section 9.2. This data must be generated using the same instrument operating conditions and calibration routine to be used for sample analysis. These documented data must be kept on file and be available for review by the data user.

11.0 Procedure

11.1 Aqueous Sample Preparation -- Total Recoverable Analytes

11.1.1 Add 2 mL (1+1) nitric acid to the beaker containing 100 mL of sample. Place the beaker on a hot plate for solution evaporation. The hot plate should be located in a fume hood and previously adjusted to provide evaporation at a temperature of approximately but no higher than 85°C. (See the following note.) The beaker should be covered with an elevated watch glass or other necessary steps should be taken to prevent sample contamination from the fume hood environment.

Note: For proper heating adjust the temperature control of the hot plate such that an uncovered Griffin beaker containing 50 mL of water placed in the center of the hot plate can be maintained at a temperature approximately but no higher than 85°C. (Once the beaker is covered with a watch glass the temperature of the water will rise to approximately 95°C.)

11.1.2 Reduce the volume of the sample aliquot to about 20 mL by gentle heating at 85°C. DO NOT BOIL. This step takes about 2 h for a 100-mL aliquot with the rate of evaporation rapidly increasing as the sample volume approaches 20 mL. (A spare beaker containing 20 mL of water can be used as a gauge.)

11.1.3 Cover the lip of the beaker with a watch glass to reduce additional evaporation and gently reflux the sample for 30 min.

11.1.4 Allow the beaker to cool. Quantitatively transfer the sample solution to a 100-mL volumetric flask, dilute to volume with reagent water, stopper and mix.

11.1.5 Allow any undissolved material to settle overnight, or centrifuge a portion of the prepared sample until clear. (If after centrifuging or standing overnight the sample contains suspended solids, a portion of the sample may be filtered prior to analysis. However, care should be exercised to avoid potential contamination from filtration.) The sample is now ready for analysis. Because the effects of various matrices on the stability of diluted samples cannot be characterized, all analyses should be performed as soon as possible after the completed preparation.

11.2 Sample Analysis

11.2.1 Prior to daily calibration of the instrument, inspect the graphite tube and contact rings for salt buildup, etc. Generally, it will be necessary to clean the contact rings and replace the graphite tube daily. The contact rings are a cooler environment in which salts can deposit after atomization. A cotton swab dipped in a 50/50 mixture of isopropyl alcohol (IPA) and H_2O (such that it is damp but not dripping) can be used to remove the majority of the salt buildup. A second cotton swab is dipped in IPA and the contact rings are wiped down to assure they are clean. The rings are then allowed to thoroughly dry and then a new tube is placed in the furnace and conditioned according to instrument manufacturer's specifications.

11.2.2 Configure the instrument system to the selected optimized operating conditions as determined in Sections 10.1 and 10.2.

11.2.3 Before beginning daily calibration the instrument should be reconfigured to the optimized conditions. Initiate the data system and allow a period of not less than 15 min for instrument and hollow cathode lamp warm up. If an EDL is to be used, allow 30 min for warm up.

11.2.4 After the warm up period but before calibration, instrument stability must be demonstrated by analyzing a standard solution with a concentration 20 times the IDL a minimum of five times. The resulting relative standard deviation of absorbance signals must be $\leq$ 5%. If the

relative standard deviation is > 5%, determine and correct the cause before calibrating the instrument.

11.2.5 For initial and daily operation, calibrate the instrument according to the instrument manufacturer's recommended procedures using the calibration blank (Section 7.8.1) and calibration standards (Section 7.7) prepared at three or more concentrations within the usable linear dynamic range of the analyte (Sections 4.4 and 9.2.2).

11.2.6 An autosampler must be used to introduce all solutions into the graphite furnace. Once the sample and the matrix modifier are injected, the furnace controller completes a set of furnace cycles and a cleanout period as programmed. Analyte signals must be reported on an integrated absorbance basis. Background absorbances, background heights and the corresponding peak profiles should be displayed to the CRT for review by the analyst and be available as hard copy for documentation to be kept on file. Flush the autosampler solution uptake system with the rinse blank (Section 7.8.4) between each solution injected.

11.2.7 After completion of the initial requirements of this method (Section 9.2), samples should be analyzed in the same operational manner used in the calibration routine.

11.2.8 During sample analyses, the laboratory must comply with the required quality control described in Sections 9.3 and 9.4.

11.2.9 For every new or unusual matrix, when practical, it is highly recommended that an inductively coupled plasma atomic emission spectrometer be used to screen for high element concentration. Information gained from this may be used to prevent potential damage to the instrument and to better estimate which elements may require analysis by graphite furnace.

11.2.10 Determined sample analyte concentrations that are $\geq$ 90% of the upper limit of calibration must either be diluted with acidified reagent water and reanalyzed with concern for memory effects (Section 4.4), or determined by another approved but less sensitive procedure. Samples with background absorbances > 1 must be diluted with appropriate acidified reagent water such that the background absorbance is < 1 (Section 9.4.4). If the method of standard additions is required, follow the instructions described in Section 11.3.

11.2.11 When it is necessary to assess an operative matrix interference (e.g., signal reduction due to high dissolved solids), the test described in Section 9.5 is recommended.

11.2.12 Report data as directed in Section 12.

11.3 Standard Additions -- If the method of standard addition is required, the following procedure is recommended:

11.3.1 The standard addition technique[9] involves preparing new standards in the sample matrix by adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interference, which causes a baseline shift. The simplest version of this technique is the single-addition method. The procedure is as follows: Two identical aliquots of the sample solution, each of volume V_x, are taken. To the first (labeled A) is added a small volume V_S of a standard analyte solution of concentration C_S. To the second (labeled B) is added the same volume V_S of the solvent. The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration C_X is calculated:

$$C_x = \frac{S_B V_S C_S}{(S_A - S_B) V_X}$$

where, S_A and S_B are the analytical signals (corrected for the blank) of solutions A and B, respectively. V_S and C_S should be chosen so that S_A is roughly twice S_B on the average. It is best if V_S is made much less than V_X, and thus C_S is much greater than C_X, to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure. For the results from this technique to be valid, the following limitations must be taken into consideration:

1. The analytical curve must be linear.

2. The chemical form of the analyte added must respond in the same manner as the analyte in the sample.

3. The interference effect must be constant over the working range of concern.

4. The signal must be corrected for any additive interference.

12.0 Data Analysis and Calculations

12.1 Sample data should be reported in units of μg/L for aqueous samples.

12.2 For total recoverable aqueous analytes (Section 11.1), when 100-mL aliquot is used to produce the 100 mL final solution, round the data to the tenths place and report the data in μg/L up to three significant figures. If a different aliquot volume other than 100 mL is used for sample preparation, adjust the dilution factor accordingly. Also, account for any additional dilution of the prepared sample solution needed to complete the determination of analytes exceeding the upper limit of the calibration curve. Do not report data below the determined analyte MDL concentration or below an adjusted detection limit reflecting smaller sample aliquots used in processing or additional dilutions required to complete the analysis.

12.3 The QC data obtained during the analyses provide an indication of the quality of the sample data and should be provided with the sample results.

13.0 Method Performance

13.1 Instrument operating conditions used for single laboratory testing of the method and MDLs are listed in Tables 1 & 2.

13.2 Table 3 contains precision and recovery data obtained from a single laboratory analysis of four fortified sample replicates of NASS-3. Five unfortified replicates were analyzed, and their average concentration was used to determine the sample concentration. Samples were prepared using the procedure described in Section 11.1. Four samples were fortified at the levels reported in Table 3. Average percent recovery and percent relative standard deviation are reported in Table 3 for the fortified samples.

14.0 Pollution Prevention

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions, consult Less is Better: Laboratory Chemical Management for Waste Reduction, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington D.C. 20036, (202)872-4477.

15.0 Waste Management

15.1 The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management consult *The Waste Management Manual for Laboratory Personnel,* available from the American Chemical Society at the address listed in the Section 14.2.

16.0 References

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9. Winefordner, J.D., Trace Analysis: Spectroscopic Methods for Elements, *Chemical Analysis,* Vol. 46, pp. 41-42, 1976.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

Table 1. Furnace Conditions for Determination of Metals in Seawater [1]

Element	Wavelength (nm) Slit Width (nm)	Method of Analysis	Modifier [2,3]	Furnaces[5] Cycle	Temp °C	Temp Ramp	Hold Time (sec)
As	193.7	Direct	Pd/Mg	Dry	130	1	60
	0.7			Char	1400[4]	10	60
				Atomization	2200	0	5
Cd	228.8	Matrix Match	Pd/Mg	Dry	130	1	60
	0.7	Standard	+	Char 1	350	45	30
		or	600 µg	Char 2	850	1	30
		Std. Addition	NH_4NO_3	Atomization	1500	0	5
Cr	357.9	Direct	Pd/Mg	Dry	130	1	60
	0.7			Char	1500	5	30
				Atomization	2600	0	5
Cu	324.8	Direct	Pd/Mg	Dry	130	1	60
	0.7			Char	1300	10	30
				Atomization	2600	0	5
Ni	232.4	Direct	Pd/Mg	Dry	130	1	60
	0.2			Char	1400[4]	10	30
				Atomization	2600	0	7
Pb	283.3	Direct	Pd/Mg	Dry	130	1	60
	0.7			Char	1200	10	45
				Atomization	2200	0	5
Se	196.0	Matrix Match	Pd/Mg	Dry	130	1	60
	2.0	Standard	9% HNO_3 on	Char	1000	5	60
		or	Platform	Atomization	2100	0	5
		Std. Addition					

[1] 10-µL sample size.
[2] 5µL of (30 mg Pd Powder and 20 mg $Mg(NO_3)_2 \cdot 6H_2O$ to 10 mL).
[3] A gas mixture of 5% H_2 in 95% Ar is used during the dry and char.
[4] Sodium emission is visibly exiting from the sample inlet port.
[5] The furnace program has a cool down step of 20° between char and atomization and a clean out step of 2600° C after atomization.

Table 2. MDLs and Background Absorbances Associated with a Fortified NASS-3[1-3]

Element	MDL[5] µg/L	Typical Integrated Background Absorbances[6]
Cd	0.1	1.2
Cr	-	0.2
Cu	2.8	0.2
Ni	1.8	0.1
Pb	2.4	0.4
Se[4]	9.5	1.4
As[4]	2.6	0.3

[1] Matrix Modifier = 0.015 mg Pd + 0.01 mg $Mg(NO_3)_2$.
[2] A 5% H_2 in Ar gas mix is used during the dry and char steps at 300 mL/min for all elements.
[3] 10-µL sample size.
[4] An electrodeless discharge lamp was used for this element.
[5] MDL calculated based on fortifying NASS-3 with metal analytes.
[6] Background absorbances are affected by the atomization temperature for analysis, therefore, lowering atomization temperatures may be advantageous if large backgrounds are observed.
- Not Determined.

Table 3. Precision and Recovery Data for Fortified NASS-3

Element	Certified Value µg/L	Observed Value µg/L	Fortified Conc. µg/L[2]	Avg. Recovery, %	%RSD	Fortified Conc. µg/L	Avg. Recovery, %	% RSD
As	1.65 ± 0.19	< MDL	15	89	3.6	37.5	85	1.6
Cd[1]	0.029 ± 0.004	< MDL	1.0	107	4.5	2.5	104	3.8
Cr	0.175 ± 0.010	< MDL	5	88	0.7	12.5	85	1.6
Cu	0.109 ± 0.011	< MDL	15	95	4.4	37.5	91	0.9
Pb	0.039 ± 0.006	< MDL	15	103	2.3	37.5	99	3.4
Ni	0.257 ± 0.027	< MDL	15	92	10.1	37.5	93	7.1
Se[1]	0.024 ± 0.004	< MDL	25	101	2.9	62.5	99	3.9

[1] Standards were made in 10,000 ppm NaCl for this analysis.
[2] Determined from four sample replicates.

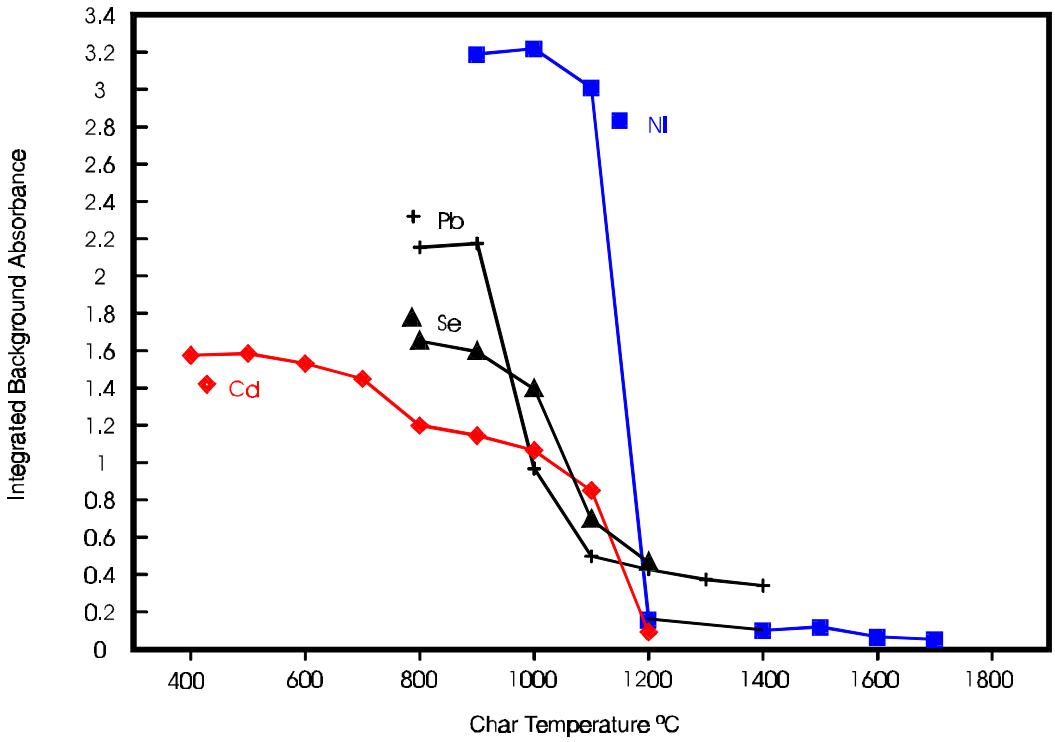

Figure 1. Integrated Background Absorbance vs. Char Temperature.

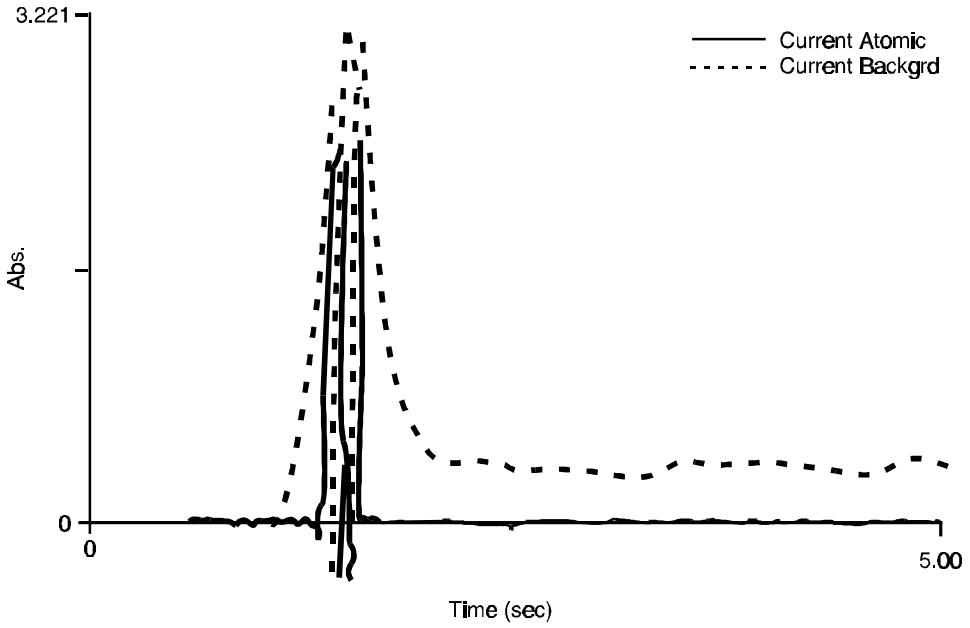

Figure 2. Pb atomization Profile Utilizing a 800° Char.

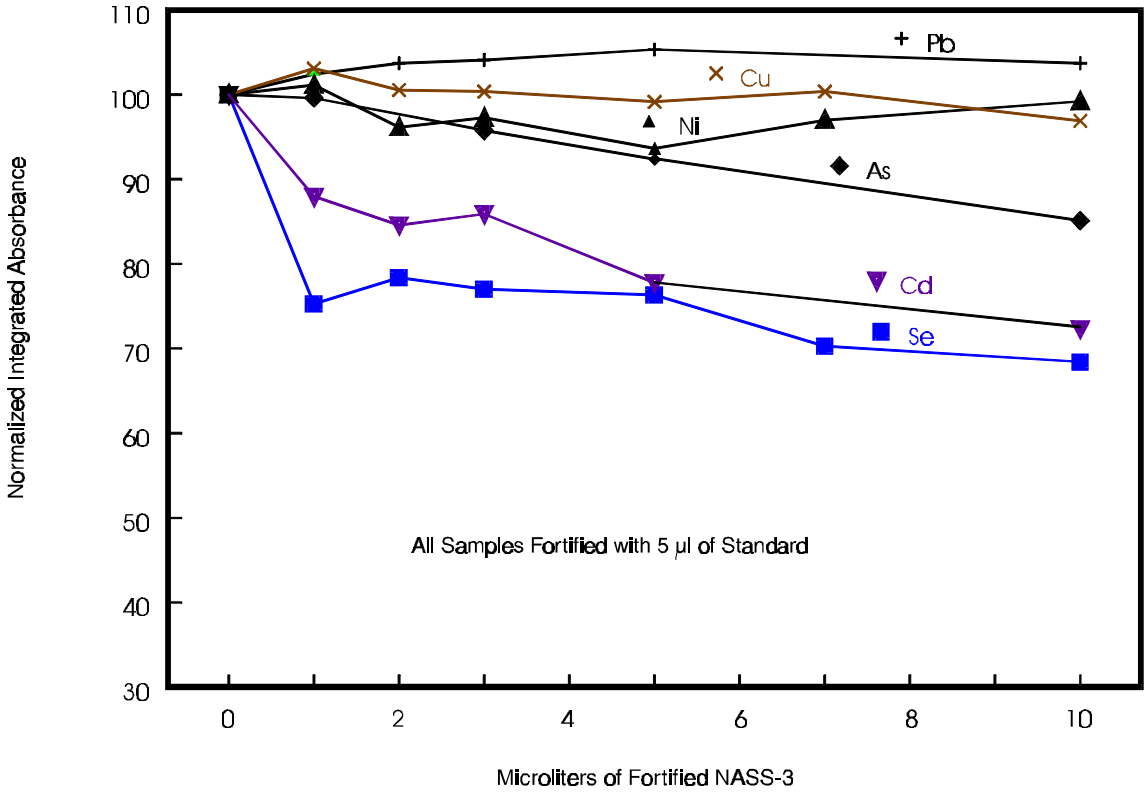

Figure 3. Normalized Integrated Absorbance vs. Microliters of Fortified NASS-3.

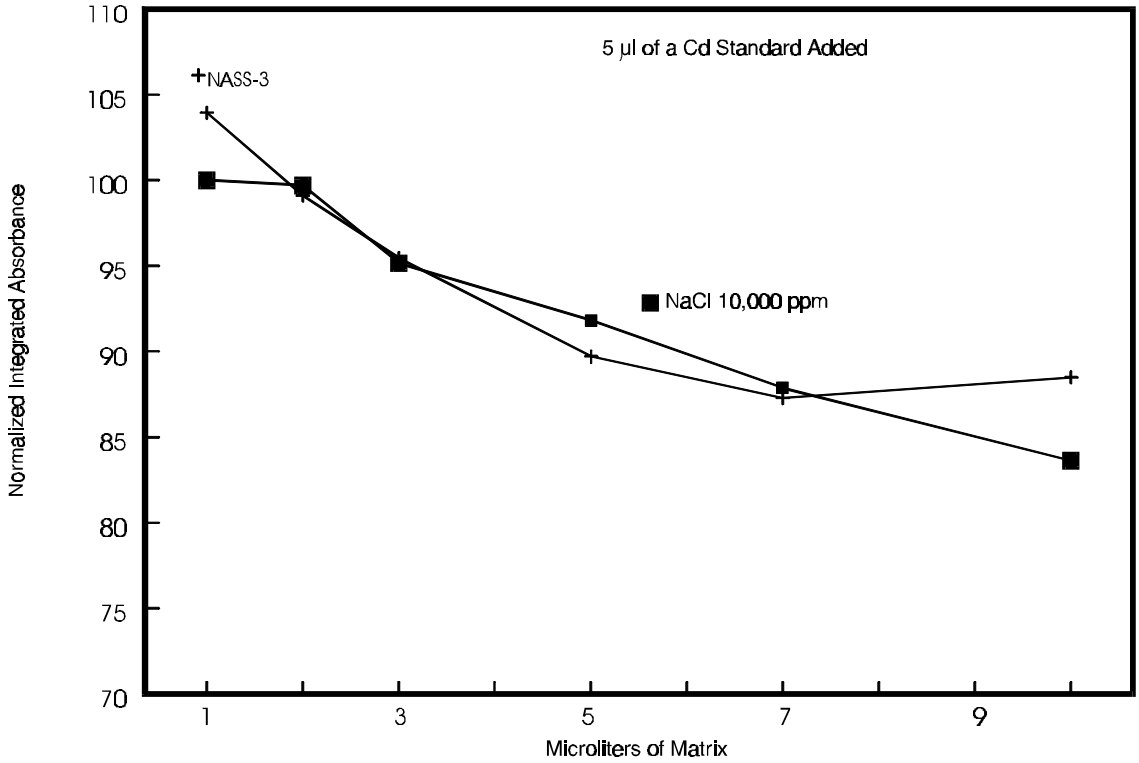

Figure 4. Cd Response in NASS-3 and 10,000 ppm NaCl.

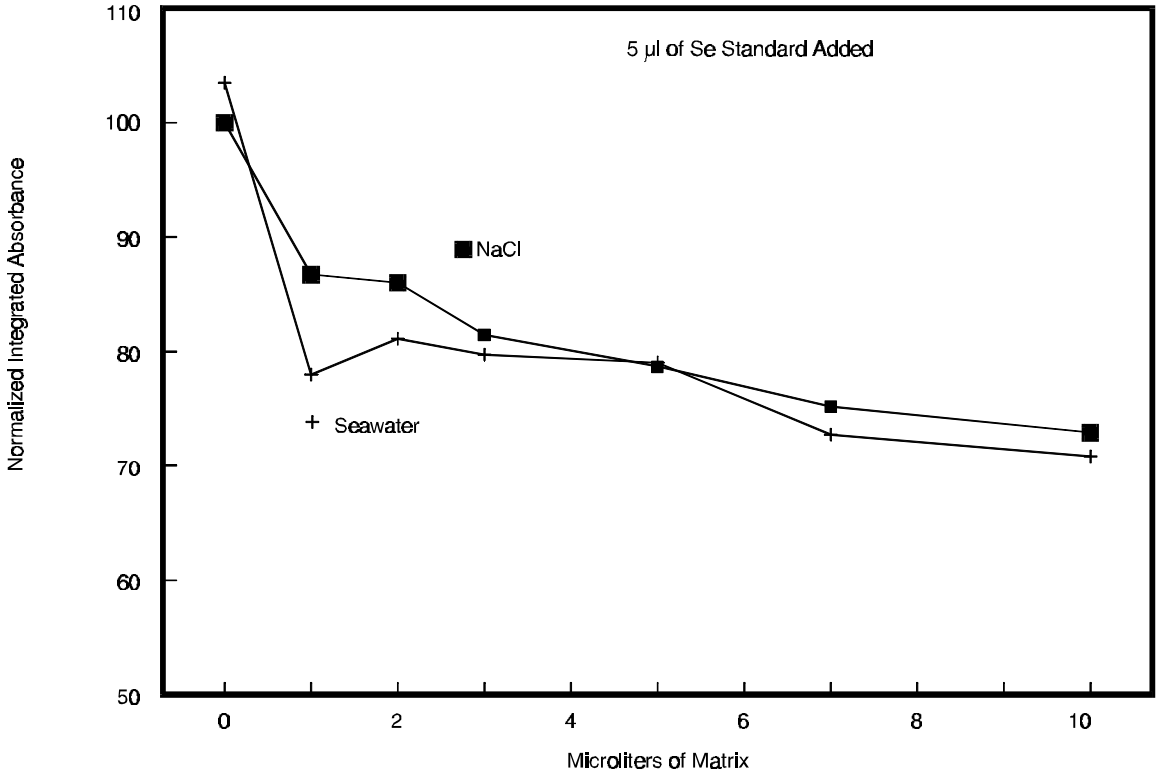

Figure 5. Se Response in Seawater vs 10,000 ppm NaCl

(1) Poor Transfer
(2) Sample Heterogeneity
(3) Digestion/Precipitation
(4) Matrix Suppression/Enhancements
(5) Contamination

IFA = In Furnace Analyte Addition

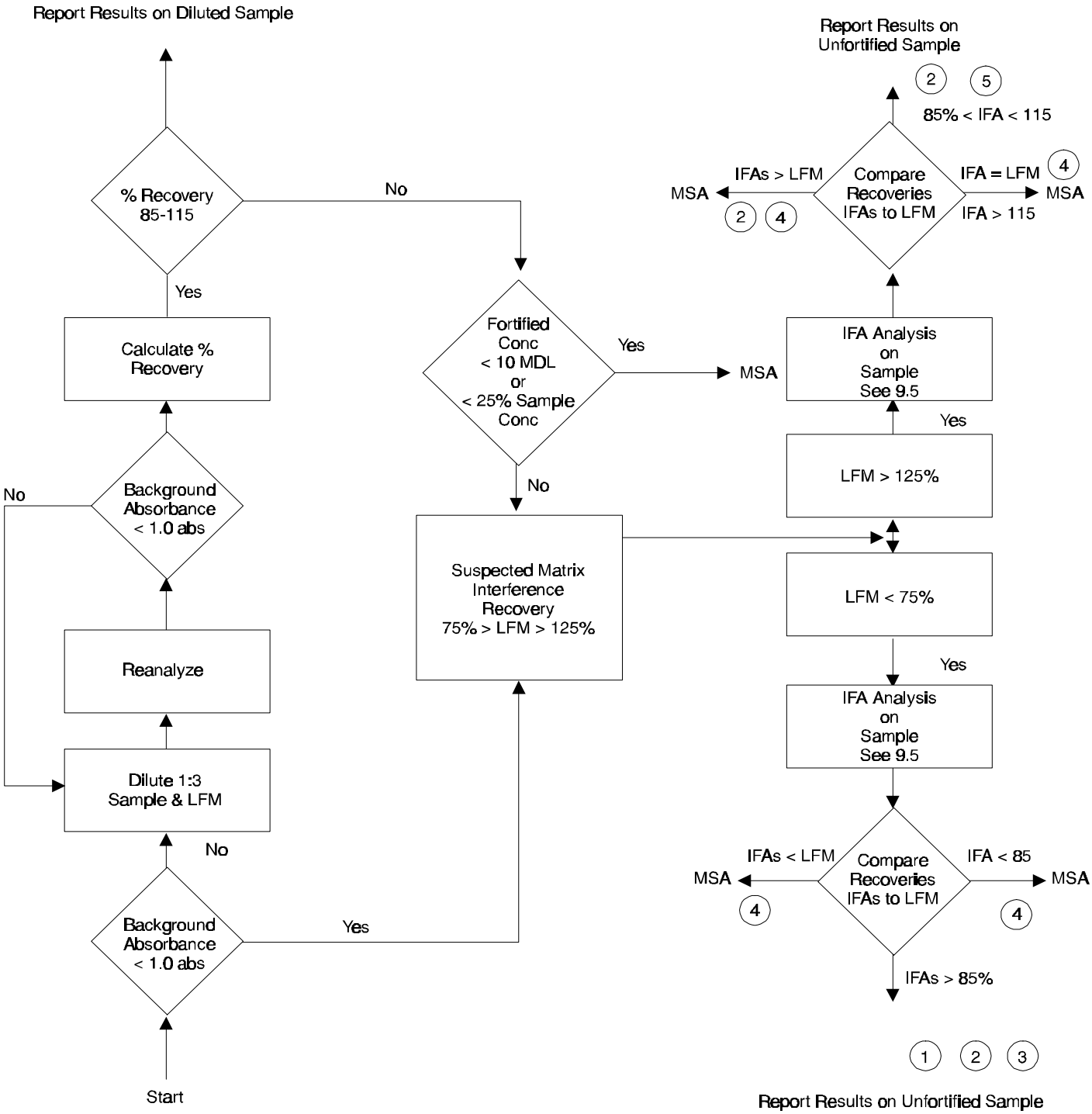

Figure 6. Matrix Interference Flowchart.