Method 200.10

Determination of Trace Elements in Marine Waters by On-Line Chelation Preconcentration and Inductively Coupled Plasma - Mass Spectrometry

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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 the determination of total recoverable elements to facilitate breakdown of complexes or colloids that 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
Uranium	(U)	7440-61-1
Vanadium	(V)	7440-62-2

1.4 Method detection limits (MDLs) for these elements will be dependent on the specific instrumentation employed and the selected operating conditions. However, the MDLs should be essentially independent of the matrix because elimination of the matrix is a feature of the method. Reagent water MDLs, which were determined using the procedure described in Section 9.2.4, are listed in Table 1.

1.5 A minimum of 6-months experience in the use of commercial instrumentation for inductively coupled plasma mass spectrometry (ICP-MS) is recommended.

2.0 Summary of Method

2.1 This method is used to preconcentrate trace elements using an iminodiacetate functionalized chelating resin.[1,2] Following acid solubilization, the sample is buffered prior to the chelating column using an on-line system. Groups 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 dilute nitric acid and are determined by ICP-MS using a directly coupled on-line configuration.

2.2 The determinative step in this method is ICP-MS.[3-5] Sample material in solution is introduced by pneumatic nebulization into a radio frequency plasma where energy transfer processes cause desolvation, atomization and ionization. The ions are extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of their mass-to-charge ratio by a quadrupole mass spectrometer having a minimum resolution capability of 1 amu peak width at 5% peak height. The ions transmitted through the quadrupole are registered by a continuous dynode electron multiplier or Faraday detector and the ion information is processed by a data handling system. Interferences relating to the technique (Section 4) must be recognized and corrected. Such corrections must include compensation for isobaric elemental interferences and interferences from polyatomic ions derived from the plasma gas, reagents or sample matrix. Instrumental drift must be corrected for by the use of internal standardization.

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 ***Instrument Detection Limit (IDL) --*** The minimum quantity of analyte or the concentration equivalent that 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.

3.4 ***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 ***Internal Standard (IS) --*** A pure analyte(s) added to a sample, extract, or standard solution in known amount(s) and used to measure the relative responses of other method analytes and surrogates that are components of the same sample or solution. The internal standard must be an analyte that is not a sample component.

3.6 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.

3.7 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.

3.8 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.

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

3.10 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.

3.11 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.

3.12 Quality Control Sample (QCS) -- A solution of method analytes of known concentrations that 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.

3.13 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.

3.15 Tuning Solution (TS) -- A solution that is used to adjust instrument performance prior to calibration and sample analyses.

4.0 Interferences

4.1 Several interference sources may cause inaccuracies in the determination of trace elements by ICP-MS. These are:

4.1.1 Isobaric elemental interferences -- Are caused by isotopes of different elements that form singly or doubly charged ions of the same nominal mass-to-charge ratio and that cannot be resolved by the mass spectrometer in use. All elements determined by this method have, at a minimum, one isotope free of isobaric elemental interference. The analytical isotopes recommended for use with this method are listed in Table 1.

4.1.2 Abundance sensitivity -- Is a property defining the degree to which the wings of a mass peak contribute to adjacent masses. The abundance sensitivity is affected by ion energy and quadrupole operating pressure. Wing overlap interferences may result when a small ion peak is being measured adjacent to a large one. The potential for these interferences should be recognized and the spectrometer resolution adjusted to minimize them.

4.1.3 Isobaric polyatomic ion interferences -- Are caused by ions consisting of more than one atom that have the same nominal mass-to-charge ratio as the isotope of interest and that cannot be resolved by the mass spectrometer in use. These ions are commonly formed in the plasma or interface system from support gases or sample components. Such interferences must be recognized, and when they cannot be avoided by the selection of alternative analytical isotopes, appropriate corrections must be made to the data. Equations for the correction of data should be established at the time of the analytical run sequence as the polyatomic ion interferences will be highly dependent on the sample matrix and chosen instrument conditions.

4.1.4 Physical interferences -- Are associated with the physical processes that govern the transport of sample into the plasma, sample conversion processes in the plasma, and the transmission of ions through the plasma mass spectrometer interface. These interferences may result in differences between instrument responses for the sample and the calibration standards. Physical interferences may occur in the transfer of solution to the nebulizer (e.g., viscosity effects), at the point of aerosol formation and transport to the plasma (e.g., surface tension), or during excitation and ionization processes within the plasma itself. Internal standardization may be effectively used to compensate for many physical interference effects.[6] Internal standards ideally should have similar analytical behavior to the elements being determined.

4.1.5 *Memory interferences* -- Result when isotopes of elements in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the sampler and skimmer cones and from the buildup of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the element and can be minimized by flushing the system with a rinse blank between samples. Memory interferences from the chelating system may be encountered especially after analyzing a sample containing high concentrations of the analytes. A thorough column rinsing sequence following elution of the analytes is necessary to minimize such interferences.

4.2 A principal advantage of this method is the selective elimination of species giving rise to polyatomic spectral interferences on certain transition metals (e.g., removal of the chloride interference on vanadium). As the majority of the sample matrix is removed, matrix induced physical interferences are also substantially reduced.

4.3 Low recoveries may be encountered in the preconcentration cycle if the trace elements are complexed by competing chelators 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.

5.0 Safety

5.1 Each chemical reagent used in this method should be regarded as a potential health hazard and exposure to these reagents 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.[7,8] A reference file of material data handling sheets should also be available to all personnel involved in the chemical analysis.

5.2 Analytical plasma sources emit radio frequency radiation in addition to intense UV radiation. Suitable precautions should be taken to protect personnel from such hazards.

5.3 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 performed in a fume hood.

5.4 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.

5.5 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 ***Preconcentration System --*** System containing no metal parts in the analyte flow path, configured as shown in Figure 1.

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

6.1.2 *Sample loop* -- 10-mL loop constructed from narrow bore, high-pressure inert tubing, Tefzel ethylene tetra-fluoroethylene (ETFE) or equivalent.

6.1.3 *Eluent pumping system (Pl)* -- Programmable flow, high pressure pumping system, capable of delivering either one of two eluents at a pressure up to 2000 psi and a flow rate of 1-5 mL/min.

6.1.4 *Auxiliary pumps -- On line buffer pump (P2),* piston pump (Dionex QIC pump or equivalent) for delivering 2M ammonium acetate buffer solution; *carrier pump (P3),* peristaltic pump (Gilson Minipuls or equivalent) for delivering 1% nitric acid carrier solution; *sample pump (P4),* peristaltic pump for loading sample loop.

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

6.1.5.1 Argon gas supply regulated at 80-100 psi.

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

6.1.7 *Tubing* -- High pressure, narrow bore, inert tubing (e.g., Tefzel ETFE or equivalent) for interconnection of pumps/valve assemblies and a minimum length for connection of the preconcentration system to the ICP-MS instrument.

6.2 *Inductively Coupled Plasma - Mass Spectrometer*

6.2.1 Instrument capable of scanning the mass range 5-250 amu with a minimum resolution capability of 1 amu peak width at 5% peak height. Instrument may be fitted with a conventional or extended dynamic range detection system.

6.2.2 Argon gas supply (high-purity grade, 99.99%).

6.2.3 A mass-flow controller on the nebulizer gas supply is recommended. A water-cooled spray chamber may be of benefit in reducing some types of interferences (e.g., polyatomic oxide species).

6.2.4 *Operating conditions* -- Because of the diversity of instrument hardware, no detailed instrument operating conditions are provided. The analyst is advised to follow the recommended operating conditions provided by the manufacturer.

6.2.5 If an electron multiplier detector is being used, precautions should be taken, where necessary, to prevent exposure to high ion flux. Otherwise changes in instrument response or damage to the multiplier may result. Samples having high concentrations of elements beyond the linear range of the instrument and with isotopes falling within scanning windows should be diluted prior to analysis.

6.3 ***Labware --*** For the determination of trace elements, contamination and loss are of **critical** concern. 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 the determination of trace elements by (1) contributing contaminants through surface desorption or leaching or (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 hr 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 10 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 ± 0.01g.

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°C±5°C.

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

7.0 Reagents and Standards

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

7.2 Reagents may contain elemental impurities that might affect the integrity of analytical data. Because of the high sensitivity of this method, ultra high-purity reagents must be used unless otherwise specified. To minimize contamination, reagents should be prepared directly in their designated containers where possible.

7.2.1 Acetic acid, glacial (sp. gr. 1.05).

7.2.2 Ammonium hydroxide (20%).

7.2.3 *Ammonium acetate buffer 1M, pH 5.5* -- Add 58-mL (60.5 g) of glacial acetic acid to 600-mL of ASTM type 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.

7.2.4 *Ammonium acetate buffer 2M, pH 5.5* -- Prepare as for Section 7.2.3 using 116 mL (121g) glacial acetic acid and 130 mL (120 g) 20% ammonium hydroxide, diluted to 1000 mL with ASTM type I water.

Note: 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. With reference to Figure 1, pump the buffer solution through the column using pump P1, with valves A and B off and valve C on. Collect the purified solution in a container at the waste outlet. Following this, elute the collected contaminants from the column using 1.25M nitric acid for 5 min at a flow rate of 4.0 mL/min.

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

7.2.5.1 Nitric acid 1.25M -- Dilute 79 mL (112 g) conc. nitric acid to 1000-mL with ASTM type I water.

7.2.5.2 Nitric acid 1% -- Dilute 10 mL conc. nitric acid to 1000 mL with ASTM type I water.

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

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

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

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 1 h 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 that 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 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 Indium solution, stock 1 mL = 1000 μg In: Pickle indium metal in (1+1) nitric acid to an exact weight 0.100 g. Dissolve in 10 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with ASTM type I water.

7.3.5 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.

7.3.6 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.

7.3.7 Scandium solution, stock 1 mL = 1000 μg Sc: Dissolve 0.1534 g Sc_2O_3 in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with ASTM type I water.

7.3.8 Terbium solution, stock 1 mL = 1000 μg Tb: Dissolve 0.1176 g Tb_4O_7 in 5 mL conc. nitric acid, heating to effect solution. Cool and dilute to 100 mL with ASTM type I water.

7.3.9 Uranium solution, stock 1 mL = 1000 μg U: Dissolve 0.2110 g $UO_2(NO_3)_2 \cdot 6H_2O$ (Do Not Dry) in 20 mL ASTM type I water. Add 2-mL (1+1) nitric acid and dilute to 100-mL with ASTM type I water.

7.3.10 Vanadium solution, stock 1 mL = 1000 μg V: Pickle vanadium 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.

7.3.11 Yttrium solution, stock 1 mL = 1000 μg Y: Dissolve 0.1270 g Y_2O_3 in 5 mL (1+1) 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 impurities that 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 the elements, cadmium, cobalt, copper, lead, nickel, uranium, and vanadium (1 mL = 10 μg) may be prepared by diluting 1 mL 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. A suggested mid-range concentration is 10 μg /L.

7.5 Blanks -- Four types of blanks are required for this method. A calibration blank is used to establish the analytical calibration curve, and the laboratory reagent blank is used to assess possible contamination from the sample preparation procedure. The laboratory fortified blank is used to assess the recovery of the method analytes and the rinse blank is used between samples to minimize memory from the nebulizer/spray chamber surfaces.

7.5.1 Calibration blank -- Consists of 1% (v/v) nitric acid in ASTM type I water (Section 7.2.5.2).

7.5.2 Laboratory reagent blank (LRB) -- Must contain all the reagents in the same volumes as used in processing the samples. The LRB must be carried through the entire sample digestion and preparation scheme.

7.5.3 Laboratory Fortified Blank (LFB) -- To an aliquot of LRB, add aliquots from the multielement stock standard (Section 7.4) to produce a final concentration of 10 μg/L for each analyte. The fortified blank must be carried through the entire sample pretreatment and analytical scheme.

7.5.4 Rinse Blank (RB) -- Is a 1% (v/v) nitric acid solution that is delivered to the ICP-MS between samples (Section 7.2.5.2).

7.6 Tuning Solution -- This solution is used for instrument tuning and mass calibration prior to analysis (Section 10.2). The solution is prepared by mixing nickel, yttrium, indium, terbium, and lead stock solutions (Section 7.3) in 1% (v/v) nitric acid to produce a concentration of 100 μg/L of each element.

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.

7.8 Instrument Performance Check (IPC) Solution -- The IPC solution is used to periodically verify instrument performance during analysis. It should be prepared 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.

7.9 Internal Standards Stock Solution, 1 mL = 100 μg -- Dilute 10-mL of scandium, yttrium, indium, terbium, and bismuth stock standards (Section 7.3) to 100-mL with ASTM type I water, and store in a Teflon bottle. Use this solution concentrate for addition to blanks, calibration standards and samples (Method A, Section 10.5), or dilute by an appropriate amount using 1% (v/v) nitric acid, if the internal standards are being added by peristaltic pump (Method B, Section 10.5).

Note: Bismuth should not be used as an internal standard using the direct addition method (Method A, Section 10.5) as it is not efficiently concentrated on the iminodiacetate column.

8.0 Sample Collection, Preservation, and Storage

8.1 Prior to the 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 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 the determination of total recoverable elements in aqueous samples, acidify with (1+1) nitric acid (high purity) at the time of collection to pH<2; normally, 3 mL of (1+1) acid per liter of sample is sufficient for most 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 >pH2 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 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 calibration ranges -- The upper limit of the linear calibration range should be established for each analyte. Linear calibration ranges should be determined every six months or whenever a significant change in instrument response is expected.

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 ± 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 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.[9] 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:

$$MDL = (t) \times (S)$$

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. 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) can give confidence to the MDL value determined in reagent water. Typical single laboratory MDL values using this method are given in Table 1.

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.

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 (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:

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

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

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 established 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 7.8) and a calibration blank immediately following daily calibration, after every tenth sample (or more frequently, if required) and at the end of the sample run. Analysis of the IPC solution and calibration blank immediately following calibration must verify that the instrument is within ±10% of calibration. Subsequent analyses of the IPC solution must verify the calibration within ±15%. 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 the quality of the data. 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.

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:

$$R = \frac{(C_s - C)}{S} x\ 100$$

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 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.

9.4.5 If analysis of 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 the successful analysis 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. The analysis of reference samples is a valuable tool for demonstrating the ability to perform the method acceptably.

10.0 Calibration and Standardization

10.1 Initiate proper operating configuration of ICP-MS instrument and data system. Allow a period of not less than 30 min for the instrument to warm up. During this process conduct mass calibration and resolution checks using the tuning solution. Resolution at low mass is indicated by nickel isotopes 60, 61, 62. Resolution at high mass is indicated by lead isotopes 206, 207, 208. For good performance adjust spectrometer resolution to produce a peak width of approximately 0.75 amu at 5% peak height. Adjust mass calibration if it has shifted by more than 0.1 amu from unit mass.

10.2 Instrument stability must be demonstrated by analyzing the tuning solution (Section 7.6) a minimum of five times with resulting relative standard deviations of absolute signals for all analytes of less than 5%.

10.3 Prior to initial calibration, setup proper instrument software routines for quantitative analysis and connect the ICP-MS instrument to the preconcentration apparatus. The instrument must be calibrated for the analytes of interest using the calibration blank (Section 7.5.1) and calibration standard (Section 7.4.1) prepared at one or more concentration levels. The calibration solutions should be processed through the preconcentration system using the procedures described in Section 11.

10.4 Demonstration and documentation of acceptable initial calibration is required before any samples are analyzed. After initial calibration is successful, a calibration check is required at the beginning and end of each period during which analyses are performed and at requisite intervals.

10.4.1 After the calibration has been established, it must be initially verified for all analytes by analyzing the IPC (Section 7.8). If the initial calibration verification exceeds ±10% of the established IPC value, the analysis should be terminated, the source of the problem identified and corrected, the instrument recalibrated, and the new calibration verified before continuing analyses.

10.4.2 To verify that the instrument is properly calibrated on a continuing basis, analyze the calibration blank (Section 7.5.1) and IPC (Section 7.8) after every 10 analyses. The results of the analyses of the standards will indicate whether the calibration remains valid. If the indicated concentration of any analyte deviates from the true concentration by more than 15%, reanalyze the standard. If the analyte is again outside the 15% limit, the instrument must be recalibrated and the previous 10 samples reanalyzed. The instrument responses from the calibration check may be used for recalibration purposes.

10.5 Internal Standardization -- Internal standardization must be used in all analyses to correct for instrument drift and physical interferences. For full mass range scans, a minimum of three internal standards must be used. Internal standards must be present in all samples, standards and blanks at identical levels. This may be achieved by directly adding an aliquot of the internal standards to the CAL standard, blank or sample solution (Method A), or alternatively by mixing with the solution prior to nebulization using a second channel of the peristaltic pump and a mixing coil (Method B). The concentration of the internal standard should be sufficiently high that good precision is obtained in the measurement of the isotope used for data correction and to minimize the possibility of correction errors if the internal standard is naturally present in the sample. Internal standards should be added to blanks, samples and standards in a like manner, so that dilution effects resulting from the addition may be disregarded.

Note: Bismuth should not be used as an internal standard using the direct addition method (Method A, Section 10.5) because it is not efficiently concentrated on the iminodiacetate column.

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 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, 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 Place approximately 500-mL 0.2M oxalic acid in all the eluent/solution containers and fill the sample loop with 0.2M oxalic acid using the sample pump (P4) at a flow rate of 3-5 mL/min. With the preconcentration system disconnected from the ICP-MS instrument, use the pump program sequence listed in Table 2 to flush the complete system with oxalic acid. Repeat the flush sequence three times.

11.2.2 Repeat the sequence described in Section 11.2.1 using 1.25M nitric acid and again using ASTM type I water in place of the 0.2M oxalic acid.

11.2.3 Rinse the containers thoroughly with ASTM type I water, fill them with their designated reagents (see Figure 1) and run through the sequence in Table 2 once to prime the pump and all eluent lines with the correct reagents.

11.3 Initiate ICP-MS instrument operating configuration. Tune the instrument for the analytes of interest (Section 10).

11.4 Establish instrument software run procedures for quantitative analysis. Because the analytes are eluted from the preconcentration column in a transient manner, it is recommended that the instrument software is configured in a rapid scan/peak hopping mode. The instrument is now ready to be calibrated.

11.5 Reconnect the preconcentration system to the ICP-MS instrument. With valves A and B in the off position and valve C in the on position, load sample through the sample loop to waste using pump P4 for 4 min at 4 mL/min. Switch on the carrier pump (P3) and pump 1% nitric acid to the nebulizer of the ICP-MS instrument at a flow rate of 0.8-1.0-mL/min.

11.6 Switch on the buffer pump (P2), and pump 2M ammonium acetate at a flow rate of 1.0 mL/min.

11.7 Preconcentration of the sample may be achieved by running through an eluent pump program (P1) sequence similar to that illustrated in Table 2. The exact timing of this sequence should be modified according to the internal volume of the connecting tubing and the specific hardware configuration used.

11.7.1 *Inject sample* -- With valves A, B, and C on, load sample from the loop onto the column using 1M ammonium acetate for 4.5 min at 4.0 mL/min. The analytes are retained on the column, while the majority of the matrix is passed through to waste.

11.7.2 *Elute analytes* -- Turn off valves A and B and begin eluting the analytes by pumping 1.25M nitric acid through the column at 4.0 mL/min, then turn off valve C and pump the eluted analytes into the ICP-MS instrument at 1.0 mL/min. Initiate ICP-MS software data acquisition and integrate the eluted analyte profiles.

11.7.3 *Column Reconditioning* -- Turn on valve C to direct column effluent to waste, and pump 1.25M nitric acid, 1M ammonium acetate, 1.25M nitric acid and 1M ammonium acetate alternately through the column at 4.0 mL/min. During this process, the next sample can be loaded into the sample loop using the sample pump (P4).

11.8 Repeat the sequence described in Section 11.7 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.

11.9 Samples having concentrations higher than the established linear dynamic range should be diluted into range with 1% HNO_3 (v/v) and reanalyzed.

12.0 Data Analysis and Calculations

12.1 Analytical isotopes and elemental equations recommended for sample data calculations are listed in Table 3. Sample data should be reported in units of µg/L. Do not report element concentrations below the determined MDL.

12.2 For data values less than 10, two significant figures should be used for reporting element concentrations. For data values greater than or equal to 10, three significant figures should be used.

12.3 Reported values should be calibration blank subtracted. If additional dilutions were made to any samples, the appropriate factor should be applied to the calculated sample concentrations.

12.4 Data values should be corrected for instrument drift by the application of internal standardization. Corrections for characterized spectral interferences should be applied to the data.

12.5 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 4.

13.2 Data obtained from single laboratory testing of the method are summarized in Tables 5 and 6 for two reference water samples consisting of National Research Council Canada (NRCC) Estuarine Water (SLEW-1) and Seawater (NASS-2). The samples were prepared using the procedure described in Section 11.1.1. For each matrix, three replicates were analyzed and the average of the replicates was used to determine the sample concentration for each analyte. Two further sets of three replicates were fortified at different concentration levels, one set at 0.5 μg/L, the other at 10 µg/L. The sample concentration, mean percent recovery, and the relative standard deviation of the fortified replicates are listed for each method analyte. The reference material certificate 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 place 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 recy-cling 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 Section 14.2.

16.0 References

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7. OSHA Safety and Health Standards, General Industry, (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206, (Revised, January 1976).
8. Safety in Academic Chemistry Laboratories, American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.
9. Code of Federal Regulations 40, Ch. 1, Pt. 136 Appendix B.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

Table 1. Total Recoverable Method Detection Limits for Reagent Water

Element	Recommended Analytical Mass	MDL[1] μg/L
Cadmium	111	0.041
Cobalt	59	0.021
Copper	63	0.023
Lead	206, 207,208	0.074
Nickel	60	0.081
Uranium	238	0.031
Vanadium	51	0.014

[1] Determined using 10-mL sample loop.

Table 2. Eluent Pump Programming Sequence for Preconcentration of Trace Elements

Time (min)	Flow (mL/min)	Eluent	Valve A,B	Valve C
0.0	4.0	1M ammonium acetate	ON	ON
4.5	4.0	1.25M nitric acid	ON	ON
5.1	1.0	1.25M nitric acid	OFF	ON
5.5	1.0	1.25M nitric acid	OFF	OFF
7.5	4.0	1.25M nitric acid	OFF	ON
8.0	4.0	1M ammonium acetate	OFF	ON
10.0	4.0	1.25M nitric acid	OFF	ON
11.0	4.0	1M ammonium acetate	OFF	ON
12.5	0.0		OFF	ON

Table 3. Recommended Analytical Isotopes and Elemental Equations for Data Calculations

Element	Isotope	Elemental Equation	Note
Cd	106, 108, *111,* 114	(1.000)(^{111}C)-(1.073)[(^{108}C)-(0.712)(^{106}C)]	(1)
Co	59	(1.000)(^{59}C)	
Cu	*63,* 65	(1.000)(^{63}C)	
Pb	*206, 207, 208*	(1.000)(^{206}C)+(1.000)(^{207}C)+(1.000)(^{208}C)	(2)
Ni	60	(1.000)(^{60}C)	
U	238	(1.000)(^{238}C)	
V	51	(1.000)(^{51}C)	

C - calibration blank subtracted counts at specified mass.
(1) - correction for MoO interference. An additional isobaric elemental correction should be made if palladium is present.
(2) - allowance for isotopic variability of lead isotopes.
NOTE: As a minimum, all isotopes listed should be monitored. Isotopes recommended for analytical determination are italized.

Table 4. Experimental Conditions for Single Laboratory Validation

Chromatography	
Instrument	Dionex chelation system
Preconcentration column	Dionex MetPac CC-1
ICP-MS Instrument Conditions	
Instrument	VG PlasmaQuad Type I
Plasma forward power	1.35 kW
Coolant flow rate	13.5 L/min
Auxiliary flow rate	0.6 L/min
Nebulizer flow rate	0.78 L/min
Internal standards	Sc, Y, In, Tb
Data Acquisition	
Detector mode	Pulse counting
Mass range	45-240 amu
Dwell time	160 μs
Number of MCA channels	2048
Number of scan sweeps	250

Table 5. Precision and Recovery Data for Estuarine Water (SLEW-1)

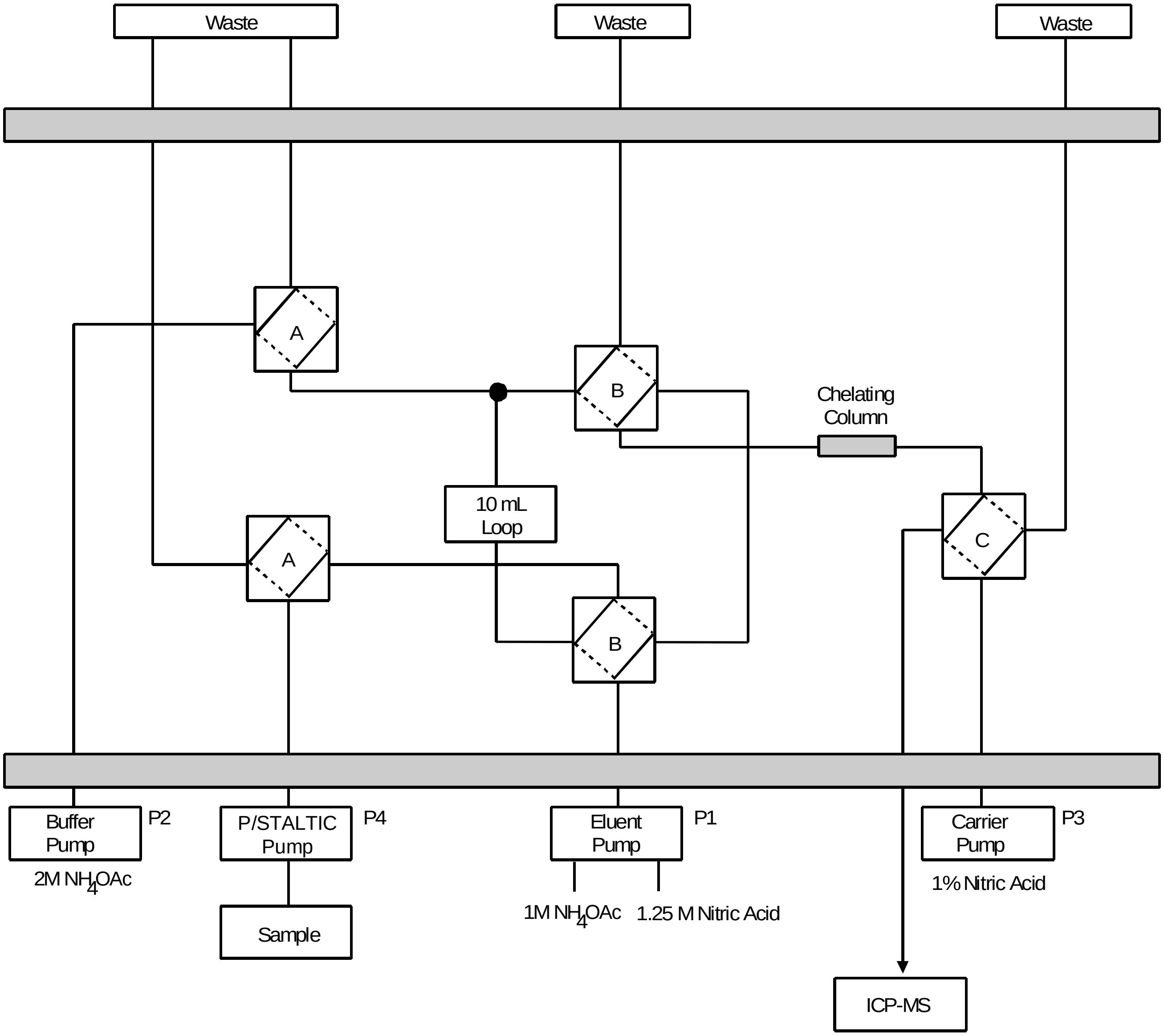
Analyte	Certificate (μg/L)	Sample Conc. (μg/L)	Spike Addition (μg/L)	Average Recovery (%)	RSD (%)	Spike Addition (μg/L)	Average Recovery (%)	RSD (%)
Cd	0.018	<0.041	0.5	94.8	9.8	10	99.6	1.1
Co	0.046	0.078	0.5	102.8	4.0	10	96.6	1.4
Cu	1.76	1.6	0.5	106.0	2.7	10	96.0	4.8
Pb	0.028	<0.074	0.5	100.2	4.0	10	106.9	5.8
Ni	0.743	0.83	0.5	100.0	1.5	10	102.0	2.1
U	--	1.1	0.5	96.7	7.4	10	98.1	3.6
V	--	1.4	0.5	100.0	3.2	10	97.0	4.5

-- No certificate value

Table 6. Precision and Recovery Data for Seawater (NASS-2)

Analyte	Certificate (μg/L)	Sample Conc. (μg/L)	Spike Addition (μg/L)	Average Recovery (%)	RSD (%)	Spike Addition (μg/L)	Average Recovery (%)	RSD (%)
Cd	0.029	<0.041	0.5	101.8	1.0	10	96.4	3.7
Co	0.004	<0.021	0.5	98.9	3.0	10	99.2	1.7
Cu	0.109	0.12	0.5	95.8	2.3	10	93.1	0.9
Pb	0.039	<0.074	0.5	100.6	8.5	10	92.1	2.6
Ni	0.257	0.23	0.5	102.2	2.3	10	98.2	1.2
U	3.00	3.0	0.5	94.0	0.7	10	98.4	1.7
V	--	1.7	0.5	104.0	3.4	10	109.2	3.7

--No certificate value



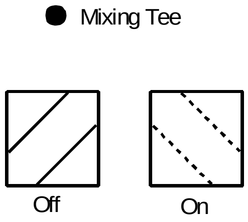


Figure 1. Configuration of Preconcentration System.