

Method 200.13

Determination of Trace Elements in Marine Waters by Off-Line Chelation Preconcentration with Graphite Furnace Atomic Absorption

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1.0 Scope and Application

1.1 This method describes procedures for preconcentration and determination of total recoverable trace elements in marine waters, including estuarine water, seawater and brines.

1.2 Acid solubilization is required prior to determination of total recoverable elements to facilitate breakdown of complexes or colloids which might influence trace element recoveries. This method should only be used for preconcentration and determination of trace elements in aqueous samples.

1.3 This method is applicable to the following elements:

Element		Chemical Abstracts Service Registry Numbers (CASRN)
Cadmium	(Cd)	7440-43-9
Cobalt	(Co)	7440-48-4
Copper	(Cu)	7440-50-8
Lead	(Pb)	7439-92-1
Nickel	(Ni)	7440-02-0

1.4 Method detection limits (MDLs) for these elements will be dependent on the specific instrumentation employed and the selected operating conditions. MDLs in NASS-3 (Reference Material, National Research Council of Canada) were determined using the procedure described in Section 9.2.4 and are listed in Table 1.

1.5 A minimum of 6 months experience in graphite furnace atomic absorption (GFAA) is recommended.

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. The sample volume is reduced to approximately 20 mL and then covered and allowed to reflux. The resulting solution is diluted to volume and is ready for analysis.

2.2 This method is used to preconcentrate trace elements using an iminodiacetate functionalized chelating resin.^{1,2} Following acid solubilization, the sample is buffered using an on-line system prior to entering the chelating column. Group I and II metals, as well as most anions, are selectively separated from the analytes by elution with ammonium acetate at pH 5.5. The analytes are subsequently eluted into a simplified matrix consisting of 0.75 M nitric acid and are determined by GFAA.

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 if method analytes or other interferences are present in the field environment.

3.4 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.

3.5 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.

3.6 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.

3.7 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.

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

3.9 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.

3.10 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.

3.11 Quality Control Sample - 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.

3.12 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.

3.13 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.

3.14 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. Some of these interferences can be minimized via the preconcentration step, which reduces the Ca, Mg, Na, and Cl concentration in the sample prior to GFAA analysis.

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 (Stabilized Temperature Platform Graphite Furnace Atomic Absorption) 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 manometers, 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. Because 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 emissions from 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 formation of free atomic analyte atoms during the atomization cycle. In this method the use of a delayed atomization device which provides warmer gas phase temperatures 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, a possible matrix effect should be suspected (Section 9.4).

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 Low recoveries may be encountered in the preconcentration cycle if the trace elements are complexed by competing chelators (humic/fulvic) in the sample or are present as colloidal material. Acid solubilization pretreatment is employed to improve analyte recovery and to minimize adsorption, hydrolysis and precipitation effects.

4.6 Memory interferences from the chelating system may be encountered, especially after analyzing a sample containing high analyte concentrations. A thorough column rinsing sequence following elution of the analytes is necessary to minimize such interferences.

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.³⁻⁶ 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 Acidification of samples containing reactive materials may result in release of toxic gases, such as cyanides or sulfides. Samples should be acidified 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 HCl 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 should be equipped with an adequate background correction device capable of removing undesirable non-specific absorbance over the spectral region of interest. The capability to record relatively fast (< 1 sec) 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. The data shown in the tables were obtained using the stabilized temperature platform and Zeemar) background correction.

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%).

6.1.4 A 5% hydrogen in argon gas mix and the necessary hardware to use this gas mixture during specific furnace cycles.

6.1.5 Autosampler - Although not specifically required, the use of an autosampler is highly recommended.

6.1.6 Graphite Furnace Operating Conditions- A guide to experimental conditions for the applicable elements is provided in Table 1

6.2 Preconcentration System - System containing no metal parts in the analyte flow path, configured as shown with a sample loop in Figure 1 and without a sample loop in Figure 2.

6.2.1 Column - Macroporous iminodiacetate chelating resin (Dionex Metpac CC-1 or equivalent).

6.2.2 Control valves - Inert double stack, pneumatically operated four-way slider valves with connectors.

6.2.2.1 Argon gas supply regulated at 80-100 psi.

6.2.3 Solution reservoirs - Inert containers, e.g., high density polyethylene (HDPE), for holding eluent and carrier reagents.

6.2.4 Tubing - High pressure, narrow bore, inert tubing such as Tefzel ETFE (ethylene tetrafluoroethylene) or equivalent for interconnection of pumps/valve assemblies and a minimum length for connection of the preconcentration system with the sample collection vessel.

6.2.5 Eluent pumping system (Gradient Pump) - Programmable flow, high-pressure pumping system, capable of delivering either one of three eluents at a pressure up to 2000 psi and a flow rate of 1-5 mL/min.

6.2.6 System setup, including sample loop (See Figure 1).

6.2.6.1 Sample loop - 10-mL loop constructed from narrow bore, high-pressure inert tubing, Tefzel ETFE or equivalent.

6.2.6.2 Auxiliary pumps - On-line buffer pump, piston pump (Dionex QIC pump or equivalent) for delivering 2M ammonium acetate buffer solution, carrier pump, peristaltic pump (Gilson Minipuls or

equivalent) for delivering 1% nitric acid carrier solution; sample pump, peristaltic pump for loading sample loop.

6.2.7 System setup without sample loop (See Figure 2).

6.2.7.1 Auxiliary Pumps - Sample pump (Dionex QIC Pump or equivalent) for loading sample on the column. Carrier pump (Dionex DIC Pump or equivalent) used to flush collection line between samples.

6.3 Labware - For determination of trace elements, contamination and loss are of critical consideration. Potential contamination sources include improperly cleaned laboratory apparatus and general contamination within the laboratory environment. A clean laboratory work area, designated for trace element sample handling must be used. Sample containers can introduce positive and negative errors in determination of trace elements by (1) contributing contaminants through surface desorption or leaching and (2) depleting element concentrations through adsorption processes. For these reasons, borosilicate glass is not recommended for use with this method. All labware in contact with the sample should be cleaned prior to use. Labware may be soaked overnight and thoroughly washed with laboratory-grade detergent and water, rinsed with water, and soaked for 4 h in a mixture of dilute nitric and hydrochloric acids, followed by rinsing with ASTM type I water and oven drying.

6.3.1 Griffin beakers, 250 mL, polytetrafluoroethylene (PTFE) or quartz.

6.3.2 *Storage bottles* - Narrow mouth bottles, Teflon FEP (fluorinated ethylene propylene), or HDPE, 125-mL and 250-mL capacities.

6.4 Sample Processing Equipment

6.4.1 *Air displacement pipetter* - Digital pipet system capable of delivering volumes from 100 to 2500 μL with an assortment of metal-free, disposable pipet tips.

6.4.2 *Balances* - Analytical balance, capable of accurately weighing to ± 0.1 mg; top pan balance, accurate to ± 0.01 g.

6.4.3 *Hot plate* - Corning PC100 or equivalent.

6.4.4 *Centrifuge* - Steel cabinet with guard bowl, electric timer and brake.

6.4.5 *Drying oven* - Gravity convection oven with thermostatic control capable of maintaining $105^\circ\text{C} \pm 5^\circ\text{C}$.

6.4.6 *pH meter* - Bench mounted or hand-held electrode system with a resolution of ± 0.1 pH units.

6.4.7 Class 100 hoods are recommended for all sample handling.

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 specifications⁷ 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.

7.1.1 Nitric acid, concentrated (sp.gr. 1.41).

7.1.1.1 Nitric acid 0.75 M - Dilute 47.7 mL (67.3g) conc. nitric acid to 1000 mL with ASTM type I water.

7.1.1.2 Nitric acid (1+1) - Dilute 500 mL conc. nitric acid to 1000 mL with ASTM type I water.

7.1.1.3 Nitric acid (1+9) - Dilute 100 mL conc. nitric acid to 1000 mL with ASTM type I water.

7.1.2 Matrix Modifier, dissolve 300 mg Palladium (Pd) powder in a minimum amount of concentrated HNO_3 , (1 mL of HNO_3 , adding concentrated HCl only if necessary). Dissolve 200 mg of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in ASTM type 1 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 overall laboratory blank.

7.1.3 Acetic acid, glacial (sp.gr. 1.05). High purity acetic acid is recommended.

7.1.4 Ammonium hydroxide (20%). High purity ammonium hydroxide is recommended.

7.1.5 Ammonium acetate buffer 1M, pH 5.5 - Add 58 mL (60.5 g) of glacial acetic acid to 600 mL of ASTM type I water. Add 65 mL (60 g) of 20% ammonium hydroxide and mix. Check the pH of the resulting solution by withdrawing a small aliquot and testing with a calibrated pH meter, adjusting the solution to pH 5.5 ± 0.1 with small volumes of acetic acid or ammonium hydroxide as necessary. Cool and dilute to 1 L with ASTM type I water.

7.1.6 Ammonium acetate buffer 2M, pH 5.5 - Prepare as for Section 7.1.5 using 116 mL (121 g) glacial acetic acid and 130 mL (120 g) 20% ammonium hydroxide, diluted to 1000 mL with ASTM type I water.

Note: If the system is configured as shown in Figure 1, the ammonium acetate buffer solutions may be further purified by passing them through the chelating column at a flow rate of 5.0 mL/min. Collect the purified solution in a container. Following this, elute the collected contaminants from the column using 0.75M nitric acid for 5 min at a flow rate of 4.0 mL/min. If the system is configured as shown in Figure 2, the majority of the buffer is being purified in an on-line configuration via the clean-up column.

7.1.7 Oxalic acid dehydrate (CASRN 6153-56-6), 0.2M - Dissolve 25.2 g reagent grade $C_2H_2O_4 \cdot 2H_2O$ in 250 mL with ASTM type I water and dilute to 1000 mL with ASTM type I water. **CAUTION** - Oxalic acid is toxic; handle with care.

7.2 **Water** - For all sample preparation and dilutions, ASTM type I water (ASTM D1193) is required.

7.3 **Standard Stock Solutions** - May be purchased from a reputable commercial source or prepared from ultra high-purity grade chemicals or metals (99.99 - 99.999% pure). All salts should be dried for one hour at 105°C, unless otherwise specified. (CAUTION - Many metal salts are extremely toxic if inhaled or swallowed. Wash hands thoroughly after handling.) Stock solutions should be stored in plastic bottles. The following procedures may be used for preparing standard stock solutions:

Note: Some metals, particularly those which form surface oxides require cleaning prior to being weighed. This may be achieved by pickling the surface of the metal in acid. An amount in excess of the desired weight should be pickled repeatedly, rinsed with water, dried and weighed until the desired weight is achieved.

7.3.1 Cadmium solution, stock 1 mL = 1000 µg Cd - Pickle cadmium metal in (1+9) nitric acid to an exact weight of 0.100 g. Dissolve in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with ASTM type I water.

7.3.2 Cobalt solution, stock 1 mL = 1000 µg Co - Pickle cobalt metal in (1+9) nitric acid to an exact weight of 0.100 g. Dissolve in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with ASTM type I water.

7.3.3 Copper solution, stock 1 mL = 1000 µg Cu - Pickle copper metal in (1+9) nitric acid to an exact weight of 0.100 g. Dissolve in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with ASTM type I water.

7.3.4 Lead solution, stock 1 mL = 1000 µg Pb - Dissolve 0.1599 g $PbNO_3$ in 5 mL (1+1) nitric acid. Dilute to 100 mL with ASTM type I water.

7.3.5 Nickel solution, stock 1 mL = 1000 µg Ni - Dissolve 0.100 g nickel powder in 5 mL conc. nitric acid, heating to effect solution. Cool and dilute to 100 mL with ASTM type I water.

7.4 **Multielement Stock Standard Solution** - Care must be taken in the preparation of multielement stock standards that the elements are compatible and stable. Originating element stocks should be checked for the presence of impurities which might influence the accuracy of the standard. Freshly prepared standards should be transferred to acid cleaned, new FEP or HDPE bottles for storage and monitored periodically for stability. A multielement stock standard solution containing cadmium, cobalt, copper, lead, and nickel may be prepared by diluting an appropriate aliquot of each single element stock in the list to 100 mL with ASTM type I water containing 1% (v/v) nitric acid.

7.4.1 **Preparation of calibration standards** - Fresh multielement calibration standards should be prepared weekly. Dilute the stock multielement standard solution in 1% (v/v) nitric acid to levels appropriate to the required operating range. The

element concentrations in the standards should be sufficiently high to produce good measurement precision and to accurately define the slope of the response curve.

7.5 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 7.1) and ASTM Type I water.

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

7.5.2 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.

7.5.3 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.

7.5.4 The rinse blank is prepared as needed by adding 1.0 mL of conc. HNO_3 and 1.0 mL conc. HCl to 1 L of ASTM Type I water and stored in a convenient manner.

7.6 Instrument Performance Check (IPC) Solution - The IPC solution is used to periodically verify instrument performance during analysis. The IPC solution should be a fortified seawater prepared in the same acid mixture as the calibration standards and should contain method analytes such that the resulting absorbances are near 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.

7.7 Quality Control Sample (QCS) -A quality control sample having certified concentrations of the analytes of interest should be obtained from a source outside the laboratory. Dilute the QCS if necessary with 1% nitric acid, such that the analyte concentrations fall within the proposed instrument calibration range.

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, so that appropriate preservation and pretreatment steps can be taken. Acid preservation, etc., 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, acidity with (1+1) nitric acid at the time of collection to $\text{pH} < 2$. Normally 3 mL of (1+1) acid per liter of sample is sufficient. 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 have $\text{pH} > 2$ because of high alkalinity should be acidified with nitric acid to $\text{pH} < 2$ 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 type 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 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 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 6 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 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 nickel. For this reason, the upper limit of the linear calibration range may not correspond to the upper 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 7.7). If the determined concentrations are not within $\pm 10\%$ 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:

$$\text{MDL} = (t) \times (S)$$

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 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 the 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 for a more appropriate MDL estimate. 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 LFM's (Section 9.4) can give confidence to the MDL value determined in reagent water. Typical single laboratory MDL values using this method are given in Table I MDLs should be determined every 6 months, when a new operator begins work, or whenever there is a significant change in the background or instrument response.

9.3 Assessing Laboratory Performance (Mandatory)

9.3.1 Laboratory reagent blank (LRB) - the laboratory must analyze at least one LRB (Section 7.5.2) 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 7.5.3) 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% (Section 9.3.2). 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 (\bar{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:

$$\text{Upper Control Limit} = \bar{x} + 3S$$

$$\text{Lower Control Limit} = \bar{x} - 3S$$

The optional control limits must be equal to or better than the required control limits of 85-115%. After each 5-10 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 7.6) and a calibration blank immediately following each

calibration, after every tenth sample (or more frequently, if required) and at the end of the sample run. The IPC solution should be a fortified seawater matrix. Analysis of the IPC solution and calibration blank immediately following calibration must verify that the instrument is within $\pm 1.0\%$ of calibration. Subsequent analyses of the IPC solution must be within $\pm 10\%$ of calibration. 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. The analysis data of the calibration blank and IPC solution must be kept on file with the sample analyses data.

9.3.5 The overall sensitivity and precision of this method are strongly influenced by a laboratory's ability to control the method blank. Therefore, it is recommended that the calibration blank response be recorded for each set of samples. This record will aid the laboratory in assessing both its long and short term ability to control the method blank.

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 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 (Sect 9.4.2) is required.

9.4.2 The laboratory must add a known amount of each analyte to a minimum of 10% of 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 7.5.3). Over time, samples from all routine sample sources should be fortified.

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 < 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 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. This situation should be rare given the matrix elimination preconcentration step prior to analysis. If a low recovery is found, check the pH of the sample plus the buffer mixture. The resulting pH should be about 5.5. The pH of the sample strongly influences the column's ability to preconcentrate the metals, therefore, a low recovery may be caused by a low pH. If the pH for the LFM/buffer mixture is about 5.5, the analyst is advised to make an in furnace analyte addition to the LFM using the preconcentrated standard solution. If recovery of the in furnace aname addition is shown to be out of control, a matrix interference is confirmed and the sample must be analyzed by MSA.

9.5 Utilizing Reference Materials

9.5.1 It is recommended that a reference material such as NASS-3 (from the Research Council of Canada) be fortified and used as an Instrument Performance Check Solution.

10. Calibration and Standardization

10.1 The preconcentration system can be

configured utilizing a sample loop to define the sample volume (Figure 1) or the system can be configured such that a sample pump rate and a pumping time defines the sample volume (Figure 2). The system illustrated in Figure 1 is recommended for sample sizes of < 10 mL. A thorough rinsing of the sample loop between samples with HNO_3 is required. This rinsing will minimize the cross-contamination which may be caused by the sample loop. The system in Figure 2 should be used for sample volumes of >10 mL. The sample pump used in Figure 2 must be calibrated to assure that a reproducible/defined volume is being delivered.

10.2 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.

10.3 Prior to the use of this method, 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. Of particular importance is the determination of the charring temperature limit for each analyte. This limit is the furnace temperature setting where a loss in analyte will occur prior to atomization. This limit should be determined by conducting char temperature profiles for each analyte and when necessary, in the matrix of question. The charring temperature selected should minimize background absorbance while providing some furnace temperature variation without loss of analyte. For routine analytical operation the charring temperature is usually set at least 100°C below this limit. The optimum conditions selected should provide the lowest reliable MDLs and be similar to those listed in Table 1. Once the optimum operating conditions are determined, they should be recorded and available for daily reference.

10.4 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.

10.5 Before using the procedure (Section 11.0) to analyze samples, data must be available to document 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 (Section 11.4) 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 *Sample Preparation - Total Recoverable Elements*

11.1.1 Add 2 mL (1+1) nitric acid to the beaker containing 100 mL of sample. Place the beaker on the 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 (ribbed) 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. Slight boiling may occur, but vigorous boiling must be avoided.

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 that would clog or affect the sample introduction system, 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 Prior to first use, the preconcentration system should be thoroughly cleaned and decontaminated using 0.2M oxalic acid.

11.2.1 *Precleaning the Preconcentration System*

11.2.1.1 Place approximately 500 mL 0.2 M oxalic acid in each of the sample/eluent containers. Flush the entire system by running the program used for sample analysis 3 times.

11.2.1.2 Rinse the containers with ASTM Type I water and repeat the sequence described in Section 11.2.1.1 using 0.75M nitric acid and again using ASTM type I water in place of the 0.2M oxalic acid.

11.2.1.3 Rinse the containers thoroughly with ASTM type I water, fill them with their designated reagents and run through the program used for sample analysis in order to prime the pump and all eluent lines with the correct reagents.

11.2.2 *Peak Profile Determination*

11.2.2.1 The peak elution time or the collection window should be determined using an ICP-AES (inductively Coupled Plasma Atomic Emission Spectrometer) or Flame AA. Figure 3 is a plot of time vs. emission intensity for Cd, Pb, Ni, and Cu. The collection window is marked in Figure 3 and should provide about 30 sec buffer on either side of the peak. If an ICP-AES is not available, it is recommended that the peak profile be determined by collecting 200- μ L samples during the elution part of the preconcentration cycle and then reconstructing the peak profile from the analysis of the 200- μ L samples.

11.3 Sample Preconcentration

11.3.1 Preconcentration utilizing a sample loop.

11.3.1.1 Loading Sample Loop - With valve 1 in the off position and valve 2 in the on position, load sample through the sample loop to waste using the sample pump for 4 min at 4 mL/min. Switch on the carrier pump and pump 1% nitric acid to flush the sample collection line.

11.3.1.2 Column Loading - With valve 1 in the on position, load sample from the loop onto the column using 1M ammonium acetate for 4.5 min at 4.0 mL/min. Switch on the buffer pump, and pump 2M ammonium acetate at a flow rate of 1 mL/min. The analytes are retained on the column, while the majority of the matrix is passed through to waste.

11.3.1.3 Elution Matrix - With valve 1 in the on position the gradient pump is allowed to elute the matrix using the 1M ammonium acetate. During which time the carrier, buffer and the sample pumps are all off.

11.3.1.4 Elute Analytes - Turn off valve 1 and begin eluting the analytes by pumping 0.75M nitric acid through the column and turn off valve 2 and pump the eluted analytes into the collection flask. The analytes should be eluted into a 2-mL sample volume.

11.3.1.5 Column Reconditioning - Turn on valve 2 to direct column effluent to waste, and pump 0.75M nitric acid, 1 M ammonium acetate, 0.75M nitric acid and 1M ammonium acetate alternately through the column at 4.0 mL/min. Each solvent should be pumped through the column for 2 min. During this process, the next sample can be loaded into the sample loop using the sample pump.

11.3.1.6 Preconcentration of the sample may be achieved by running through an eluent pump program. The exact timing of this sequence should be modified according to the internal volume of the connecting tubing and the specific hardware configuration used.

11.3.2 Preconcentration utilizing an auxiliary pump to determine sample volume.

11.3.2.1 Sample Loading - With the valves 1 and 2 on and the sample pump on, load the sample

on the column buffering the sample utilizing the gradient pump and the 2M buffer. The actual sample volume is determined by knowing the sample pump rate and the time. While, the sample is being loaded the carrier pump can be used to flush the collection line.

11.3.2.2 Elution Matrix - With valve 1 in the off position the gradient pump is allowed to elute the matrix using the 1 M ammonium acetate. During which time the carrier, buffer and the sample pumps are all off.

11.3.2.3 Elution of Analytes - with valves 1 and 2 in the off position the gradient pump is switched to 0.75M HNO₃ and the analytes are eluted into the collection vessel. The analytes should be eluted into a 2 mL sample volume.

11.3.2.4 Column Reconditioning - Turn on valve 2 to direct column effluent to waste, and pump 0.75M nitric acid, 1M ammonium acetate, 0.75M nitric acid and 1M ammonium acetate alternately through the column at 4.0 mL/min.

Note: When switching the gradient pump from nitric acid back to the ammonium acetate it is necessary to flush the line connecting the gradient pump to valve 2 with the ammonium acetate prior to switching the valve. If the line contains nitric acid it will elute the metals from the cleanup column.

11.3.2.5 Preconcentration of the sample may be achieved by running through an eluent pump program. The exact timing of this sequence should be modified according to the internal volume of the connecting tubing and the specific hardware configuration used.

11.4 Repeat the sequence described in Section 11.3.1 or 11.3.2 for each sample to be analyzed. At the end of the analytical run leave the column filled with 1M ammonium acetate buffer until it is next used.

11.5 Samples having concentrations higher than the established linear dynamic range should be diluted into range and reanalyzed.

11.6 Sample Analysis

11.6.1 Prior to daily instrument calibration, inspect the graphite furnace, the sample uptake system and autosampler injector for any change that would affect instrument performance. Clean

the system and replace the graphite tube and/or platform when needed or on a daily basis. A cotton swab dipped in a 50/50 mixture of isopropyl alcohol (IPA) and H₂O (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 dngs 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 manufacturers specifications.

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

11.6.3 Before beginning daily calibration the instrument should be reconfigured to the optimized conditions. Initiate 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.

11.6.4 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 < 5%. If the relative standard deviation is > 5%, determine and correct the cause before calibrating the instrument.

11.6.5 For initial and daily operation calibrate the instrument according to the instrument manufacturer's recommended procedures using the calibration blank (Section 7.5.1) and calibration standards (Section 7.4) prepared at three or more concentrations within the usable linear dynamic range of the analyte (Sections 4.4 & 9.2.2).

11.6.6 An autosampler must be used to introduce all solutions into the graphite furnace. Once the standard, sample or QC solution plus the matrix modifier is injected, the furnace controller completes furnace cycles and cleanout period as programmed. Analyte signals must be integrated and collected as peak area measurements. Background absorbances, background corrected analyte signals, and determined analyte concentrations on all solutions must be able to be displayed on a CRT for immediate 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 7.5.4) between each solution injected.

11.6.7 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.

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

11.6.9 Determined sample analyte concentrations that are ≥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 test procedure that is less sensitive. Samples with a background absorbance > 1.0 must be appropriately diluted with acidified reagent water and reanalyzed (Section 9.4.6). If the method of standard additions is required, follow the instructions described in Section 11.5.

11.6.10 Report data as directed in Section 12.

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

11.7.1 The standard addition techniques 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:

$$C = \frac{S_B V_S C_S}{(S_A - S_B) V_x}$$

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 $\mu\text{g/L}$ 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 $\mu\text{g/L}$ up to three significant figures. If an 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 Experimental conditions used for single laboratory testing of the method are summarized in Table 1.

13.2 Table 2 contains precision and recovery data obtained from a single laboratory analysis of a fortified and a non-fortified sample of NASS-3. The samples were prepared using the procedure described in Sect. 11.1. Four replicates of the non-fortified samples were analyzed and the average of the replicates was used for determining the sample analyte concentration. The fortified samples of NASS-3 were also analyzed and the average percent recovery and the percent relative standard deviation is reported. The reference material

certified values are also listed for comparison.

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 (e.g., Section 7.8). 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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17.0 Tables, Diagrams, Flowcharts, and Validation Data

Table 1. Method Detection Limits for Total Recoverable Analytes in Reagent Water ¹

Element	Slit, nm	Recommended Analytical Wavelengths, nm	Char Temp, °C	Atomization Temp, °C	MDL ² , µg/L
Cadmium	0.7	228.8	800	1600	0.016
Cobalt	0.2	242.5	1400	2500	-
Copper	0.7	324.8	1300	2600	0.36
Lead	0.7	283.3	1250	2000	0.28
Nickel	0.2	232.4	1400	2500	*

¹ MDLs were calculated using NASS-3 as the matrix.

² MDLs were calculated based on a 10-mL sample loop.

* MDL was not calculated because the concentration in the matrix exceeds the MDL spike level.

- Not Determined.

Table 2. Precision and Recovery Data for NASS-3 using System Illustrated in Figure 1 ^{1,2}

Analyte	Certified Value, µg/L ³	Sample Conc., µg/L ³	Fortified Conc., µg/L	Avg. Recovery, %	% RSD
Cd	0.029 ± 0.004	0.026 ± 0.012	0.25	93	3.3
Co	0.004 ± 0.001	-	-	-	-
Cu	0.109 ± 0.011	<0.36	5.0	87	1.4
Pb	0.039 ± 0.006	<0.28	5.0	90	3.7
Ni	0.257 ± 0.027	0.260 ± 0.04	5.0	117	8.3

¹ Data collected using 10-mL sample loop.

² Matrix modifier is Pd/Mg(NO₃)₂/H₂.

³ Uncertainties based on 95% confidence limits.

- Not determined.

	Valves		Buffer Pump	Carrier Pump	Sample Pump
	1	2			
Sample Loop Loading	Off	On	Off	On	On
Column Loading	On	On	On	Off	Off
Elution of Matrix	On	On	Off	Off	Off
Elution of Analytes	Off	Off	Off	Off	Off
Column Recondition	Off	On	Off	Off	Off

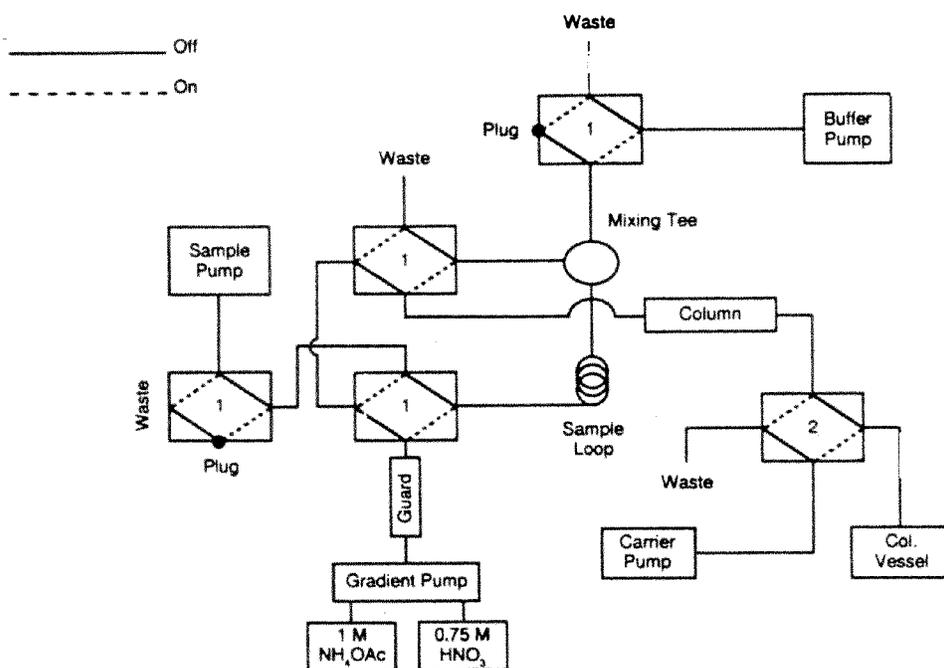


Figure 1. Sample Loop Configuration.

Event	Valves		Carrier Pump	Sample Pump
	1	2		
Sample Loading	On	On	On	On
Elution of Matrix	Off	On	Off	Off
Elution of Analytes	Off	Off	Off	Off
Column Recondition	Off	On	Off	On

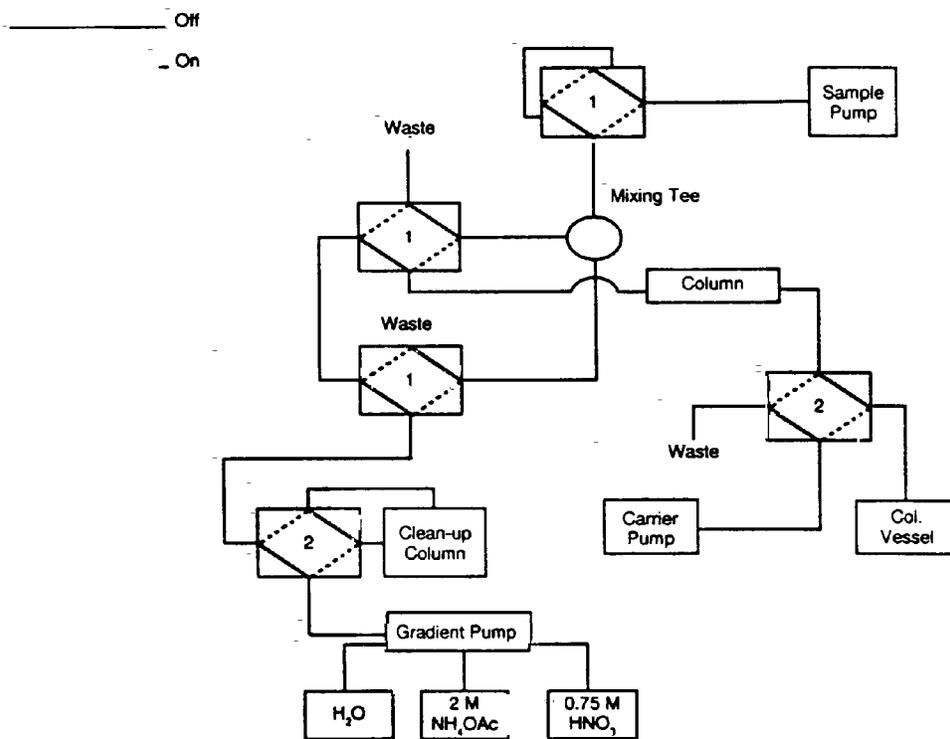


Figure 2. System Diagram without Sample Loop.

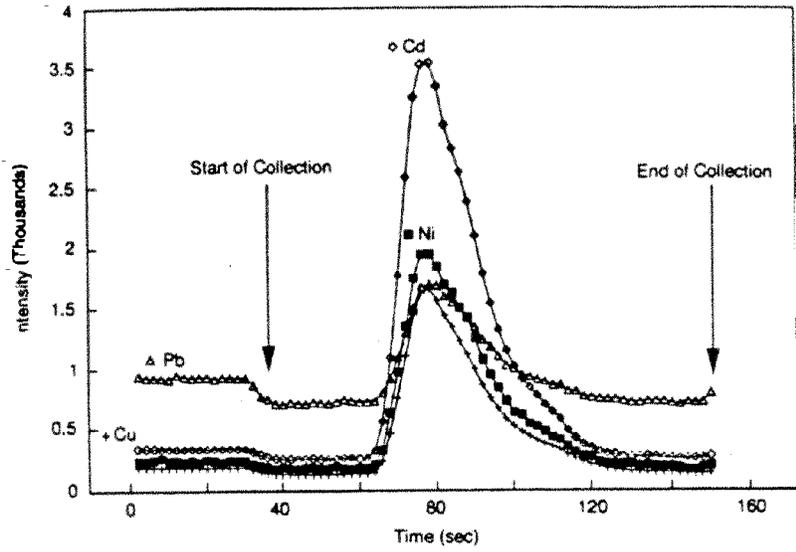


Figure 3. Peak Collection Window from ICP-AES.