

Method 200.2, Revision 2.8: Sample Preparation Procedure for Spectrochemical Determination of Total Recoverable Elements

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**SAMPLE PREPARATION PROCEDURE FOR SPECTROCHEMICAL
DETERMINATION OF TOTAL RECOVERABLE ELEMENTS**

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T.D. Martin, E.R. Martin, and S.E. Long (Technology Applications, Inc.) - Method 200.2,
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T.D. Martin, S.E. Long (Technology Applications Inc.), and J.T. Creed - Method 200.2,
Revision 2.3 (1991)

T.D. Martin, J.T. Creed, and C.A. Brockhoff - Method 200.2, Revision 2.8 (1994)

**ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U. S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268**

METHOD 200.2

SAMPLE PREPARATION PROCEDURE FOR SPECTROCHEMICAL DETERMINATION OF TOTAL RECOVERABLE ELEMENTS

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.¹ Aqueous samples containing suspended or particulate material $\geq 1\%$ (W/V) should be extracted as a solid type sample. This method is applicable to the following analytes:

Analyte		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

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

Analyte		Chemical Abstract Services Registry Number (CASRN)
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

- 1.2 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 Regulation (40 CFR Part 136 Table 1B for NPDES, and Part 141 § 141.23 for drinking water), and the latest Federal Register announcements.
- 1.3 Samples prepared by this method can be analyzed by the following methods given in this supplement: Method 200.7, Determination of Metals and Trace Elements by Inductively Coupled Plasma-Atomic Emission Spectrometry; Method 200.8, Determination of Trace Elements By Inductively Coupled Plasma-Mass Spectrometry; and Method 200.9, Determination of Trace Elements by Stabilized Temperature Graphite Furnace Atomic Absorption Spectrometry. Also, this method can be used prior to analysis by direct aspiration flame atomic absorption for the above list of analytes with the exception of the following: As, B, Hg, P, Se, SiO₂, Th, and U.
- 1.4 The preparation procedures described in this method are *not* recommended prior to analysis by the conventional graphite furnace technique, commonly referred to as "off-the-wall", non-platform or non-delayed atomization. It is believed that the resulting chloride concentration in the prepared solutions can cause either analyte volatilization loss prior to atomization or an unremediable chemical vapor state interference for some analytes when analyzed using the conventional graphite furnace technique.
- 1.5 This method is suitable for preparation of aqueous samples containing silver concentrations up to 0.1 mg/L. For the analysis of wastewater samples containing higher concentrations of silver, succeeding smaller volume, well mixed aliquots must be prepared until the analysis solution contains <0.1 mg/L silver. The extraction of solid samples containing concentrations of silver >50 mg/kg should be treated in a similar manner. Also, the extraction of tin from solid samples should be prepared again using aliquots <1 g when determined sample concentrations exceed 1%.
- 1.6 When using this method for determination of boron and silica in aqueous samples, only plastic or quartz labware should be used from the time of sample collection to the completion of the analysis. For accurate determinations of boron in 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 will solubilize and hold in solution only minimal concentrations of barium in the presence of free sulfate. For the analysis of barium in samples having varying and unknown concentrations of sulfate, analysis should be completed as soon as possible after sample preparation.
- 1.8 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 beaker 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 beaker with a watch glass and refluxing the sample in the dilute acid mixture for 30 minutes. After extraction, the solubilized analytes are diluted to specified volumes with ASTM Type I water, mixed and either 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 **Field Reagent Blank (FRB)** - An aliquot of reagent water or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to the sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment (Section 8.3).
- 3.2 **Solid Sample** - For the purpose of this method, a sample taken from material classified as either soil, sediment or sludge.
- 3.3 **Total Recoverable Analyte** - The concentration of analyte determined to be in either a solid sample or an unfiltered aqueous sample following treatment by refluxing with hot dilute mineral acid.
- 3.4 **Water Sample** - For the purpose of this method, a sample taken from one of the following sources: drinking, surface, ground, storm runoff, industrial or domestic wastewater.

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 in order to eliminate environmental contamination.
- 4.2 Chemical interferences are matrix dependent and cannot be documented previous to analysis.
- 4.3 Boron and silica from the glassware will grow into the sample solution during and following sample processing. For critical determinations of boron and silica, only quartz and/or PTFE plastic labware should be used. When quartz beakers are not available for extraction of solid samples, to reduce boron contamination, immediately transfer an aliquot of the diluted extract to a plastic centrifuge tube for storage until time of analysis. A series of laboratory reagent blanks can be used to monitor and indicate the contamination effect.

5.0 **SAFETY**

- 5.1 All personnel handling environmental samples known to contain or to have been in contact with human waste should be immunized against known disease causative agents.
- 5.2 The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. Acidification of samples should be done in a fume hood.
- 5.3 Material safety data sheets for all chemical reagents should be available to and understood by all personnel using this method. Specifically, concentrated hydrochloric acid and concentrated nitric acid are moderately toxic and extremely irritating to skin and mucus membranes. Use these reagents in a hood whenever possible and if eye or skin contact occurs, flush with large volumes of water. Always wear safety glasses or a shield for eye protection when working with these reagents.^{2,3,4}

6.0 **EQUIPMENT AND SUPPLIES**

- 6.1 Analytical balance, with capability to measure to 0.1 mg, for use in weighing solids, and for determining dissolved solids in extracts.
- 6.2 Single pan balance, with capability of weighing to 0.01 g, for use in rapid weighing solids and liquids or samples in excess of 10 g.
- 6.3 A temperature adjustable hot plate capable of maintaining a temperature of 95°C.
- 6.4 (Optional) A temperature adjustable block digester capable of maintaining a temperature of 95°C and equipped with 250 mL constricted digestion tubes.

- 6.5 (Optional) A steel cabinet centrifuge with guard bowl, electric timer and brake.
- 6.6 A gravity convection drying oven with thermostatic control capable of maintaining $180^{\circ}\text{C} \pm 5^{\circ}\text{C}$.
- 6.7 (Optional) An air displacement pipetter capable of delivering volumes ranging from 0.1 to 2500 μL with an assortment of high quality disposable pipet tips.
- 6.8 Mortar and pestle, ceramic or nonmetallic material.
- 6.9 Polypropylene sieve, 5-mesh (4 mm opening).
- 6.10 Labware - For determination of trace levels of elements, contamination and loss are of prime 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 processes. All reusable labware (glass, quartz, polyethylene, PTFE, FEP, etc.) should be sufficiently clean for the task objectives. Several procedures found to provide clean labware include soaking overnight and thoroughly washing with laboratory-grade detergent and water, rinsing with tap water, and soaking for four hours or more in 20% (V/V) nitric acid or a mixture of dilute nitric and hydrochloric acid (1+2+9), followed by rinsing with ASTM Type I grade water and storing clean.

Note: Chromic acid must not be used for cleaning glassware.

- 6.10.1 Glassware - Volumetric flasks, graduated cylinders, funnels and centrifuge tubes (glass and/or metal free plastic).
- 6.10.2 Assorted calibrated pipettes.
- 6.10.3 Conical Phillips beakers (Corning 1080-250 or equivalent), 250 mL with 50 mm watch glasses.
- 6.10.4 Griffin beakers, 250 mL with 75 mm watch glasses and (optional) 75 mm ribbed watch glasses.
- 6.10.5 (Optional) PTFE and/or quartz beakers, 250 mL with PTFE covers.
- 6.10.6 Evaporating dishes or high-form crucibles, porcelain, 100 mL capacity.
- 6.10.7 Wash bottle - One piece stem, Teflon FEP bottle with Tefzel ETFE screw closure, 125 mL capacity.

7.0 REAGENTS AND STANDARDS

- 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.
- 7.1.1 Nitric acid, concentrated (sp.gr. 1.41).
- 7.1.2 Nitric acid (1+1) -- Add 500 mL conc. nitric acid to 400 mL of ASTM Type I water and dilute to 1 L.
- 7.1.3 Hydrochloric acid, concentrated (sp.gr. 1.19).
- 7.1.4 Hydrochloric acid (1+1) -- Add 500 mL conc. hydrochloric acid to 400 mL of ASTM Type I water and dilute to 1 L.
- 7.1.5 Hydrochloric acid (1+4) -- Add 200 mL conc. hydrochloric acid to 400 mL of ASTM Type I water and dilute to 1 L.
- 7.2 Reagent water -- For all sample preparation and dilutions, ASTM Type I water (ASTM D1193)⁵ is required. Suitable water may be prepared by passing distilled water through a mixed bed of anion and cation exchange resins.
- 7.3 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 STORAGE

- 8.1 For determination of total recoverable elements in aqueous samples, the samples must be acid preserved prior to aliquoting for either sample processing or determination by direct spectrochemical analysis. For proper preservation samples are *not* filtered, but acidified with (1+1) nitric acid to pH <2. Preservation may be done at the time of sample collection, however, to avoid the hazards of strong acids in the field, transport restrictions, and possible contamination it is recommended that the samples be returned to the laboratory within two weeks of collection and acid preserved upon receipt in the laboratory. Following acidification, the sample should 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). 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 16 hours until verified to be pH <2. If properly acid preserved, the sample can be held up to six months before analysis.

Note: When the nature of the sample is either unknown or is known to be hazardous, acidification should be done in a fume hood. See Section 5.2.

- 8.2 Solid samples require no preservation prior to analysis other than storage at 4°C. There is no established holding time limitation for solid samples.
- 8.3 For aqueous samples, a field blank should be prepared and analyzed as required by the data user. Use the same container and acid as used in sample collection.

9.0 QUALITY CONTROL

- 9.1 Each laboratory determining total recoverable elements is required to operate a formal quality control (QC) program. The minimum requirements of a QC program consist of an initial demonstration of laboratory capability, and the analysis of laboratory reagent blanks, fortified blanks and quality control samples as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of data generated.
- 9.2 Specific instructions on accomplishing the described aspects of the QC program are discussed in the analytical methods (Section 1.3).

10. 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 For the determination of total recoverable analytes in aqueous samples, transfer a 100 mL (± 1 mL) aliquot from a well mixed, acid preserved sample to a 250 mL Griffin beaker (Sections 1.2, 1.5, 1.6, 1.7, and 1.8). (When necessary, smaller sample aliquot volumes may be used.)

Note: If the sample contains undissolved solids >1%, a well mixed, acid preserved aliquot containing no more than 1 g particulate material should be cautiously evaporated to near 10 mL and extracted using the acid-mixture procedure described in Sections 11.2.3 through 11.2.8.

- 11.1.2 Add 2 mL (1+1) nitric acid and 1.0 mL of (1+1) hydrochloric acid to the beaker containing the measured volume of sample. Place the beaker on the hot plate for solution evaporation. The hot plate should be located in a fume hood and previously adjusted to provide evaporation at a temperature of approximately but no higher than 85°C. (See the following note.) The beaker should be covered with an elevated watch

glass or other necessary steps should be taken to prevent sample contamination from the fume hood environment.

Note: For proper heating adjust the temperature control of the hot plate such that an uncovered Griffin beaker containing 50 mL of water placed in the center of the hot plate can be maintained at a temperature approximately but no higher than 85°C. (Once the beaker is covered with a watch glass the temperature of the water will rise to approximately 95°C.)

- 11.1.3 Reduce the volume of the sample aliquot to about 20 mL by gentle heating at 85°C. DO NOT BOIL. This step takes about two hours for a 100 mL aliquot with the rate of evaporation rapidly increasing as the sample volume approaches 20 mL. (A spare beaker containing 20 mL of water can be used as a gauge.)
- 11.1.4 Cover the lip of the beaker with a watch glass to reduce additional evaporation and gently reflux the sample for 30 minutes. (Slight boiling may occur, but vigorous boiling must be avoided to prevent loss of the HCl-H₂O azeotrope.)
- 11.1.5 Allow the beaker to cool. Quantitatively transfer the sample solution to a 50 mL volumetric flask, make to volume with reagent water, stopper and mix.
- 11.1.6 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.) The sample is now ready for analysis by either inductively coupled plasma-atomic emission spectrometry or direct aspiration flame and stabilized temperature graphite furnace atomic absorption spectroscopy (Sections 1.3 and 1.4).
- 11.1.7 To ready the sample for analyses by inductively coupled plasma-mass spectrometry (Section 1.3), 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 extraction and/or skimmer cones. Internal standards are added at the time of analysis.)
- 11.1.8 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 1.0 ± 0.01 g aliquot (W) of the sample and transfer to a 250 mL Phillips beaker for acid extraction (Sections 1.5, 1.6, 1.7, and 1.8).
- 11.2.3 To the beaker add 4 mL of (1+1) HNO₃ and 10 mL of (1+4) HCl. Cover the lip of the beaker with a watch glass. Place the beaker on a hot plate for reflux extraction of the analytes. The hot plate should be located in a fume hood and previously adjusted to provide a reflux temperature of approximately 95°C. (See the following note.)
- Note:** For proper heating adjust the temperature control of the hot plate such that an uncovered Griffin beaker containing 50 mL of water placed in the center of the hot plate can be maintained at a temperature approximately but no higher than 85°C. (Once the beaker is covered with a watch glass the temperature of the water will rise to approximately 95°C.) Also, a block digester capable of maintaining a temperature of 95°C and equipped with 250 mL constricted volumetric digestion tubes may be substituted for the hot plate and conical beakers in the extraction step.
- 11.2.4 Heat the sample and gently reflux for 30 minutes. Very slight boiling may occur, however vigorous boiling must be avoided to prevent loss of the HCl-H₂O azeotrope. Some solution evaporation will occur (3-4 mL).
- 11.2.5 Allow the sample to cool and quantitatively transfer the extract to a 100 mL volumetric flask. Dilute to volume with reagent water, stopper and mix.
- 11.2.6 Allow the sample extract solution to stand overnight to separate insoluble material or centrifuge a portion of the sample solution until clear. (If after centrifuging or standing overnight the extract solution contains suspended solids that would clog the nebulizer, a portion of the extract solution may be filtered for their removal prior to analysis. However, care should be exercised to avoid potential contamination

from filtration.) The sample is now ready for analysis by either inductively coupled plasma-atomic emission spectrometry or direct aspiration flame and stabilized temperature graphite furnace atomic absorption spectroscopy (Sections 1.3 and 1.4).

11.2.7 To ready the sample for analyses by inductively coupled plasma-mass spectrometry (Section 1.3), 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 extraction and/or skimmer cones. Internal standards are added at the time of analysis.)

11.2.8 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 1.3.

12.0 DATA ANALYSIS AND CALCULATIONS

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

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

where:

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 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 1.3.

13.0 METHOD PERFORMANCE

13.1 Not applicable. Available data included in analytical methods listed in Section 1.3.

14.0 POLLUTION PREVENTION

- 14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.
- 14.2 For information about pollution prevention that may be applicable to laboratories and research institutions, consult "Less is Better: Laboratory Chemical Management for Waste Reduction", available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington D.C. 20036, (202)872-4477.

15.0 WASTE MANAGEMENT

- 15.1 The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management consult "The Waste Management Manual for Laboratory Personnel", available from the American Chemical Society at the address listed in the Section 14.2.

16.0 REFERENCES

1. Martin, T.D. and E.R. Martin, "Evaluation of Method 200.2 Sample Preparation Procedure for Spectrochemical Analyses of Total Recoverable Elements", December 1989, U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring Systems Laboratory, Cincinnati, Ohio 45268.
2. "OSHA Safety and Health Standards, General Industry", (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206, revised January 1976.
3. "Safety in Academic Chemistry Laboratories", American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.
4. "Proposed OSHA Safety and Health Standards, Laboratories", Occupational Safety and Health Administration, Federal Register, July 24, 1986.
5. Annual Book of ASTM Standards, Volume 11.01.