

STANDARD OPERATING PROCEDURE

For USEPA MODIFIED METHOD 200.2

SAMPLE PREPARATION PROCEDURE FOR SPECTROCHEMICAL DETERMINATION OF TOTAL RECOVERABLE ELEMENTS

SOP #: EPA 200.2

REVISION #: 2.0

DATE: October 2022

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LIST OF REVISIONS

Rev. #	Date	Description of Revision	Page #
0	November 2000	None	
0	February 2007	Replaced Old DEP Logo with State Seal	
1.0	January 2011	Converting method from using a hot plate to using an Environmental Express Hot Block™	Throughout document
1.1	September 2017	Section 2.1 – Clarified refluxing until volume reduced to 10 - 15 mL Section 6.5 – Clarified digestion tube specifications Section 6.7 – Clarified filter specifications Section 11.1.2 – Clarified final volume and monitoring of solution temperature Section 11.3.7 – Clarified diluent Section 11.3.7.1 – Added dilution for ICP-MS analyses	
1.2	October 2018	Sections 7.4, 7.6, and 7.7 – Acid preparation steps refer to Bench Sheet for acid preparation. New Acid Standards (1+1) HNO ₃ , (1+1) HCl, (1+4) HCl Preparation Bench Sheet for EPA 200.2 Solid Sample Preparation Digestion Sheet for Aqueous Sample Preparation Digestion Sheet for Solid Sample Preparation Section 11.3.7.1 – Changed 20 mL to 10 mL of digestate.	
1.3	March 2020	U.S. EPA 2019 Audit Corrective Actions: Section 6.6 – Digital Thermometer added Section 6.8 – Description of digestion tubes clarified	
2.0	October 2022	Section 1.1 – Added full list of analytes that can be analyzed by either EPA Method 200.7 or EPA Method 200.8 Section 1.2 – Added EPA Method 200.8 Section 3.0 – Removed irrelevant definitions Section 9.0 – Clarified frequency of quality control samples Section 11.1.2 – Updated HNO ₃ and HCl matrix for the reduced volume digestion process. Section 11.2 – Updated digestion procedure for solid samples to better follow EPA 200.2 reference method.	



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NOT APPLICABLE



1.0 SCOPE AND APPLICATION

- 1.1 This method provides sample preparation procedures for the determination of total recoverable analytes in groundwaters, surface waters, drinking waters, wastewaters, and, with the exception of silica, in solid type samples such as sediments, sludges, and soils. Aqueous samples containing suspended or particulate material $\geq 1\%$ (w/v) should be extracted as a high solid aqueous sample. This method is applicable to the following analytes:

Analyte	Symbol	Chemical Abstract Services Registry Number (CASRN)
Aluminum	Al	7429-90-5
Antimony	Sb	7440-36-0
Arsenic	As	7440-38-2
Boron	B	7440-42-8
Barium	Ba	7440-39-3
Beryllium	Be	7440-41-7
Cadmium	Cd	7440-43-9
Calcium	Ca	7440-70-2
Chromium	Cr	7440-47-3
Cobalt	Co	7440-48-4
Copper	Cu	7440-50-8
Iron	Fe	7439-89-6
Lead	Pb	7439-92-1
Lithium	Li	7439-93-2
Magnesium	Mg	7439-95-4
Manganese	Mn	7439-96-5
Mercury	Hg	7439-97-6
Molybdenum	Mo	7439-98-7
Nickel	Ni	7440-02-0
Phosphorus	P	7723-14-0
Potassium	K	7440-09-7
Selenium	Se	7782-49-2
Silica ^a	SiO ₂	7631-86-9
Silver	Ag	7440-22-4
Sodium	Na	7440-23-5
Strontium	Sr	7440-24-6
Thallium	Tl	7440-28-0
Thorium	Th	7440-29-1
Tin	Sn	7440-31-5
Uranium	U	7440-61-1
Vanadium	V	7440-62-2
Zinc	Zn	7440-66-6

^a This method is not suitable for the determination of silica in solids.

- 1.2 Samples prepared by this method can be analyzed by EPA Method 200.7, Determination of Metals and Trace Elements by Inductively Coupled Plasma-Atomic Emission Spectrometry and EPA Method 200.8, Determination of Trace Elements by Inductively Coupled Plasma-Mass Spectrometry.
- 1.3 For reference where this method is approved for use in compliance monitoring programs [e.g., Clean Water Act (NPDES) or Safe Drinking Water Act (SDWA)], consult both the appropriate



sections of the Code of Federal Regulations (40 CFR Part 136 Table 1B for NPDES, and Part 141 & 141.23 for drinking water) and the latest Federal Register announcements.

- 1.4 For the analysis of wastewater samples containing silver (Ag) concentrations > 0.1 mg/L, dilution must be prepared until the analysis solution contains < 0.1 mg/L. The extraction of solid samples containing concentrations of silver > 50 mg/kg should be treated in a similar manner. Also, the extraction of tin (Sn) from solid samples should be prepared again using aliquots < 1g when determined sample concentrations exceed 1%.
- 1.5 This method will solubilize and hold in solution only minimal concentrations of barium (Ba) in the presence of free sulfate. For the analysis of barium in samples having varied and unknown concentrations of sulfate, analysis should be completed as soon as possible after sample preparation.
- 1.6 When using this method for the determination of boron in aqueous samples, only plastic or quartz labware should be used from the time of sample collection to the completion of the analysis. For solid samples, only quartz or PTFE beakers should be used during acid extraction with immediate transfer of an extract aliquot to a plastic centrifuge tube following dilution of the extract to volume. When possible, borosilicate glass should be avoided to prevent contamination of these analytes.
- 1.7 This method is not suitable for the determination of volatile low boiling point organo-mercury compounds.

2.0 SUMMARY OF METHOD

- 2.1 Solid and aqueous samples are prepared in a similar manner for analysis. Nitric and hydrochloric acids are dispensed into a polypropylene Environmental Express digestion vessel containing an accurately weighed or measured, well-mixed, homogeneous aqueous or solid sample. Aqueous samples are first reduced in volume by gentle heating. Then, metals and toxic elements are extracted from either solid samples or the undissolved portion of aqueous samples by covering the vessel with a reflux cap and refluxing the sample in the dilute acid mixture until reduced to 10 to 15 mL.
- 2.2 After extraction, the solubilized analytes are diluted to specified volumes with ASTM Type I reagent water and either filtered, centrifuged, or allowed to settle overnight before analysis. Diluted samples are to be analyzed by the appropriate mass and/or atomic spectrometry methods as soon as possible after preparation.

3.0 DEFINITIONS

- 3.1 **Solid Sample** – For the purpose of this method, a sample taken from material classified as either soil, sediment, or sludge.
- 3.2 **Water Sample** – For the purpose of this method, a sample taken from one of the following sources: drinking, surface, ground, storm runoff, or industrial or domestic wastewater.
- 3.3 **Total Recoverable Analyte** – The concentration of analyte determined to be either in a solid sample or an unfiltered aqueous sample following treatment by refluxing with hot dilute mineral acid.
- 3.4 **Laboratory Reagent Blank (LRB)** – An aliquot of reagent water that is treated exactly as a sample. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, reagents, or apparatus.



- 3.5 **Laboratory Fortified Blank (LFB)** – An aliquot of LRB to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.
- 3.6 **Laboratory Duplicates (DUP)** – Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses for LD1 and LD2 indicate precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.
- 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.
- 3.8 **Minimum Reporting Level (MRL) Check** – An aliquot of LRB spiked at the lowest analyte concentration that can be quantitated with acceptable accuracy and precision under stated analytical conditions.

4.0 INTERFERENCES

- 4.1 In sample preparation, contamination is of prime concern. The work area, including bench top and fume hood, should be periodically cleaned to eliminate environmental contamination.
- 4.2 Chemical interferences are matrix dependent and cannot be documented prior to analysis.
- 4.3 Interferences are discussed in the reference analytical methods.

5.0 SAFETY

- 5.1 Acidification of samples should be done in a fume hood.
- 5.2 Safety Data Sheets for all chemical reagents are available to and understood by all personnel using this method.
- 5.3 Concentrated nitric acid and concentrated hydrochloric acid are moderately toxic and extremely irritating to skin and mucus membranes; if eye or skin contact occurs, flush with large volumes of water.
- 5.4 Always wear safety glasses or a shield for eye protection and protective clothing.

6.0 EQUIPMENT AND SUPPLIES

- 6.1 Analytical balance, with capability to measure to 0.0001 g.
- 6.2 Fume hood.
- 6.3 Hot Block™ – Adjustable and able to maintain a temperature of 95°C (Environmental Express).
- 6.4 Reflux cap, 30 mm #SC506 (Environmental Express).



- 6.5 Polypropylene digestion tubes with screw caps (68 mL) (Environmental Express), Cat # SC475 or similar. All digestion tubes must come with a by lot Certificate of Analysis which certifies both the volume markings and the background elemental concentrations.
- 6.6 Digital Thermometer and PTFE Holder: Environmental Express # SC984, Hi-Temperature Probe with PTFE Holder, - 50 to 250°C
- Digital Thermometer only: Environmental Express # SC980C, Hi-Temperature Probe only
- Digital Thermometer Holder only: Environmental Express # SC985C, Thermometer Adaptor/PTFE Holder for # SC985.
- 6.7 Graduated cylinder or equivalent volume measuring device – 100 mL.
- 6.8 Filtermate – Cat # SC0401 – Environmental Express or similar. All filters must come with a by lot Certificate of Analysis which certifies the background elemental concentrations and volume accuracy.
- 6.9 Calibrated pipettes.
- 6.10 Wash bottle.

7.0 REAGENTS

- 7.1 Reagents may contain elemental impurities which might affect analytical data. High-purity reagents should be used whenever possible. All acids used for this method must be of ultra-high purity grade.
- 7.2 Hydrochloric acid (HCl), concentrated.
- 7.2.1 Hydrochloric acid (1:4) - Add 2 mL of *conc.* HCl to 4 mL reagent water and dilute to 10 mL.
- 7.3 Nitric acid (HNO₃), concentrated.
- 7.3.1 Nitric acid (1:1) - Add 5 mL of *conc.* HNO₃ to 4 mL reagent water and dilute to 10 mL.
- 7.4 30% Hydrogen peroxide (H₂O₂).
- 7.5 Reagent Water, ASTM Type I, is required for all sample preparation and dilutions.
- 7.6 Refer to the appropriate analytical method for the preparation of standard stock solutions, calibration standards, and quality control solutions.

8.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

- 8.1 Plastic and glass containers are both suitable.
- 8.2 All sample containers must be free of contamination.
- 8.3 Aqueous samples must be acidified to a pH of < 2 with HNO₃. Following acidification, the sample must be mixed and held for 16 hours. Normally, 3 mL of (1+1) nitric acid per liter of sample is sufficient for most ambient and drinking water samples. Preservation may be done at the time of sample collection or upon receipt in the laboratory, preferably within two weeks of collection. The



pH of all aqueous samples must be tested immediately prior to withdrawing an aliquot for processing to ensure the sample has been properly preserved. If for some reason, such as high alkalinity, the sample pH is verified to be > 2 , more acid must be added, and the sample held for **sixteen hours** until verified to be at a $\text{pH} < 2$.

- 8.4 All labware used should be washed with a detergent solution, rinsed with tap water, soaked for 4 hours or more in 20% (v/v) nitric acid or a mixture of dilute nitric and hydrochloric acid (1+2+9) and rinsed with reagent water.
- 8.5 If properly acid-preserved, aqueous samples can be held up to 6 months before analysis.
- 8.6 Solid samples require no preservation prior to analysis other than storage at 4°C . There is no established holding time limitation for solid samples.

9.0 QUALITY CONTROL

- 9.1 For every 20 field samples processed, a laboratory reagent blank (LRB) and a laboratory fortified blank (LFB) must be carried throughout the entire sample preparation.
- 9.2 Minimum reporting level (MRL) check standards are run with each batch of samples.
- 9.3 A duplicate sample (DUP) and a spiked duplicate sample (LFM) are run with every 10 field samples.
- 9.4 All quality control data must be maintained and added to the final analysis report to be available for reference or inspection.

10.0 CALIBRATION AND STANDARDIZATION

- 10.1 Not applicable. Follow instructions given in the analytical method selected.

11.0 PROCEDURE

- 11.1 Aqueous Sample Preparation – Total Recoverable Analytes.
 - 11.1.1 Transfer a 50 mL representative aliquot of the well-mixed, acid-preserved sample to a 68-mL Environmental Express polypropylene digestion vessel (tube). When necessary, smaller sample aliquot volumes may be used.
 - 11.1.2 Add 0.5 mL *conc.* HNO_3 acid and 0.25 mL *conc.* HCl acid to the tube containing the measured volume of sample. Place the tube in the Hot Block™. The Hot Block™ is located in a fume hood and it should be previously adjusted to provide evaporation at a temperature of approximately, but no higher than, 85°C . However, the tube should be covered with a reflux cap to prevent sample contamination from the fume hood environment. Once the tube is covered with a reflux cap, the temperature of the sample will rise to approximately 95°C .

Note: For proper heating, adjust the temperature control of the Hot Block™ such that a covered sample tube containing 50 mL of 2% acid placed in the Hot Block can be maintained at a temperature approximately but no higher than 95°C . Record on Digestion Sheet the time and temperature of the blank solution at intervals during the digestion. If a metal thermometer is used, then use reagent water instead of the acid blank solution to measure the temperature throughout the digestion.



- 11.1.3 Reduce the volume of the sample aliquot to 10 mL to 15 mL by gentle heating at 95°C (covered). DO NOT BOIL. This step takes about 5 to 7 hours for a 50-mL aliquot with the rate of evaporation rapidly increasing as the sample volume approaches 20 mL.
- 11.1.4 Remove the samples from the Hot Block™ and allow to cool. After cooling, dilute to 50 mL with reagent water.
- 11.1.5 Allow any undissolved material to settle overnight or centrifuge a portion of the prepared sample until clear. (If after centrifuging or standing overnight the sample contains suspended solids that would clog the nebulizer, a portion of the sample may be filtered for their removal prior to analysis. However, care should be exercised to avoid potential contamination from filtration.)
- 11.1.5.1 Use the Filtermate for sample filtration. This step should be performed slowly with little pressure placed on the plunger. Applying pressure to the plunger may cause “blow through” and allow sediment to pass through the filter into the digestate. If excessive backpressure occurs, stop filtration, and allow sediments to settle out.
- 11.1.6 MRL Check Standards, LRB, LFB, DUP, and LFM are treated in the same manner as the samples. Sections 9.1 – 9.3 specify the frequency needed for each quality control element depending on the number of field samples.
- 11.1.7 The sample is now ready for analysis by inductively coupled plasma-atomic emission spectrometry (Section 1.2).
- 11.1.8 To ready the sample for analyses by inductively coupled plasma-mass spectrometry (Section 1.2), adjust the chloride concentration by pipetting 20 mL of the prepared solution into a 50 mL volumetric flask, dilute to volume with reagent water and mix. (If the dissolved solids in this solution are > 0.2%, additional dilution may be required to prevent clogging of the sampler and/or skimmer cones. Internal standards are added at the time of analysis.) The sample is now ready for analysis by inductively coupled plasma-mass spectrometry.
- 11.1.9 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 Solid Sample Preparation – Total Recoverable Analytes
- 11.2.1 For the determination of total recoverable analytes in solid samples, mix the sample thoroughly and transfer a portion (> 20 g) to tared weighing dish, weigh the sample, and record the wet weight. (For samples with < 35% moisture, a 20-g portion is sufficient. For samples with moisture > 35%, a larger aliquot 50-100 g is required.) Dry the sample to a constant weight at 60°C and record the dry weight for calculation of percent solids (Section 12.1). The sample is dried at 60°C to prevent the loss of mercury and other possible volatile metallic compounds, to facilitate sieving, and to ready the sample for grinding.
- 11.2.2 To achieve homogeneity, sieve the dried sample using a 5-mesh polypropylene sieve and grind in a mortar and pestle. (The sieve, mortar and pestle should be cleaned between samples.) From the dried ground material, weigh accurately a representative 0.5 ± 0.01 g aliquot of the sample into a 68-mL digestion tube.



- 11.2.3 Add 2 mL of 1:1 HNO₃ and 5 mL of 1:4 HCl to the digestion tube. Cover tube with a reflux cap. Place the tube in the Hot Block™ previously adjusted to provide a gentle reflux temperature of approximately 95°C, for reflux extraction of the analytes.

Note: For proper heating, adjust the temperature control of the Hot Block™ such that an uncovered digestion tube containing 50 mL of reagent water placed in the Hot Block™ can be maintained at a temperature approximately but no higher than 85°C. Once the tube is covered with a reflux cap, the temperature of the water will rise to approximately 95°C

- 11.2.4 Heat the sample and gently reflux for 30 minutes. Very slight boiling may occur; however, vigorous boiling must be avoided.

- 11.2.5 If the sample is suspected of having a high concentration of organic compounds, the Hot Block™ manufacturer recommends the step described in Section 11.2.5.1, which is not included in EPA Method 200.2. The step is optional and is only warranted if the sample has high concentrations of organic compounds. Otherwise, continue onto Section 11.2.6.

11.2.5.1 Add 2 mL of a 30% H₂O₂ to the well-cooled sample. Allow the exothermic reaction to occur (approximately 10 minutes) and place the sample back in the Hot Block™ at a temperature of 10°C LESS than the original set point for an additional 30 minutes. The reaction with the H₂O₂ raises the sample temperature and boiling should not occur if the temperature of the Hot Block™ is lowered. The H₂O₂ helps aid in the breakdown of high organic compounds in the sample thus creating a more complete digestion.

- 11.2.6 Remove samples from the Hot Block™ and allow them to cool completely. Bring the volume to 50 mL with Type I Reagent Water.

- 11.2.7 Allow any undissolved material to settle overnight or centrifuge a portion of the prepared sample until clear. (If after centrifuging or standing overnight the sample contains suspended solids that would clog the nebulizer, a portion of the sample may be filtered for their removal prior to analysis. However, care should be exercised to avoid potential contamination from filtration.)

11.2.7.1 Use the Filtermate for sample filtration. This step should be performed slowly with little pressure placed on the plunger. Applying pressure to the plunger may cause “blow through” and allow sediment to pass through the filter into the digestate. If excessive backpressure occurs, stop filtration, and allow sediments to settle out.

- 11.2.8 The sample is now ready for analysis by inductively coupled plasma-atomic emission spectrometry (Section 1.2).

- 11.2.9 To ready the sample for analyses by inductively coupled plasma-mass spectrometry (Section 1.2), adjust the chloride concentration by pipetting 10 mL of the prepared solution into a 50-mL volumetric flask, dilute to volume with reagent water and mix. (If the dissolved solids in this solution are > 0.2%, additional dilution may be required to prevent clogging of the sampler and/or skimmer cones. Internal standards are added at the time of analysis.) The sample is now ready for analysis by inductively coupled plasma-mass spectrometry.



11.2.10 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.

11.3 Sample Analysis – Use an analytical method listed in Section 1.2.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 To report percent solids in solid samples (Section 11.2), calculate as follows:

$$\% \text{ Solids (S)} = \frac{DW}{WW} \times 100$$

where:

DW = Sample weight (g) dried at 60°C

WW = Sample weight (g) before drying

Note: If the data user or program requires that the reported percent solids be determined by drying at 105°C, repeat the procedure given in Section 11.2.1 using a separate portion (> 20 g) of the sample and dry to constant weight at 103-105°C.

12.2 Calculation and treatment of determined analyte data are discussed in analytical methods listed in Section 1.2.

13.0 METHOD PERFORMANCE

13.1 Not applicable. Available data included in analytical methods listed in Section 1.2.

14.0 POLLUTION PREVENTION

14.1 The quantity of chemicals purchased should be based on expected usage during its shelf life.

14.2 Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

14.1 Refer to the WES Environmental Management System (EMS) policy and SOPs regarding pollution prevention.

15.0 WASTE MANAGEMENT

15.1 WES laboratories fully comply with all applicable federal, state, and local environmental regulations. WES is also committed to protecting the air, water, and land by minimizing and controlling all chemical releases from fume hoods, biological safety cabinets, and bench operations. Refer to the WES EMS policy and SOPs regarding waste management.

15.2 All acid waste is collected in sealed waste containers. Once the waste containers reach capacity, they are transferred to the WES hazardous waste storage room where they are emptied into a waste inorganic chemical drum. Within 180-days of waste accumulation, the waste drum is transported off the premises by a licensed hazardous waste management contractor. Under the WES EMS, a chemical inventory database has been developed to track purchases and use of acids and other hazardous materials, and the waste generated by the use of these chemicals.



16.0 REFERENCES

- 16.1 U.S. Environmental Protection Agency. Method 200.2 – *Sample Preparation Procedure for Spectrochemical Determination of Total Recoverable Elements*, Revision 2.8 EMMC Version, 1994.
- 16.2 Environmental Express Hot Block™ 200 Digestion Systems Operation & Instruction Manual, August 2018.

17.0 TABLES AND VALIDATION DATA

Not applicable.