<u>**Georgia Department of Natural Resources**</u>
Environmental Protection Division Laboratory

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Laboratory Manager Approval: Shene A. Jones / 08/19/2021
QA Manager Approval: Jeffrey Moore / 08/19/2021

EPA 200.2 Sample Preparation Procedure for Spectrochemical Determination of Total Recoverable Elements

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1 Scope and Application

This method is used for preparation of samples for the determination of total recoverable metals in groundwaters, surface waters, drinking waters, wastewaters, soils, sludges, and sediments. Samples prepared by this procedure are analyzed by EPA-200.8 and EPA-200.7.

Compound	CAS No.
Aluminum	7429-90-5
Antimony	7440-36-0
Arsenic	7440-38-2
Barium	7440-39-3
Beryllium	7440-41-7
Cadmium	7440-43-9
Calcium	7440-70-2
Chromium	7440-47-3
Cobalt	7440-48-4
Copper	7440-50-8
Iron	7439-89-6
Magnesium	7439-95-4
Manganese	7439-96-5
Molybdenum	7439-98-7
Nickel	7440-02-0
Potassium	7440-09-7
Selenium	7782-49-2
Silver	7440-22-4
Sodium	7440-23-5
Strontium	7440-24-6
Thallium	7440-28-0
Tin	7440-31-5
Vanadium	7440-62-2
Zinc	7440-66

1.2 Restricted Procedure
This procedure is restricted to use by an analyst experienced in the handling of hazardous materials. Additionally, the analyst must complete the requirements of the GaEPD Initial Demonstration of Analyst Proficiency prior to the analysis of actual samples. Analysts are further warned that performance of this analysis involves the use of potentially hazardous chemicals; refer to the GaEPD Chemical Hygiene Plan for additional information regarding chemicals required by this method.

2 Definitions

2.1 Refer to Sections 3 and 4 of the Georgia EPD Laboratory Quality Assurance Manual for Quality Control Definitions. (See SOP reference 13.7)

2.2 MDL standard (ML) = Method Detection Limit Spike Standard (MDL_{spike}): A standard equal to concentration of lowest calibration curve standard. An MDL_{spike} is analyzed with every batch of samples and is carried through the same procedure as the samples being analyzed.

2.3 Dissolved Samples: Samples filtered through a 0.45µm filter before analysis.

3 Interferences

3.1 Contamination is the prime concern. The work area (including counters and hoods) is cleaned weekly to eliminate sources of contamination. All reagents and apparatus must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks.

3.1.1 Glassware must be scrupulously cleaned. Any glassware used must be triple washed in reagent grade or equivalent 1+1 nitric acid followed by a triple rinse in 18 MΩ water. After washing, all glassware is dried in a clean environment then covered with parafilm and stored in a closed cabinet until used. Virgin plasticware (HDPE) is used as much as possible and discarded after use.

3.1.2 The use of Ultra purity reagents helps to minimize interference problems. Ultra-pure and Trace acids are used in the preparation of samples for ICP-MS analysis. While reagent grade acids can be used for all other metal analysis, EPD lab prefers using Ultra-pure or Trace acids for all metals analysis because some sample digestates are analyzed by both ICP-EOS and ICP-MS

4 Safety

Refer to Laboratory Chemical Hygiene Plan, online revision.

5 Apparatus and Equipment

5.1 Appropriately sized new pre-washed HDPE sample bottle with screw caps for sample collection.
5.2 New 50 ml flat bottom HDPE graduated tubes with screw caps for digesting sample in.
5.3 Air displacement pipettes of capable of delivering volumes ranging from 0.1-2500uL., auto-pipettors, and pipette tips in various sizes. Air displacement pipettes and auto-pipettors may also be described as mechanical pipettes.
5.3.1 Each day of use, the volume dispensed by each mechanical pipette must be verified for the specific volume for which the pipette is being used.
5.3.1.1 Mechanical pipette volumes are verified by measuring the weight of a volume of water dispensed by the unit. At room temperature, 1 ml of water is equal to 1 g. Pipettes must be capable of ± 2.5% accuracy and within 2.5% precision RSD.
5.3.1.2 Auto-pipettors may be verified by measuring the volume dispensed with a graduated cylinder. The volume dispensed must be within ±2.5% of the nominal weight.
5.3.1.3 Air displacement pipettes must be professionally calibrated every 6 months.
5.4 Hot block capable of maintaining a temperature of 95ºC.
5.5 Balance: analytical, capable of accurately measuring to the nearest 0.1mg.
5.6 Steel cabinet centrifuge with electric timer and brake.
5.7 Gravity convection drying oven with thermostatically control capable of maintaining 180ºC ± 5ºC.
5.8 Plastic wash bottles for cleaning.
5.9 Wood spatulas.
5.10 Disposable polypropylene ribbed watch glasses
5.11 Digital Thermometer (replaced every three months)
5.12 Digestion vessel sample holding trays
5.13 7-inch cervical scrappers (used for soil prep)
5.14 0.45µm Filter

6 Reagents and Standards

6.1 Concentrated nitric acid, Ultra or Trace grades or equivalent (for ICP-MS preps).
6.2 Concentrated nitric acid (sp. gr. 1.41), reagent grade or equivalent (for ICP-OES analysis only).
6.3 1+1 nitric acid, Ultra or Trace grades or equivalent (for ICP-MS preps).
6.4 1+1 nitric acid, reagent grade or equivalent (for ICP-OES analysis only).
6.5 Concentrated hydrochloric acid, Ultra or Trace grades or equivalent (for ICP-MS preps).
6.6 Concentrated hydrochloric acid, (sp. gr. 1.19), reagent grade or equivalent (for ICP-OES analysis only).
6.7 1+1 Hydrochloric acid, Ultra or Trace grades or equivalent (for ICP-MS preps)
6.8 1+1 Hydrochloric acid, reagent grade or equivalent (for ICP-OES analysis only).
6.9 1+4 Hydrochloric acid, Ultra, Trace grades or equivalent (for ICP-MS preps)
6.10 1+4 Hydrochloric acid, reagent grade or equivalent (for ICP-OES analysis only).
6.11 18 MΩ.Water – Purified water which does not contain any measurable quantities of target elements or interfering elements for each element of interest. Milli-Q water is

used by the EPD Metals Lab. Milli-Q water has a resistivity of 18.2[MΩ.cm] @ 25°C and a TOC of 50 µg/L or less.

6.12 Acidified Blank Solution, 18 MΩ water acidified with 3ml-5ml 1:1 concentrated Ultra or Trace grade Nitric Acid (see 6.3) and stored in a HDPE container. The Acidified Blank Solution must be allowed to stand for at least 16 hours before use.

6.13 Sand, standard washed and ignited, EMD SX0075 or equivalent

6.14 Spiking solution for preparing all matrix spikes, laboratory control samples and ML standards

6.15 All reagents and standards must be logged into the standard log notebook with the following: standard number, expiration date and initials.

7 Sample Collection

Water samples and liquid waste samples for metal analysis are collected in a narrow mouth and wide mouth plastic (HDPE) bottles. The samples must be preserved prior to aliquoting for either sample processing or determination by direct spectrochemical analysis. Samples are preserved with sufficient 1+1 HNO_3 to lower the pH below 2, usually 5 mls per liter. One to two bottles are required for each sample. The pH is checked after addition of acid. If the pH is above 2, add more 1+1 HNO3 in 1 to 2 ml increments until pH of <2 less is reached. Following acidification, the sample is mixed and held for a minimum of 16 hours before analysis can begin. The pH of all samples must be tested immediately prior to withdrawing an aliquot for processing to ensure the sample has been properly preserved. Metals require analysis within 180 days. *Please note: Dissolved samples are preserved after filtration.*

Soil and sediment samples for metal analysis are collected in a 500 ml wide mouth plastic (HDPE) bottle. Samples are stored at 0-6^{0}C (not frozen) after sample collection. Analysis must be performed within 180 days.

8 Calibration

Not applicable.

9 Quality Control - Refer to analytical method

Refer to SOP Table 14.1 for Reporting Limits (PQLs), Table 14.2 for Quality Control Acceptance Criteria, and Table 14.2 for Quality Control Procedures associated with each analytical method using this digestion method. (See SOP references 13.9 & 13.10)

9.1 Record all reagents used, volumes, standard or lot numbers, time, temperature, and sample IDs on the digestion log. Fill out a run log with every use of the instrument. The run log must include all samples and standards analyzed in the order they were analyzed.

9.2 Verify the pipette calibration by following procedure outlined in section 5.3. Record the pipette number, the volumes and the weights on the digestion sheet.

10 Procedure

10.1 Aqueous Samples, Aqueous Dissolved Samples (filtered using a 0.45µm filter).

10.1.1 Transfer 50mL aliquot of well mixed, acid preserved sample to a 50ml Hotblock digestion tube. For dissolved samples-Transfer 50ml well mixed filter preserved sample to a 50ml Hotblock digestion tube. (When necessary, smaller sample aliquot volumes may be used.)
NOTE: If the sample contains more than 1% suspended solids, a 50mL well mixed, acid preserved aliquot should be cautiously evaporated to near 5mL and extracted using the acid mixture procedure described in sections 10.2.3 thru 10.2.10.

10.1.2 Check pipettes for accuracy.

10.1.3 Transfer 50ml of acidified 18 MΩ water blank solution (see 6.12) for the $MDL(MB)_{blank}$ and $MDL(ML)_{spike}$ standard to a 50 ml digestion tube. For dissolved samples-Transfer 50ml of acidified 18 MΩ water blank solution (see 6.12) for the MDL (Filter blank also known as $FB)_{blank}$ and $MDL(ML)_{spike}$ standard. Add spiking solution so that MDL $(ML)_{spike}$ standard is at lowest point on calibration curve.

10.1.4 Transfer 50 ml of acidified 18 MΩ water blank solution (see 6.12) for the matrix blank (MB), laboratory control sample (LCS) and laboratory control sample duplicate (LCSD) to a 50 ml digestion tube. For dissolved samples-Transfer 50ml filtered acidified 18 MΩ water blank solution (see 6.12) for Filter Blank (FB), LCS and LCSD. Add spiking solution to LCS and LCSD. Be sure to alternate position of LCS and LCSD in hotblock for each digestion. Please note: Do not filter MB for dissolved samples.

10.1.5 Transfer an additional 50 mL of one routine well mixed sample for the matrix spike (MS) and another 50 mL for the matrix spike duplicate (MSD) for every ten samples digested in the batch to a 50 ml digestion tube. For dissolved samples- Transfer two filtered 50ml aliquots for the MS and MSD for every ten samples in digestion batch. Add spiking solution to MS and MSD.
Note: Be sure to alternate positions of the QC samples in the hotblock for each digestion batch. This allows for all positions of the hotblock to be evaluated over time.

10.1.6 Add 1mL (1+1) nitric acid and 0.5mL (1+1) hydrochloric acid to all samples and standards.

10.1.7 Place digestion vessels in the Hotblock (located in a fume hood). Adjust the temperature to 85°C ±5°C. Place a thermometer in a digestion vessel filled with 50mL water to monitor the temperature. Be sure to alternate position of digestion vessel in hotblock for each digestion. If the sample boils or sample is lost due to spattering discard the sample and redigest.

10.1.8 Reduce the volume of sample aliquot to about 10mL by gentle heating at 85°C ± 5°C. DO NOT BOIL. Please note: If samples evaporate to dryness while heating, please discard samples and QC and start the procedure again from 10.1.

10.1.9 Cover the lip of the digestion vessel with a Disposable polypropylene ribbed watch glass to reduce additional evaporation and gently reflux the sample for 30 minutes (slight boiling may occur, but vigorous boiling must be avoided).

10.1.10 Remove the samples from the hotblock and cool inside a vented fume hood.

10.1.11 Bring the sample volume up to 50 ml with 18 MΩ water and mix well by inverting slowly.

10.1.12 Allow any undissolved material to settle overnight or centrifuge a portion of the prepared sample until clear (if the sample still contains suspended solids that would clog the nebulizer, a portion of the sample may be filtered for their removal prior to analysis).

10.2 Solids Samples

10.2.1 Mix the sample thoroughly and transfer a portion (>20 grams) to a tared weighing dish, weigh the sample and record the wet weight. (For sample with <35% moisture a 20 grams portion is sufficient. For sample with moisture >35% moisture a larger aliquot 50-100 grams is required.) Dry the sample to a constant weight at 60°C and record the dry weight for calculation of percent solids (see SOP section 11). **Note:** 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.

10.2.2 Sieve then grind the dried sample in a mortar and pestle if needed to reduce particle size.

10.2.3 Transfer 0.5 grams ±0.01 grams of sample to a 50 ml hotblock digestion vessel.

10.2.4 Transfer 0.5 grams ±0.01 grams of Sand each for the matrix blank (MB), laboratory control sample (LCS), laboratory control sample duplicate (LCSD), and MDL spike. For the LCS and LCSD add appropriate spiking solution to each. Add spiking solution so that MDL spike (ML) is at lowest point on calibration curve.
Note: Be sure to alternate positions of QC samples in the hotblock for each digestion batch. This allows for all positions of the hotblock to be evaluated over time.

10.2.5 Transfer an additional 0.5 grams ±0.01 grams of one routine well mixed sample for the matrix spike (MS) and another 0.5 grams ±0.01 grams for the matrix spike duplicate (MSD) for every ten samples digested in the batch. For the MS and MSD add appropriate spiking solution to each.

10.2.6 Add 2mls of 1+1 nitric acid and 5mls of 1+4 hydrochloric acid to each vessel.

10.2.7 Cover each vessel with a watch glass and reflux at 85ºC for 30 minutes, once covered the temperature of the water will rise to approximately 95°C. Place a thermometer in a digestion vessel filled with water to monitor the temperature. If the sample boils or sample is lost due to spattering discard the sample and redigest.

10.2.8 Remove the samples from the hotblock and cool.

10.2.9 Bring the sample volume up to 50mls with 18 MΩ water and mix well.

10.2.10 Allow any undissolved material to settle overnight or centrifuge a portion of the prepared sample until clear. (if the sample still contains suspended solids that would clog the nebulizer, a portion of the sample may be filtered prior to analysis.

11 Calculations

11.1 To report percent solids in solid samples calculate as follows:

$$\% \text{ solids (S)} = \frac{DW}{WW} \times 10$$

DW = Sample weight (g) dried at 60°C
WW = Sample weight (g) before drying

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

12 Waste Management

12.1 See GA EPD Laboratory SOP-EPD Laboratory Waste Management Standard Operating procedures, SOP 6-015, online revision.

13 References

13.1 *Methods for the Determination of Metals in Environmental Samples Supplement I;* U.S. EPA Office of Research and Development: Cincinnati, OH, 1994, EPA-600/R-94/111 May 1994
13.2 EPA Method 200.2, SAMPLE PREPARATION PROCEDURE FOR SPECTROCHEMICAL DETERMINATION OF TOTAL RECOVERABLE ELEMENTS, U.S. EPA Office of Research and Development: Cincinnati, OH, Revision 2.8, May 1994
13.3 GA EPD Laboratory SOPs – Initial Demonstration of Capability, SOP 6-001 online revision and/or Continuing Demonstration of Capability, SOP 6-002, online revision.
13.4 GA EPD Laboratory SOP – EPD Laboratory Procedures for Control Charting and Control Limits SOP, SOP 6-025, online revision.
13.5 GA EPD Laboratory SOP – EPD Laboratory Waste Management SOP, SOP 6-015, online revision.
13.6 GA EPD Laboratory SOP – Determination of Method Detection Limit, SOP 6-007, online revision.
13.7 GA EPD: Laboratory Quality Assurance Plan, online revision.
13.8 GA EPD Laboratory Safety/Chemical Hygiene Plan & Fire Safety Plan, online revision.

13.9 EPA Method 200.7, Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry, EMMC Version, Revision 4.4, 1994.

13.10 EPA Method 200.8, Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma – Mass Spectrometry, EMMC Version, Revsion 5.4, 1994.

14 Practical Quantitation Limits (PQLs), Precision and Accuracy Criteria, and Quality Control Approach

Refer to SOP Table 14.1 for Reporting Limits (PQLs), Table 14.2 for Quality Control Acceptance Criteria, and Table 14.2 for Quality Control Procedures associated with each analytical method using this digestion method. (See SOP references 13.9 & 13.10.)