



Designation: D6800 – 18

# Standard Practice for Preparation of Water Samples Using Reductive Precipitation Preconcentration Technique for ICP-MS Analysis of Trace Metals<sup>1</sup>

This standard is issued under the fixed designation D6800; 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 ( $\epsilon$ ) 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 [D5673](#)). 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 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 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.5 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the*

*Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

## 2. Referenced Documents

### 2.1 ASTM Standards:<sup>2</sup>

- [D1129 Terminology Relating to Water](#)
- [D1193 Specification for Reagent Water](#)
- [D5673 Test Method for Elements in Water by Inductively Coupled Plasma—Mass Spectrometry](#)
- [D5810 Guide for Spiking into Aqueous Samples](#)
- [D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis](#)

### 2.2 Other Documents:

- [U.S. Federal Register 40 CFR 131.36, Minimum Requirements for Water Quality Standards Submission, Ch. I \(7-1-00 Edition\)](#)<sup>3</sup>
- [U.S. EPA Method 1640, Determination of Trace Elements in Water by Preconcentration and Inductively Coupled Plasma-Mass Spectrometry \(1997\)](#)<sup>4</sup>
- [U.S. EPA Method 1669, Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels](#)<sup>4</sup>

## 3. Terminology

### 3.1 Definitions:

3.1.1 For definitions of terms used in this standard, refer to Terminology [D1129](#).

### 3.2 Definitions of Terms Specific to This Standard:

3.2.1 *continuing calibration blank, n*—a solution containing no analytes (of interest) which is used to verify blank response and freedom from carryover.

<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

<sup>3</sup> Available from DLA Document Services, Building 4/D, 700 Robbins Ave., Philadelphia, PA 19111-5094, <http://quicksearch.dla.mil>.

<sup>4</sup> Available from United States Environmental Protection Agency (EPA), William Jefferson Clinton Bldg., 1200 Pennsylvania Ave., NW, Washington, DC 20460, <http://www.epa.gov>.

<sup>1</sup> 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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\*A Summary of Changes section appears at the end of this standard

3.2.2 *continuing calibration verification, n*—a solution (or set of solutions) of known concentration used to verify freedom from excessive instrumental drift; the concentration is to cover the range of calibration curve.

3.2.3 *intermediate stock-standard solution, n*—a diluted solution prepared from one or more of the stock-standard solutions.

3.2.4 *laboratory control sample (LCS), n*—an aliquot of solution with known concentrations of method analytes.

3.2.4.1 *Discussion*—The LCS 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.

3.2.5 *laboratory duplicate (LD), n*—a second sample aliquot that is analyzed using the same sample preparation, analytical method and QA/QC procedure used for test samples.

3.2.5.1 *Discussion*—The purpose of the LD is to determine whether method performance is within accepted control limits.

3.2.6 *matrix spike (MS), n*—a second sample aliquot to which known concentrations of target analyte(s) are added in the laboratory and which are analyzed using the same sample preparation and analytical method used for test samples.

3.2.6.1 *Discussion*—The purpose of the MS 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](#).

3.2.7 *method blank (MB), n*—suitable reagent-water aliquots that are analyzed using the same sample preparation, analytical method, and QA/QC procedure used for test samples.

3.2.7.1 *Discussion*—The MB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents or apparatus.

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

3.2.9 *reagent water, n*—standard laboratory water purified to meet Specification [D1193](#) Type I or better.

3.2.10 *reporting detection limit (RDL), n*—the lowest concentration at which an analyte can be reliably quantified.

3.2.10.1 *Discussion*—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

3.2.11 *spiked blank (SB), n*—a reagent-water aliquot to which known concentrations of analyte(s) are added in the laboratory, using the same solution as used to prepare the matrix spike.

3.2.11.1 *Discussion*—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: (1) spike-solution and spiking-technique problems, and (2) matrix interferences. Recommended spike levels are listed in Annex, [Table A1.3](#).

3.2.12 *stock-standard solution, n*—a concentrated solution (containing one or more analytes), obtained as a certified solution from a reputable source.

3.2.13 *surrogate spikes, n*—lanthanum and terbium are added at a concentration of 5 ng/mL (each) in the initial 100-mL sample.

3.2.13.1 *Discussion*—The surrogate spikes are then preconcentrated to approximately 50 ng/mL in the final 10-mL sample without 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.

3.2.14 *total recoverable, n*—the concentration of analyte determined on a whole, unfiltered water or solid sample following vigorous digestion as described in U.S. 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 0.4 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 µm 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 D5673. 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  $^{107}\text{Ag}$  and  $^{109}\text{Ag}$  due to the formation of the  $\text{PdH}^+$  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 safety data sheets (SDS) 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  $\text{HNO}_3$  to 500-mL sample). Samples are kept at room temperature in plastic bins. Use the minimum amount of acid necessary to reduce the sample  $\text{pH} < 2$ . Excess acid will complicate the  $\text{pH}$  adjustment during the reductive precipitation reaction.

8.3 Use only acid washed sample containers prepared as described in U.S. 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  $\text{pH} < 2$  (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  $\text{HNO}_3$  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  $\text{pH} < 2$  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 0.4  $\mu\text{m}$  membrane filter or equivalent. Acidify the filtrate with ultra pure nitric acid to  $\text{pH} < 2$  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 ( $\mu\text{L}$ ) 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- $\mu$ m pore size.

10.1.6.2 47-mm diameter, 0.4- $\mu$ m pore size.

10.1.6.3 47-mm diameter, 0.2- $\mu$ m 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 **D1193**).

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<sub>3</sub> 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 % <sup>6</sup>Li*.<sup>5</sup>

10.12 *<sup>6</sup>Li Internal Standard Solution*—Dissolve 0.6312 g lithium carbonate 95 atom % enriched <sup>6</sup>Li in 100 mL of 2 % nitric acid.

10.13 *Gallium 1000  $\mu$ g/mL Stock Standard ICP-MS Grade Solution*.

10.14 *Indium 1000  $\mu$ g/mL Stock Standard ICP-MS Grade Solution*.

10.15 *Iron 1000  $\mu$ g/mL Stock Standard ICP-MS Grade Solution*.

10.16 *Lutetium 1000  $\mu$ g/mL Stock Standard ICP-MS Grade Solution*.

10.17 *Lanthanum 1000  $\mu$ g/mL Stock Standard ICP-MS Grade Solution*.

10.18 *Palladium 1000  $\mu$ g/mL Stock Standard ICP-MS Grade Solution*.

10.19 *Scandium 1000  $\mu$ g/mL Stock Standard ICP-MS Grade Solution*.

10.20 *Terbium 1000  $\mu$ g/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  $\mu$ g/mL ICP-MS grade stock standard.

10.23 *Reductive Precipitation Solution*—Prepare an iron/palladium/lanthanum/terbium mixed solution. Prepare 500  $\mu$ g/mL Fe, Pd, 0.500  $\mu$ g/mL La, Tb in 5 % HCl, 1 % HNO<sub>3</sub>. 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- $\mu$ m 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- $\mu$ m 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.

<sup>5</sup> <sup>6</sup>Li is available from ICP-MS standards suppliers.