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An American National Standard

# Standard Practice for Preparation of Water Samples Using Reductive Precipitation Preconcentration Technique for ICP-MS Analysis of Trace Metals[1]

This standard is issued under the fixed designation D 6800; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 Toxic elements may be present in ambient waters and may enter the food chain via uptake by plants and animals; the actual concentrations of toxic metals are usually sub-ng/mL. The U.S. EPA has published its Water Quality Standards in the U.S. Federal Register 40 CFR 131.36, Minimum requirements for water quality standards submission, Ch. I (7-1-00 Edition), see Annex, Table A1.1. The U.S. EPA has also developed Method 1640 to meet these requirements, see Annex, Table A1.2.

1.2 Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) is a technique with sufficient sensitivity to routinely measure toxic elements in ambient waters, both fresh and saline (Test Method D 5673). However saline and hard water matrices pose analytical challenges for direct multielement analysis by ICP-MS at the required sub-ng/mL levels.

1.3 This standard practice describes a method used to prepare water samples for subsequent multielement analysis using ICP-MS. The practice is applicable to seawater and fresh water matrices, which may be filtered or digested. Samples prepared by this method have been analyzed by ICP-MS for the elements listed in Annex, Table A1.3).

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

## 2. Referenced Documents

2.1 *ASTM Standards:*

D 1129 Terminology Relating to Water[2]

D 1193 Specification for Reagent Water[2]

D 5673 Test Method for Elements in Water by Inductively Coupled Plasma Mass Spectrometry[2]

D 5810 Guide for Spiking into Aqueous Samples[2]

D 5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis[3]

2.2 *Other Documents:*

U.S. Federal Register 40 CFR 131.36, Minimum Requirements for Water Quality Standards Submission, Ch. I (7-1-00 Edition)[4]

U.S. EPA Method 1640, Determination of Trace Elements in Water by Preconcentration and Inductively Coupled Plasma-Mass Spectrometry (1997)[5]

U.S. EPA Method 1669, Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels[5]

## 3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method refer to Terminology D 1129.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *dissolved*—the concentration of elements determined on a filtered fraction of a sample. Samples are filtered through a 0.45 µm membrane filter before acid preservation.

3.2.2 *intermediate stock standard solution*—a diluted solution prepared from one or more of the stock standard solutions.

3.2.3 *laboratory control sample (LCS)*—an aliquot of solution with known concentrations of method analytes. It should be obtained from a reputable source or prepared at the laboratory from a separate source from the calibration standards. The LCS is analyzed using the same sample preparation, analytical method and QA/QC procedure used for test samples. Its purpose is to determine whether method performance is within accepted control limits.

3.2.4 *laboratory duplicate (LD)*—a second aliquot of a sample should be analyzed using the same sample preparation, analytical method and QA/QC procedure used for test samples. Its purpose is to determine whether method performance is within accepted control limits.

3.2.5 *matrix spike (MS)*—a second aliquot of a sample to which known concentrations of target analyte(s) are added in the laboratory and should be analyzed using the same sample

[1] This practice is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.05 on Inorganic Constituents in Water.

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[2] *Annual Book of ASTM Standards*, Vol 11.01.

[3] *Annual Book of ASTM Standards*, Vol 11.02.

[4] Available from DODSSP, Bldg. 4, Section D, 700 Robbins Ave., Philadelphia, PA 19111–5098.

[5] Available from U.S. EPA, Ariel Rios Bldg., 1200 Pennsylvania Ave., NW, Washington, DC 20460.

preparation and analytical method used for test samples. Its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentration of the matrix must be determined in a separate aliquot and the measured values in the MS corrected for the concentrations found. Recommended spike levels are listed in Annex, Table A1.3.

3.2.6 *method blank (MB)*—suitable aliquots of reagent water are analyzed using the same sample preparation technique, analytical method and QA/QC procedure used for test samples. The MB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents or apparatus.

3.2.7 *method detection limit (MDL)*—determined as described in the U.S. Federal Register (see 40 CFR Part 136, Appendix B).

3.2.8 *reagent water*—standard laboratory water purified to meet Specification D 1193 Type I or better.

3.2.9 *reporting detection limit (RDL)*—the lowest concentration at which an analyte can be reliably quantified. The RDL represents the minimum concentration at which method performance becomes quantitative and is not subject to the degree of variation observed at concentrations between the MDL and the RDL.

3.2.10 *spiked blank (SB)*—an aliquot of reagent water to which known concentrations of analyte(s) is added in the laboratory, using the same solution as used to prepare the matrix spike. The spike blank is analyzed using the same sample preparation, analytical method and QA/QC procedure used for test samples. The purpose of the spike blank is to determine whether method performance is within acceptable limits. The spike blank is also useful for troubleshooting matrix spike results that are outside the acceptance limits, by allowing the analyst to differentiate between spike solution and spiking technique problems and matrix interferences. Recommended spike levels are listed in Annex, Table A1.3.

3.2.11 *stock standard solution*—a concentrated solution containing one or more analytes, obtained as a certified solution form a reputable source.

3.2.12 *surrogate spikes*—lanthanum and terbium are added at a concentration of 5 ng/mL in the initial 100-mL sample. The surrogate spikes are then preconcentrated to approximately 50 ng/mL in the final 10-mL sample not correcting for the final preconcentration. The surrogate spikes are used to determine potential method problems such as improper pH adjustment or faulty filters used when collecting the precipitate.

3.2.13 *total recoverable*—the concentration of analyte determined on a whole, unfiltered water or solid sample following vigorous digestion as described in US EPA Method 1640.

## 4. Summary of Practice

4.1 In this practice, trace elements are separated from seawater matrix elements (in particular Na, Ca, and Mg) and preconcentrated by a factor of 10 by reductive precipitation using sodium borohydride as a reducing agent.

4.2 Iron (Fe) and palladium (Pd) are added to the samples to aid co-precipitation of metal borides and to enhance the precipitation of metals in their elemental form.

4.3 For total metals, the whole sample is acidified at the time of collection with ultrapure nitric acid at an equivalent concentration of 0.20 % to a pH < 2.

4.4 For dissolved metals, the sample is filtered through a 0.45 µm filter at the time of collection then acidified with ultrapure nitric acid at an equivalent concentration of 0.20 % to a pH < 2.

NOTE 1—It is important to minimize the amount of nitric acid used to preserve the samples. A pH adjustment to a pH between 8 and 10 using ammonium hydroxide is performed during the co-precipitation reaction and it is important to minimize the amount of ammonium hydroxide required for this adjustment to reduce potential contamination of the samples.

4.5 The precipitate is collected by filtration through a 0.4 mm filter and the salt matrix is eliminated with the filtrate. The filter and precipitate are digested with nitric acid and hydrogen peroxide for analysis by ICP-MS.

## 5. Significance and Use

5.1 Ambient marine waters generally contain very low concentrations of toxic metals that require sensitive analytical methods, such as ICP-MS, to detect and measure the metal's concentrations.

5.2 Due to the high dissolved salt concentrations present in seawater, sample pretreatment is required to remove signal suppression and significant polyatomic interferences due to the matrix both of which compromise detection limits.

## 6. Interferences

6.1 *Contamination*—Concentrations of trace metals in ambient marine waters may be very low and it is imperative that extreme care be taken to avoid contamination when collecting, preparing and analyzing ambient water samples. U.S. EPA Method 1669 details appropriate clean sampling protocols.

6.2 Isobaric polyatomic ion interferences are caused by ions consisting of more than one atom which have the same nominal mass-to-charge ratio as the isotope of interest, and which may not 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. Most of the common interferences have been identified, and are listed in Test Method D 5673. 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 operating parameters. Major interfering ions from seawater matrixes are eliminated in this practice by the selective precipitation of metals.

6.3 Palladium reagent in the analyzed samples interferes with both silver masses $^{107}Ag$ and $^{109}Ag$ due to the formation of the $PdH^+$ ion.

## 7. Hazards

7.1 The toxicity or carcinogenicity of reagents 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. A reference file of material data handling sheets (MSDS) for each chemical used in this procedure should be available to all personnel involved in the chemical analysis.

## 8. Sample Collection, Containers, Preservation, and Storage

8.1 All samples must be collected using a sampling plan that addresses the considerations discussed in U.S. EPA Method 1669. Contamination control is critical at all steps of sample handling due to the low measurement limit goals of this method.

8.2 Water samples must be acidified with an equivalent concentration of 0.2 % ultrapure nitric acid (that is, 1 mL $HNO_3$ to 500 mL sample). Samples are kept at room temperature in plastic bins. Use the minimum amount of acid necessary to reduce the sample pH < 2. Excess acid will complicate the pH adjustment during the reductive precipitation reaction.

8.3 Use only acid washed sample containers prepared as described in US EPA Method 1669. High-density polyethylene (HDPE) is preferred.

8.4 *Sample Preservation*:

8.4.1 *Total Recoverable Metals*—For determination of total recoverable elements in aqueous samples, preserve the whole sample by adding ultra pure nitric acid to pH < 2 (normally 1 mL per 500 mL of sample) at the time of collection or upon receipt with an equivalent concentration of 0.2 % ultrapure nitric acid (that is, 1 mL $HNO_3$ to 500 mL sample).

NOTE 2—Samples that cannot be acid preserved at the time of collection because of sampling limitations or transport restrictions, should be acidified with ultra pure acid to pH < 2 upon receipt in the laboratory. These samples must be then held for 16 h prior to sample preparation.

8.4.2 *Dissolved Metals*—For the determination of dissolved elements, the samples are filtered through a 0.45 µm membrane filter or equivalent. Acidify the filtrate with ultra pure nitric acid to pH < 2 immediately following filtration.

## 9. Apparatus and Equipment

9.1 *Laboratory Equipment*—For the determination of trace levels of elements, contamination and loss are of primary consideration. Potential contamination sources include improperly cleaned laboratory apparatus and general contamination within the laboratory environment from dust, etc. 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, (*2*) depleting element concentrations through adsorption process. Equipment should be dedicated to trace metals analysis and thorough cleaning procedures will minimize contamination. All equipment used for sample preparation is cleaned by first soaking in a 2 % detergent solution, second in 20 % hydrochloric acid, third in 20 % nitric acid followed by rinsing copiously with reagent water. Equipment cleanliness is monitored by the method blanks. Refer to U.S. EPA Method 1669 for guidance.

9.2 *Hot Block*, capable of 70°C.

9.3 *Vacuum Filter Holder*, with a viton o-ring and a silicone stopper.

9.4 *25 mm Polysulphone Filter Funnel*, 200 mL capacity.

9.5 *PVC Vacuum Manifold*.

9.6 *Filter Dome*, 2000 mL capacity.

9.7 *Oil-Free Vacuum Pump*.

9.8 *Analytical Balance*.

9.9 *Metal-Free Pipettes*, capable of delivering varying amounts from microlitres (µL) to millilitres (mL).

9.10 *500 mL Fluoropolymer Separatory Funnel*.

9.11 *125 mL High-Density Polyethylene (HDPE) Bottles*.

9.12 *125 mL and 250 mL Wide-Mouth Fluoropolymer Bottles*.

9.13 *Fluoropolymer Tweezers*.

9.14 *Automated Pipette*, for acid dispensing. Capable of accurately delivering 0.25 to 5.0 mL.

9.15 *Polypropylene Specimen Cups and Polypropylene Lids*.

9.16 *250 mL Polypropylene Graduated Cylinders*.

9.17 *100 mL Polymethylpentene (PMP) Graduated Cylinders*.

9.18 *Laminar Flow Polypropylene Fume Hood.*

## 10. Standards, Reagents, and Consumables

10.1 *Consumables*:

10.1.1 125 mL environmental sampling bottles, high-density polyethylene (HDPE), wide mouth.

10.1.2 15 mL calibrated disposable polypropylene centrifuge tubes.

10.1.3 20 mm polypropylene caps.

10.1.4 50 mL or 100 mL volumetric flask, polypropylene.

10.1.5 pH test papers, dual tint, pH range 7.0 to 10.0, accurate to 0.1.

10.1.6 *Polycarbonate Filters*:

10.1.6.1 25 mm diameter, 0.4 µm pore size.

10.1.6.2 47 mm diameter, 0.4 µm pore size.

10.1.6.3 47 mm diameter, 0.2 µm pore size.

10.1.7 *Metal-Free Laboratory Gloves*.

10.2 *Purity of Reagents*—All reagents may contain impurities that may affect the integrity of the analytical results. Due to the high sensitivity of ICP-MS, high-purity reagents, water, and acids must be used whenever possible. All acids used for this method must be of ultra high-purity grade. Nitric acid is preferred for the ICPMS in order to minimize polyatomic interferences.

10.3 *Reagent Water*, equivalent to ASTM Type I water (see Specification D 1193).

10.4 *Nitric Acid, Concentrated*—Ultra-pure from sub-boiling distillation is preferred.

10.5 *2 % Nitric Acid Rinse Solution*—Fill an acid washed 100 mL polypropylene volumetric flask with approximately 90 mL of reagent water. Add 2 mL of concentrated nitric acid. Dilute to 100 mL with reagent water and mix well. Transfer to an acid washed 125 mL HPDE bottle and label.

NOTE 3—Use this 2 % nitric acid rinse solution to rinse pipette tips. Prior to using a pipette tip, pick up a volume of the 2 % $HNO_3$ solution and then dispense it to waste.

10.6 *Hydrogen Peroxide*, ultra-pure.

10.7 *Ammonium Hydroxide*, ultra-pure.

10.8 *Sodium Borohydride*, 99 %.

10.9 *Pyrrolidinecarbodithioic Acid, Ammonium Salt (APDC)*.

10.10 *Methyl Isobutyl Ketone (MIBK)*.

10.11 *Lithium Carbonate 95 Atom % $^{6}Li^{6}$*.

10.12 *$^{6}Li$ Internal Standard Solution*—Dissolve 0.6312 g lithium carbonate 95 atom % enriched $^{6}Li$ in 100 mL of 2 % nitric acid.

10.13 *Gallium 1000 µg/mL Stock Standard ICP-MS Grade Solution*.

10.14 *Indium 1000 µg/mL Stock Standard ICP-MS Grade Solution*.

10.15 *Iron 1000 µg/mL Stock Standard ICP-MS Grade Solution*.

10.16 *Lutetium 1000 µg/mL Stock Standard ICP-MS Grade Solution*.

10.17 *Lanthanum 1000 µg/mL Stock Standard ICP-MS Grade Solution*.

10.18 *Palladium 1000 µg/mL Stock Standard ICP-MS Grade Solution*.

10.19 *Scandium 1000 µg/mL Stock Standard ICP-MS Grade Solution*.

10.20 *Terbium 1000 µg/mL Stock Standard ICP-MS Grade Solution*.

10.21 *Mixed Standard Solutions*—Prepare standard solutions containing antimony, arsenic, beryllium, cadmium, chromium, cobalt, copper, lead, nickel, selenium, thallium, vanadium and zinc can be made from single element 1000 mg/mL ICP-MS grade stock standards or appropriate mixed ICP-MS grade standard solutions.

10.22 *Standard Solutions*—Prepare standard solutions for silver from a 1000 µg/mL ICP-MS grade stock standard.

10.23 *Reductive Precipitation Solution*—Prepare an iron/palladium/lanthanum/terbium mixed solution. Prepare 500 µg/mL Fe, Pd, 0.500 µg/mL La, Tb in 5 % HCl, 1 % $HNO_3$. Lanthanum and terbium are used as surrogate spikes for this method.

10.24 *2 % Ammonium 1-Pyrrolidinedithiocarbamate (APDC) Solution*—Weigh out 4.0 g of APDC into a 250 mL acid-washed container. Add approximately 200 mL of reagent water into the bottle. Gently heat the bottle in a water bath to facilitate salt dissolution. Cleanse the solution of chelated impurities using an acid-washed 500 mL separatory funnel and MIBK as follows: Add approximately 200 mL of the MIBK to the APDC solution in a 500 mL fluoropolymer separatory funnel. Shake for one minute and allow at least 30 min for complete separation. The APDC forms the layer on the bottom of the separatory funnel and the MIBK is the top layer. Withdraw the APDC solution into the initial mixing bottle. Withdraw the MIBK into a waste jar and repeat the extraction with 200 mL of fresh MIBK. Withdraw the APDC solution into a new acid-washed bottle. Allow the solution to sit for 24 h, then further cleanse the APDC solution of impurities by filtering through a 47 mm diameter, 0.4 µm pore size acid-washed polycarbonate filter.

10.25 *5 % Sodium Borohydride Solution*—Weigh out 5.0 g per 100 mL solution volume needed of 99 % pure sodium borohydride into a 250 mL acid washed, wide mouth fluoropolymer bottle. Slowly add 100 mL reagent water to the fluoropolymer bottle. Let the solution stand for at least one hour before filtration to allow impurities to precipitate. Keep cap loose to allow gases to escape preventing pressure build up. Purify by filtering solution through a 47 mm diameter, 0.2 µm pore size acid-washed polycarbonate filter and collect the filtrate in a clean bottle. Dispose of sodium borohydride solution after use. Do not store. Always keep cap loose to prevent pressure build up.

10.26 *Quality Control Solutions*—Prepare solutions at concentrations within the instrument calibration range from an alternative supplier from the source of the calibration solutions. Recommended spike levels are listed in Table A1.3.

10.27 *Internal Standard Stock Solution*—Prepare 20 mg/L $^{6}Li$, In, Lu, Sc and 40 mg/L Ga in 5 % nitric acid in an acid-washed HDPE bottle.

10.28 *Certified Reference Materials*:

10.28.1 National Research Council Canada (NRCC) SLEW-2 Estuarine Water.

10.28.2 NRCC CASS-4 Coastal Seawater.

## 11. Procedure

11.1 Prior to sample preparation, the following must be completed:

11.1.1 *Acid-Wash Filters*—Using the metal-free tweezers, place the individual polycarbonate filters in the cup. Fill the polypropylene specimen cup with approximately 50 mL reagent water and then add approximately 150 mL of ultra-pure concentrated HCl. Place cover on the cup and let allow the filters to soak for at least one week, preferably one month. Drain acid into waste acid container. Fill the sample cup with filters with reagent water, mix, and then drain off the reagent water. Repeat until the filters are thoroughly rinsed. Store the filters in a container filled with reagent water.

11.1.2 Pre-clean and condition pipette tips for ammonium hydroxide and sodium borohydride.

NOTE 4—Due to the variable contaminant levels found in the pipette tips extraordinary steps need to be taken to insure pipette cleanliness.

11.1.2.1 *Pre-Cleaning Pipette Storage Container*—Fill an acid-washed 125 mL wide mouth fluoropolymer bottle with approximately 20 mL of concentrated ammonium hydroxide, cap and swirl the solution in the bottle to rinse all inner surfaces of bottle and cap. Discard the 20 mL of ammonium hydroxide. Fill the bottle with concentrated ammonium hydroxide, cap and let stand overnight. The following day, prepare fresh 5 % sodium borohydride solution. Discard the concentrated ammonium hydroxide solution. Add approximately 20 mL of 5 % sodium borohydride, cap and then swirl the solution in the bottle to rinse all inner surfaces of bottle and cap. Discard the 20 mL of 5 % sodium borohydride. Fill the bottle with 5 % sodium borohydride, cap loosely and let stand overnight. The bottle is now ready for cleaning and storing pipette tips.

11.1.2.2 Fill the container from 11.1.2.1 with concentrated ammonium hydroxide, cap and let stand 4 h. The container can hold approximately four pipette tips. Each tip should be pre-rinsed at least 10 times. Pre-rinse pipette tips by picking up

[6] $^{6}Li$ is available from ICP-MS standards suppliers.

an aliquot of the concentrated ammonium hydroxide from the bottle and discard. Discard the remaining concentrated ammonium hydroxide from the 125 mL bottle. Place the pre-rinsed pipette tips into the bottle and fill with concentrated ammonium hydroxide, cap and let stand overnight.

11.1.2.3 Prepare 5 % sodium borohydride (see 10.25). Remove the pipette tips from the container and then discard the concentrated ammonium hydroxide. Fill the container with 20 mL of 5 % sodium borohydride, cap and swirl the solution in the bottle to rinse all inner surfaces of bottle and cap. Discard the 20 mL of 5 % sodium borohydride. Fill the container with 5 % sodium borohydride, cap loosely and let stand 4 h. Each tip should be pre-rinsed at least 10 times. Pre-rinse pipette tips by picking up an aliquot of the 5 % sodium borohydride from the bottle and discard. Discard the remaining 5 % sodium borohydride from the 125 mL bottle. Place the pre-rinsed pipette tips into the bottle and fill with 5 % sodium borohydride, cap loosely and let stand overnight.

11.1.2.4 Remove the pipette tips. Discard the 5 % sodium borohydride. Fill the container with 20 mL concentrated ammonium hydroxide, cap and swirl the solution in the bottle to rinse all the inner surfaces of bottle and cap. Discard the 20 mL of concentrated ammonium hydroxide. Place the pipette tips into the container. Fill the container with a solution of approximately 20 % (v/v) ammonium hydroxide. The pipette tips are stored in this solution until needed.

NOTE 5—These pipette tips are used for the additions of both ammonium hydroxide and 5 % sodium borohydride during sample preparation. After the tips are used during sample preparation, do not throw the tips away. The pipette tips should be returned to the storage bottle for later reuse.

11.1.3 Prepare APDC solution (see 10.23).

11.1.4 Prepare fresh 5 % sodium borohydride solution (see 10.24).

11.1.5 Prepare reagent water for method blanks and spike blanks by adding 2mL concentrated ultrapure $HNO_3$ per 1 L reagent water and store in acid-washed fluoropolymer bottles.

11.2 *Prepare Samples*:

11.2.1 *Method Blank (MB)*—Tare an acid-washed 125 mL HDPE bottle on the balance. Pour approximately 100 g (100 to 102 g) of acidified reagent water into the bottle and record the weight.

11.2.2 *Laboratory Duplicate (LD)*—Tare an acid-washed 125 mL HDPE bottle on the balance. Pour approximately 100 g (100 to 102 g) of acidified reagent water into the bottle and record the weight.

11.2.3 *Spike Blank (SB)*—Tare an acid-washed 125 mL HDPE bottle on the balance. Pour approximately 100 g (100 to 102 g) of acidified reagent water into the bottle and record the weight. Add 1.00 mL of the spike solution.

11.2.4 *Samples*—Tare an acid-washed 125 mL HDPE bottle on the balance. Pour approximately 100 g (100 to 102 g) of acidified sample into the bottle and record the weight.

11.2.5 *Matrix Spike (MS)*—Tare an acid-washed 125 mL HDPE bottle on the balance. Pour approximately 100 g (100 to 102 g) of acidified sample into the bottle and record the weight. Add 1.00 mL of the spike solution.

11.2.6 Add 1.0 mL of the 500 µg/mL Fe/Pd, 0.500 µg/mL La/Tb mixed solution to all solutions.

11.2.7 Use a replicate of each sample type suspected of exhibiting different pH characteristics (freshwater, seawater, blanks) to determine the volume of ammonium hydroxide required to adjust the sample pH to between 8 and 10 (target a pH of 8.5). Gently swirl the replicate sample to adequately mix ammonium hydroxide with sample and measure the pH by pipetting a small aliquot of the solution (3 to 10 µL) onto a pH test strip. Add additional ammonium hydroxide, swirl to mix, and measure pH. Continue ammonium hydroxide additions until desired pH is achieved and discard the replicate sample. Once the volume of ammonium hydroxide required to adjust the pH is determined for each sample type, add the appropriate volume of ammonium hydroxide to the samples to be analyzed.

11.2.8 Adjust the pH using ammonium hydroxide. Pre-cleaned clear pipette tips must be used for adding ammonium hydroxide solution. Rinse with fresh ammonium hydroxide by dispensing repeatedly (at least 10 times) before using on actual samples.

11.2.9 Add 1.0 mL of 5 % sodium borohydride solution to each sample using a clear pipette tip and gently swirl to mix.

NOTE 6—Addition of sodium borohydride solution must be done with a clear pipette tip that has been immersed in a 5 % sodium borohydride solution for a minimum of 3 h. A period of several days or longer is preferred to help ensure cleanliness. Ensure the tips are clean by rinsing and dispensing repeatedly with fresh sodium borohydride before using on actual samples.

11.2.10 Add 0.25 mL of 2 % APDC solution to each sample and gently swirl to mix.

11.2.11 Allow samples to stand at least 20 h but not more than 40 h if Zn, Mn, Be, or Al are in the analysis suite, otherwise let samples stand for at least 1 h but not more than 40 h.

11.2.12 *Precipitate Collection by Filtration*:

11.2.12.1 Assemble acid-washed (see 9.1) 25 mm vacuum filtering apparatus.

11.2.12.2 Rinse the filter apparatus (without a filter in place) with a minimum of 200 mL of reagent water.

11.2.12.3 Remove the filter funnel from the filter support. Using fluoropolymer tweezers place a 25 mm diameter, 0.4 µm pore size, acid-washed polycarbonate filter on the filter support. Reassemble the filter funnel to the filter support. Rinse with a minimum of 100 mL of reagent water.

11.2.12.4 Gently swirl the prepared sample to mix and then pour into the filter funnel. Turn on the vacuum pump. Wash down the sides of the sample bottle with a small amount of reagent water and pour into the filter funnel.

11.2.12.5 After all prepared sample has passed through the filter, rinse down the sides of the filter funnel with a small amount reagent water, ensuring the filter has been covered and rinsed with a small amount of reagent water to remove any residual matrix.

11.2.12.6 Stop the vacuum. Remove the filter funnel from the filter support. With tweezers, fold the precipitate-deposited filter (25 mm diameters filters must be folded twice into quarters). Place folded filter into an acid-washed 15 mL centrifuge tube, then cap. Filtrate may be discarded.

11.2.12.7 Reassemble the filtering apparatus without a filter and rinse filter apparatus with a minimum of 150 mL reagent water before placing filter on filter support.

11.2.12.8 Repeat steps 11.2.12.1-11.2.12.7 for each sample.

11.3 *Digestion of the Precipitate*:

11.3.1 Ensure the filter is resting at the bottom of the centrifuge tube.

11.3.2 With the tubes inside of a fume hood, remove the cap of the centrifuge tube and add 0.25 mL concentrated nitric acid. Replace cap.

11.3.3 Before heating the centrifuge tubes, loosen the caps to prevent pressure buildup during digestion. Place tubes in block that has been preset to heat samples at 70°C for at least 30 min but no longer than one hour.

11.3.4 Allow the samples to cool. Add 0.5 mL of hydrogen peroxide to each tube. The caps should be loose to prevent pressure build up during the next digestion step. Place tubes in block that has been preset to heat samples at 70°C for at least 30 min but no longer than one hour.

11.3.5 Let samples cool. Once samples have cooled to room temperature, tighten caps.

11.3.6 Before analysis, depending on instrument sensitivity, add an appropriate volume of internal standard solution and dilute to 10 mL volume with reagent water.

## 12. Quality Control

12.1 *Initial Demonstration of Method Performance*:

12.1.1 *Method Detection Limits (MDL)*—See Test Method D 5673 and Practice D 5847 for guidance.

12.1.2 *Assessing Laboratory Performance*:

12.1.2.1 *Method Blank Used for the Reductive Precipitation Technique (MB and MBRP)*—A method blank is an aliquot of reagent water taken through the preparation method and analyzed using the same sample preparations and analytical method used for test samples.

*(1)* Analyze three method blanks (MB) with each batch (20 unknown samples) to determine background contamination from the method.

*(2)* The average of the three blanks is used for blank subtraction calculations.

12.1.2.2 *Filters*—One filter blank is required for each group of samples filtered.

*(1) Surrogate Spikes*—Recoveries should be > 75 % to ensure sample preparation integrity.

12.1.2.3 *Spike Blank (SB)*—Spike blanks should be two to ten times the MDL or estimated sample concentrations. One SB should be prepared and analyzed for each analytical batch and after five SB samples control limits for each analyte should be determined from the mean percent recovery and the standard deviation of the percent recovery. All upper and lower control limits should be calculated using the following equations:

$$\text{Upper control limit} = X + 3S$$

$$\text{Lower control limit} = X - 3S$$

where:

$S$ = Standard Deviation of the percent recovery, and
$X$ = Mean Value of the percent recovery.

All control limit data should be evaluated and be updated for each analyte on a regular basis. All such data should be kept on file and available for review.

12.1.2.4 *Certified Reference Material (CRM)*—A Certified Reference Material (SLEW (10.28.1) or CASS (10.28.2) is recommended) should be prepared and analyzed at a 2 % frequency. Calculate accuracy as percent recovery. When sufficient internal performance data becomes available (usually a minimum of 20-30 analyses) control limits for the CRM should be determined from the mean percent recovery. All upper and lower control limits should be calculated using the following equations:

$$\text{Upper control limit} = X + 3S$$

$$\text{Lower control limit} = X - 3S$$

where:

$S$ = Standard Deviation of the last 20 measurements, and
$X$ = Mean Value.

12.1.2.5 *Laboratory Duplicate (LD)*—Analyze one duplicate sample for every matrix in a QC batch of 20 samples or less (minimum frequency of 5 %). A control limit of 20 % RPD should not be exceeded for analyte values greater than the RDL. If the control limit is exceeded, the reason for the out of control situation should be corrected and any samples analyzed during the out of control condition reanalyzed.

12.1.2.6 *Matrix Spike (MS)*—The MS results are used to determine whether the sample matrix contributes bias to the analytical results. Matrix spike and spike blank concentrations are dependent on the expected sample concentrations and project requirements. The concentration of target analyte(s) added to the spike blank should be the same as the concentration of target analyte(s) added to the matrix spike. Matrix spike and spike blanks should be two to ten times the MDL or estimated sample concentrations. Analyze one duplicate sample for every matrix in a QC batch of 20 samples or less (minimum frequency of 5 %). After five MS samples control limits for each analyte in the MS should be determined from the mean percent recovery and the standard deviation of the percent recovery. All upper and lower control limits should be calculated using the following equations:

$$\text{Upper control limit} = X + 3S$$

$$\text{Lower control limit} = X - 3S$$

where:

$S$ = Standard Deviation of the percent recovery, and
$X$ = Mean Value of the percent recovery.

## 13. Keywords

13.1 ambient; brackish; brine; elements; estuarine; inductively coupled plasma-mass spectrometry; pre-concentration; seawater; water

# ANNEX

## (Mandatory Information)

## A1. TABLES

**TABLE A1.1 U.S. EPA National Recommended Water Quality Criteria[A]**

| Element | Freshwater | | Seawater | | Human Health[B] for Consumption of: | |
|---|---|---|---|---|---|---|
| | CMC[C] (ng/mL) | CCC[D] (ng/mL) | CMC[C] (ng/mL) | CCC[D] (ng/mL) | Water + Organisms (ng/mL) | Organisms Only (ng/mL) |
| Antimony | | | | | 14 | 4300 |
| Arsenic | 360 | 190 | 69 | 36 | 0.018 | 0.14 |
| Beryllium | | | | | | |
| Cadmium | 3.7 | 1 | 42 | 9.3 | | |
| Chromium III | 550 | 180 | | | | |
| Chromium VI | 15 | 10 | 1100 | 50 | | |
| Copper | 17 | 11 | 2.4 | 2.4 | | |
| Lead | 65 | 2.5 | 210 | 8.1 | | |
| Mercury | 2.1 | 0.012 | 1.8 | 0.025 | 0.14 | 0.15 |
| Nickel | 1400 | 160 | 74 | 8.2 | 610 | 4600 |
| Selenium | 20 | 5 | 290 | 71 | | |
| Silver | 3.4 | | 1.9 | | | |
| Thallium | | | | | 1.7 | 6.3 |
| Zinc | 110 | 100 | 90 | 81 | | |

[A] U.S. Federal Register 40 CFR 131.36, Minimum Requirements for Water Quality Standards Submission, Ch. I (7-1-00 Edition).
[B] $10^{-6}$ risk for carcinogens.
[C] The Criteria Maximum Concentration (CMC) is an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed briefly without resulting in an unacceptable effect.
[D] The Criterion Continuous Concentration (CCC) is an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed indefinitely without resulting in an unacceptable effect.

**TABLE A1.2 List of Analytes Amenable to Analysis Using Method 1640[A]: Lowest Water Quality Criterion for Each Metal Species, Method Detection Limits, Minimum Levels, and Recommended Analytical Masses 1,2,3**

| Element | Lowest Ambient Water Quality Criterion[B] (ng/mL) | Method Detection Limit[C] (MDL) (ng/mL) | Minimum Level[D] (ML) (ng/mL) |
|---|---|---|---|
| Arsenic[E] | 0.018 | 0.0018 | TBD |
| Cadmium | 0.37 | 0.0024 | 0.01 |
| Copper | 2.5 | 0.024 | 0.1 |
| Lead | 0.54 | 0.0081 | 0.02 |
| Nickel | 8.2 | 0.029 | 0.1 |
| Silver | 0.32 | 0.032 | TBD |
| Zinc | 32 | 0.32 | TBD |

[A] Method 1640 Determination of Trace Elements in Water by Preconcentration and Inductively Coupled Plasma-Mass Spectrometry, U.S. Environmental Protection Agency, Office of Water, Office of Science and Technology, Engineering and Analysis Division (4303), 401 M Street SW, Washington, DC 20460, (April 1997).
[B] Lowest of the freshwater, marine, or human health WQC at 40 CFR Part 131 (57 FR 60848 for human health criteria and 60 FR 22228 for aquatic criteria). Hardness-dependent freshwater aquatic life criteria also calculated to reflect a hardness of 25 mg/L $CaCO_3$, and all aquatic life criteria adjusted to reflect dissolved levels in accordance with equations provided in 60 FR 22228. Hardness-dependent dissolved criteria conversion factors for Cd and Pb also calculated at a hardness of 25 mg/L per 60 FR 22228.
[C] Method Detection Limit as determined by 40 CFR Part 136, Appendix B.
[D] Minimum Level (ML) calculated by multiplying laboratory-determined MDL by 3.18 and rounding result to nearest multiple of 1, 2, 5, 10, etc. in accordance with procedures used by EAD and described in the EPA Draft National Guidance for the Permitting, Monitoring, and Enforcement of Water Quality-Based Effluent Limitations Set Below Analytical Detection/Quantitation Levels, March 22, 1994.
[E] Target MDL based on objective of 1/10 lowest WQC.

**TABLE A1.3 Elements, Recommended Masses, Method Detection Limits and Recommended Quality Control Spiking Levels[A]**

| Element | Mass (m/z) | MDL (ng/mL) | Spiking Level (ng/mL) |
|---|---|---|---|
| Anitmony | 123 | 0.01 | 0.3 |
| Arsenic | 75 | 0.03 | 2 |
| Beryllium | 9 | 0.015 | 0.1 |
| Cadmium | 114 | 0.005 | 0.3 |
| Chromium | 52 | 0.03 | 1 |
| Cobalt | 59 | 0.004 | 0.1 |
| Copper | 65 | 0.02 | 2 |
| Lead | 208 | 0.005 | 0.3 |
| Nickel | 60 | 0.05 | 2 |
| Selenium | 82 | 0.15 | 1 |
| Silver | 107 | 0.06 | 0.5 |
| Thallium | 205 | 0.005 | 0.1 |
| Vanadium | 51 | 0.02 | 4 |
| Zinc | 66 | 0.15 | 4 |

[A] Method Detection Limit Data and Recommended Spiking Levels using a Thermo Elemental PlasmaQuad 2 ICP-MS. Data supplied courtesy of King County Environmental Laboratory, 322 West Ewing Street, Seattle, WA 98119.