3030 PRELIMINARY TREATMENT OF SAMPLES*

3030 A. Introduction

Samples containing particulates or organic material generally require pretreatment before spectroscopic analysis. "Total metals" includes all metals, inorganically and organically bound, both dissolved and particulate. Colorless, transparent samples (primarily drinking water) having a turbidity of <1 NTU, no odor, and single phase may be analyzed directly by atomic absorption spectroscopy (flame or electrothermal vaporization) or inductively coupled plasma spectroscopy (atomic emission or mass spectrometry) for total metals without digestion. For further verification or if changes in existing matrices are encountered, compare digested and undigested samples to ensure comparable results. On collection, acidify such samples to pH <2 with conc nitric acid (1.5 mL HNO_3/L is usually adequate for drinking water) and analyze directly. Digest all other samples before determining total metals. Conc HNO_3 preservative must be present in sample bottle for at least 16 h before removal of portion for digestion. To analyze for dissolved metals, filter sample, acidify filtrate, and store until analyses can be performed. To determine suspended metals, filter sample, digest filter and the material on it, and analyze. To determine acid-extractable metals, extract metals as indicated in 3030E–K and analyze extract.

This section describes general pretreatment for samples in which metals are to be determined according to Sections 3110–3500-Zn with several exceptions. The special digestion techniques for mercury are given in Sections 3112B.4*b* and *c*, and those for arsenic and selenium in Sections 3114B.4*c* and *d* and 3500-Se.B.2–5.

Take care not to introduce metals into samples during preliminary treatment. During pretreatment avoid contact with rubber, metal-based paints, cigarette smoke, paper tissues, and all metal products including those made of stainless steel, galvanized metal, and brass. Conventional fume hoods can contribute significantly to sample contamination, particularly during acid digestion in open containers. Keep vessels covered with watch glasses and turn spouts away from incoming air to reduce airborne contamination. Plastic pipet tips often are contaminated with copper, iron, zinc, and cadmium; before use soak in 2*N* HCl or HNO_3 for several days and rinse with deionized water. Avoid using colored plastics, which can contain metals. Use certified metal-free plastic containers and pipet tips when possible. Avoid using glass if analyzing for aluminum or silica.

Use metal-free water (see Section 3111B.3*c*) for all operations. Check reagent-grade acids used for preservation, extraction, and digestion for purity. If excessive metal concentrations are found, purify the acids by distillation or use ultra-pure acids. Inductively coupled plasma mass spectrometry (ICP-MS) may require use of ultra-pure acids and reagents to avoid measurable contamination. Process blanks through all digestion and filtration steps and evaluate blank results relative to corresponding sample results. Either apply corrections to sample results or take other corrective actions as necessary or appropriate.

3030 B. Filtration for Dissolved and Suspended Metals

1. Filtration Procedures

If dissolved or suspended metals (see Section 3010A.3) are to be determined, filter sample at time of collection using a preconditioned plastic filtering device with either vacuum or pressure, containing a filter support of plastic or fluorocarbon, through a prewashed ungridded 0.4- to 0.45-μm-pore-diam membrane filter (polycarbonate or cellulose esters). Before use filter a blank consisting of metal-free (deionized) water to ensure freedom from contamination. Precondition filter and filter device by rinsing with 50 mL deionized water. If the filter blank contains significant metals concentrations, soak membrane filters in approximately 0.5*N* HCl or 1*N* HNO_3 (recommended for electrothermal atomic absorption spectrometry and ICP–MS analyses) and rinse with deionized water before use. NOTE: Take care to avoid potential contamination during filtration of samples.

Before filtering, centrifuge highly turbid samples in acid-washed fluorocarbon or high-density plastic tubes to reduce loading on filters. Stirred, pressure filter units foul less readily than vacuum filters; filter at a pressure of 70 to 130 kPa. After filtration acidify filtrate to pH 2 with conc HNO_3 and store until analyses can be performed. If a precipitate forms on acidification, digest acidified filtrate before analysis as directed (see 3030E). Retain filter and digest it for direct determination of suspended metals.

If it is not possible to field-filter the sample without contaminating it, obtain sample in an "unpreserved" bottle as above and promptly cool to 4°C. Do not acid-preserve the sample. Then, without delay, filter sample under cleaner conditions in the laboratory.

---

* Approved by Standard Methods Committee, 2004.

Joint Task Group: 20th Edition—Jonathan Talbott (chair), Paul R. Fritschel, Elly M. Gabrelian, David Eugene Kimbrough, H.M. Kingston, Nimi Kocherlakota, Dennis Neuin, Mark E. Tatro, Mark M. Ultis, Melissa Weekley, Aaron D. Weiss, Ruth E. Wolf.

https://doi.org/10.2105/SMWW.2882.041

Test pH of a portion of aqueous sample upon receipt in the laboratory to ensure that the sample has been properly filtered and acid-preserved.[1]

NOTE: Different filters display different sorption and filtration characteristics[2]; for trace analysis, test filter and filtration sytem to verify complete recovery of metals.

If suspended metals (see Section 3010A.3) are to be determined, filter sample as above for dissolved metals, but do not centrifuge before filtration. Retain filter and digest it for direct determination of suspended metals. Record sample volume filtered and include a filter in determination of the blank.

CAUTION: Do not use perchloric acid to digest membrane filters. (See 3030H for more information on handling $HClO_4$).

2. References

1. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1994. Sample Preparation Procedure for Spectrochemical Determination of Total Recoverable Elements; Method 200.2. Environmental Monitoring Systems Lab., Cincinnati, Ohio.
2. HOROWITZ, A.J., K.R. LUM, J.R. GARBARINO, G.E.M. HALL, C. LEMIEUX & C.R. DEMAS. 1996. Problems with using filtration to define dissolved trace element concentrations in natural water samples. *Environ. Sci. Technol.* 30:954.

3030 C. Treatment for Acid-Extractable Metals

Extractable metals (see Section 3010A.3) are lightly adsorbed on particulate material. Because some sample digestion may be unavoidable use rigidly controlled conditions to obtain meaningful and reproducible results. Maintain constant sample volume, acid volume, and contact time. Express results as extractable metals and specify extraction conditions.

At collection, acidify entire sample to pH <2 using 5 mL conc HNO_3/L sample. To prepare sample, mix well, transfer 100 mL to a beaker or flask, and add 5 mL $1 + 1$ high-purity HCl. Heat 15 min on a steam bath. Filter through a membrane filter (preconditioned as in 3030B) and carefully transfer filtrate to a tared volumetric flask. Adjust volume to 100 mL with metal-free water, mix, and analyze. If volume is greater than 100 mL, determine volume to nearest 0.1 mL by weight, analyze, and correct final concentration measurement by multiplying by the dilution factor (final volume ÷ 100).

3030 D. Digestion for Metals

To reduce interference by organic matter and to convert metals associated with particulates to a form (usually the free metal ion) that can be determined by electrothermal atomic absorption spectrometry or inductively-coupled plasma spectroscopy, use one of the digestion techniques presented below. Use the least rigorous digestion method required to provide acceptable and consistent recovery compatible with the analytical method and the metal being analyzed.[1–3]

1. Selection of Acid

Nitric acid will digest most samples adequately (3030E). Nitrate is an acceptable matrix for both flame and electrothermal atomic absorption and the preferred matrix for ICP-MS.[4] Some samples may require addition of perchloric, hydrochloric, hydrofluoric, or sulfuric acid for complete digestion. These acids may interfere in the analysis of some metals and all provide a poorer matrix for both electrothermal and ICP-MS analysis. Confirm metal recovery for each digestion and analytical procedure used. Use Table 3030:I as a guide in determining which acids (in addition to HNO_3) to use for complete digestion. As a general rule, HNO_3 alone is adequate for clean samples or easily oxidized materials; HNO_3-H_2SO_4 or HNO_3-HCl digestion is adequate for readily oxidizable organic matter; HNO_3-$HClO_4$ or HNO_3-$HClO_4$-HF digestion is necessary for difficult-to-oxidize organic matter or minerals containing silicates. Although dry ashing is not generally recommended because of the loss of many volatile elements, it may be helpful if large amounts of organic matter are present.

TABLE 3030:I. ACIDS USED WITH HNO_3 FOR SAMPLE PREPARATION

Acid	Recommended for	May Be Helpful for	Not Recommended for
HCl	Ag	Sb, Ru, Sn	Th, Pb
H_2SO_4	Ti	—	Ag, Pb, Ba
$HClO_4$	—	Organic materials	—
HF	—	Siliceous materials	—

2. Digestion Procedures

Dilute samples with Ag concentrations greater than 1 mg/L to contain less than 1 mg Ag/L for flame atomic absorption methods and 25 μg/L or less for electrothermal analysis.[2,5,6] To address problems with silver halide solubility in HNO_3, digest using method 3030F.3*b*.

Report digestion technique used.

Acid digestion techniques (3030E–I) generally yield comparable precision and bias for most sample types that are totally digested by the technique. Because acids used in digestion will add metals to the samples and blanks, minimize the volume of acids used.

Because the acid digestion techniques (3030E and F) normally are not total digestions, the microwave digestion procedure

(3030K) may be used as an alternative. The microwave method is a closed-vessel procedure and thus is expected to provide improved precision when compared with hot-plate techniques. Microwave digestion is recommended for samples being analyzed by ICP-MS. The microwave digestion method is recommended for the analysis of Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Tl, V, and Zn. Microwave digestion may be acceptable for additional analytes provided its performance for those elements is validated.

Suggested sample volumes are indicated below for flame atomic absorption spectrometry. Lesser volumes, to a minimum of 5 mL, are appropriate for graphite furnace, ICP, and ICP-MS. Do not subsample volumes less than 5 mL, especially when particulates are present. Instead dilute samples with elevated analyte concentrations after digestion. If the recommended volume exceeds digestion vessel capacity, add sample as evaporation proceeds. For samples containing particulates, wide-bore pipets may be useful for volume measurement and transfer.

When samples are concentrated during digestion (e.g., >100 mL sample used) determine metal recovery for each matrix digested, to verify method validity. Using larger samples will require additional acid, which also would increase the concentration of impurities.

Estimated Metal Concentration *mg/L*	Sample Volume* *mL*
<0.1	1000
0.1–10	100
10–100+	10

* For flame atomic absorption spectrometry.

Report results as follows:

$$\text{Metal concentration, mg/L} = A \times \frac{B}{C}$$

where:

A = concentration of metal in digested solution, mg/L,
B = final volume of digested solution, mL, and
C = sample size, mL.

Prepare solid samples or liquid sludges with high solids contents on a weight basis. Mix sample and transfer a suitable amount (typically 1 g of a sludge with 15% total solids) directly into a preweighed digestion vessel. Reweigh and calculate weight of sample. Proceed with one of the digestion techniques presented below. However, as these digestion methods are predominantly for dissolved and extractable metals in aqueous samples, other approaches may be more appropriate for solid samples. For complete mineralization of solid samples, consult methods available elsewhere.[1,4,6,7] Report results on wet- or dry-weight basis as follows:

$$\text{Metal concentrations, mg/kg (wet-weight basis)} = \frac{A \times B}{\text{g sample}}$$

$$\text{Metal concentration, mg/kg (dry-weight basis)} = \frac{A \times B}{\text{g sample}} \times \frac{100}{D}$$

where:

A = concentration of metal in digested solution, mg/L,
B = final volume of digested solution, mL, and
D = total solids, % (see Section 2540G).

Always prepare acid blanks for each type of digestion performed. Although it is always best to eliminate all relevant sources of contamination, a reagent blank prepared with the same acids and subjected to the same digestion procedure as the sample can correct for impurities present in acids and reagent water.

3. References

1. BOUMANS, P.W.J.M., ed. 1987. Inductively Coupled Plasma Emission Spectroscopy, Part II: Applications and Fundamentals. John Wiley & Sons, New York, N.Y.
2. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1992. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods; SW-846, 3rd ed. Update 1, Methods 3005A, 3010A, 3020A & 3050A. Off. Solid Waste & Emergency Response, Washington, D.C.
3. HOENIG, M. & A.M. DE KERSABIEC. 1996. Sample preparation steps for analysis by atomic spectroscopy methods: Present status. *Spectrochim. Acta.* B51:1297.
4. JARVIS, K.E., A.L. GRAY & R.S. HOUK, eds. 1992. Sample preparation for ICP-MS. Chapter 7 *in* Handbook of Inductively Coupled Plasma Mass Spectrometry. Blackie, Glasgow & London, U.K.
5. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1994. Sample Preparation Procedure for Spectrochemical Determination of Total Recoverable Elements; Method 200.2. Environmental Monitoring Systems Lab., Cincinnati, Ohio.
6. KINGSTON, H.M. & S. HASWELL, eds. 1997. Microwave Enhanced Chemistry: Fundamentals, Sample Preparation and Applications. American Chemical Soc., Washington, D.C.
7. BOCK, R. 1979. A Handbook of Decomposition Methods in Analytical Chemistry. Blackie, Glasgow, U.K.

3030 E. Nitric Acid Digestion

Because of the wide variation in concentration levels detected by various instrumental techniques and the need to deal adequately with sources of contamination at trace levels, this method presents one approach for high-level analytes (>0.1 mg/L) and another for trace levels (≤0.1 mg/L).

1. Digestion for Flame Atomic Absorption and High-Level Concentrations

a. Apparatus:

1) *Hot plate.*

2) *Conical (Erlenmeyer) flasks,* 125-mL, or *Griffin beakers,* 150-mL, acid-washed and rinsed with water.

3) *Volumetric flasks,* 100-mL.

4) *Watch glasses,* ribbed and unribbed.
5) *Safety shield.*
6) *Safety goggles.*

b. Reagent:

Nitric acid, HNO_3, conc, or trace-metals grade or ultrapure.

c. Procedure: Use protective equipment listed in ¶s *a*5) and 6) above. Transfer a measured volume (100 mL recommended) of well-mixed, acid-preserved sample appropriate for the expected metals concentrations to a flask or beaker (see 3030D for sample volume). In a hood, add 5 mL conc HNO_3. If a beaker is used, cover with a ribbed watch glass to minimize contamination. Boiling chips, glass beads, or Hengar granules may be added to aid boiling and minimize spatter when high concentration levels (>10 mg/L) are being determined. Bring to a reflux temperature of approximately 95°C to achieve a slow boil and evaporate on a hot plate to the lowest volume possible (about 10 to 20 mL) before precipitation occurs. Continue heating and adding conc HNO_3 as necessary until digestion is complete as shown by a light-colored, clear solution. Do not let sample dry during digestion.

Wash down flask or beaker walls and watch glass cover (if used) with metal-free water. Filter if necessary, using TFE or glass fiber filters (see 3030B). Transfer filtrate to a 100-mL volumetric flask with two portions of reagent water, adding these rinsings to the volumetric flask. Cool, dilute to mark, and mix thoroughly. Take portions of this solution for required metal determinations.

2. Digestion for Trace-Level (≤0.1 mg/L) Concentrations for ICP and ICP-MS[1]

a. Apparatus:

1) *Block heater,* dry, with temperature control.

2) *Polypropylene tubes,** graduated, round-bottom tubes with caps, 17 × 100 mm, acid-washed and rinsed with metal-free water. Preferably use tubes that simultaneously match the analysis instrument autosampler and the block digester. A fit with the centrifuge is secondary but also desirable.

3) *Pipettors,* assorted sizes or adjustable.
4) *Pipet tips.*
5) *Centrifuge.*
6) *Safety shield.*
7) *Safety goggles.*

b. Reagent:

Nitric acid (HNO_3), conc, double distilled.†

c. Procedure: Use protective equipment listed in 3030E.1*a*5) and 6). Soak new polypropylene tubes and caps overnight or for several days in 2*N* HNO_3. Triple rinse with metal-free water, and preferably dry in poly rackets or baskets in a low-temperature oven overnight. Store cleaned tubes in plastic bags before use. Pipet tips also may need to be cleaned; evaluate before use.

Pipet 10 mL well-mixed, acid-preserved sample into a precleaned, labeled tube with a macropipet. With a minimum volume change (<0.5 mL), add appropriate amount of analyte for matrix fortified samples. With a pipet, add 0.5 mL conc HNO_3 (or 1.0 mL 1 + 1 HNO_3) to all samples, blanks, standards, and quality control samples.

Place tubes in block heater in a hood and adjust temperature to 105°C. Drape caps over each tube to allow escape of acid vapors while preventing contamination. NOTE: Do not screw on caps at this time. Digest samples for a minimum of 2 h. Do not let samples boil. Add more conc nitric acid as necessary until digestion is complete by observation of a clear solution.

Remove tubes from heat and cool. Dilute back to original 10 mL volume with metal-free water. Adjust over-volume samples to next convenient gradation for calculations and note volume. (Apply concentration correction from 3030D.2.) If tubes contain particulates, centrifuge and decant clear portion into another precleaned tube. Tighten screw caps and store at 4°C until ready for analysis.

3. Reference

1. JARVIS, K.E., A.L. GRAY & R.S. HOUK, eds. 1992. Sample preparation for ICP-MS. Chapter 7 *in* Handbook of Inductively Coupled Plasma Mass Spectrometry. Blackie & Son, Ltd., Glasgow & London, U.K.

---

* Falcon tubes, or equivalent.

† Ultrex, Optima grade, or equivalent.

3030 F. Nitric Acid-Hydrochloric Acid Digestion

1. Apparatus

See 3030E.1*a*. The following also may be needed:

Steam bath.

2. Reagents

a. Nitric acid, HNO_3, conc, trace-metals grade or ultrapure.
b. Hydrochloric acid, HCl, 1 + 1.
c. Nitric acid, HNO_3, 1 + 1.

3. Procedure

a. Total HNO_3/HCl: Use protective equipment specified in 3030E.1*a*5) and 6). Transfer a measured volume of well-mixed, acid-preserved sample appropriate for the expected metals concentrations to a flask or beaker (see 3030D for sample volume). In a hood add 3 mL conc HNO_3 and cover with a ribbed watch glass. Place flask or beaker on a hot plate and cautiously evaporate to less than 5 mL, making certain that sample does not boil and that no area of the bottom of the container is allowed to go dry. Cool. Rinse down walls of beaker and watch glass with a minimum of metal-free water and add 5 mL conc HNO_3. Cover container with a nonribbed watch glass and return to hot plate. Increase temperature of hot plate so that a gentle reflux action occurs. Continue heating, adding additional acid as necessary, until digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). Cool. Add 10 mL 1 + 1 HCl and 15 mL water per 100 mL anticipated final volume. Heat for an additional 15 min to dissolve any precipitate or residue. Cool, wash down beaker walls and watch glass with water, filter to remove insoluble material that could clog the nebulizer (see 3030B), and transfer filtrate to a 100-mL volumetric flask with rinsings. Alternatively centrifuge or let settle overnight. Adjust to volume and mix thoroughly.

b. Recoverable HNO_3/HCl: For this less rigorous digestion procedure, transfer a measured volume of well-mixed, acid-preserved sample to a flask or beaker. Add 2 mL 1 + 1 HNO_3 and 10 mL 1 + 1 HCl and cover with a ribbed watch glass. Heat on a steam bath or hot plate until volume has been reduced to near 25 mL, making certain sample does not boil. Cool and filter to remove insoluble material or alternatively centrifuge or let settle overnight. Quantitatively transfer sample to volumetric flask, adjust volume to 100 mL, and mix.

For trace-level digestion, use precautionary measures similar to those detailed in 3030E.

3030 G. Nitric Acid-Sulfuric Acid Digestion

1. Apparatus

See 3030E.1*a*.

2. Reagents

a. Nitric acid, HNO_3, conc, trace-metals grade or ultrapure.

b. Sulfuric acid, H_2SO_4, conc.

3. Procedure

Use protective equipment specified in 3030E.1*a*5) and 6). Transfer a measured volume of well-mixed, acid-preserved sample appropriate for the expected metals concentrations to a flask or beaker (see 3030D for sample volume). Add 5 mL conc HNO_3 and cover with a ribbed watch glass. Bring to slow boil on hot plate and evaporate to 15 to 20 mL. Add 5 mL conc HNO_3 and 10 mL conc H_2SO_4, cooling flask or beaker between additions. Evaporate on a hot plate until dense white fumes of SO_3 just appear. If solution does not clear, add 10 mL conc HNO_3 and repeat evaporation to fumes of SO_3. Heat to remove all HNO_3 before continuing treatment. All HNO_3 will be removed when the solution is clear and no brownish fumes are evident. Do not let sample dry during digestion.

Cool and dilute to about 50 mL with water. Heat to almost boiling to dissolve slowly soluble salts. Filter if necessary, then complete procedure as directed in 3030E.1*c* beginning with, "Transfer filtrate . . ."

3030 H. Nitric Acid-Perchloric Acid Digestion

1. Apparatus

See 3030E.1*a*.

2. Reagents

a. Nitric acid, HNO_3, conc, trace-metals grade or ultrapure.

b. Perchloric acid, $HClO_4$.

c. Ammonium acetate solution: Dissolve 500 g $NH_4C_2H_3O_2$ in 600 mL water.

3. Procedure

CAUTION: Heated mixtures of $HClO_4$ and organic matter may explode violently. Avoid this hazard by taking the following precautions:

- **do not add $HClO_4$ to a hot solution containing organic matter;**
- **always pretreat samples containing organic matter with HNO_3 before adding $HClO_4$;**
- **avoid repeated fuming with $HClO_4$ in ordinary hoods (For routine operations, use a water pump attached to a glass fume eradicator. Stainless steel fume hoods with adequate water washdown facilities are available commercially and are acceptable for use with $HClO_4$); and**
- **never let samples being digested with $HClO_4$ evaporate to dryness.**

Use protective equipment specified in 3030E.1*a*5) and 6).

Transfer a measured volume of well-mixed, acid-preserved sample appropriate for the expected metals concentrations to a flask or beaker (see 3030D for sample volume). In a hood add 5 mL conc HNO_3 and cover with a ribbed watch glass. Evaporate sample to 15 to 20 mL on a hot plate. Add 10 mL each of conc HNO_3 and $HClO_4$, cooling flask or beaker between additions. Evaporate gently on a hot plate until dense white fumes of $HClO_4$ just appear. If solution is not clear, keep solution just boiling until it clears. If necessary, add 10 mL conc HNO_3 to complete digestion. Cool, dilute to about 50 mL with water, and boil to expel any chlorine or oxides of nitrogen. Filter, then complete procedure as directed in 3030E.1*c* beginning with, "Transfer filtrate . . ."

If lead is to be determined in the presence of high amounts of sulfate (e.g., determination of Pb in power plant fly ash samples), dissolve $PbSO_4$ precipitate as follows: Add 50 mL ammonium acetate solution to flask or beaker in which digestion was carried out and heat to incipient boiling. Rotate container occasionally to wet all interior surfaces and dissolve any deposited residue. Reconnect filter and slowly draw solution through it. Transfer filtrate to a 100-mL volumetric flask, cool, dilute to mark, mix thoroughly, and set aside for determination of lead.

3030 I. Nitric Acid-Perchloric Acid-Hydrofluoric Acid Digestion

1. Apparatus

a. Hot plate.

b. TFE beakers, 250-mL, acid-washed and rinsed with water.

c. Volumetric flasks, 100-mL, polypropylene or other suitable plastic.

d. Safety shield.

e. Safety goggles.

2. Reagents

a. Nitric acid, HNO_3, conc and 1 + 1, trace-metals grade or ultrapure.

b. Perchloric acid, $HClO_4$.

c. Hydrofluoric acid, HF, 48 to 51%.

3. Procedure

CAUTION: See precautions for using $HClO_4$ in 3030H; handle HF with extreme care and provide adequate ventilation, especially for the heated solution. Avoid all contact with exposed skin. Provide medical attention for HF burns.

Use safety shield and goggles.

Transfer a measured volume of well-mixed, acid-preserved sample appropriate for the expected metals concentrations into a 250-mL TFE beaker (see 3030D for sample volume). Evaporate on a hot plate to 15 to 20 mL. Add 12 mL conc HNO_3 and evaporate to near dryness. Repeat HNO_3 addition and evaporation. Let solution cool, add 20 mL $HClO_4$ and 1 mL HF, and boil until solution is clear and white fumes of $HClO_4$ have appeared. Cool, add about 50 mL water, filter, and proceed as directed in 3030E.1*c* beginning with, "Transfer filtrate . . ."

3030 J. Dry Ashing

The procedure appears in the 18th Edition of *Standard Methods*. It has not been included in subsequent versions of this publication.

3030 K. Microwave-Assisted Digestion

1. Apparatus

a. Microwave unit with programmable power (minimum 545 W) to within ±10 W of required power, having a corrosion-resistant, well-ventilated cavity and having all electronics protected against corrosion for safe operation. Use a unit having a rotating turntable with a minimum speed of 3 rpm to ensure homogeneous distribution of microwave radiation. Use only laboratory-grade microwave equipment and closed digestion containers with pressure relief that are specifically designed for hot acid.[1]

b. Vessels: Construction requires an inner liner of perfluoroalkoxy (PFA) Teflon™,* other TFE, or composite fluorinated polymers,† capable of withstanding pressures of at least 760 ± 70 kPa (110 ± 10 psi), and capable of controlled pressure relief at the manufacturer's maximum pressure rating.

Acid wash all digestion vessels and rinse with water (3030K.2*a*). For new vessels or when changing between high- and low-concentration samples, clean by leaching with hot‡ hydrochloric acid (1:1) for a minimum of 2 h and then with hot nitric acid (1:1) for a minimum of 2 h; rinse with water and dry in a clean environment. Use this procedure whenever the previous use of digestion vessels is unknown or cross-contamination from vessels is suspected.

c. Temperature feedback control system, using shielded thermocouple, fiber-optic probe, or infrared detector.

d. Bottles, polyethylene, 125-mL, with caps.

e. Thermometer, accurate to ±0.1°C.

f. Balance, large-capacity (1500 g), accurate to 0.1 g.

g. Filtration or centrifuge equipment (optional).

h. Plastic container with cover, 1-L, preferably made of PFA Teflon.™§

---

* Or equivalent.

† Such as TFM™, or equivalent.

‡ At temperatures >80°C, but not boiling.

§ Or equivalent.

2. Reagents

a. Metal-free water: See Section 3111B.3*c*.

b. Nitric acid (HNO_3), conc, sub-boiling distilled: Non-sub-boiling acids can be used if they are shown not to contribute blanks.

3. Calibration of Microwave Unit

NOTE: For microwave units equipped with temperature feedback electronic controls, calibration of the microwave unit is not required provided performance specifications can be duplicated.

For cavity-type microwave equipment, evaluate absolute power (watts) by measuring the temperature rise in 1 kg water exposed to microwave radiation for a fixed time. With this measurement, the relationship between available power (W) and the partial power setting (%) of the unit can be estimated, and any absolute power in watts may be transferred from one unit to another. The calibration format required depends on type of electronic system used by manufacturer to provide partial microwave power. Few units have an accurate and precise linear relationship between percent power settings and absorbed power. Where linear circuits have been used, determine calibration curve by a three-point calibration method; otherwise, use the multiple-point calibration method.

a. Three-point calibration method: Measure power at 100% and 50% power using the procedure described in ¶ *c* below and calculate power setting corresponding to required power in watts as specified in the procedure from the two-point line. Measure absorbed power at the calculated partial power setting. If the measured absorbed power does not correspond to the calculated power within ±10 W, use the multiple-point calibration method, ¶ *b* below. Use this point periodically to verify integrity of calibration.

b. Multiple-point calibration method: For each microwave unit, measure the following power settings: 100, 99, 98, 97, 95, 90, 80, 70, 60, 50, and 40% using the procedure described in ¶ *c* below. These data are clustered about the customary working power ranges. Nonlinearity commonly is encountered at the upper end of the calibration curve. If the unit's electronics are known to have nonlinear deviations in any region of proportional power control, make a set of measurements that bracket the power to be used. The final calibration point should be at the partial power setting that will be used in the test. Check this setting periodically to evaluate the integrity of the calibration. If a significant change (±10 W) is detected, re-evaluate entire calibration.

c. Equilibrate a large volume of water to room temperature (23 ± 2°C). Weigh 1 kg water (1000 g ± 1 g) or measure (1000 mL ± 1 mL) into a plastic, not glass, container, and measure the temperature to ±0.1°C. Condition microwave unit by heating a glass beaker with 500 to 1000 mL tap water at full power for 5 min with the exhaust fan on. Loosely cover plastic container to reduce heat loss and place in normal sample path (at outer edge of rotating turntable); circulate continuously through the microwave field for 120 s at desired power setting with exhaust fan on as it will be during normal operation. Remove plastic container and stir water vigorously. Use a magnetic stirring bar inserted immediately after microwave irradiation; record maximum temperature within the first 30 s to ±0.1°C. Use a new sample for each additional measurement. If the water is reused, return both water and beaker to 23 ± 2°C. Make three measurements at each power setting. When any part of the high-voltage circuit, power source, or control components in the unit have been serviced or replaced, recheck calibration power. If power output has changed by more than ±10 W, re-evaluate entire calibration. Compute absorbed power by the following relationship:

$$P = \frac{(K)(Cp)(m)(\Delta T)}{t}$$

where:

P = apparent power absorbed by sample, W,
K = conversion factor for thermochemical calories sec^{-1} to watts (4.184),
Cp = heat capacity, thermal capacity, or specific heat (cal g^{-1} $°C^{-1}$) of water,
m = mass of water sample, g,
ΔT = final temperature minus initial temperature, °C, and
t = time, s.

For the experimental conditions of 120 s and 1 kg water (Cp at 25°C = 0.9997), the calibration equation simplifies to:

$$P = (\Delta T)(34.85)$$

Stable line voltage within the manufacturer's specification is necessary for accurate and reproducible calibration and operation. During measurement and operation it must not vary by more than ±2 V. A constant power supply may be necessary if line voltage is unstable.

4. Procedure

CAUTION: This method is designed for microwave digestion of waters only. It is not intended for the digestion of solids, for which high concentrations of organic compounds may result in high pressures and possibly unsafe conditions.

CAUTION: As a safety measure, never mix different manufacturers' vessels in the same procedure. Vessels constructed differently will retain heat at different rates; control of heating conditions assumes that all vessels have the same heat-transfer characteristics. Inspect casements for cracks and chemical corrosion. Failure to maintain the vessels' integrity may result in catastrophic failure.

Both prescription controls and performance controls are provided for this procedure. Performance controls are the most general and most accurate. When equipment capability permits, use the performance criterion.

a. Performance criterion: The following procedure is based on heating acidified samples in two stages where the first stage is to reach 160 ± 4°C in 10 min and the second stage is to permit a slow rise to 165 to 170°C during the second 10 min. This performance criterion is based on temperature feedback control system capability that is implemented in various ways by different manufacturers. Because the temperature of the acid controls the reaction, this is the essential condition that will reproduce results in this preparation method. Verification of temperature conditions inside the vessel at these specific times is sufficient to verify the critical procedural requirements.

b. Prescription criterion: For all PFA vessels without liners, a verified program that meets the performance-based temperature-time profile is 545 W for 10 min followed by 344 W for 10 min using five single-wall PFA Teflon™‖ digestion vessels.[2] Any verified program for a given microwave unit depends on unit power and operational power settings, heating times, number, type, and placement of digestion vessels within the unit, and sample and acid volumes. The change in power, time, and temperature profile is not directly proportional to the change in the number of sample vessels. Any deviations from the verified program conditions will require verification of the time-temperature profile to conform to the given two-stage profile. This may be done by laboratory personnel if suitable test equipment is available, or by the manufacturer of the microwave equipment.

c. General conditions: Weigh entire digestion vessel assembly to 0.1 g before use and record (*A*). Accurately transfer 45 mL of well-shaken sample into the digestion vessel. Pipet 5 mL conc HNO_3 into each vessel. Attach all safety equipment required for appropriate and safe vessel operation following manufacturer's specifications. Tighten cap to manufacturer's specifications. Weigh each capped vessel to the nearest 0.1 g (*B*).

Place appropriate number of vessels evenly distributed in the carousel. Treat sample blanks, known additions, and duplicates in the same manner as samples. For prescription control only, when fewer samples than the appropriate number are digested, fill remaining vessels with 45 mL water and 5 mL conc HNO_3 to obtain full complement of vessels for the particular program being used.

Place carousel in unit and seat it carefully on turntable. Program microwave unit to heat samples to 160 ± 4°C in 10 min and then, for the second stage, to permit a slow rise to 165 to 170°C for 10 min. Start microwave generator, making sure that turntable is turning and that exhaust fan is on.

At completion of the microwave program, let vessels cool for at least 5 min in the unit before removal. Cool samples further outside the unit by removing the carousel and letting them cool on a bench or in a water bath. When cooled to room temperature, weigh each vessel (to 0.1 g) and record weight (*C*).

If the net weight of sample plus acid decreased by more than 10%, discard sample.

Complete sample preparation by carefully uncapping and venting each vessel in a fume hood. Follow individual manufacturer's specifications for relieving pressure in individual vessel types. Transfer to acid-cleaned noncontaminating plastic bottles. If the digested sample contains particulates, filter, centrifuge, or settle overnight and decant.

5. Calculations

a. Dilution correction: Multiply results by 50/45 or 1.11 to account for the dilution caused by the addition of 5 mL acid to 45 mL sample.

b. Discarding of sample: To determine if the net weight of sample plus acid decreased by more than 10% during the digestion process, use the following calculation

$$\frac{[(B-A)-(C-A)]}{(B-A)} \times 100 > 10\% \text{ (1\% for multilayer vessels)}$$

6. Quality Control

NOTE: When nitric acid digestion is used, recoveries of silver and antimony in some matrices may be unacceptably low. Verify recoveries using appropriate known additions.

Preferably include a quality-control sample in each loaded carousel. Prepare samples in batches including preparation blanks, sample duplicates, and pre-digestion known additions. Determine size of batch and frequency of quality-control samples by method of analysis and laboratory practice. The power of the microwave unit and batch size may prevent including one or more of the quality-control samples in each carousel. Do not group quality-control samples together but distribute them throughout the various carousels to give the best monitoring of digestion.

7. References

1. KINGSTON, H.M. & S. HASWELL, eds. 1997. Microwave Enhanced Chemistry: Fundamentals, Sample Preparation and Applications. American Chemical Soc., Washington, D.C.
2. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1990. Microwave assisted acid digestion of aqueous samples and extracts; SW-846. Method 3015, Test Methods for Evaluating Solid Waste. Washington, D.C.

‖ Or equivalent.

3110 METALS BY ATOMIC ABSORPTION SPECTROMETRY

Because requirements for determining metals by atomic absorption spectrometry vary with metal and/or concentration to be determined, the method is presented as follows:

Metals by Flame Atomic Absorption Spectrometry (Section 3111) encompasses:

- Determination of antimony, bismuth, cadmium, calcium, cesium, chromium, cobalt, copper, gold, iridium, iron, lead, lithium, magnesium, manganese, nickel, palladium, platinum, potassium, rhodium, ruthenium, silver, sodium, strontium, thallium, tin, and zinc by direct aspiration into an air-acetylene flame (Section 3111B),
- Determination of low concentrations of cadmium, chromium, cobalt, copper, iron, lead, manganese, nickel, silver, and zinc by chelation with ammonium pyrrolidine dithiocarbamate (APDC), extraction into methyl isobutyl ketone (MIBK), and aspiration into an air-acetylene flame (Section 3111C),
- Determination of aluminum, barium, beryllium, calcium, molybdenum, osmium, rhenium, silicon, thorium, titanium, and vanadium by direct aspiration into a nitrous oxide-acetylene flame (Section 3111D), and
- Determination of low concentrations of aluminum and beryllium by chelation with 8-hydroxyquinoline, extraction into MIBK, and aspiration into a nitrous oxide-acetylene flame (Section 3111E).

Section 3112 covers determination of mercury by the cold vapor technique.

Section 3113 concerns determination of micro quantities of aluminum, antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, iron, lead, manganese, molybdenum, nickel, selenium, silver, and tin by electrothermal atomic absorption spectrometry.

Section 3114 covers determination of arsenic and selenium by conversion to their hydrides and aspiration into an argon-hydrogen or nitrogen-hydrogen flame.

https://doi.org/10.2105/SMWW.2882.042

3111 METALS BY FLAME ATOMIC ABSORPTION SPECTROMETRY*

3111 A. Introduction

1. Principle

In flame atomic absorption spectrometry, a sample is aspirated into a flame and atomized. A light beam is directed through the flame, into a monochromator, and onto a detector that measures the amount of light absorbed by the atomized element in the flame. For some metals, atomic absorption exhibits superior sensitivity over flame emission. Because each metal has its own characteristic absorption wavelength, a source lamp composed of that element is used; this makes the method relatively free from spectral or radiation interferences. The amount of energy at the characteristic wavelength absorbed in the flame is proportional to the concentration of the element in the sample over a limited concentration range. Most atomic absorption instruments also are equipped for operation in an emission mode, which may provide better linearity for some elements.

2. Selection of Method

See Section 3110.

3. Interferences

a. Chemical interference: Many metals can be determined by direct aspiration of sample into an air-acetylene flame. The most troublesome type of interference is termed "chemical" and results from the lack of absorption by atoms bound in molecular combination in the flame. This can occur when the flame is not hot enough to dissociate the molecules or when the dissociated atom is oxidized immediately to a compound that will not dissociate further at the flame temperature. Such interferences may be reduced or eliminated by adding specific elements or compounds to the sample solution. For example, the interference of phosphate in the magnesium determination can be overcome by adding lanthanum. Similarly, introduction of calcium eliminates silica interference in the determination of manganese. However, silicon and metals such as aluminum, barium, beryllium, and vanadium require the higher-temperature, nitrous oxide-acetylene flame to dissociate their molecules. The nitrous oxide-acetylene flame also can be useful in minimizing certain types of chemical interferences encountered in the air-acetylene flame. For example, the interference caused by high concentrations of phosphate in the determination of calcium in the air-acetylene flame is reduced in the nitrous oxide-acetylene flame.

MIBK extractions with APDC (see 3111C) are particularly useful where a salt matrix interferes, for example, in seawater. This procedure also concentrates the sample so that the detection limits are lowered.

Brines and seawater can be analyzed by direct aspiration but sample dilution is recommended. Aspiration of solutions containing high concentrations of dissolved solids often results in solids buildup on the burner head. This requires frequent shutdown of the flame and cleaning of the burner head. Preferably use background correction when analyzing waters that contain in excess of 1% solids, especially when the primary resonance line of the element of interest is below 240 nm. Make more frequent recovery checks when analyzing brines and seawaters to ensure accurate results in these concentrated and complex matrices.

Barium and other metals ionize in the flame, thereby reducing the ground state (potentially absorbing) population. The addition of an excess of a cation (sodium, potassium, or lithium) having a similar or lower ionization potential will overcome this problem. The wavelength of maximum absorption for arsenic is 193.7 nm and for selenium 196.0 nm—wavelengths at which the air-acetylene flame absorbs intensely. The sensitivity for arsenic and selenium can be improved by conversion to their gaseous hydrides and analyzing them in either a nitrogen-hydrogen or an argon-hydrogen flame with a quartz tube (see Section 3114).

b. Background correction: Molecular absorption and light scattering caused by solid particles in the flame can cause erroneously high absorption values resulting in positive errors. When such phenomena occur, use background correction to obtain accurate values. Use any one of three types of background correction: continuum-source, Zeeman, or Smith-Hieftje correction.

1) Continuum-source background correction—A continuum-source background corrector utilizes either a hydrogen-filled hollow cathode lamp with a metal cathode or a deuterium arc lamp. When both the line source hollow-cathode lamp and the continuum source are placed in the same optical path and are time-shared, the broadband background from the elemental signal is subtracted electronically, and the resultant signal will be background-compensated.

Both the hydrogen-filled hollow-cathode lamp and deuterium arc lamp have lower intensities than either the line source hollow-cathode lamp or electrodeless discharge lamps. To obtain a valid correction, match the intensities of the continuum source with the line source hollow-cathode or electrodeless discharge lamp. The matching may result in lowering the intensity of the line source or increasing the slit width; these measures have the disadvantage of raising the detection limit and possibly causing nonlinearity of the calibration curve. Background correction using a continuum source corrector is susceptible to interference from other absorbing lines in the spectral bandwidth. Miscorrection occurs from significant atomic absorption of the continuum source radiation by elements other than that being determined. When a line source hollow-cathode lamp is used without background correction, the presence of an absorbing line from another element in the spectral bandwidth will not cause an interference unless it overlaps the line of interest.

---

* Approved by Standard Methods Committee, 1999. Editorial revisions, 2011.

https://doi.org/10.2105/SMWW.2882.043

Continuum-source background correction will not remove direct absorption spectral overlap, where an element other than that being determined is capable of absorbing the line radiation of the element under study.

2) Zeeman background correction—This correction is based on the principle that a magnetic field splits the spectral line into two linearly polarized light beams parallel and perpendicular to the magnetic field. One is called the pi (π) component and the other the sigma (σ) component. These two light beams have exactly the same wavelength and differ only in the plane of polarization. The π line will be absorbed by both the atoms of the element of interest and by the background caused by broadband absorption and light scattering of the sample matrix. The σ line will be absorbed only by the background.

Zeeman background correction provides accurate background correction at much higher absorption levels than is possible with continuum source background correction systems. It also virtually eliminates the possibility of error from structured background. Because no additional light sources are required, the alignment and intensity limitations encountered using continuum sources are eliminated.

Disadvantages of the Zeeman method include reduced sensitivity for some elements, reduced linear range, and a “rollover” effect whereby the absorbance of some elements begins to decrease at high concentrations, resulting in a two-sided calibration curve.

3) Smith–Hieftje background correction—This correction is based on the principle that absorbance measured for a specific element is reduced as the current to the hollow cathode lamp is increased while absorption of nonspecific absorbing substances remains identical at all current levels. When this method is applied, the absorbance at a high-current mode is subtracted from the absorbance at a low-current mode. Under these conditions, any absorbance due to nonspecific background is subtracted out and corrected for.

Smith–Hieftje background correction provides a number of advantages over continuum-source correction. Accurate correction at higher absorbance levels is possible and error from structured background is virtually eliminated. In some cases, spectral interferences also can be eliminated. The usefulness of Smith-Hieftje background correction with electrodeless discharge lamps has not yet been established.

4. Sensitivity, Detection Levels, and Optimum Concentration Ranges

The sensitivity of flame atomic absorption spectrometry is defined as the metal concentration that produces an absorption of 1% (an absorbance of approximately 0.0044). The instrument detection level is defined here as the concentration that produces absorption equivalent to twice the magnitude of the background fluctuation. Sensitivity and detection levels vary with the instrument, the element determined, the complexity of the matrix, and the technique selected. The optimum concentration range usually starts from the concentration of several times the detection level and extends to the concentration at which the calibration curve starts to flatten. To achieve best results, use concentrations of samples and standards within the optimum concentration range of the spectrometer. See Table 3111:I for indication of concentration ranges measurable with conventional atomization. In many instances the concentration range shown in Table 3111:I may be extended downward either by scale expansion or by integrating the absorption signal over a long time. The range may be extended upward by dilution, using a less sensitive wavelength, rotating the burner head, or utilizing a microprocessor to linearize the calibration curve at high concentrations.

TABLE 3111:I. ATOMIC ABSORPTION CONCENTRATION RANGES WITH DIRECT ASPIRATION ATOMIC ABSORPTION

Element	Wave-length *nm*	Flame Gases*	Instrument Detection Level *mg/L*	Sensitivity *mg/L*	Optimum Concentration Range *mg/L*
Ag	328.1	A–Ac	0.01	0.06	0.1–4
Al	309.3	N–Ac	0.1	1	5–100
Au	242.8	A–Ac	0.01	0.25	0.5–20
Ba	553.6	N–Ac	0.03	0.4	1–20
Be	234.9	N–Ac	0.005	0.03	0.05–2
Bi	223.1	A–Ac	0.06	0.4	1–50
Ca	422.7	A–Ac	0.003	0.08	0.2–20
Cd	228.8	A–Ac	0.002	0.025	0.05–2
Co	240.7	A–Ac	0.03	0.2	0.5–10
Cr	357.9	A–Ac	0.02	0.1	0.2–10
Cs	852.1	A–Ac	0.02	0.3	0.5–15
Cu	324.7	A–Ac	0.01	0.1	0.2–10
Fe	248.3	A–Ac	0.02	0.12	0.3–10
Ir	264.0	A–Ac	0.6	8	—
K	766.5	A–Ac	0.005	0.04	0.1–2
Li	670.8	A–Ac	0.002	0.04	0.1–2
Mg	285.2	A–Ac	0.0005	0.007	0.02–2
Mn	279.5	A–Ac	0.01	0.05	0.1–10
Mo	313.3	N–Ac	0.1	0.5	1–20
Na	589.0	A–Ac	0.002	0.015	0.03–1
Ni	232.0	A–Ac	0.02	0.15	0.3–10
Os	290.9	N–Ac	0.08	1	—
Pb†	283.3	A–Ac	0.05	0.5	1–20
Pt	265.9	A–Ac	0.1	2	5–75
Rh	343.5	A–Ac	0.5	0.3	—
Ru	349.9	A–Ac	0.07	0.5	—
Sb	217.6	A–Ac	0.07	0.5	1–40
Si	251.6	N–Ac	0.3	2	5–150
Sn	224.6	A–Ac	0.8	4	10–200
Sr	460.7	A–Ac	0.03	0.15	0.3–5
Ti	365.3	N–Ac	0.3	2	5–100
V	318.4	N–Ac	0.2	1.5	2–100
Zn	213.9	A–Ac	0.005	0.02	0.05–2

* A–Ac = air-acetylene; N–Ac = nitrous oxide-acetylene.

† The more sensitive 217.0 nm wavelength is recommended for instruments with background correction capabilities.

5. Preparation of Standards

Prepare standard solutions of known metal concentrations in water with a matrix similar to the sample. Use standards that bracket expected sample concentration and are within the method’s working range. Very dilute standards should be prepared daily from stock solutions in concentrations greater than 500 mg/L. Stock standard solutions can be obtained from several commercial sources. They also can be prepared from National

Institute of Standards and Technology (NIST) reference materials or by procedures outlined in the following sections.

For samples containing high and variable concentrations of matrix materials, make the major ions in the sample and the dilute standard similar. If the laboratory has reason to believe the sample matrix is complex and the components, surface tension, or viscosity cannot be matched accurately with the standards, use the method of standard additions [Section 3113B.4*d*2)] to correct for matrix effects. If digestion is used, carry standards through the same digestion procedure used for samples.

6. Apparatus

a. Atomic absorption spectrometer, consisting of a light source emitting the line spectrum of an element (hollow-cathode lamp or electrodeless discharge lamp), a device for vaporizing the sample (usually a flame), a means of isolating an absorption line (monochromator or filter and adjustable slit), and a photoelectric detector with its associated electronic amplifying and measuring equipment.

b. Burner: The most common type of burner is a premix, which introduces the spray into a condensing chamber for removal of large droplets. The burner may be fitted with a conventional head containing a single slot; a three-slot Boling head, which may be preferred for direct aspiration with an air-acetylene flame; or a special head for use with nitrous oxide and acetylene.

c. Readout: Most instruments are equipped with either a digital or null meter readout mechanism. Most modern instruments are equipped with microprocessors or stand-alone control computers capable of integrating absorption signals over time and linearizing the calibration curve at high concentrations.

d. Lamps: Use either a hollow-cathode lamp or an electrodeless discharge lamp (EDL). Use one lamp for each element being measured. Multi-element hollow-cathode lamps generally provide lower sensitivity than single-element lamps. EDLs take a longer time to warm up and stabilize.

e. Pressure-reducing valves: Maintain supplies of fuel and oxidant at pressures somewhat higher than the controlled operating pressure of the instrument by using suitable reducing valves. Use a separate reducing valve for each gas.

f. Vent: Place a vent about 15 to 30 cm above the burner to remove fumes and vapors from the flame. This precaution protects laboratory personnel from toxic vapors, protects the instrument from corrosive vapors, and prevents flame stability from being affected by room drafts. A damper or variable-speed blower is desirable for modulating air flow and preventing flame disturbance. Select blower size to provide the air flow recommended by the instrument manufacturer. In laboratory locations with heavy particulate air pollution, use clean laboratory facilities (Section 3010C).

7. Quality Assurance/Quality Control

Some data typical of the precision and bias obtainable
T2 with the methods discussed are presented in Tables 3111:II
T3 and III.

Analyze a blank between sample or standard readings to verify baseline stability. Rezero when necessary.

TABLE 3111:II. INTERLABORATORY PRECISION AND BIAS DATA FOR ATOMIC ABSORPTION METHODS—DIRECT ASPIRATION AND EXTRACTED METALS

Metal	Conc*	SD*	Relative SD %	Relative Error %	No. of Participants
Direct determination:					
Aluminum[1]	4.50	0.19	4.2	8.4	5
Barium[2]	1.00	0.089	8.9	2.7	11
Beryllium[1]	0.46	0.0213	4.6	23.0	11
Cadmium[3]	0.05	0.0108	21.6	8.2	26
Cadmium[1]	1.60	0.11	6.9	5.1	16
Calcium[1]	5.00	0.21	4.2	0.4	8
Chromium[1]	3.00	0.301	10.0	3.7	9
Cobalt[1]	4.00	0.243	6.1	0.5	14
Copper[3]	1.00	0.112	11.2	3.4	53
Copper[1]	4.00	0.331	8.3	2.8	15
Iron[1]	4.40	0.260	5.8	2.3	16
Iron[3]	0.30	0.0495	16.5	0.6	43
Lead[1]	6.00	0.28	4.7	0.2	14
Magnesium[3]	0.20	0.021	10.5	6.3	42
Magnesium[1]	1.10	0.116	10.5	10.0	8
Manganese[1]	4.05	0.317	7.8	1.3	16
Manganese[3]	0.05	0.0068	13.5	6.0	14
Nickel[1]	3.93	0.383	9.8	2.0	14
Silver[3]	0.05	0.0088	17.5	10.6	7
Silver[1]	2.00	0.07	3.5	1.0	10
Sodium[1]	2.70	0.122	4.5	4.1	12
Strontium[1]	1.00	0.05	5.0	0.2	12
Zinc[3]	0.50	0.041	8.2	0.4	48
Extracted determination:					
Aluminum[2]	300	32	10.7	0.7	15
Beryllium[2]	5	1.7	34.0	20.0	9
Cadmium[3]	50	21.9	43.8	13.3	12
Cobalt[1]	300	28.5	9.5	1.0	6
Copper[1]	100	71.7	71.7	12.0	8
Iron[1]	250	19.0	7.6	3.6	4
Manganese[1]	21.5	2.4	11.2	7.4	8
Molybdenum[1]	9.5	1.1	11.6	1.3	5
Nickel[1]	56.8	15.2	26.8	13.6	14
Lead[3]	50	11.8	23.5	19.0	8
Silver[1]	5.2	1.4	26.9	3.0	7

* For direct determinations, mg/L; for extracted determinations, μg/L.
Superscripts refer to reference numbers.
SOURCE: AMERICAN SOCIETY FOR TESTING & MATERIALS. 1986. Annual Book of ASTM Standards, Vol. 11.01: Water and Environmental Technology. Philadelphia, Pa. Copyright © ASTM. Reprinted with permission.

To one sample out of every ten (or one sample from each group of samples if less than ten are being analyzed) add a known amount of the metal of interest and reanalyze to confirm recovery. The amount of metal added should be approximately equal to the amount found. If little metal is present add an amount close to the middle of the linear range of the test. Recovery of added metal should be between 85 and 115%.

Analyze an additional standard solution after every ten samples or with each batch of samples, whichever is less, to confirm that the test is in control. Recommended concentrations of standards to be run, limits of acceptability, and

TABLE 3111:III. SINGLE-OPERATOR PRECISION AND RECOMMENDED CONTROL RANGES FOR ATOMIC ABSORPTION METHODS—DIRECT ASPIRATION AND EXTRACTED METALS

Metal	Conc*	SD*	Relative SD %	No. of Participants	QC Std.*	Acceptable Range*
Direct determination:						
Aluminum[1]	4.50	0.23	5.1	15	5.00	4.3–5.7
Beryllium[1]	0.46	0.012	2.6	10	0.50	0.46–0.54
Calcium[1]	5.00	0.05	1.0	8	5.00	4.8–5.2
Chromium[1]	7.00	0.69	9.9	9	5.00	3.3–6.7
Cobalt[1]	4.00	0.21	5.3	14	4.00	3.4–4.6
Copper[1]	4.00	0.115	2.9	15	4.00	3.7–4.3
Iron[1]	5.00	0.19	3.8	16	5.00	4.4–5.6
Magnesium[1]	1.00	0.009	0.9	8	1.00	0.97–1.03
Nickel[4]	5.00	0.04	0.8	—	5.00	4.9–5.1
Silver[1]	2.00	0.25	12.5	10	2.00	1.2–2.8
Sodium[4]	8.2	0.1	1.2	—	5.00	4.8–5.2
Strontium[1]	1.00	0.04	4.0	12	1.00	0.87–1.13
Potassium[4]	1.6	0.2	12.5	—	1.6	1.0–2.2
Molybdenum[4]	7.5	0.07	0.9	—	10.0	9.7–10.3
Tin[4]	20.0	0.5	2.5	—	20.0	18.5–21.5
Titanium[4]	50.0	0.4	0.8	—	50.0	48.8–51.2
Vanadium	50.0	0.2	0.4	—	50.0	49.4–50.6
Extracted determination:						
Aluminum[1]	300	12	4.0	15	300	264– 336
Cobalt[1]	300	20	6.7	6	300	220– 380
Copper[1]	100	21	21	8	100	22– 178
Iron[1]	250	12	4.8	4	250	180– 320
Manganese[1]	21.5	202	10.2	8	25	17– 23
Molybdenum[1]	9.5	1.0	10.5	5	10	5.5–14.5
Nickel[1]	56.8	9.2	16.2	14	50	22– 78
Silver[1]	5.2	1.2	23.1	7	5.0	0.5–9.5

* For direct determinations, mg/L; for extracted determinations, μg/L.

Superscripts refer to reference numbers.

SOURCE: AMERICAN SOCIETY FOR TESTING & MATERIALS. 1986. Annual Book of ASTM Standards, Vol. 11.01: Water and Environmental Technology. Philadelphia, Pa. Copyright © ASTM. Reprinted with permission.

reported single-operator precision data are listed in Table 3111:III.

The QC practices considered to be an integral part of each method can be found in Section 3020.

8. References

1. AMERICAN SOCIETY FOR TESTING & MATERIALS. 1986. Annual Book of ASTM Standards, Vol. 11.01, Water and Environmental Technology. Philadelphia, Pa.
2. U.S. DEPARTMENT HEALTH, EDUCATION AND WELFARE. 1970. Water Metals No. 6, Study No. 37; U.S. Public Health Serv. Pub. No. 2029, Cincinnati, Ohio.
3. U.S. DEPARTMENT HEALTH, EDUCATION AND WELFARE. 1968. Water Metals No. 4, Study No. 30; U.S. Public Health Serv. Pub. No. 999-UTH-8, Cincinnati, Ohio.
4. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1983. Methods for Chemical Analysis of Water and Wastes. Cincinnati, Ohio.

9. Bibliography

KAHN, H.L. 1968. Principles and Practice of Atomic Absorption; Advan. Chem. Ser. No. 73. Div. Water, Air & Waste Chemistry, American Chemical Soc., Washington, D.C.

RAMIRIZ-MUNOZ, J. 1968. Atomic Absorption Spectroscopy and Analysis by Atomic Absorption Flame Photometry. American Elsevier Publishing Co., New York, N.Y.

SLAVIN, W. 1968. Atomic Absorption Spectroscopy. John Wiley & Sons, New York, N.Y.

PAUS, P.E. 1971. The application of atomic absorption spectroscopy to the analysis of natural waters. *Atomic Absorption Newsletter* 10:69.

EDIGER, R.D. 1973. A review of water analysis by atomic absorption. *Atomic Absorption Newsletter* 12:151.

PAUS, P.E. 1973. Determination of some heavy metals in seawater by atomic absorption spectroscopy. *Fresenius Zeitschr. Anal. Chem.* 264:118.

BURRELL, D.C. 1975. Atomic Spectrometric Analysis of Heavy-Metal Pollutants in Water. Ann Arbor Science Publishers, Inc., Ann Arbor, Mich.

3111 B. Direct Air-Acetylene Flame Method

1. General Discussion

This method is applicable to the determination of antimony, bismuth, cadmium, calcium, cesium, chromium, cobalt, copper, gold, iridium, iron, lead, lithium, magnesium, manganese, nickel, palladium, platinum, potassium, rhodium, ruthenium, silver, sodium, strontium, thallium, tin, and zinc.

2. Apparatus

Atomic absorption spectrometer and associated equipment: See 3111A.6. Use burner head recommended by the manufacturer.

3. Reagents

a. Air, cleaned and dried through a suitable filter to remove oil, water, and other foreign substances. The source may be a compressor or commercially bottled gas.

b. Acetylene, standard commercial grade. Acetone, which always is present in acetylene cylinders, can be prevented from entering and damaging the burner head by replacing a cylinder when its pressure has fallen to 689 kPa (100 psi) acetylene.

CAUTION: Acetylene gas represents an explosive hazard in the laboratory. Follow instrument manufacturer's directions in plumbing and using this gas. Do not allow gas contact with copper, brass with >65% copper, silver, or liquid mercury; do not use copper or brass tubing, regulators, or fittings with >65% copper content.

c. Metal-free water: Use metal-free water for preparing all reagents and calibration standards and as dilution water. Prepare metal-free water by deionizing tap water and/or by using one of the following processes, depending on the metal concentration in the sample: single distillation, redistillation, or sub-boiling. Always check deionized or distilled water to determine whether the element of interest is present in trace amounts. (NOTE: If the source water contains Hg or other volatile metals, single- or redistilled water may not be suitable for trace analysis because these metals distill over with the distilled water. In such cases, use sub-boiling to prepare metal-free water.)

d. Calcium solution: Dissolve 630 mg calcium carbonate, $CaCO_3$, in 50 mL of 1 + 5 HCl. If necessary, boil gently to obtain complete solution. Cool and dilute to 1000 mL with water.

e. Hydrochloric acid (HCl), 1%, 10%, 20% (all v/v), 1 + 5, 1 + 1, and conc.

f. Lanthanum solution: Dissolve 58.65 g lanthanum oxide, La_2O_3, in 250 mL conc HCl. Add acid slowly until the material is dissolved and dilute to 1000 mL with water.

g. Hydrogen peroxide, 30%.

h. Nitric acid (HNO_3), 2% (v/v), 1 + 1, and conc.

i. Aqua regia: Add 3 volumes conc HCl to 1 volume conc HNO_3.

j. Standard metal solutions: Prepare a series of standard metal solutions in the optimum concentration range by appropriate dilution of the following stock metal solutions with water containing 1.5 mL conc HNO_3/L. Stock standard solutions are available from a number of commercial suppliers. Alternatively, prepare as described below. Thoroughly dry reagents before use. In general, use reagents of the highest purity. For hydrates, use fresh reagents.

1) *Antimony*—Dissolve 0.2669 g $K(SbO)C_4H_4O_6$ in water, add 10 mL 1 + 1 HCl and dilute to 1000 mL with water; 1.00 mL = 100 μg Sb.

2) *Bismuth*—Dissolve 0.100 g bismuth metal in a minimum volume of 1 + 1 HNO_3. Dilute to 1000 mL with 2% (v/v) HNO_3; 1.00 mL = 100 μg Bi.

3) *Cadmium*—Dissolve 0.100 g cadmium metal in 4 mL conc HNO_3. Add 8.0 mL conc HNO_3 and dilute to 1000 mL with water; 1.00 mL = 100 μg Cd.

4) *Calcium*—Suspend 0.2497 g $CaCO_3$ (dried at 180° for 1 h before weighing) in water and dissolve cautiously with a minimum amount of 1 + 1 HNO_3. Add 10.0 mL conc HNO_3 and dilute to 1000 mL with water; 1.00 mL = 100 μg Ca.

5) *Cesium*—Dissolve 0.1267 g cesium chloride, CsCl, in 1000 mL water; 1.00 mL = 100 μg Cs.

6) *Chromium*—Dissolve 0.1923 g CrO_3 in water. When solution is complete, acidify with 10 mL conc HNO_3 and dilute to 1000 mL with water; 1.00 mL = 100 μg Cr.

7) *Cobalt*—Dissolve 0.1000 g cobalt metal in a minimum amount of 1 + 1 HNO_3. Add 10.0 mL 1 + 1 HCl and dilute to 1000 mL with water; 1.00 mL = 100 μg Co.

8) *Copper*—Dissolve 0.100 g copper metal in 2 mL conc HNO_3, add 10.0 mL conc HNO_3 and dilute to 1000 mL with water; 1.00 mL = 100 μg Cu.

9) *Gold*—Dissolve 0.100 g gold metal in a minimum volume of aqua regia. Evaporate to dryness, dissolve residue in 5 mL conc HCl, cool, and dilute to 1000 mL with water; 1.00 mL = 100 μg Au.

10) *Iridium*—Dissolve 0.1147 g ammonium chloroiridate, $(NH_4)_2IrCl_6$, in a minimum volume of 1% (v/v) HCl and dilute to 100 mL with 1% (v/v) HCl; 1.00 mL = 500 μg Ir.

11) *Iron*—Dissolve 0.100 g iron wire in a mixture of 10 mL 1 + 1 HCl and 3 mL conc HNO_3. Add 5 mL conc HNO_3 and dilute to 1000 mL with water; 1.00 mL = 100 μg Fe.

12) *Lead*—Dissolve 0.1598 g lead nitrate, $Pb(NO_3)_2$, in a minimum amount of 1 + 1 HNO_3, add 10 mL conc HNO_3, and dilute to 1000 mL with water; 1.00 mL = 100 μg Pb.

13) *Lithium*—Dissolve 0.5323 g lithium carbonate, Li_2CO_3, in a minimum volume of 1 + 1 HNO_3. Add 10.0 mL conc HNO_3 and dilute to 1000 mL with water; 1.00 mL = 100 μg Li.

14) *Magnesium*—Dissolve 0.1658 g MgO in a minimum amount of 1 + 1 HNO_3. Add 10.0 mL conc HNO_3 and dilute to 1000 mL with water; 1.00 mL = 100 μg Mg.

15) *Manganese*—Dissolve 0.1000 g manganese metal in 10 mL conc HCl mixed with 1 mL conc HNO_3. Dilute to 1000 mL with water; 1.00 mL = 100 μg Mn.

16) *Nickel*—Dissolve 0.1000 g nickel metal in 10 mL hot conc HNO_3, cool, and dilute to 1000 mL with water; 1.00 mL = 100 μg Ni.

17) *Palladium*—Dissolve 0.100 g palladium wire in a minimum volume of aqua regia and evaporate just to dryness. Add 5 mL conc HCl and 25 mL water and warm until dissolution is complete. Dilute to 1000 mL with water; 1.00 mL = 100 μg Pd.

https://doi.org/10.2105/SMWW.2882.043

18) *Platinum*—Dissolve 0.100 g platinum metal in a minimum volume of aqua regia and evaporate just to dryness. Add 5 mL conc HCl and 0.1 g NaCl and again evaporate just to dryness. Dissolve residue in 20 mL of 1 + 1 HCl and dilute to 1000 mL with water; 1.00 mL = 100 μg Pt.

19) *Potassium*—Dissolve 0.1907 g potassium chloride, KCl, (dried at 110°C) in water and make up to 1000 mL; 1.00 mL = 100 μg K.

20) *Rhodium*—Dissolve 0.386 g ammonium hexachlororhodate, $(NH_4)_3RhCl_6 \cdot 1.5H_2O$, in a minimum volume of 10% (v/v) HCl and dilute to 1000 mL with 10% (v/v) HCl; 1.00 mL = 100 μg Rh.

21) *Ruthenium*—Dissolve 0.205 g ruthenium chloride, $RuCl_3$, in a minimum volume of 20% (v/v) HCl and dilute to 1000 mL with 20% (v/v) HCl; 1.00 mL = 100 μg Ru.

22) *Silver*—Dissolve 0.1575 g silver nitrate, $AgNO_3$, in 100 mL water, add 10 mL conc HNO_3, and make up to 1000 mL; 1.00 mL = 100 μg Ag.

23) *Sodium*—Dissolve 0.2542 g sodium chloride, NaCl, dried at 140°C, in water, add 10 mL conc HNO_3 and make up to 1000 mL; 1.00 mL = 100 μg Na.

24) *Strontium*—Suspend 0.1685 g $SrCO_3$ in water and dissolve cautiously with a minimum amount of 1 + 1 HNO_3. Add 10.0 mL conc HNO_3 and dilute to 1000 mL with water: 1 mL = 100 μg Sr.

25) *Thallium*—Dissolve 0.1303 g thallium nitrate, $TlNO_3$, in water. Add 10 mL conc HNO_3 and dilute to 1000 mL with water; 1.00 mL = 100 μg Tl.

26) *Tin*—Dissolve 1.000 g tin metal in 100 mL conc HCl and dilute to 1000 mL with water; 1.00 mL = 1.00 mg Sn.

27) *Zinc*—Dissolve 0.100 g zinc metal in 20 mL 1 + 1 HCl and dilute to 1000 mL with water; 1.00 mL = 100 μg Zn.

4. Procedure

a. Sample preparation: Required sample preparation depends on the metal form being measured.

If dissolved metals are to be determined, see Section 3030B for sample preparation. If total or acid-extractable metals are to be determined, see Sections 3030C–K. For all samples, make certain that the concentrations of acid and matrix modifiers are the same in both samples and standards.

When determining Ca or Mg, dilute and mix 100 mL sample or standard with 10 mL lanthanum solution (3111B.3*f*) before aspirating. When determining Fe or Mn, mix 100 mL with 25 mL of Ca solution (3111B.3*d*) before aspirating. When determining Cr, mix 1 mL 30% H_2O_2 with each 100 mL before aspirating. Alternatively use proportionally smaller volumes.

b. Instrument operation: Because of differences between makes and models of atomic absorption spectrometers, it is not possible to formulate instructions applicable to every instrument. See manufacturer's operating manual. In general, proceed according to the following: Install a hollow-cathode lamp for the desired metal in the instrument and roughly set the wavelength dial according to Table 3111:I. Set slit width according to manufacturer's suggested setting for the element being measured. Turn on instrument, apply to the hollow-cathode lamp the current suggested by the manufacturer, and let instrument warm up until energy source stabilizes, generally about 10 to 20 min. Readjust current as necessary after warmup. Optimize wavelength by adjusting wavelength dial until optimum energy gain is obtained. Align lamp in accordance with manufacturer's instructions.

Install suitable burner head and adjust burner head position. Turn on air and adjust flow rate to that specified by manufacturer to give maximum sensitivity for the metal being measured. Turn on acetylene, adjust flow rate to value specified, and ignite flame. Let flame stabilize for a few minutes. Aspirate a blank consisting of deionized water containing the same concentration of acid in standards and samples. Zero the instrument. Aspirate a standard solution and adjust aspiration rate of the nebulizer to obtain maximum sensitivity. Adjust burner both vertically and horizontally to obtain maximum response. Aspirate blank again and rezero the instrument. Aspirate a standard near the middle of the linear range. Record absorbance of this standard when freshly prepared and with a new hollow-cathode lamp. Refer to these data on subsequent determinations of the same element to check consistency of instrument setup and aging of hollow-cathode lamp and standard.

The instrument now is ready to operate. When analyses are finished, extinguish flame by turning off first acetylene and then air.

c. Standardization: Select at least three concentrations of each standard metal solution (prepared as in 3111B.3*j*) to bracket the expected metal concentration of a sample. Aspirate blank and zero the instrument. Then aspirate each standard in turn into flame and record absorbance.

Prepare a calibration curve by plotting on linear graph paper absorbance of standards versus their concentrations. For instruments equipped with direct concentration readout, this step is unnecessary. With some instruments it may be necessary to convert percent absorption to absorbance by using a table generally provided by the manufacturer. Plot calibration curves for Ca and Mg based on original concentration of standards before dilution with lanthanum solution. Plot calibration curves for Fe and Mn based on original concentration of standards before dilution with Ca solution. Plot calibration curve for Cr based on original concentration of standard before addition of H_2O_2.

d. Analysis of samples: Rinse nebulizer by aspirating water containing 1.5 mL conc HNO_3/L. Aspirate blank and zero instrument. Aspirate sample and determine its absorbance.

5. Calculations

Calculate concentration of each metal ion, in micrograms per liter for trace elements, and in milligrams per liter for more common metals, by referring to the appropriate calibration curve prepared according to 3111B.4*c*. Alternatively, read concentration directly from the instrument readout if the instrument is so equipped. If the sample has been diluted, multiply by the appropriate dilution factor.

6. Bibliography

Willis, J.B. 1962. Determination of lead and other heavy metals in urine by atomic absorption spectrophotometry. *Anal. Chem.* 34:614.

Also see 3111A.8 and 9.

3111 C. Extraction/Air-Acetylene Flame Method

1. General Discussion

This method is suitable for the determination of low concentrations of cadmium, chromium, cobalt, copper, iron, lead, manganese, nickel, silver, and zinc. The method consists of chelation with ammonium pyrrolidine dithiocarbamate (APDC) and extraction into methyl isobutyl ketone (MIBK), followed by aspiration into an air-acetylene flame.

2. Apparatus

a. Atomic absorption spectrometer and associated equipment: See 3111A.6.

b. Burner head, conventional. Consult manufacturer's operating manual for suggested burner head.

3. Reagents

a. Air: See 3111B.3*a*.

b. Acetylene: See 3111B.3*b*.

c. Metal-free water: See 3111B.3*c*.

d. Methyl isobutyl ketone (MIBK), reagent grade. For trace analysis, purify MIBK by redistillation or by sub-boiling distillation.

e. Ammonium pyrrolidine dithiocarbamate (APDC) solution: Dissolve 4 g APDC in 100 mL water. If necessary, purify APDC with an equal volume of MIBK. Shake 30 s in a separatory funnel, let separate, and withdraw lower portion. Discard MIBK layer.

f. Nitric acid (HNO_3), conc, ultrapure.

g. Standard metal solutions: See 3111B.3*j*.

h. Potassium permanganate solution ($KMnO_4$), 5% (w/v) aqueous.

i. Sodium sulfate (Na_2SO_4), anhydrous.

j. Water-saturated MIBK: Mix one part purified MIBK with one part water in a separatory funnel. Shake 30 s and let separate. Discard aqueous layer. Save MIBK layer.

k. Hydroxylamine hydrochloride solution, 10% (w/v): This solution can be purchased commercially.

4. Procedure

a. Instrument operation: See 3111B.4*b*. After final adjusting of burner position, aspirate water-saturated MIBK into flame and gradually reduce fuel flow until flame is similar to that before aspiration of solvent.

b. Standardization: Select at least three concentrations of standard metal solutions (prepared as in 3111B.3*j*) to bracket expected sample metal concentration and to be, after extraction, in the optimum concentration range of the instrument. Adjust 100 mL of each standard and 100 mL of a metal-free water blank to pH 3 by adding 1*N* HNO_3 or 1*N* NaOH. For individual element extraction, use the following pH ranges to obtain optimum extraction efficiency:

Element	pH Range for Optimum Extraction
Ag	2–5 (complex unstable)
Cd	1–6
Co	2–10
Cr	3–9
Cu	0.1–8
Fe	2–5
Mn	2–4 (complex unstable)
Ni	2–4
Pb	0.1–6
Zn	2–6

NOTE: For Ag and Pb extraction the optimum pH value is 2.3 ± 0.2. The Mn complex deteriorates rapidly at room temperature, resulting in decreased instrument response. Chilling the extract to 0°C may preserve the complex for a few hours. If this is not possible and Mn cannot be analyzed immediately after extraction, use another analytical procedure.

Transfer each standard solution and blank to individual 200-mL volumetric flasks, add 1 mL APDC solution, and shake to mix. Add 10 mL MIBK and shake vigorously for 30 s. (The maximum volume ratio of sample to MIBK is 40.) Let contents of each flask separate into aqueous and organic layers, then carefully add water (adjusted to the same pH at which the extraction was carried out) down the side of each flask to bring the organic layer into the neck and accessible to the aspirating tube.

Aspirate organic extracts directly into the flame (zeroing instrument on a water-saturated MIBK blank) and record absorbance.

Prepare a calibration curve by plotting on linear graph paper absorbances of extracted standards against their concentrations before extraction.

c. Analysis of samples: Prepare samples in the same manner as the standards. Rinse atomizer by aspirating water-saturated MIBK. Aspirate organic extracts treated as above directly into the flame and record absorbances.

With the above extraction procedure only hexavalent chromium is measured. To determine total chromium, oxidize trivalent chromium to hexavalent chromium by bringing sample to a boil and adding sufficient $KMnO_4$ solution dropwise to give a persistent pink color while the solution is boiled for 10 min. Destroy excess $KMnO_4$ by adding 1 to 2 drops hydroxylamine hydrochloride solution to the boiling solution, allowing 2 min for the reaction to proceed. If pink color persists, add 1 to 2 more drops hydroxylamine hydrochloride solution and wait 2 min. Heat an additional 5 min. Cool, extract with MIBK, and aspirate.

During extraction, if an emulsion forms at the water-MIBK interface, add anhydrous Na_2SO_4 to obtain a homogeneous organic phase. In that case, also add Na_2SO_4 to all standards and blanks.

https://doi.org/10.2105/SMWW.2882.043

To avoid problems associated with instability of extracted metal complexes, determine metals immediately after extraction.

5. Calculations

Calculate the concentration of each metal ion in micrograms per liter by referring to the appropriate calibration curve.

6. Bibliography

Allan, J.E. 1961. The use of organic solvents in atomic absorption spectrophotometry. *Spectrochim. Acta* 17:467.

Sachdev, S.L. & P.W. West. 1970. Concentration of trace metals by solvent extraction and their determination by atomic absorption spectrophotometry. *Environ. Sci. Technol.* 4:749.

3111 D. Direct Nitrous Oxide-Acetylene Flame Method

1. General Discussion

This method is applicable to the determination of aluminum, barium, beryllium, calcium, molybdenum, osmium, rhenium, silicon, thorium, titanium, and vanadium.

2. Apparatus

a. Atomic absorption spectrometer and associated equipment: See 3111A.6.

b. Nitrous oxide burner head: Use special burner head as suggested in manufacturer's manual. At roughly 20-min intervals of operation it may be necessary to dislodge the carbon crust that forms along the slit surface with a carbon rod or appropriate alternative.

c. T-junction valve or other switching valve for rapidly changing from nitrous oxide to air, so that flame can be turned on or off with air as oxidant to prevent flashbacks.

3. Reagents

a. Air: See 3111B.3*a*.

b. Acetylene: See 3111B.3*b*.

c. Metal-free water: See 3111B.3*c*.

d. Hydrochloric acid (HCl), 1*N*, 1+1, and conc.

e. Nitric acid (HNO_3), conc.

f. Sulfuric acid (H_2SO_4), 1% (v/v).

g. Hydrofluoric acid (HF), 1*N*.

h. Nitrous oxide, commercially available cylinders. Fit nitrous oxide cylinder with a special nonfreezable regulator or wrap a heating coil around an ordinary regulator to prevent flashback at the burner caused by reduction in nitrous oxide flow through a frozen regulator. (Most modern atomic absorption instruments have automatic gas control systems that will shut down a nitrous oxide-acetylene flame safely in the event of a reduction in nitrous oxide flow rate.)

CAUTION: Use nitrous oxide with strict adherence to manufacturer's directions. Improper sequencing of gas flows at startup and shutdown of instrument can produce explosions from flashback.

i. Potassium chloride solution: Dissolve 250 g KCl in water and dilute to 1000 mL.

j. Aluminum nitrate solution: Dissolve 139 g $Al(NO_3)_3 \cdot 9H_2O$ in 150 mL water. Acidify slightly with conc HNO_3 to preclude possible hydrolysis and precipitation. Warm to dissolve completely. Cool and dilute to 200 mL.

k. Standard metal solutions: Prepare a series of standard metal solutions in the optimum concentration ranges by appropriate dilution of stock metal solutions with water containing 1.5 mL conc HNO_3/L. Stock standard solutions are available from a number of commercial suppliers. Alternatively, prepare as described below.

1) *Aluminum*—Dissolve 0.100 g aluminum metal in an acid mixture of 4 mL 1 + 1 HCl and 1 mL conc HNO_3 in a beaker. Warm gently to effect solution. Transfer to a 1-L flask, add 10 mL 1 + 1 HCl, and dilute to 1000 mL with water; 1.00 mL = 100 μg Al.

2) *Barium*—Dissolve 0.1516 g $BaCl_2$ (dried at 250° for 2 h), in about 10 mL water with 1 mL 1+ 1 HCl. Add 10.0 mL 1 + 1 HCl and dilute to 1000 mL with water; 1.00 mL = 100 μg Ba.

3) *Beryllium—Do not dry.* Dissolve 1.966 g $BeSO_4 \cdot 4H_2O$ in water, add 10.0 mL conc HNO_3, and dilute to 1000 mL with water; 1.00 mL = 100 μg Be.

4) *Calcium*—See 3111B.3*j*4).

5) *Molybdenum*—Dissolve 0.2043 g $(NH_4)_2$ MoO_4 in water and dilute to 1000 mL; 1.00 mL = 100 μg Mo.

6) *Osmium*—Obtain standard 0.1*M* osmium tetroxide solution* and store in glass bottle; 1.00 mL = 19.02 mg Os. Make dilutions daily as needed using 1% (v/v) H_2SO_4. **CAUTION: OsO_4 is extremely toxic and highly volatile.**

7) *Rhenium*—Dissolve 0.1554 g potassium perrhenate, $KReO_4$, in 200 mL water. Dilute to 1000 mL with 1% (v/v) H_2SO_4; 1.00 mL = 100 μg Re.

8) *Silica—Do not dry.* Dissolve 0.4730 g $Na_2SiO_3 \cdot 9H_2O$ in water. Add 10.0 mL conc HNO_3 and dilute to 1000 mL with water. 1.00 mL = 100 μg SiO_2. Store in polyethylene.

9) *Thorium*—Dissolve 0.238 g thorium nitrate, $Th(NO_3)_4 \cdot 4H_2O$ in 1000 mL water; 1.00 mL = 100 μg Th.

10) *Titanium*—Dissolve 0.3960 g pure (99.8 or 99.9%) titanium chloride, $TiCl_4$,† in a mixture of equal volumes of 1*N* HCl and 1*N* HF. Make up to 1000 mL with this acid mixture; 1.00 mL = 100 μg Ti.

11) *Vanadium*—Dissolve 0.2297 g ammonium metavanadate, NH_4VO_3, in a minimum amount of conc HNO_3. Heat to dissolve. Add 10 mL conc HNO_3, and dilute to 1000 mL with water; 1.00 mL = 100 μg V.

---

* GFS Chemicals, Inc., Columbus, OH, Cat. No. 64, or equivalent.

† Alpha Ventron, P.O. Box 299, 152 Andover St., Danvers, MA 01923, or equivalent.

https://doi.org/10.2105/SMWW.2882.043

4. Procedure

a. Sample preparation: See 3111B.4*a*.

When determining Al, Ba, or Ti, mix 2 mL KCl solution into 100 mL sample and standards before aspiration. When determining Mo and V, mix 2 mL $Al(NO_3)_3 \cdot 9H_2O$ into 100 mL sample and standards before aspiration.

b. Instrument operation: See 3111B.4*b*. After adjusting wavelength, install a nitrous oxide burner head. Turn on acetylene (without igniting flame) and adjust flow rate to value specified by manufacturer for a nitrous oxide-acetylene flame. Turn off acetylene. With both air and nitrous oxide supplies turned on, set T-junction valve to nitrous oxide and adjust flow rate according to manufacturer's specifications. Turn switching valve to the air position and verify that flow rate is the same. Turn acetylene on and ignite to a bright yellow flame. With a rapid motion, turn switching valve to nitrous oxide. The flame should have a red cone above the burner. If it does not, adjust fuel flow to obtain red cone. After nitrous oxide flame has been ignited, let burner come to thermal equilibrium before beginning analysis.

Aspirate a blank consisting of deionized water containing 1.5 mL conc HNO_3/L and check aspiration rate. Adjust if necessary to a rate between 3 and 5 mL/ min. Zero the instrument. Aspirate a standard of the desired metal with a concentration near the midpoint of the optimum concentration range and adjust burner (both horizontally and vertically) in the light path to obtain maximum response. Aspirate blank again and re-zero the instrument. The instrument now is ready to run standards and samples.

To extinguish flame, turn switching valve from nitrous oxide to air and turn off acetylene. This procedure eliminates the danger of flashback that may occur on direct ignition or shutdown of nitrous oxide and acetylene.

c. Standardization: Select at least three concentrations of standard metal solutions (prepared as in 3111D.3*k*) to bracket the expected metal concentration of a sample. Aspirate each in turn into the flame and record absorbances.

Most modern instruments are equipped with microprocessors and digital readout which permit calibration in direct concentration terms. If instrument is not so equipped, prepare a calibration curve by plotting on linear graph paper absorbance of standards versus concentration. Plot calibration curves for Al, Ba, and Ti based on original concentration of standard before adding KCl solution. Plot calibration curves for Mo and V based on original concentration of standard before adding $Al(NO_3)_3$ solution.

d. Analysis of samples: Rinse atomizer by aspirating water containing 1.5 mL conc HNO_3/L and zero instrument. Aspirate a sample and determine its absorbance.

5. Calculations

Calculate concentration of each metal ion in micrograms per liter by referring to the appropriate calibration curve prepared according to 3111D.4*c*.

Alternatively, read the concentration directly from the instrument readout if the instrument is so equipped. If sample has been diluted, multiply by the appropriate dilution factor.

6. Bibliography

Willis, J.B. 1965. Nitrous oxide-acetylene flame in atomic absorption spectroscopy. *Nature* 207:715.

Also see 3111A.8 and 9.

3111 E. Extraction/Nitrous Oxide-Acetylene Flame Method

1. General Discussion

a. Application: This method is suitable for the determination of aluminum at concentrations less than 900 μg/L and beryllium at concentrations less than 30 μg/L. The method consists of chelation with 8-hydroxyquinoline, extraction with methyl isobutyl ketone (MIBK), and aspiration into a nitrous oxide-acetylene flame.

b. Interferences: Concentrations of Fe greater than 10 mg/L interfere by suppressing Al absorption. Iron interference can be masked by addition of hydroxylamine hydrochloride/1,10-phenanthroline. Mn concentrations up to 80 mg/L do not interfere if turbidity in the extract is allowed to settle. Mg forms an insoluble chelate with 8-hydroxyquinoline at pH 8.0 and tends to remove Al complex as a coprecipitate. However, the Mg complex forms slowly over 4 to 6 min; its interference can be avoided if the solution is extracted immediately after adding buffer.

2. Apparatus

Atomic absorption spectrometer and associated equipment: See 3111A.6.

3. Reagents

a. Air: See 3111B.3*a*.

b. Acetylene: See 3111B.3*b*.

c. Ammonium hydroxide (NH_4OH), conc.

d. Buffer: Dissolve 300 g ammonium acetate, $NH_4C_2H_3O_2$, in water, add 105 mL conc NH_4OH, and dilute to 1 L.

e. Metal-free water: See 3111B.3*c*.

f. Hydrochloric acid (HCl), conc.

g. 8-Hydroxyquinoline solution: Dissolve 20 g 8-hydroxyquinoline in about 200 mL water, add 60 mL glacial acetic acid, and dilute to 1 L with water.

h. Methyl isobutyl ketone: See 3111C.3*d*.

i. Nitric acid (HNO_3), conc.

j. Nitrous oxide: See 3111D.3*h*.

k. Standard metal solutions: Prepare a series of standard metal solutions containing 5 to 1000 μg/L by appropriate dilution of the stock metal solutions prepared according to 3111D.3*k*.

https://doi.org/10.2105/SMWW.2882.043

l. Iron masking solution: Dissolve 1.3 g hydroxylamine hydrochloride and 6.58 g 1,10-phenanthroline monohydrate in about 500 mL water and dilute to 1 L with water.

4. Procedure

a. Instrument operation: See 3111B.4*b*, C.4*a*, and D.4*b*. After final adjusting of burner position, aspirate MIBK into flame and gradually reduce fuel flow until flame is similar to that before aspiration of solvent. Adjust wavelength setting according to Table 3111:I.

b. Standardization: Select at least three concentrations of standard metal solutions (prepared as in 3111E.3*k*) to bracket the expected metal concentration of a sample and transfer 100 mL of each (and 100 mL water blank) to four different 200-mL volumetric flasks. Add 2 mL 8-hydroxyquinoline solution, 2 mL masking solution (if required), and 10 mL buffer to one flask, immediately add 10 mL MIBK, and shake vigorously. The duration of shaking affects the forms of aluminum complexed. A fast, 10-s shaking time favors monomeric Al, whereas 5 to 10 min of shaking also will complex polymeric species. Adjustment of the 8-hydroxyquinoline to sample ratio can improve recoveries of extremely high or low concentrations of aluminum. Treat each blank, standard, and sample in similar fashion. Continue as in 3111C.4*b*.

c. Analysis of samples: Rinse atomizer by aspirating water-saturated MIBK. Aspirate extracts of samples treated as above, and record absorbances.

5. Calculations

Calculate concentration of each metal in micrograms per liter by referring to the appropriate calibration curve prepared according to 3111E.4*b*.

3112 METALS BY COLD-VAPOR ATOMIC ABSORPTION SPECTROMETRY*

3112 A. Introduction

For general introductory material on atomic absorption spectrometric methods, see Section 3111A.

---

* Approved by Standard Methods Committee, 2009. Editorial revisions, 2011.

3112 B. Cold-Vapor Atomic Absorption Spectrometric Method

1. General Discussion

This method is applicable to the determination of mercury.

The QC practices considered to be an integral part of each method can be found in Section 3020.

2. Apparatus

When possible, dedicate glassware for use in Hg analysis. Avoid using glassware previously exposed to high levels of Hg, such as those used in COD, TKN, or Cl^- analysis.

a. Atomic absorption spectrometer and associated equipment: See Section 3111A.6. Instruments and accessories specifically designed for measuring mercury via the cold vapor technique are available commercially and may be substituted.

b. Absorption cell, a glass or plastic tube approximately 2.5 cm in diameter. An 11.4-cm-long tube has been found satisfactory, but a 15-cm-long tube is preferred. Grind tube ends perpendicular to the longitudinal axis, and cement quartz windows in place. Attach gas inlet and outlet ports (6.4 mm diam) 1.3 cm from each end.

c. Cell support: Strap cell to the flat nitrous-oxide burner head or other suitable support and align in light beam to give maximum transmittance.

d. Air pumps: Use any peristaltic pump with electronic speed control capable of delivering an air flow of 2 L/min. Any other regulated compressed air system or air cylinder also is satisfactory.

e. Flowmeter, capable of measuring an air flow of 2 L/min.

f. Aeration tubing, a straight glass frit having a coarse porosity for use in reaction flask.

g. Reaction flask, 250-mL Erlenmeyer flask or a BOD bottle, fitted with a rubber stopper to hold aeration tube.

h. Drying tube, 150-mm × 18-mm-diam, containing 20 g $Mg(ClO_4)_2$. A 60-W light bulb with a suitable shade may be substituted to prevent condensation of moisture inside the absorption cell. Position bulb to maintain cell temperature at 10°C above ambient.

i. Connecting tubing, glass tubing to pass mercury vapor from reaction flask to absorption cell and to interconnect all other components. Clear vinyl plastic tubing* may be substituted for glass.

3. Reagents†

a. Metal-free water: See Section 3111B.3*c*.

b. Stock mercury solution: Dissolve 0.1354 g mercuric chloride ($HgCl_2$) in about 70 mL water, add 1 mL conc HNO_3, and dilute to 100 mL with water; 1.00 mL = 1.00 mg Hg.

c. Standard mercury solutions: Prepare a series of standard mercury solutions containing 0 to 5 μg/L by appropriate dilution of stock mercury solution with water containing 10 mL conc HNO_3/L. Prepare standards daily.

d. Nitric acid (HNO_3), conc.

e. Potassium permanganate solution: Dissolve 50 g $KMnO_4$ in water and dilute to 1 L.

f. Potassium persulfate solution: Dissolve 50 g $K_2S_2O_8$ in water and dilute to 1 L.

g. Sodium chloride-hydroxylamine sulfate solution: Dissolve 120 g NaCl and 120 g $(NH_2OH)_2 \cdot H_2SO_4$ in water and dilute to 1 L. A 10% hydroxylamine hydrochloride solution may be substituted for the hydroxylamine sulfate.

h. Stannous ion (Sn^{2+}) solution: Use either stannous chloride, ¶ *h*1) below, or stannous sulfate, ¶ *h*2) below, to prepare this solution containing about 7.0 g Sn^{2+}/100 mL.

1) Dissolve 10 g $SnCl_2$ in water containing 20 mL conc HCl and dilute to 100 mL.

2) Dissolve 11 g $SnSO_4$ in water containing 7 mL conc H_2SO_4 and dilute to 100 mL.

Both solutions decompose with aging. If a suspension forms, stir reagent continuously during use. Reagent volume is sufficient to process about 20 samples; adjust volumes prepared to accommodate number of samples processed.

i. Sulfuric acid (H_2SO_4), conc.

4. Procedure

a. Instrument operation: See Section 3111B.4*b*. Set wavelength to 253.7 nm. Install absorption cell and align in light path to give maximum transmission. Connect associated equipment to absorption cell with glass or vinyl plastic tubing, as indicated in Figure 3112:1. Turn on air and adjust flow rate to 2 L/min. Allow air to flow continuously. Alternatively, follow manufacturer's directions for operation. NOTE: Fluorescent lighting may increase baseline noise.

---

* Tygon, or equivalent.

† Use specially prepared reagents low in mercury.

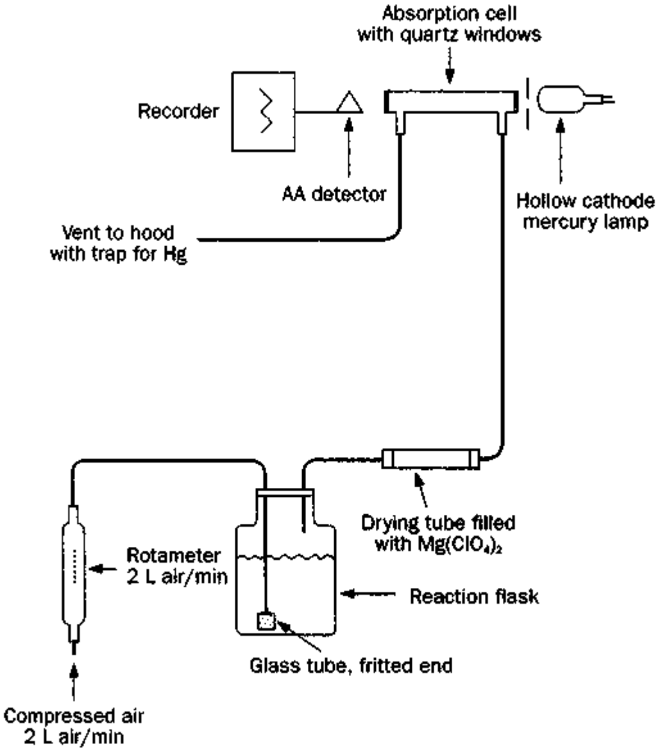

Figure 3112:1. **Schematic arrangement of equipment for measuring mercury by cold-vapor atomic absorption technique.**

b. Standardization: Transfer 100 mL each of the 1.0, 2.0, and 5.0 μg/L Hg standard solutions and a blank of 100 mL water to 250-mL Erlenmeyer reaction flasks. Add 5 mL conc H_2SO_4 and 2.5 mL conc HNO_3 to each flask. Add 15 mL $KMnO_4$ solution to each flask and let stand at least 15 min. Add 8 mL $K_2S_2O_8$ solution to each flask and heat for 2 h in a water bath at 90 to 95°C. Cool to room temperature.

Treating each flask individually, add enough NaCl-hydroxylamine solution to reduce excess $KMnO_4$, then add 5 mL $SnCl_2$ or $SnSO_4$ solution and immediately attach flask to aeration apparatus. As Hg is volatilized and carried into the absorption cell, absorbance will increase to a maximum within a few seconds. As soon as recorder returns approximately to the baseline, remove stopper holding the frit from reaction flask, and replace with a flask containing water. Flush system for a few seconds, and run the next standard in the same manner. Construct a standard curve by plotting peak height versus micrograms Hg.

c. Analysis of samples: Transfer 100 mL sample or portion diluted to 100 mL containing not more than 5.0 μg Hg/L to a reaction flask. Treat as in 3112B.4*b*. Seawaters, brines, and effluents high in chlorides require as much as another 25 mL $KMnO_4$ solution. During oxidation step, chlorides are converted to free chlorine, which absorbs at 253 nm. Remove all free chlorine before the Hg is reduced and swept into the cell by using an excess (25 mL) of hydroxylamine reagent.

Remove free chlorine by sparging sample gently with air or nitrogen after adding hydroxylamine reducing solution. Use a separate tube and frit to avoid carryover of residual stannous chloride, which could cause reduction and loss of mercury.

TABLE 3112:I. INTERLABORATORY PRECISION AND BIAS OF COLD-VAPOR ATOMIC ABSORPTION SPECTROMETRIC METHOD FOR MERCURY[1]

Form	Conc. *µg/L*	SD *µg/L*	Relative SD %	Relative Error %	No. of Participants
Inorganic	0.34	0.077	22.6	21.0	23
Inorganic	4.2	0.56	13.3	14.4	21
Organic	4.2	0.36	8.6	8.4	21

5. Calculation

Determine peak height of sample from recorder chart and read mercury value from standard curve prepared according to 3112B.4*b*.

6. Precision and Bias

Data on interlaboratory precision and bias for this method are given in Table 3112:I.

7. Reference

1. Kopp, J.F., M.C. Longbottom & L.B. Lobring. 1972. “Cold vapor” method for determining mercury. *J. Amer. Water Works Assoc.* 64:20.

8. Bibliography

Hatch, W.R. & W.L. Ott. 1968. Determination of submicrogram quantities of mercury by atomic absorption spectrophotometry. *Anal. Chem.* 40:2085.

Uthe, J.F., F.A.J. Armstrong & M.P. Stainton. 1970. Mercury determination in fish samples by wet digestion and flameless atomic absorption spectrophotometry. *J. Fish. Res. Board Can.* 27:805.

Feldman, C. 1974. Preservation of dilute mercury solutions. *Anal. Chem.* 46:99.

Bothner, M.H. & D.E. Robertson. 1975. Mercury contamination of sea water samples stored in polyethylene containers. *Anal. Chem.* 47:592.

Hawley, J.E. & J.D. Ingle, Jr. 1975. Improvements in cold vapor atomic absorption determination of mercury. *Anal. Chem.* 47:719.

Lo, J.M. & C.M. Wal. 1975. Mercury loss from water during storage: Mechanisms and prevention. *Anal. Chem.* 47:1869.

El-Awady, A.A., R.B. Miller & M.J. Carter. 1976. Automated method for the determination of total and inorganic mercury in water and wastewater samples. *Anal. Chem.* 48:110.

Oda, C.E. & J.D. Ingle, Jr. 1981. Speciation of mercury by cold vapor atomic absorption spectrometry with selective reduction. *Anal. Chem.* 53:2305.

Suddendorf, R.F. 1981. Interference by selenium or tellurium in the determination of mercury by cold vapor generation atomic absorption spectrometry. *Anal. Chem.* 53:2234.

Heiden, R.W. & D.A. Aikens. 1983. Humic acid as a preservative for trace mercury (II) solutions stored in polyolefin containers. *Anal. Chem.* 55:2327.

Chou, H.N. & C.A. Naleway. 1984. Determination of mercury by cold vapor atomic absorption spectrometry. *Anal. Chem.* 56:1737.

3113 METALS BY ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY*

3113 A. Introduction

1. Applications

Electrothermal atomic absorption permits determination of most metallic elements with sensitivities and detection levels from 20 to 1000 times better than those of conventional flame techniques without extraction or sample concentration. This increase in sensitivity results from an increase in atom density within the furnace as compared to flame atomic absorption. Many elements can be determined at concentrations of, or below, 1.0 μg/L. An additional advantage of electrothermal atomic absorption is that only a very small volume of sample is required.

The electrothermal technique is used only at concentration levels below the optimum range of direct flame atomic absorption because it is subject to more interferences than the flame procedure and requires increased analysis time. The method of standard additions may be required to ensure validity of data. Because of the high sensitivity of this technique, it is extremely susceptible to contamination; extra care in sample handling and analysis may be required.

2. Principle

Electrothermal atomic absorption spectroscopy is based on the same principle as direct flame atomization but an electrically heated atomizer or graphite furnace replaces the standard burner head. A discrete sample volume is dispensed into the graphite sample tube (or cup). Typically, determinations are made by heating the sample in three or more stages. First, a low current heats the tube to dry the sample. The second, or charring, stage destroys organic matter and volatilizes other matrix components at an intermediate temperature. Finally, a high current heats the tube to incandescence and, in an inert atmosphere, atomizes the element being determined. Additional stages frequently are added to aid in drying and charring, and to clean and cool the tube between samples. The resultant ground-state atomic vapor absorbs monochromatic radiation from the source. A photoelectric detector measures the intensity of transmitted radiation. The inverse of the transmittance is related logarithmically to the absorbance, which is directly proportional to the number density of vaporized ground-state atoms (the Beer-Lambert law) over a limited concentration range.

3. Interferences

Electrothermal atomization determinations may be subject to significant interferences from molecular absorption as well as chemical and matrix effects. Molecular absorption may occur when components of the sample matrix volatilize during atomization, resulting in broadband absorption. Several background correction techniques are available commercially to compensate for this interference. A continuum source such as a deuterium arc can correct for background up to absorbance levels of about 0.8. Continuum lamp intensity diminishes at long wavelengths and use of continuum background correction is limited to analytical wavelengths below 350 nm. Zeeman effect background correctors can handle background absorbance up to 1.5 to 2.0. The self-reversal (e.g., Smith-Hieftje) correction technique can accommodate background absorbance levels as large as 2.5 to 3.0 (see Section 3111A.3*b*). Both Zeeman and self-reversal background corrections are susceptible to rollover (development of a negative absorbance-concentration relationship) at high absorbances. The rollover absorbance for each element should be available in the manufacturer's literature. Curvature due to rollover should become apparent during calibration; dilution produces a more linear calibration plot. Use background correction when analyzing samples containing high concentrations of acid or dissolved solids and in determining elements for which an absorption line below 350 nm is used.

Matrix modification can be useful in minimizing interference and increasing analytical sensitivity. Determine need for a modifier by evaluating recovery of a sample with a known addition. Recovery near 100% indicates that sample matrix does not affect analysis. Chemical modifiers generally modify relative volatilities of matrix and metal. Some modifiers enhance matrix removal, isolating the metal, while other modifiers inhibit metal volatilization, allowing use of higher ashing/charring temperatures and increasing efficiency of matrix removal. Chemical modifiers are added at high concentration (percent level) and can lead to sample contamination from impurities in the modifier solution. Heavy use of chemical modifiers may reduce the useful life (normally 50 to 100 firings) of the graphite tube. Nonetheless, the use of matrix modifiers is encouraged. Some specific chemical modifiers and approximate concentrations are listed in Table 3113:I.

Addition of a chemical modifier directly to the sample before analysis is restricted to inexpensive additives (e.g., phosphoric acid). Use of palladium salts for matrix modification normally requires methods of co-addition, in which sample and modifier are added consecutively to the furnace either manually or, preferably, with an automatic sampler. Palladium salts (nitrate is preferred, chloride is acceptable) are listed in Table 3113:I as a modifier for many metals. The palladium solution (50 to 2000 mg/L) generally includes citric or ascorbic acid, which aids reduction of palladium in the furnace. Citric acid levels of 1 to 2% are typical. Use of hydrogen (5%) in the purge gas (available commercially as a mixture) also reduces palladium, eliminating need for organic reducing acids. CAUTION: **Do not mix hydrogen and other gases in the laboratory; hydrogen gas is very flammable—handle with caution**. Use low levels of pal-

---

* Approved by Standard Methods Committee, 2010.
Joint Task Group: 20th Edition—Raymond J. Lovett (chair), David J. Kaptain.

https://doi.org/10.2105/SMWW.2882.045

TABLE 3113:I. POTENTIAL MATRIX MODIFIERS FOR ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY*

Modifier	Analyses for Which Modifier May Be Useful
1500 mg Pd/L + 1000 mg $Mg(NO_3)_2$/L[1]	Ag, As, Au, Bi, Cu, Ge, Mn, Hg, In, Sb, Se, Sn, Te, Tl
500–2000 mg Pd/L + reducing agent[2]†	Ag, As, Bi, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb
5000 mg $Mg(NO_3)_2$/L[1]	Be, Co, Cr, Fe, Mn, V
100–500 mg Pd/L[2]	As, Ga, Ge, Sn
50 mg Ni/L[2]	As, Se, Sb
2% PO_4^{3-} + 1000 mg Mg $(NO_3)_2$/L[1]	Cd, Pb

* Assumes 10 μL modifier/10 μL sample.

† Citric acid (1–2%) preferred; ascorbic acid or H_2 acceptable.

TABLE 3113:II. DETECTION LEVELS AND CONCENTRATION RANGES FOR ELECTROTHERMAL ATOMIZATION ATOMIC ABSORPTION SPECTROMETRY

Element	Wavelength *nm*	Estimated Detection Level *μg/L*	Optimum Concentration Range *μg/L*
Al	309.3	3	20–200
Sb	217.6	0.8	20–300
As	193.7	0.5	5–100
Ba	553.6	2	10–200
Be	234.9	0.02	1–30
Cd	228.8	0.05	0.5–10
Cr	357.9	0.1	5–100
Co	240.7	0.7	5–100
Cu	324.7	0.7	5–100
Fe	248.3	1	5–100
Pb*	283.3	0.7	5–100
Mn	279.5	0.2	1–30
Mo	313.3	1	3–60
Ni	232.0	0.6	5–100
Se	196.0	0.6	5–100
Ag	328.1	0.2	1–25
Sn	224.6	1.7	20–300

* The more sensitive 217.0-nm wavelength is recommended for instruments with background correction capabilities.

ladium (50 to 250 mg/L) for normal samples and higher levels for complex samples. Addition of excess palladium modifier may widen atomization peaks; in such cases peak area measurements may provide higher quality results. The recommended mode of modifier use is through co-addition to the furnace of about 10 μL of the palladium (or other) modifier solution. Palladium may not be the best modifier in all cases and cannot be recommended unconditionally. Test samples requiring a modifier first with palladium; test other modifiers only if palladium is unsuccessful or to minimize modifier cost. See 3113B.3*d* for preparation of modifier solution.

Temperature ramping (i.e., gradual heating) can be used to decrease background interferences and permits analysis of samples with complex matrices. Ramping permits a controlled, continuous increase of furnace temperature in any of the various steps of the temperature sequence. Ramp drying is used for samples containing mixtures of solvents or for samples with a high salt content (to avoid spattering). If spattering is suspected, develop drying ramp by visual inspection of the drying stage, using a mirror. Samples that contain a complex mixture of matrix components sometimes require ramp charring to effect controlled, complete thermal decomposition. Ramp atomization may minimize background absorption by permitting volatilization of the element being determined before the matrix. This is especially applicable in the determination of such volatile elements as cadmium and lead. Use of time-resolved absorbance profiles (available on most modern instruments) greatly aids method development. Changes in atomization, notably the element peak appearance time and magnitude of background and metal absorbances, can be monitored directly.

Improve analysis by using a graphite platform, inserted into the graphite tube, as the atomization site. The platform is not heated as directly by the current flowing through the graphite tube; thus the metal atomizes later and under more uniform conditions.

Use standard additions to compensate for matrix interferences. When making standard additions, determine whether the added metal and that in the sample behave similarly under the specified conditions. [See 3113B.4*d*2)]. In the extreme, test every sample for recovery (85 to 115% recovery desired) to determine whether modification of the temperature program or use of the method of standard additions is needed. Test every new sample type for recovery. Recovery of only 40 to 85% generally indicates that standard addition is required. Often, as long as the samples are from sources of consistent properties, a representative recovery can be used to characterize the analysis and determine the necessity of standard addition. Test samples of unknown origin or of complex composition (digestates, for example) individually for metal recovery. Ideally, chemical modifiers and graphite platforms render the sample fit to be analyzed using a standard analytical calibration curve. Always verify this assumption; however, a properly developed method with judicious use of chemical modifiers should eliminate the necessity for standard addition in all but the most extreme samples.

Chemical interaction of the graphite tube with various elements to form refractory carbides occurs at high charring and atomization temperatures. Elements that form carbides are barium, molybdenum, nickel, titanium, vanadium, and silicon. Carbide formation is characterized by broad, tailing atomization peaks and reduced sensitivity. Using pyrolytically coated tubes for these metals minimizes the problem.

4. Sensitivity, Detection Levels, and Optimum Concentration Range

Estimated detection levels and optimum concentration ranges are listed in Table 3113:II. These values may vary with the chemical form of the element being determined, sample composition, or instrumental conditions.

For a given sample, increased sensitivity may be achieved by using a larger sample volume or by reducing flow rate of the purge gas or by using gas interrupt during atomization. Note, however, that these techniques also will increase the effects of any interferences present. Sensitivity can be decreased by diluting the sample, reducing sample volume, increasing purge-gas flow, or using a less sensitive wavelength. Use of argon, rather than nitrogen, as the purge gas generally improves sensitivity and reproducibility. Hydrogen mixed with the inert gas may suppress chemical interference and increase sensitivity by acting as a reducing agent, thereby aiding in producing more ground-state atoms. Pyrolytically coated graphite tubes can increase sensitivity for the more refractory elements and are recommended. The optical pyrometer/maximum power accessory available on some instruments also offers increased sensitivity with lower atomization temperatures for many elements.

Using the Stabilized Temperature Platform Furnace (STPF) technique, which is a combination of individual techniques, also offers significant interference reduction with improved sensitivity. Sensitivity changes with sample tube age. Discard graphite tubes when significant variations in sensitivity or poor reproducibility are observed. The use of high acid concentrations, brine samples, and matrix modifiers often drastically reduces tube life. Preferably use the graphite platform in such situations.

5. References

1. Perkin-Elmer Corp. 1991. Summary of Standard Conditions for Graphite Furnace. Perkin-Elmer Corp., Norwalk, Conn.
2. Rothery, E., ed. 1988. Analytical Methods for Graphite Tube Atomizers. Varian Techtron Pty, Ltd., Mulgrave, Victoria, Australia.

6. Bibliography

Fernandez, F.J. & D.C. Manning. 1971. Atomic absorption analyses of metal pollutants in water using a heated graphite atomizer. *Atomic Absorption Newsletter* 10:65.

Segar, D.A. & J.G. Gonzalez. 1972. Evaluation of atomic absorption with a heated graphite atomizer for the direct determination of trace transition metals in sea water. *Anal. Chim. Acta* 58:7.

Barnard, W.M. & M.J. Fishman. 1973. Evaluation of the use of heated graphite atomizer for the routine determination of trace metals in water. *Atomic Absorption Newsletter* 12:118.

Kahn, H.L. 1973. The detection of metallic elements in wastes and waters with the graphite furnace. *Int. J. Environ. Anal. Chem.* 3:121.

Martin, T.D. & J.F. Kopp. 1978. Methods for Metals in Drinking Water. U.S. Environmental Protection Agency, Environmental Monitoring and Support Lab., Cincinnati, Ohio.

Hydes, D.J. 1980. Reduction of matrix effects with a soluble organic acid in the carbon furnace atomic absorption spectrometric determination of cobalt, copper, and manganese in seawater. *Anal. Chem.* 52:289.

Sotera, J.J. & H.L. Kahn. 1982. Background correction in AAS. *Amer. Lab.* 14:100.

Smith, S.B. & G.M. Hieftje. 1983. A new background-correction method for atomic absorption spectrometry. *Appl. Spectrosc.* 37:419.

Grosser, Z. 1985. Techniques in Graphite Furnace Atomic Absorption Spectrophotometry. Perkin-Elmer Corp., Ridgefield, Conn.

Slavin, W. & G.R. Carnick. 1985. A survey of applications of the stabilized temperature platform furnace and Zeeman correction. *Atomic Spectrosc.* 6:157.

Brueggemeyer, T. & F. Fricke. 1986. Comparison of furnace & atomization behavior of aluminum from standard & thorium-treated L'vov platforms. *Anal. Chem.* 58:1143.

3113 B. Electrothermal Atomic Absorption Spectrometric Method

1. General Discussion

This method is suitable for determination of micro quantities of aluminum, antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, iron, lead, manganese, molybdenum, nickel, selenium, silver, and tin.

2. Apparatus

a. Atomic absorption spectrometer: See Section 3111A.6*a*. The instrument must have background correction capability.

b. Source lamps: See Section 3111A.6*d*.

c. Graphite furnace: Use an electrically heated device with electronic control circuitry designed to carry a graphite tube or cup through a heating program that provides sufficient thermal energy to atomize the elements of interest. Furnace heat controllers with only three heating steps are adequate only for fresh waters with low dissolved solids content. For salt waters, brines, and other complex matrices, use a furnace controller with up to seven individually programmed heating steps. Fit the furnace into the sample compartment of the spectrometer in place of the conventional burner assembly. Use argon as a purge gas to minimize oxidation of the furnace tube and to prevent the formation of metallic oxides. Use graphite tubes with platforms to minimize interferences and to improve sensitivity.

d. Readout: See Section 3111A.6*c*.

e. Sample dispensers: Use microliter pipets (5 to 100 μL) or an automatic sampling device designed for the specific instrument.

f. Vent: See Section 3111A.6*f*.

g. Cooling water supply: Cool with tap water flowing at 1 to 4 L/min or use a recirculating cooling device.

h. Membrane filter apparatus: Use an all-glass filtering device and 0.45-μm or smaller-pore-diameter membrane filters. For trace analysis of aluminum, use polypropylene or TFE devices.

3. Reagents

a. Metal-free water: See Section 3111B.3*c*.

b. Hydrochloric acid (HCl), 1 + 1 and conc.

c. Nitric acid (HNO_3), 1 + 1 and conc.

d. Matrix modifier stock solutions:

1) *Magnesium nitrate*, 10 000 mg Mg/L—Dissolve 10.5 g $Mg(NO_3)_2 \cdot 6H_2O$ in water. Dilute to 100 mL.

2) *Nickel nitrate*, 10 000 mg Ni/L—Dissolve 4.96 g $Ni(NO_3)_2 \cdot 6H_2O$ in water. Dilute to 100 mL.

https://doi.org/10.2105/SMWW.2882.045

3) *Phosphoric acid*, 10% (v/v)—Add 10 mL conc H_3PO_4 to water. Dilute to 100 mL.

4) *Palladium nitrate*, 4000 mg Pd/L—Dissolve 9.34 g $Pd(NO_3)_2 \cdot H_2O$ in water. Dilute to 1 L.

5) *Citric acid*, 4%—Dissolve 40 g citric acid in water. Dilute to 1 L.

NOTE: All of the modifier solutions recommended in Table 3113:I can be prepared with volumetric combination of the above solutions and water. For preparation of other matrix modifiers, see references or follow manufacturers' instructions.

e. Stock metal solutions: Refer to Sections 3111B.3*j* and 3114B.3.

f. Chelating resin: 100 to 200 mesh* purified by heating at 60°C in 10*N* NaOH for 24 h. Cool resin and rinse 10 times each with alternating portions of 1*N* HCl, metal-free water, 1*N* NaOH, and metal-free water.

g. Metal-free seawater (or brine): Fill a 1.4-cm-ID × 20-cm-long borosilicate glass column to within 2 cm of the top with purified chelating resin. Elute resin with successive 50-mL portions of 1*N* HCl, metal-free water, 1*N* NaOH, and metal-free water at the rate of 5 mL/min just before use. Pass salt water or brine through the column at a rate of 5 mL/min to extract trace metals present. Discard the first 10 bed volumes (300 mL) of eluate.

4. Procedures

a. Sample pretreatment: Before analysis, pretreat all samples as indicated below. Rinse all glassware with 1 + 1 HNO_3 and water. Carry out digestion procedures in a clean, dust-free laboratory area to avoid sample contamination. For digestion of trace aluminum, use polypropylene or TFE utensils to avoid leachable aluminum from glassware.

1) Dissolved metals and metals where sample turbidity is <1 NTU—See Section 3030B. For samples requiring arsenic and/or selenium analysis add 3 mL 30% hydrogen peroxide/100 mL sample and an appropriate volume of nickel nitrate solution (see Table 3113:I) before analysis. Nickel may be deleted if palladium is co-added during analysis. For all other metals no further pretreatment is required except for adding a matrix modifier when necessary.

2) Total recoverable metals (Al, Sb, Ba, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Mo, Ni, Ag, and Sn)—NOTE: Sb and Sn are not recovered unless HCl is used in the digestion. See Section 3030D. Quantitatively transfer digested sample to a 100-mL volumetric flask, add an appropriate amount of matrix modifier (see Table 3113:I), and dilute to volume with water.

3) Total recoverable metals (As, Se)—Transfer 100 mL of shaken sample, 1 mL conc HNO_3, and 2 mL 30% H_2O_2 to a clean, acid-washed 250-mL beaker. Heat on a hot plate without allowing solution to boil until volume has been reduced to about 50 mL. Remove from hot plate and let cool to room temperature. Add an appropriate concentration of nickel (see Table 3113:I), and dilute to volume in a 100-mL volumetric flask with water. Substitution of palladium is uneconomical. Nickel may be deleted if palladium is co-added during analysis. Simultaneously prepare a digested blank by substituting water for sample and proceed with digestion as described above.

b. Instrument operation: Mount and align furnace device according to manufacturer's instructions. Turn on instrument and data collection system. Select appropriate light source and adjust to recommended electrical setting. Select proper wavelength and set all conditions according to manufacturer's instructions, including background correction. Background correction is important when elements are determined at short wavelengths or when sample has a high level of dissolved solids. Background correction normally is not necessary at wavelengths longer than 350 nm. If background correction above 350 nm is needed, deuterium arc background correction is not useful and other types must be used.

Select proper inert- or sheath-gas flow. In some cases, it is desirable to interrupt the inert-gas flow during atomization. Such interruption results in increased sensitivity by increasing residence time of the atomic vapor in the optical path. Gas interruption also increases background absorption and intensifies interference effects, but modern background correction methods usually eliminate these problems. Consider advantages and disadvantages of this option for each matrix when optimizing analytical conditions.

To optimize graphite furnace conditions, carefully adjust furnace temperature settings to maximize sensitivity and precision and to minimize interferences. Follow manufacturer's instructions.

Use drying temperatures slightly above the solvent boiling point and provide enough time and temperature for complete evaporation without boiling or spattering.

Select atomization temperature by determining the lowest temperature providing maximum sensitivity without significantly eroding precision. Optimize by a series of successive determinations at various atomization temperatures using a standard solution giving an absorbance of 0.2 to 0.5.

The charring temperature must be high enough to maximize volatilization of interfering matrix components yet too low to volatilize the element of interest. With the drying and atomization temperatures set to their optimum values, analyze a standard solution at a series of charring temperatures in increasing increments of 50 to 100°C. When the optimum charring temperature is exceeded, there will be a significant drop in sensitivity. Plot charring temperature versus sample absorbance: the optimum charring temperature is the highest temperature without reduced sensitivity. Verify optimization with major changes in sample matrix.

c. Instrument calibration: Prepare standard solutions for instrument calibration by diluting metal stock solutions. Prepare standard solutions every 2 weeks, or more frequently as needed if standard response indicates degradation of standard. A decrease in signal of more than 10% requires investigation and indicates the possible need for fresh standards.

Prepare a blank and at least three calibration standards in the appropriate concentration range (see Table 3113:II) for correlating element concentration and instrument response. Match the matrix of the standard solutions to those of the samples as closely as possible. In most cases, this simply requires matching the acid background of the samples. For seawaters or brines, however, use the metal-free matrix (3113B.3*g*) as the standard solution diluent. In addition, add the same concentration of matrix modifier (if required for sample analysis) to the standard solutions.

---

* Chelex 100, Bio-Rad Laboratories, Richmond, CA, or equivalent.

Inject a suitable portion of each standard solution, in order of increasing concentration. Analyze each standard solution in duplicate to verify method precision.

Construct an analytical curve by plotting the average peak absorbances or peak areas of the standard solution versus concentration on linear graph paper. Alternatively, use electronic instrument calibration if the instrument has this capability.

d. Sample analysis: Analyze all samples except those demonstrated to be free of matrix interferences (based on recoveries of 85 to 115% for known additions) using the method of standard additions. Analyze all samples at least in duplicate or until reproducible results are obtained. A variation of $\leq$10% is considered acceptable reproducibility. Average replicate values.

1) Direct determination—Inject a measured portion of pretreated sample into the graphite furnace. Use the same volume as was used to prepare the calibration curve. Usually add modifier immediately after the sample, preferably using an automatic sampler or a micropipet. Some methods require modifier to be injected before the sample. Co-addition of the modifier is acceptable. Use the same volume and concentration of modifier for all standards and samples. Dry, char, and atomize according to the preset program. Repeat until reproducible results are obtained.

Compare the average absorbance value or peak area to the calibration curve to determine concentration of the element of interest. Alternatively, read results directly if the instrument is equipped with this capability. If absorbance (or concentration) or peak area of the sample is greater than absorbance (concentration) or peak area of the most concentrated standard solution, dilute sample and reanalyze. If very large dilutions are required, another technique (e.g., flame AA or ICP) may be more suitable for this sample. Large dilution factors magnify small errors on final calculation. Keep acid background and concentration of matrix modifier (if present in the solutions) constant. Dilute the sample in a blank solution of acid and matrix modifiers.

Proceed to 3113B.5*a*.

2) Method of standard additions—Refer to ¶ *c* above. The method of standard additions is valid only when it falls in the linear portion of the calibration curve. Once instrument sensitivity has been optimized for the element of interest and the linear range for the element has been established, proceed with sample analyses.

Inject a measured volume of sample into furnace device. Dry, char or ash, and atomize samples according to preset program. Repeat until reproducible results are obtained. Record instrument response in absorbance or concentration as appropriate. Add a known concentration of the element of interest to a separate portion of sample so as not to change significantly the sample volume. Repeat the determination.

Add a known concentration (preferably twice that used in the first addition) to a separate sample portion. Mix well and repeat the determination. NOTE: These steps must yield results within the linear range of the method.

Using linear graph paper, plot average absorbance or instrument response for the sample and the additions on the vertical axis against the concentrations of the added element on the horizontal axis, using zero as the concentration for the sample. Draw a straight line connecting the three points and extrapolate to zero absorbance. The intercept at the horizontal axis is the negative of the element concentration in the sample. The concentration axis to the left of the origin should be a mirror image of the axis to the right.

Some instruments can perform and calculate methods of standard additions. Use of these capabilities is acceptable.

5. Calculations

a. Direct determination:

$$\mu\text{g metal/L} = C \times F$$

where:

C = metal concentration as read directly from the instrument or from the calibration curve, μg/L, and
F = dilution factor.

b. Method of additions:

$$\mu\text{g metal/L} = C \times F$$

where:

C = metal concentration as read from the method of additions plot, μg/L, and
F = dilution factor.

6. Precision and Bias

Data typical of the precision and bias obtainable are presented in Tables 3113:III, IV, and V.

7. Quality Control

The QC practices considered to be an integral part of each method can be found in Section 3020. Although previous indications were that very low optimum concentration ranges were attainable for most metals (see Table 3113:II), data in Table 3113:III using variations of these protocols show that this may not be so. Exercise extreme care when applying this method to the lower concentration ranges. Verify analyst precision at the beginning of each analytical run by making triplicate analyses. Verify autosampler precision by checking volumes (by weight) delivered by the autosampler at routinely used injection volume settings.

8. Reference

1. COPELAND, T.R. & J.P. MANEY. 1986. EPA Method Study 31: Trace Metals by Atomic Absorption (Furnace Techniques); EPA-600/S4-85-070. U.S. Environmental Protection Agency, Environmental Monitoring and Support Lab., Cincinnati, Ohio.

9. Bibliography

RENSHAW, G.D. 1973. The determination of barium by flameless atomic absorption spectrophotometry using a modified graphite tube atomizer. *Atomic Absorption Newsletter* 12:158.

YANAGISAWA, M., T. TAKEUCHI & M. SUZUKI. 1973. Flameless atomic absorption spectrometry of antimony. *Anal. Chim. Acta* 64:381.

TABLE 3113:III. INTERLABORATORY SINGLE-ANALYST PRECISION DATA FOR ELECTROTHERMAL ATOMIZATION METHODS[1]

		Single-Analyst Precision *% RSD*					
Element	Concentration *μg/L*	Lab Pure Water	Drinking Water	Surface Water	Effluent 1	Effluent 2	Effluent 3
Al	28	66	108	70	—	—	66
	125	27	35	24	—	—	34
	11 000	11	—	—	22	—	—
	58 300	27	—	—	19	—	—
	460	9	—	—	—	30	—
	2 180	28	—	—	—	4	—
	10.5	20	13	13	13	56	18
	230	10	18	13	21	94	14
As	9.78	40	25	15	74	23	11
	227	10	6	8	11	15	6
Ba	56.5	36	21	29	59	23	27
	418	14	12	20	24	24	18
Be	0.45	18	27	15	30	2	11
	10.9	14	4	9	7	12	12
Cd	0.43	72	49	1	121	35	27
	12	11	17	22	14	11	15
Cr	9.87	24	33	10	23	15	10
	236	16	7	11	13	16	7
Co	29.7	10	17	10	19	24	12
	420	8	11	13	14	9	5
Cu	10.1	49	47	17	17	—	30
	234	8	15	6	21	—	11
	300	6	—	—	—	11	—
	1 670	11	—	—	—	6	—
Fe	26.1	144	52	153	—	—	124
	455	48	37	45	—	—	31
	1 030	17	—	—	30	—	—
	5 590	6	—	—	32	—	—
	370	14	—	—	—	19	—
	2 610	9	—	—	—	18	—
Pb	10.4	6	19	17	21	19	33
	243	17	7	17	18	12	16
Mn	0.44	187	180	—	—	—	275
	14.8	32	19	—	—	—	18
	91.0	15	—	—	48	—	—
	484.0	4	—	—	12	—	—
	111.0	12	—	—	—	21	—
	666.0	6	—	—	—	20	—
Ni	26.2	20	26	25	24	18	9
	461.0	15	11	9	8	11	4
Se	10.0	12	27	16	35	41	13
	235.0	6	6	15	6	13	14
Ag	8.48	10	—	—	15	27	16
	56.5	14	—	—	7	16	23
	0.45	27	166	48	—	—	—
	13.6	15	4	10	—	—	—

TABLE 3113:IV. INTERLABORATORY OVERALL PRECISION DATA FOR ELECTROTHERMAL ATOMIZATION METHODS[1]

		Overall Precision *% RSD*					
Element	Concentration *µg/L*	Lab Pure Water	Drinking Water	Surface Water	Effluent 1	Effluent 2	Effluent 3
Al	28	99	114	124	—	—	131
	125	45	47	49	—	—	40
	11 000	19	—	—	43	—	—
	58 300	31	—	—	32	—	—
	460	20	—	—	—	47	—
	2 180	30	—	—	—	15	—
	10.5	37	19	22	50	103	39
	230	26	16	16	17	180	21
As	9.78	43	26	37	72	50	39
	227	18	12	13	20	15	14
Ba	56.5	68	38	43	116	43	65
	418	35	35	28	38	48	16
Be	0.45	28	31	15	67	50	35
	10.9	33	15	26	20	9	19
Cd	0.43	73	60	5	88	43	65
	12	19	25	41	26	20	27
Cr	9.87	30	53	24	60	41	23
	236	18	14	24	20	14	20
Co	29.7	13	26	17	18	21	17
	420	21	21	17	18	13	13
Cu	10.1	58	82	31	32	—	74
	234	12	33	19	21	—	26
	300	13	—	—	—	14	—
	1 670	12	—	—	—	13	—
Fe	26.1	115	93	306	—	—	204
	455	53	46	53	—	—	44
	1 030	32	—	—	25	—	—
	5 590	10	—	—	43	—	—
	370	28	—	—	—	22	—
	2 610	13	—	—	—	22	—
Pb	10.4	27	42	31	23	28	47
	243	18	19	17	19	19	25
Mn	0.44	299	272	—	—	—	248
	14.8	52	41	—	—	—	29
	91.0	16	—	—	45	—	—
	484.0	5	—	—	17	—	—
	111.0	15	—	—	—	17	—
	666.0	8	—	—	—	24	—
Ni	26.2	35	30	49	35	37	43
	461.0	23	22	15	12	21	17
Se	10.0	17	48	32	30	44	51
	235.0	16	18	18	17	22	34
Ag	8.48	23	—	—	16	35	34
	56.5	15	—	—	24	32	28
	0.45	57	90	368	—	—	—
	13.6	19	19	59	—	—	—

TABLE 3113:V. INTERLABORATORY RELATIVE ERROR DATA FOR ELECTROTHERMAL ATOMIZATION METHODS[1]

		Relative Error %					
Element	Concentration *μg/L*	Lab Pure Water	Drinking Water	Surface Water	Effluent 1	Effluent 2	Effluent 3
Al	28.0	86	150	54	—	—	126
	125.0	4	41	39	—	—	30
	11 000.0	2	—	—	14	—	—
	58 300.0	12	—	—	7	—	—
	460.0	2	—	—	—	11	—
	2 180.0	11	—	—	—	9	—
Sb	10.5	30	32	28	24	28	36
	230.0	35	14	19	13	73	39
As	9.78	36	1	22	106	13	16
	227.0	3	7	10	19	6	13
Ba	56.5	132	54	44	116	59	40
	418.0	4	0	0	13	6	60
Be	0.45	40	16	11	16	10	15
	10.9	13	2	9	7	8	8
Cd	0.43	58	45	37	66	16	19
	12.0	4	6	5	22	18	3
Cr	9.87	10	9	4	2	5	15
	236.0	11	0	9	13	5	8
Co	29.7	7	7	1	6	3	13
	420.0	12	8	8	11	5	18
Cu	10.1	16	48	2	5	—	15
	234.0	8	7	0	4	—	19
	300.0	4	—	—	—	21	—
	1 670.0	6	—	—	—	2	—
Fe	26.1	85	60	379	—	—	158
	455.0	43	22	31	—	—	18
	1 030.0	8	—	—	8	—	—
	5 590.0	2	—	—	12	—	—
	370.0	4	—	—	—	11	—
	2 610.0	35	—	—	—	2	—
Pb	10.4	16	10	17	1	34	14
	243.0	5	15	8	18	15	29
Mn	0.44	332	304	—	—	—	556
	14.8	10	1	—	—	—	36
	91.0	31	—	—	10	—	—
	484.0	42	—	—	4	—	—
	111.0	1	—	—	—	29	—
	666.0	6	—	—	—	23	—
Ni	26.2	9	16	10	7	33	54
	461.0	15	19	18	31	16	18
Se	10.0	12	9	6	36	17	37
	235.0	7	7	0	13	10	17
Ag	8.48	12	—	—	1	51	20
	56.5	16	—	—	8	51	22
	0.45	34	162	534	—	—	—
	13.6	3	12	5	—	—	—

Rattonetti, A. 1974. Determination of soluble cadmium, lead, silver and indium in rainwater and stream water with the use of flameless atomic absorption. *Anal. Chem.* 46:739.

Henn, E.L. 1975. Determination of selenium in water and industrial effluents by flameless atomic absorption. *Anal. Chem.* 47:428.

Martin, T.D. & J.F. Kopp. 1975. Determining selenium in water, wastewater, sediment and sludge by flameless atomic absorption spectrometry. *Atomic Absorption Newsletter* 14:109.

Maruta, T., K. Minegishi & G. Sudoh. 1976. The flameless atomic absorption spectrometric determination of aluminum with a carbon atomization system. *Anal. Chim. Acta* 81:313.

Cranston, R.E. & J.W. Murray. 1978. The determination of chromium species in natural waters. *Anal. Chim. Acta* 99:275.

Hoffmeister, W. 1978. Determination of iron in ultrapure water by atomic absorption spectroscopy. *Z. Anal. Chem.* 50:289.

Lagas, P. 1978. Determination of beryllium, barium, vanadium and some other elements in water by atomic absorption spectrometry with electrothermal atomization. *Anal. Chim. Acta* 98:261.

Carrondo, M.J.T., J.N. Lester & R. Perry. 1979. Electrothermal atomic absorption determination of total aluminum in waters and waste waters. *Anal. Chim. Acta* 111:291.

Nakahara, T. & C.L. Chakrabarti. 1979. Direct determination of traces of molybdenum in synthetic sea water by atomic absorption spectrometry with electrothermal atomization and selective volatilization of the salt matrix. *Anal. Chim. Acta* 104:99.

Timinaga, M. & Y. Umezaki. 1979. Determination of submicrogram amounts of tin by atomic absorption spectrometry with electrothermal atomization. *Anal. Chim. Acta* 110:55.

Welz, B., G. Schlemmer & J.R. Mudakavi. 1998. Palladium nitrate-magnesium nitrate modifier for graphite furnace atomic absorption spectrometry. Part 2. Determination of arsenic, cadmium, copper, manganese, lead, antimony, selenium, and thallium in water. *J. Anal. Atom. Spectrom.* 3:695.

3114 ARSENIC AND SELENIUM BY HYDRIDE GENERATION/ATOMIC ABSORPTION SPECTROMETRY*

3114 A. Introduction

For general introductory material on atomic absorption spectrometric methods, see Section 3111A.

Two methods are presented in this section: A manual method and a continuous-flow method especially recommended for selenium. Continuous-flow automated systems are preferable to manual hydride generators because the effect of sudden hydrogen generation on light-path transparency is removed and any blank response from contamination of the HCl reagent by the elements being determined is incorporated into the background baseline.

3114 B. Manual Hydride Generation/Atomic Absorption Spectrometric Method

1. General Discussion

a. Principle: This method is applicable to the determination of arsenic and selenium by conversion to their hydrides by sodium borohydride reagent and transport into an atomic absorption atomizer.

Arsenous acid and selenous acid, the As(III) and Se(IV) oxidation states of arsenic and selenium, respectively, are instantaneously converted by sodium borohydride reagent in acid solution to their volatile hydrides. The hydrides are purged continuously by argon or nitrogen into a quartz cell heated electrically or by the flame of an atomic absorption spectrometer and converted to the gas-phase atoms. The sodium borohydride reducing agent, by rapid generation of the elemental hydrides in an appropriate reaction cell, minimizes dilution of the hydrides by the carrier gas and provides rapid, sensitive determinations of arsenic and selenium.

CAUTION: Arsenic and selenium and their hydrides are toxic. Handle with care.

At room temperature and solution pH values of 1 or less, arsenic acid, the As(V) oxidation state of arsenic, is reduced relatively slowly by sodium borohydride to As(III), which is then instantaneously converted to arsine. The arsine atomic absorption peaks commonly are decreased by one-fourth to one-third for As(V) when compared to As(III). Determination of total arsenic requires that all inorganic arsenic compounds be in the As(III) state. Organic and inorganic forms of arsenic are first oxidized to As(V) by acid digestion. The As(V) then is quantitatively reduced to As(III) with sodium or potassium iodide before reaction with sodium borohydride.

Selenic acid, the Se(VI) oxidation state of selenium, is not measurably reduced by sodium borohydride. To determine total selenium by atomic absorption and sodium borohydride, first reduce Se(VI) formed during the acid digestion procedure to Se(IV), being careful to prevent reoxidation by chlorine. Efficiency of reduction depends on temperature, reduction time, and HCl concentration. For 4*N* HCl, heat 1 h at 100°C. For 6*N* HCl, boiling for 10 min is sufficient.[1–3] Alternatively, autoclave samples in sealed containers at 121°C for 1 h. NOTE: Autoclaving in sealed containers may result in incomplete reduction, apparently due to the buildup of chlorine gas. To obtain equal instrument responses for reduced Se(VI) and Se (IV) solutions of equal concentrations, manipulate HCl concentration and heating time. For further details, see Section 3500-Se.

b. Equipment selection: Certain atomic absorption atomizers and hydride reaction cells are available commercially for use with the sodium borohydride reagent. A functional manual system that can be constructed in the laboratory is presented in Figure 3114:1. Irrespective of the hydride reaction cell-atomizer system selected, it must meet the following quality-control considerations:

- it must provide a precise and reproducible standard curve between 0 and 20 μg As or Se/L and an instrument detection limit between 0.1 and 0.5 μg As or Se/L;
- when carried through the entire procedure, oxidation state couples [As(III) – As(V) or Se(IV) – Se(VI)] must cause equal instrument response; and
- sample digestion must yield 80% or greater recovery of added cacodylic acid (dimethyl arsinic acid) and 90% or greater recovery of added As(III), As(V), Se(VI), or Se(IV).

Quartz atomization cells provide for the most sensitive arsenic and selenium hydride determinations. The quartz cell can be heated electrically or by an air–acetylene flame in an atomic absorption unit.

c. Digestion techniques: Waters and wastewaters may contain varying amounts of organic arsenic compounds and inorganic compounds of As(III), As(V), Se(IV), and Se(VI). To measure total arsenic and selenium in these samples requires sample digestion to solubilize particulate forms, oxidize reduced forms of arsenic and selenium, and convert any organic compounds to inorganic ones. Organic selenium compounds rarely have been demonstrated in water. It is left to the experienced analyst's judgment whether sample digestion is required.

Various alternative digestion procedures are provided in 3114B.4*c* and *d*. Consider sulfuric–nitric–perchloric acid diges-

---

* Approved by Standard Methods Committee, 2009. Editorial revisions, 2011.

https://doi.org/10.2105/SMWW.2882.046

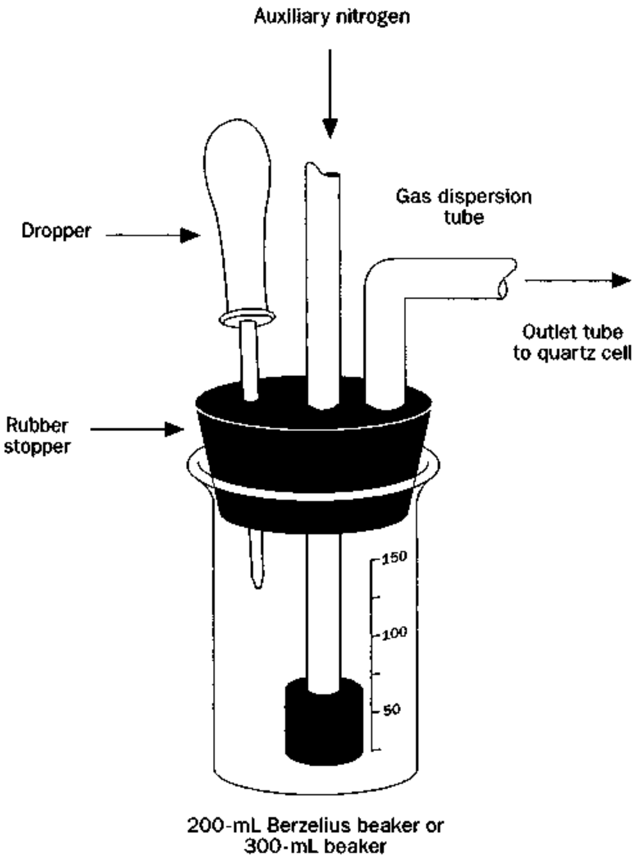

Figure 3114:1. Manual reaction cell for producing As and Se hydrides.

tion (3114B.4*c*) or sulfuric–nitric acid digestion (Section 3030F) as providing a measure of total recoverable arsenic rather than total arsenic because they do not completely convert certain organic arsenic compounds to As(V). Sulfuric–nitric–perchloric acid digestion effectively destroys organics and most particulates in untreated wastewater or solid samples, but does not convert all organic arsenicals to As(V). Potassium persulfate digestion (3114B.4*d*) is effective for converting organic arsenic and selenium compounds to As(V) and Se(VI) in potable and surface waters and in most wastewaters.[4]

The HCl–autoclave reduction of Se(VI) described above and in 3114B.4*f* is an effective digestion procedure for total inorganic selenium; however, it has not been found effective for converting benzene-substituted selenium compounds to inorganic selenium. In all cases, verify the effectiveness of digestion methods by carrying samples with known additions of organic As or Se(IV) through the entire procedure.

d. Interferences: Interferences are minimized because the As and Se hydrides are removed from the solution containing most potentially interfering substances. Slight response variations occur when acid matrices are varied. Control these variations by treating standards and samples in the same manner. Low concentrations of noble metals (approximately 100 μg/L of Ag, Au, Pt, Pd, etc.); concentrations of copper, lead, and nickel at or greater than 1 mg/L; and concentrations between 0.1 and 1 mg/L of hydride-forming elements (Bi, Sb, Sn, and Te) may suppress the response of As and Se hydrides. Interference by transition metals depends strongly on HCl concentration. Interferences are less pronounced at 4 to 6*N* HCl than at lower concentrations.[5] The presence of As or Se in each other's matrices can cause similar suppression. Reduced nitrogen oxides resulting from HNO_3 digestion and nitrite also can suppress instrumental response for both elements. Large concentrations of iodide interfere with the Se determination by reducing Se to its elemental form. When determining Se, do not use any glassware that has been used for iodide reduction of As(V).

When reducing Se(VI) to Se(IV), to prevent chlorine gas produced from reoxidizing Se(IV), generate the hydride within a few hours of the reduction steps or purge the chlorine from the samples by sparging.[6]

Interferences depend on system design and defy quantitative description because of their synergistic effects. Certain waters and wastewaters can contain interferences in sufficient concentration to suppress absorption responses of As and Se. For representative samples in a given laboratory and for initial analyses of unknown wastewaters, add appropriate inorganic forms of As or Se to digested sample portions and measure recovery. If average recoveries are less than 90%, consider using alternative analytical procedures.

e. Detection level and optimum concentration range: For both arsenic and selenium analyzed by aspiration into a nitrogen–hydrogen or argon–hydrogen flame after reduction, the method detection level is 2 μg/L or lower and the optimum concentration range is 2 to 20 μg/L.

For both arsenic and selenium analyzed by atomization into a nitrogen–hydrogen flame after reduction, the method detection limit should be 2 μg/L, with an optimum concentration range of 2 to 20 μg/L. Lower detection limits can be expected with a quartz tube atomizer.

f. Quality control (QC): The QC practices considered to be an integral part of each method can be found in Section 3020.

2. Apparatus

a. Atomic absorption spectrometer equipped with air–acetylene flame and quartz cell with mounting bracket or an electrically heated quartz cell, As and Se electrodeless discharge lamps with power supply, background correction at measurement wavelengths, and appropriate strip-chart recorder. A good-quality 10-mV recorder with high sensitivity and a fast response time is needed.

b. Atomizer: Use one of the following:

1) *Cylindrical quartz cell,* 10 to 20 cm long, bracket-mountable above air–acetylene burner.

2) *Cylindrical quartz cell*, 10 to 20 cm long, electrically heated by external nichrome wire to 800 to 900°C.[7]

3) *Cylindrical quartz cell* with internal fuel-rich hydrogen–oxygen (air) flame.[8]

The sensitivity of quartz cells deteriorates over several months of use. Sensitivity sometimes may be restored by treatment with 40% HF. **CAUTION: HF is extremely corrosive. Avoid all contact with exposed skin. Handle with care.**

c. Reaction cell for producing As or Se hydrides: See Figure 3114:1 for an example of a manual, laboratory-made system. A commercially available system is acceptable if it uses liquid sodium borohydride reagents; accepts samples digested in accordance with 3114B.4*c–e*; accepts 4 to 6*N* HCl; and is efficiently and precisely stirred by the purging gas and/or a magnetic stirrer.

d. Eye dropper or syringe capable of delivering 0.5 to 3.0 mL sodium borohydride reagent. Exact and reproducible addition is required so production of hydrogen gas does not vary significantly between determinations.

e. Vent: See Section 3111A.6*f*.

3. Reagents

a. Sodium borohydride reagent: Dissolve 8 g $NaBH_4$ in 200 mL 0.1*N* NaOH. Prepare fresh daily.

b. Sodium iodide prereductant solution: Dissolve 50 g NaI in 500 mL water. Prepare fresh daily. Alternatively, use an equivalent KI solution.

c. Sulfuric acid (H_2SO_4), 18*N*.

d. Sulfuric acid, 2.5*N:* Cautiously add 35 mL conc H_2SO_4 to about 400 mL water, let cool, and adjust volume to 500 mL.

e. Potassium persulfate, 5% solution: Dissolve 25 g $K_2S_2O_8$ in water and dilute to 500 mL. Store in glass and refrigerate. Prepare weekly.

f. Nitric acid (HNO_3), conc.

g. Perchloric acid ($HClO_4$), conc.

h. Hydrochloric acid (HCl), conc.

i. Argon (or nitrogen), commercial grade.

j. Arsenic(III) solutions:

1) *Stock As(III) solution*—Dissolve 1.320 g arsenic trioxide, As_2O_3, in water containing 4 g NaOH. Dilute to 1 L; 1.00 mL = 1.00 mg As(III).

2) *Intermediate As(III) solution*—Dilute 10 mL stock As solution to 1000 mL with water containing 5 mL conc HCl; 1.00 mL = 10.0 μg As(III).

3) *Standard As(III) solution*—Dilute 10 mL intermediate As(III) solution to 1000 mL with water containing the same concentration of acid used for sample preservation (2 to 5 mL conc HNO_3); 1.00 mL = 0.100 μg As(III). Prepare diluted solutions daily.

k. Arsenic(V) solutions:

1) *Stock As(V) solution*—Dissolve 1.534 g arsenic pentoxide (As_2O_5) in distilled water containing 4 g NaOH. Dilute to 1 L; 1.00 mL = 1.00 mg As(V).

2) *Intermediate As(V) solution*—Prepare as for As(III) above; 1.00 mL = 10.0 μg As(V).

3) *Standard As(V) solution*—Prepare as for As(III) above; 1.00 mL = 0.100 μg As(V).

l. Organic arsenic solutions:

1) *Stock organic arsenic solution*—Dissolve 1.842 g dimethylarsinic acid (cacodylic acid) [$(CH_3)_2AsOOH$] in water containing 4 g NaOH. Dilute to 1 L; 1.00 mL = 1.00 mg As. [NOTE: Check purity of cacodylic acid reagent against an intermediate arsenic standard (50 to 100 mg As/L) using flame atomic absorption.]

2) *Intermediate organic arsenic solution*—Prepare as for As(III) above; 1.00 mL = 10.0 μg As.

3) *Standard organic arsenic solution*—Prepare as for As(III) above; 1.00 mL = 0.100 μg As.

m. Selenium(IV) solutions:

1) *Stock Se(IV) solution*—Dissolve 2.190 g sodium selenite (Na_2SeO_3) in water containing 10 mL HCl and dilute to 1 L; 1.00 mL = 1.00 mg Se(IV).

2) *Intermediate Se(IV) solution*—Dilute 10 mL stock Se(IV) to 1000 mL with water containing 10 mL conc HCl; 1.00 mL = 10.0 μg Se(IV).

3) *Standard Se(IV) solution*—Dilute 10 mL intermediate Se(IV) solution to 1000 mL with water containing the same concentration of acid used for sample preservation (2 to 5 mL conc HNO_3). Prepare solution daily when checking the equivalency of instrument response for Se(IV) and Se(VI); 1.00 mL = 0.100 μg Se(IV).

n. Selenium(VI) solutions:

1) *Stock Se(VI) solution*—Dissolve 2.393 g sodium selenate (Na_2SeO_4), in water containing 10 mL conc HNO_3. Dilute to 1 L; 1.00 mL = 1.00 mg Se(VI).

2) *Intermediate Se(VI) solution*—Prepare as for Se(IV) above; 1.00 mL = 10.0 μg Se (VI).

3) *Standard Se(VI) solution*—Prepare as for Se(IV) above; 1.00 mL = 0.100 μg Se(VI).

4. Procedure

a. Apparatus setup: Either see Figure 3114:1 or follow manufacturer's instructions. Connect inlet of reaction cell with auxiliary purging gas controlled by flow meter. If a drying cell between the reaction cell and atomizer is necessary, use only anhydrous $CaCl_2$ but not $CaSO_4$ because it may retain SeH_2. Before using the hydride generation/analysis system, optimize operating parameters. Align quartz atomizers for maximum absorbance. Aspirate a blank until memory effects are removed. Establish purging gas flow, concentration and rate of addition of sodium borohydride reagent, solution volume, and stirring rate for optimum instrument response for the chemical species to be analyzed. Optimize quartz cell temperature. Rapid injection of sodium borohydride reagent will increase sensitivities, so injection rates should be both consistent and as rapid as the system will tolerate. Recommended wavelengths are 193.7 and 196.0 nm for As and Se, respectively.

b. Instrument calibration standards: Prepare at least three standards and a blank by transferring appropriate volumes of AS(III) or Se(IV) standard solutions to 100-mL volumetric flasks and bring to volume with water containing the same acid concentration used for sample preservation (typically 2 to 5 mL conc HNO_3/L). Standards should be prepared to cover the linear range of the instrument used (generally from 1 to 20 μg/L). Prepare fresh daily. In all cases, standards must be carried through the same digestion protocol as the samples to monitor digestion effectiveness.

c. Preparation of samples and standards for total recoverable arsenic and selenium: Use digestion procedure described in Section 3030F for samples and standards. Alternatively, add 50 mL sample, As(III), or Se(IV) standard to 200-mL Berzelius beaker or 100-mL micro-Kjeldahl flask. Add 7 mL 18*N* H_2SO_4 and 5 mL conc HNO_3. Add a small boiling chip or glass beads if necessary. Evaporate to SO_3 fumes. Maintain oxidizing conditions at all times by adding small amounts of HNO_3 to prevent solution from darkening. Maintain an excess of HNO_3 until all organic matter is destroyed. Complete digestion usually is indicated by a light-colored solution. Cool slightly, add 25 mL water and 1 mL conc $HClO_4$ and again evaporate to SO_3 fumes to expel oxides of nitrogen. **CAUTION: See Section 3030H for cautions on use of $HClO_4$.** Monitor effectiveness of either digestion procedure used by adding 5 mL of standard organic arsenic solution or 5 mL of a standard selenium solution to a 50-mL sample and measuring recovery, carrying standards and the sample with known addition through entire procedure. To report total recoverable arsenic as total arsenic, average recoveries of cacodylic acid must exceed 80%. After final evaporation of SO_3 fumes, dilute to 50 mL for arsenic measurements or to 30 mL for selenium measurements. For analysis of both elements in a single sample, increase sample volume to 100 mL and double the volumes of acids used in the digestion. Adjust final digestate volume to 100 mL. Use 50 mL for As and 30 mL for Se determinations, making appropriate volume corrections in calculating results.

d. Preparation of samples and standards for total arsenic and selenium: Add 50 mL undigested sample or standard to a 200-mL Berzelius beaker or 100-mL micro-Kjeldahl flask. Add 1 mL 2.5N H_2SO_4 and 5 mL 5% $K_2S_2O_8$. Boil gently on a preheated hot plate for approximately 30 to 40 min or until a final volume of 10 mL is reached. Do not let sample go to dryness. Alternatively, heat in an autoclave at 121°C for 1 h in capped containers. After manual digestion, dilute to 50 mL for subsequent arsenic measurements and to 30 mL for selenium measurements. Monitor digestion effectiveness by measuring recovery of As or Se as above. If poor recovery of arsenic added as cacodylic acid is obtained, re-analyze using double the amount of $K_2S_2O_8$. For analysis of both elements in a single sample, increase sample volume to 100 mL and double the volumes of acids used in the digestion. Adjust final digestate volume to 100 mL. Use 50 mL for As and 30 mL for Se determinations, making appropriate volume corrections in calculating results.

e. Determination of arsenic with sodium borohydride: To 50 mL digested standard or sample in a 200-mL Berzelius beaker (see Figure 3114:1), add 5 mL conc HCl and mix. Add 5 mL NaI prereductant solution, mix, and wait at least 30 min. [NOTE: The NaI reagent has not been found necessary for certain hydride reaction cell designs if a 20 to 30% loss in instrument sensitivity is not important and variables of solution acid conditions, temperatures, and volumes for production of As(V) and arsine can be controlled strictly. Such control requires an automated delivery system (see 3114C.)]

Attach one Berzelius beaker at a time to the rubber stopper containing the gas dispersion tube for the purging gas, the sodium borohydride reagent inlet, and the outlet to the quartz cell. Turn on strip-chart recorder and wait until the baseline is established by the purging gas and all air is expelled from the reaction cell. Add 0.5 mL sodium borohydride reagent. After the instrument absorbance has reached a maximum and returned to the baseline, remove beaker, rinse dispersion tube with water, and proceed to the next sample or standard. Periodically compare standard As(III) and As(V) curves for response consistency. Check for presence of chemical interferences that suppress instrument response for arsine by treating a digested sample with 10 μg/L As(III) or As(V), as appropriate. Average recoveries should be not less than 90%.

f. Determination of selenium with sodium borohydride: To 30 mL digested standard or sample in a 200-mL Berzelius beaker or 100-mL micro-Kjeldahl flask, add 15 mL conc HCl and mix. Heat for a predetermined period at 90 to 100°C. Alternatively, autoclave at 121°C in capped containers for 60 min, or heat for a predetermined time in open test tubes using a 90 to 100°C hot water bath or an aluminum block digester. Check effectiveness of the selected heating time by demonstrating equal instrument responses for calibration curves prepared either from standard Se(IV) or from Se(VI) solutions. Effective heat exposure for converting Se(VI) to Se(IV), with no loss of Se(IV), ranges between 5 and 60 min when open beakers or test tubes are used. Establish a heating time for effective conversion and apply this time to all samples and standards. Do not digest standard Se(IV) and Se(VI) solutions used for this check of equivalency. After prereduction of Se(VI) to Se(IV), attach Berzelius beakers, one at a time, to the purge apparatus. For each, turn on the strip-chart recorder and wait until the baseline is established. Add 0.50 mL sodium borohydride reagent. After the instrument absorbance has reached a maximum and returned to the baseline, remove beaker, rinse dispersion tube with water, and proceed to the next sample or standard. Check for presence of chemical interferences that suppress selenium hydride instrument response by treating a digested sample with 10 μg Se (IV)/L. Average recoveries should be not less than 90%.

5. Calculation

Construct a standard curve by plotting peak heights or areas of standards and blanks versus concentration of standards. Measure peak heights or areas of samples and read concentrations from curve. If sample was diluted (or concentrated) before sample digestion, apply an appropriate factor. On instruments so equipped, read concentrations directly after standard calibration.

6. Precision and Bias

Single-laboratory, single-operator data were collected for As(III) and organic arsenic by both manual and automated methods, and for the manual determination of selenium. Recovery values (%) from seven replicates are given below:

Method	As(III)	Org As	Se(IV)	Se(VI)
Manual with digestion	91.8	87.3	—	—
Manual without digestion	109.4	19.4	100.6	110.8
Automated with digestion	99.8	98.4	—	—
Automated without digestion	92.5	10.4	—	—

7. References

1. VIJAN, P.N. & D. LEUNG. 1980. Reduction of chemical interference and speciation studies in the hydride generation-atomic absorption method for selenium. *Anal. Chim. Acta.* 120:141.
2. VOTH-BEACH, L.M. & D.E. SHRADER. 1985. Reduction of interferences in the determination of arsenic and selenium by hydride generation. *Spectroscopy* 1:60.
3. JULSHAMN, K., O. RINGDAL, K.-E. SLINNING & O.R. BRAEKKAN. 1982. Optimization of the determination of selenium in marine samples by atomic absorption spectrometry: Comparison of a flameless graphite furnace atomic absorption system with a hydride generation atomic absorption system. *Spectrochim. Acta.* 37B:473.
4. NYGAARD, D.D. & J.H. LOWRY. 1982. Sample digestion procedures for simultaneous determination of arsenic, antimony, and selenium by inductively coupled argon plasma emission spectrometry with hydride generation. *Anal. Chem.* 54:803.

5. Welz, B. & M. Melcher. 1984. Mechanisms of transition metal interferences in hydride generation atomic-absorption spectrometry. Part 1. Influence of cobalt, copper, iron and nickel on selenium determination. *Analyst* 109:569.
6. Krivan, V., K. Petrick, B. Welz & M. Melcher. 1985. Radiotracer error-diagnostic investigation of selenium determination by hydride-generation atomic absorption spectrometry involving treatment with hydrogen peroxide and hydrochloric acid. *Anal. Chem.* 57:1703.
7. Chu, R.C., G.P. Barron & P.A.W. Baumgarner. 1972. Arsenic determination at submicrogram levels by arsine evolution and flameless atomic absorption spectrophotometric technique. *Anal. Chem.* 44:1476.
8. Siemer, D.D., P. Koteel & V. Jariwala. 1976. Optimization of arsine generation in atomic absorption arsenic determinations. *Anal. Chem.* 48:836.

8. Bibliography

Fernandez, F.J. & D.C. Manning. 1971. The determination of arsenic at submicrogram levels by atomic absorption spectrophotometry. *Atomic Absorption Newsletter* 10:86.

Jarrel-Ash Corporation. 1971. High Sensitivity Arsenic Determination by Atomic Absorption; Jarrel-Ash Atomic Absorption Applications Laboratory Bull. No. As-3.

Manning, D.C. 1971. A high sensitivity arsenic-selenium sampling system for atomic absorption spectroscopy. *Atomic Absorption Newsletter* 10:123.

Braman, R.S. & C.C. Foreback. 1973. Methylated forms of arsenic in the environment. *Science* 182:1247.

Caldwell, J.S., R.J. Lishka & E.F. McFarren. 1973. Evaluation of a low-cost arsenic and selenium determination of microgram-per-liter levels. *J. Amer. Water Works Assoc.* 65:731.

Aggett, J. & A.C. Aspell. 1976. The determination of arsenic (III) and total arsenic by atomic-absorption spectroscopy. *Analyst* 101:341.

Fiorino, J.A., J.W. Jones & S.G. Capar. 1976. Sequential determination of arsenic, selenium, antimony, and tellurium in foods via rapid hydride evolution and atomic absorption spectrometry. *Anal. Chem.* 48:120.

Cutter, G.A. 1978. Species determination of selenium in natural waters. *Anal. Chem. Acta.* 98:59.

Godden, R.G. & D.R. Thomerson. 1980. Generation of covalent hydrides in atomic absorption spectroscopy. *Analyst* 105:1137.

Brown, R.M., Jr., R.C. Fry, J.L. Moyers, S.J. Northway, M.B. Denton & G.S. Wilson. 1981. Interference by volatile nitrogen oxides and transition-metal catalysis in the preconcentration of arsenic and selenium as hydrides. *Anal. Chem.* 53:1560.

Sinemus, H.W., M. Melcher & B. Welz. 1981. Influence of valence state on the determination of antimony, bismuth, selenium, and tellurium in lake water using the hydride AA technique. *Atomic Spectrosc.* 2:81.

Dedina, J. 1982. Interference of volatile hydride forming elements in selenium determination by atomic absorption spectrometry with hydride generation. *Anal. Chem.* 54:2097.

Van Wagenen, S., D.E. Carter, A.G. Ragheb & Q. Fernando. 1987. Kinetic control of peak shapes in atomic absorption arsenic determination arsine generations. *Anal. Chem.* 59:891.

3114 C. Continuous Hydride Generation/Atomic Absorption Spectrometric Method

1. General Discussion

The continuous hydride generator offers the advantages of simplicity in operation, excellent reproducibility, low detection limits, and high sample volume throughput for selenium analysis following preparations as described in Sections 3500-Se.B or 3114B.4*c* and *d*.

a. Principle: See 3114B.1*a*

b. Interferences: Free chlorine in hydrochloric acid is a common but difficult-to-diagnose interference. (The amount of chlorine varies with manufacturer and with each lot from the same manufacturer.) Chlorine oxidizes the hydride and can contaminate the hydride generator to prevent recoveries under any conditions. When interference is encountered, or preferably before using each new bottle of HCl, eliminate chlorine from a 2.3-L bottle of conc HCl by bubbling with helium (commercial grade, 100 mL/min) for 3 h.

Excess oxidant (peroxide, persulfate, or permanganate) from the total selenium digestion can oxidize the hydride. Follow procedures in Section 3500-Se.B.2, 3, or 4 to ensure removal of all oxidizing agents before hydride generation.

Nitrite is a common trace constituent in natural and waste waters, and at levels as low as 10 μg/L, nitrite can reduce the recovery of hydrogen selenide from Se(IV) by more than 50%. Moreover, during the reduction of Se(VI) to Se(IV) by digestion with HCl (Section 3500-Se.B.5), some nitrate is converted to nitrite, which subsequently interferes. When this interference is suspected, add sulfanilamide after sample acidification (or HCl digestion). The diazotization reaction between nitrite and sulfanilamide completely removes the interferent effect (i.e., the standard addition slope is normal).

c. Quality control (QC): The QC practices considered to be an integral part of each method can be found in Section 3020.

2. Apparatus

a. Continuous hydride generator: The basic unit is composed of two parts: a precision peristaltic pump, which is used to meter and mix reagents and sample solutions, and the gas–liquid separator. At the gas–liquid separator, a constant flow of argon strips out the hydrogen and metal hydride gases formed in the reaction and carries them to the heated quartz absorption cell (3114B.1*b* and 2*b*), which is supported by a metal bracket mounted on top of the regular air acetylene burner head. The spent liquid flows out of the separator via a constant level side drain to a waste bucket. Schematics and operating parameters are shown in Figure 3114:2.

Check flow rates frequently to ensure a steady flow; an uneven flow in any tubing will cause an erratic signal. Remove tubings from pump rollers when not in use. Typical flow rates are: sample, 7 mL/min; acid, 1 mL/min; and borohydride reagent, 1 mL/min. Argon flow usually is pre-fixed, typically at 90 mL/min.

b. Atomic absorption spectrometric equipment: See Section 3111A.6.

https://doi.org/10.2105/SMWW.2882.046

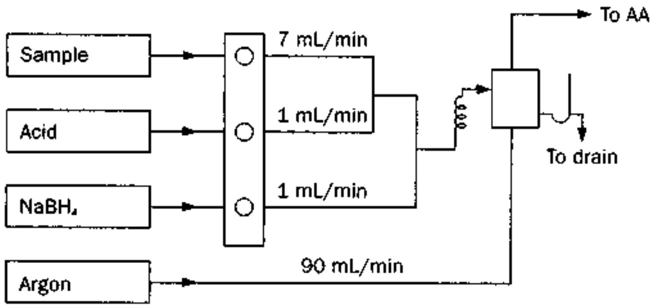

Figure 3114:2. Schematic of a continuous hydride generator.

3. Reagents

a. Hydrochloric acid (HCl), 5 + 1: Handle conc HCl under a fume hood. If necessary, remove free Cl_2 by stripping conc HCl with helium as described in 3114C.1*b*.

b. Borohydride reagent: Dissolve 0.6 g $NaBH_4$ and 0.5 g NaOH in 100 mL water. **CAUTION: Sodium borohydride is toxic, flammable, and corrosive.**

c. Selenium reference standard solution, 1000 mg/L: Use commercially available standard; verify that selenium is Se(IV).

d. Intermediate standard solution, 1 mg/L: Dilute 1 mL reference standard solution to 1 L in a volumetric flask with distilled water.

e. Working standard solutions, 5, 10, 20, 30, and 40 μg/L: Dilute 0.5, 1.0, 2.0, 3.0, and 4.0 mL intermediate standard solution to 100 mL in volumetric flasks.

f. Sulfanilamide solution: Prepare a 2.5% (w/v) solution daily; add several drops conc HCl per 50 mL solution to facilitate dissolution.

4. Procedure

a. Sample preparation: See Section 3500-Se.B or 3114B.4*c* and *d* for preparation steps for various Se fractions or total Se.

b. Preconditioning hydride generator: For newly installed tubing, turn on pump for at least 10 to 15 min before instrument calibration. Sample the highest standard for a few minutes to let volatile hydride react with the reactive sites in the transfer lines and on the quartz absorption cell surfaces.

c. Instrument calibration: Depending on total void volume in sample tubing, sampling time of 15 to 20 s generally is sufficient to obtain a steady signal. Between samples, submerge uptake tube in rinsewater. Calibrate instrument daily after a 45-min lamp warmup time. Use either the hollow cathode or the electrodeless discharge lamp.

d. Antifoaming agents: Certain samples, particularly wastewater samples containing a high concentration of proteinaceous substances, can cause excessive foaming that could carry the liquid directly into the heated quartz absorption cell and cause splattering of salty deposits onto the windows of the spectrometer. Add a drop of antifoaming agent* to eliminate this problem.

e. Nitrite removal: After samples have been acidified, or after acid digestion, add 0.1 mL sulfanilamide solution per 10 mL sample and let react for 2 min.

f. Analysis: Follow manufacturer's instructions for operation of analytical equipment.

5. Calculation

Construct a calibration curve based on absorbance vs. standard concentration. Apply dilution factors on diluted samples.

6. Precision and Bias

Working standards were analyzed together with batches of water samples on a routine production basis. The standards were compounded using chemically pure sodium selenite and sodium selenate. The values of Se(IV) + Se(VI) were determined by converting Se(VI) to Se(IV) by digestion with HCl. Results are tabulated below.

No. Analyses	Mean Se(IV) *μg/L*	Rel. Dev. *%*	Se(IV) + Se(VI) *μg/L*	Rel. Dev. *%*
21	4.3	12	10.3	7
26	8.5	12	19.7	6
22	17.2	7	39.2	8
20	52.8	5	106.0	6

7. Bibliography

REAMER, D.C. & C. VEILOON. 1981. Preparation of biological materials for determination of selenium by hydride generation-AAS. *Anal. Chem.* 53:1192.

SINEMUS, H.W., M. MELCHER & B. WELZ. 1981. Influence of valence state on the determination of antimony, bismuth, selenium, and tellurium in lake water using the hydride AA technique. *Atomic Spectrosc.* 2:81.

RODEN, D.R. & D.E. TALLMAN. 1982. Determination of inorganic selenium species in groundwaters containing organic interferences by ion chromatography and hydride generation/atomic absorption spectrometry. *Anal. Chem.* 54:307.

CUTTER, G. 1983. Elimination of nitrite interference in the determination of selenium by hydride generation. *Anal. Chim. Acta.* 149:391.

NARASAKI, H. & M. IKEDA. 1984. Automated determination of arsenic and selenium by atomic absorption spectrometry with hydride generation. *Anal. Chem.* 56:2059.

VOTH-BEACH, L.M. & D.E. SHRADER. 1985. Reduction of interferences in the determination of arsenic and selenium by hydride generation. *Spectroscopy* 1:60.

WELZ, B. & M. MELCHER. 1985. Decomposition of marine biological tissues for determination of arsenic, selenium, and mercury using hydride-generation and cold-vapor atomic absorption spectrometries. *Anal. Chem.* 57:427.

EBDON, L. & S.T. SPARKES. 1987. Determination of arsenic and selenium in environmental samples by hydride generation-direct current plasma-atomic emission spectrometry. *Microchem. J.* 36:198.

EBDON, L. & J.R. WILKINSON. 1987. The determination of arsenic and selenium in coal by continuous flow hydride-generation atomic absorption spectroscopy and atomic fluorescence spectrometry. *Anal. Chim. Acta.* 194:177.

---

* Dow Corning, or equivalent.

3120 METALS BY PLASMA EMISSION SPECTROSCOPY*

3120 A. Introduction

1. General Discussion

Emission spectroscopy using inductively coupled plasma (ICP) was developed in the mid-1960s[1,2] as a rapid, sensitive, and convenient method for the determination of metals in water and wastewater samples.[3–6] Dissolved metals are determined in filtered and acidified samples. Total metals are determined after appropriate digestion. Care must be taken to ensure that potential interferences are dealt with, especially when dissolved solids exceed 1500 mg/L.

2. References

1. Greenfield, S., I.L. Jones & C.T. Berry. 1964. High-pressure plasma-spectroscopic emission sources. *Analyst* 89: 713.
2. Wendt, R.H. & V.A. Fassel. 1965. Induction-coupled plasma spectrometric excitation source. *Anal. Chem.* 37:920.
3. U.S. Environmental Protection Agency. 1994. Method 200.7: Inductively coupled plasma-atomic emission spectrometric method for trace element analysis of water and wastes. Methods for the Determination of Metals in Environmental Samples–Supplement I; EPA 600/R-94-111, May 1994.
4. American Society For Testing & Materials. 1987. Annual Book of ASTM Standards, Vol. 11.01. Philadelphia, Pa.
5. Fishman, M.J. & W.L. Bradford, eds. 1982. A Supplement to Methods for the Determination of Inorganic Substances in Water and Fluvial Sediments; Rep. No. 82-272. U.S. Geological Survey, Washington, D.C.
6. Garbarino, J.R. & H.E. Taylor. 1985. Trace Analysis. Recent Developments and Applications of Inductively Coupled Plasma Emission Spectroscopy to Trace Elemental Analysis of Water, Vol. 4. Academic Press, New York, N.Y.

3120 B. Inductively Coupled Plasma (ICP) Method

1. General Discussion

a. Principle: An ICP source consists of a flowing stream of argon gas ionized by an applied radio frequency field typically oscillating at 27.1 MHz. This field is inductively coupled to the ionized gas by a water-cooled coil surrounding a quartz "torch" that supports and confines the plasma. A sample aerosol is generated in an appropriate nebulizer and spray chamber and is carried into the plasma through an injector tube located within the torch. The sample aerosol is injected directly into the ICP, subjecting the constituent atoms to temperatures of about 6000 to 8000°K.[1] Because this results in almost complete dissociation of molecules, significant reduction in chemical interferences is achieved. The high temperature of the plasma excites atomic emission efficiently. Ionization of a high percentage of atoms produces ionic emission spectra. The ICP provides an optically "thin" source that is not subject to self-absorption except at very high concentrations. Thus linear dynamic ranges of four to six orders of magnitude are observed for many elements.[2]

The efficient excitation provided by the ICP results in low detection limits for many elements. This, coupled with the extended dynamic range, permits effective multielement determination of metals.[3] The light emitted from the ICP is focused onto the entrance slit of either a monochromator or a polychromator that effects dispersion. A precisely aligned exit slit is used to isolate a portion of the emission spectrum for intensity measurement using a photomultiplier tube. The monochromator uses a single exit slit/photomultiplier and may use a computer-controlled scanning mechanism to examine emission wavelengths sequentially. The polychromator uses multiple fixed exit slits and corresponding photomultiplier tubes; it simultaneously monitors all configured wavelengths using a computer-controlled readout system. The sequential approach provides greater wavelength selection while the simultaneous approach can provide greater sample throughput.

b. Applicable metals and analytical limits: Table 3120:I lists elements for which this method applies, recommended analytical wavelengths, and typical estimated instrument detection levels using conventional pneumatic nebulization. Actual working detection levels are sample-dependent. Typical upper limits for linear calibration also are included in Table 3120:I. T1

c. Interferences: Interferences may be categorized as follows:

1) Spectral interferences—Light emission from spectral sources other than the element of interest may contribute to apparent net signal intensity. Sources of spectral interference include direct spectral line overlaps, broadened wings of intense spectral lines, ion-atom recombination continuum emission, molecular band emission, and stray (scattered) light from the emission of elements at high concentrations.[4] Avoid line overlaps by selecting alternate analytical wavelengths. Avoid or minimize other spectral interference by judicious choice of background correction positions. A wavelength scan of the element line region is useful for detecting potential spectral interferences and for selecting positions for background correction. Make corrections for residual spectral interference using empirically determined correction factors with the computer software supplied by the spectrometer manufacturer or with the calculation detailed below. The empirical correction method cannot be used with scanning spectrometer systems if the analytical and interfering

---

* Approved by Standard Methods Committee, 1999. Editorial revisions, 2011.

https://doi.org/10.2105/SMWW.2882.047

TABLE 3120:I. SUGGESTED WAVELENGTHS, ESTIMATED DETECTION LEVELS, ALTERNATE WAVELENGTHS, CALIBRATION CONCENTRATIONS, AND UPPER LIMITS

Element	Suggested Wavelength *nm*	Estimated Detection Level *µg/L*	Alternate Wavelength* *nm*	Calibration Concentration *mg/L*	Upper Limit Concentration† *mg/L*
Aluminum	308.22	40	237.32	10.0	100
Antimony	206.83	30	217.58	10.0	100
Arsenic	193.70	50	189.04‡	10.0	100
Barium	455.40	2	493.41	1.0	50
Beryllium	313.04	0.3	234.86	1.0	10
Boron	249.77	5	249.68	1.0	50
Cadmium	226.50	4	214.44	2.0	50
Calcium	317.93	10	315.89	10.0	100
Chromium	267.72	7	206.15	5.0	50
Cobalt	228.62	7	230.79	2.0	50
Copper	324.75	6	219.96	1.0	50
Iron	259.94	7	238.20	10.0	100
Lead	220.35	40	217.00	10.0	100
Lithium	670.78	4§	—	5.0	100
Magnesium	279.08	30	279.55	10.0	100
Manganese	257.61	2	294.92	2.0	50
Molybdenum	202.03	8	203.84	10.0	100
Nickel	231.60	15	221.65	2.0	50
Potassium	766.49	100§	769.90	10.0	100
Selenium	196.03	75	203.99	5.0	100
Silica (SiO_2)	212.41	20	251.61	21.4	100
Silver	328.07	7	338.29	2.0	50
Sodium	589.00	30§	589.59	10.0	100
Strontium	407.77	0.5	421.55	1.0	50
Thallium	190.86‡	40	377.57	10.0	100
Vanadium	292.40	8	—	1.0	50
Zinc	213.86	2	206.20	5.0	100

* Other wavelengths may be substituted if they provide the needed sensitivity and are corrected for spectral interference.

† Defines the top end of the effective calibration range. Do not extrapolate to concentrations beyond highest standard.

‡ Available with vacuum or inert gas purged optical path.

§ Sensitive to operating conditions.

lines cannot be precisely and reproducibly located. In addition, if using a polychromator, verify absence of spectral interference from an element that could occur in a sample but for which there is no channel in the detector array. Do this by analyzing single-element solutions of 100 mg/L concentration and noting for each element channel the apparent concentration from the interfering substance that is greater than the element's instrument detection limit.

2) Nonspectral interferences

a) Physical interferences are effects associated with sample nebulization and transport processes. Changes in the physical properties of samples, such as viscosity and surface tension, can cause significant error. This usually occurs when samples containing more than 10% (by volume) acid or more than 1500 mg dissolved solids/L are analyzed using calibration standards containing ≤5% acid. Whenever a new or unusual sample matrix is encountered, use the test described in 3120B.4*g*. If physical interference is present, compensate for it by sample dilution, by using matrix-matched calibration standards, or by applying the method of standard addition (see 3120B.5*d*).

High dissolved solids content also can contribute to instrumental drift by causing salt buildup at the tip of the nebulizer gas orifice. Using prehumidified argon for sample nebulization lessens this problem. Better control of the argon flow rate to the nebulizer using a mass flow controller improves instrument performance.

b) Chemical interferences are caused by molecular compound formation, ionization effects, and thermochemical effects associated with sample vaporization and atomization in the plasma. Normally these effects are not pronounced and can be minimized by careful selection of operating conditions (incident power, plasma observation position, etc.). Chemical interferences are highly dependent on sample matrix and element of interest. As with physical interferences, compensate for them by using matrix matched standards or by standard addition (3120B.5*d*). To determine the presence of chemical interference, follow instructions in 3120B.4*g*.

d. Quality control (QC): The QC practices considered to be an integral part of each method can be found in Section 3020.

2. Apparatus

a. ICP source: The ICP source consists of a radio frequency (RF) generator capable of generating at least 1.1 kW of power, torch, tesla coil, load coil, impedance matching network, nebulizer, spray chamber, and drain. High-quality flow regulators are required for both the nebulizer argon and the plasma support gas flow. A peristaltic pump is recommended to regulate sample flow to the nebulizer. The type of nebulizer and spray chamber used may depend on the samples to be analyzed as well as on the equipment manufacturer. In general, pneumatic nebulizers of the concentric or cross-flow design are used. Viscous samples and samples containing particulates or high dissolved solids content ($>$5000 mg/L) may require nebulizers of the Babington type.[5]

b. Spectrometer: The spectrometer may be of the simultaneous (polychromator) or sequential (monochromator) type with air-path, inert gas purged, or vacuum optics. A spectral bandpass of 0.05 nm or less is required. The instrument should permit examination of the spectral background surrounding the emission lines used for metals determination. It is necessary to be able to measure and correct for spectral background at one or more positions on either side of the analytical lines.

3. Reagents and Standards

Use reagents that are of ultra-high-purity grade or equivalent. Redistilled acids are acceptable. Except as noted, dry all salts at 105°C for 1 h and store in a desiccator before weighing. Use deionized water prepared by passing water through at least two stages of deionization with mixed bed cation/anion exchange resins.[6] Use deionized water for preparing all calibration standards, reagents, and for dilution.

a. Hydrochloric acid (HCl), conc and 1+1.

b. Nitric acid (HNO_3), conc.

c. Nitric acid (HNO_3), 1+1: Add 500 mL conc HNO_3 to 400 mL water and dilute to 1 L.

d. Standard stock solutions: See Sections 3111B.3, 3111D.3, and 3114B.3. **CAUTION: Many metal salts are extremely toxic and may be fatal if swallowed. Wash hands thoroughly after handling.**

1) *Aluminum*—See Section 3111D.3*k*1).
2) *Antimony*—See Section 3111B.3*j*1).
3) *Arsenic*—See Section 3114B.3*k*1).
4) *Barium*—See Section 3111D.3*k*2).
5) *Beryllium*—See Section 3111D.3*k*3).
6) *Boron—Do not dry* but keep bottle tightly stoppered and store in a desiccator. Dissolve 0.5716 g anhydrous H_3BO_3 in water and dilute to 1000 mL; 1 mL = 100 μg B.
7) *Cadmium*—See Section 3111B.3*j*3).
8) *Calcium*—See Section 3111B.3*j*4).
9) *Chromium*—See Section 3111B.3*j*6).
10) *Cobalt*—See Section 3111B.3*j*7).
11) *Copper*—See Section 3111B.3*j*8).
12) *Iron*—See Section 3111B.3*j*11).
13) *Lead*—See Section 3111B.3*j*12).
14) *Lithium*—See Section 3111B.3*j*13).
15) *Magnesium*—See Section 3111B.3*j*14).
16) *Manganese*—See Section 3111B.3*j*15).
17) *Molybdenum*—See Section 3111D.3*k*5).
18) *Nickel*—See Section 3111B.3*j*16).
19) *Potassium*—See Section 3111B.3*j*19).
20) *Selenium*—See Section 3114B.3*n*1).
21) *Silica*—See Section 3111D.3*k*8).
22) *Silver*—See Section 3111B.3*j*22).
23) *Sodium*—See Section 3111B.3*j*23).
24) *Strontium*—See Section 3111B.3*j*24).
25) *Thallium*—See Section 3111B.3*j*25).
26) *Vanadium*—See Section 3111D.3*k*11).
27) *Zinc*—See Section 3111B.3*j*27).

e. Calibration standards: Prepare mixed calibration standards containing the concentrations shown in Table 3120:I by combining appropriate volumes of the stock solutions in 100-mL volumetric flasks. Add 2 mL 1+1 HNO_3 and 10 mL 1+1 HCl and dilute to 100 mL with water. Before preparing mixed standards, analyze each stock solution separately to determine possible spectral interference or the presence of impurities. When preparing mixed standards take care that the elements are compatible and stable. Store mixed standard solutions in an FEP fluorocarbon or unused polyethylene bottle. Verify calibration standards initially using the quality control standard; monitor weekly for stability. The following are recommended combinations using the suggested analytical lines in Table 3120:I. Alternative combinations are acceptable.

1) *Mixed standard solution I*—Manganese, beryllium, cadmium, lead, selenium, and zinc.
2) *Mixed standard solution II*—Barium, copper, iron, vanadium, and cobalt.
3) *Mixed standard solution III*—Molybdenum, silica, arsenic, strontium, and lithium.
4) *Mixed standard solution IV*—Calcium, sodium, potassium, aluminum, chromium, and nickel.
5) *Mixed standard solution V*—Antimony, boron, magnesium, silver, and thallium. If addition of silver results in an initial precipitation, add 15 mL water and warm flask until solution clears. Cool and dilute to 100 mL with water. For this acid combination limit the silver concentration to 2 mg/L. Silver under these conditions is stable in a tap water matrix for 30 d. Higher concentrations of silver require additional HCl.

f. Calibration blank: Dilute 2 mL 1+1 HNO_3 and 10 mL 1+1 HCl to 100 mL with water. Prepare a sufficient quantity to be used to flush the system between standards and samples.

g. Method blank: Carry a reagent blank through entire sample preparation procedure. Prepare method blank to contain the same acid types and concentrations as the sample solutions.

h. Instrument check standard: Prepare instrument check standards by combining compatible elements at a concentration of 2 mg/L.

i. Instrument quality control sample: Obtain a certified aqueous reference standard from an outside source and prepare according to instructions provided by the supplier. Use the same acid matrix as the calibration standards.

j. Method quality control sample: Carry the instrument quality control sample (¶ *i* above) through the entire sample preparation procedure.

k. Argon: Use technical or welder's grade. If gas appears to be a source of problems, use prepurified grade.

4. Procedure

a. Sample preparation: See Section 3030F.

b. Operating conditions: Because of differences among makes and models of satisfactory instruments, no detailed operating instructions can be provided. Follow manufacturer's instructions. Establish instrumental detection limit, precision, optimum background correction positions, linear dynamic range, and interferences for each analytical line. Verify that the instrument configuration and operating conditions satisfy the analytical requirements and that they can be reproduced on a day-to-day basis. An atom-to-ion emission intensity ratio [Cu(I) 324.75 nm/Mn(II) 257.61 nm] can be used to reproduce optimum conditions for multielement analysis precisely. The Cu/Mn intensity ratio may be incorporated into the calibration procedure, including specifications for sensitivity and for precision.[7] Keep daily or weekly records of the Cu and Mn intensities and/or the intensities of critical element lines. Also record settings for optical alignment of the polychromator, sample uptake rate, power readings (incident, reflected), photomultiplier tube attenuation, mass flow controller settings, and system maintenance.

c. Instrument calibration: Set up instrument as directed (¶ *b* above). Warm up for 30 min. For polychromators, perform an optical alignment using the profile lamp or solution. Check alignment of plasma torch and spectrometer entrance slit, particularly if maintenance of the sample introduction system was performed. Make Cu/Mn or similar intensity ratio adjustment.

Calibrate instrument according to manufacturer's recommended procedure using calibration standards and blank. Aspirate each standard or blank for a minimum of 15 s after reaching the plasma before beginning signal integration. Rinse with calibration blank or similar solution for at least 60 s between each standard to eliminate any carryover from the previous standard. Use average intensity of multiple integrations of standards or samples to reduce random error.

Before analyzing samples, analyze instrument check standard. Concentration values obtained should not deviate from the actual values by more than ±5% (or the established control limits, whichever is lower).

d. Analysis of samples: Begin each sample run with an analysis of the calibration blank, then analyze the method blank. This permits a check of the sample preparation reagents and procedures for contamination. Analyze samples, alternating them with analyses of calibration blank. Rinse for at least 60 s with dilute acid between samples and blanks. After introducing each sample or blank let system equilibrate before starting signal integration. Examine each analysis of the calibration blank to verify that no carry-over memory effect has occurred. If carry-over is observed, repeat rinsing until proper blank values are obtained. Make appropriate dilutions and acidifications of the sample to determine concentrations beyond the linear calibration range.

e. Instrumental quality control: Analyze instrument check standard once per 10 samples to determine if significant instrument drift has occurred. If agreement is not within ±5% of the expected values (or within the established control limits, whichever is lower), terminate analysis of samples, correct problem, and recalibrate instrument. If the intensity ratio reference is used, resetting this ratio may restore calibration without the need for reanalyzing calibration standards. Analyze instrument check standard to confirm proper recalibration. Reanalyze one or more samples analyzed just before termination of the analytical run. Results should agree to within ±5%, otherwise all samples analyzed after the last acceptable instrument check standard analysis must be reanalyzed.

Analyze instrument quality control sample within every run. Use this analysis to verify accuracy and stability of the calibration standards. If any result is not within ±5% of the certified value, prepare a new calibration standard and recalibrate the instrument. If this does not correct the problem, prepare a new stock solution and a new calibration standard and repeat calibration.

f. Method quality control: Analyze the method quality control sample within every run. Results should agree to within ±5% of the certified values. Greater discrepancies may reflect losses or contamination during sample preparation.

g. Test for matrix interference: When analyzing a new or unusual sample matrix verify that neither a positive nor negative nonlinear interference effect is operative. If the element is present at a concentration above 1 mg/L, use serial dilution with calibration blank. Results from the analyses of a dilution should be within ±5% of the original result. Alternately, or if the concentration is either below 1 mg/L or not detected, use a post-digestion addition equal to 1 mg/L. Recovery of the addition should be either between 95% and 105% or within established control limits of ±2 standard deviations around the mean. If a matrix effect causes test results to fall outside the critical limits, complete the analysis after either diluting the sample to eliminate the matrix effect while maintaining a detectable concentration of at least twice the detection limit or applying the method of standard additions.

5. Calculations and Corrections

a. Blank correction: Subtract result of an adjacent calibration blank from each sample result to make a baseline drift correction. (Concentrations printed out should include negative and positive values to compensate for positive and negative baseline drift. Make certain that the calibration blank used for blank correction has not been contaminated by carry-over.) Use the result of the method blank analysis to correct for reagent contamination. Alternatively, intersperse method blanks with appropriate samples. Reagent blank and baseline drift correction are accomplished in one subtraction.

b. Dilution correction: If the sample was diluted or concentrated in preparation, multiply results by a dilution factor (*DF*) calculated as follows:

$$DF = \frac{\text{Final weight or volume}}{\text{Initial weight or volume}}$$

c. Correction for spectral interference: Correct for spectral interference by using computer software supplied by the instrument manufacturer or by using the manual method based on interference correction factors. Determine interference correction factors by analyzing single-element stock solutions of appropriate concentrations under conditions matching as closely as possible those used for sample analysis. Unless analysis conditions can be reproduced accurately from day to day, or for longer periods, redetermine interference correction factors found to affect the results significantly each time samples are analyzed.[7, 8] Calculate interference correction factors (K_{ij}) from apparent concentrations observed in the analysis of the high-purity stock solutions:

$$K_{ij} = \frac{\text{Apparent concentration of element } i}{\text{Actual concentration of interfering element } j}$$

where the apparent concentration of element i is the difference between the observed concentration in the stock solution and the observed concentration in the blank. Correct sample concentrations observed for element i (already corrected for baseline drift), for spectral interferences from elements j, k, and l; for example:

$$\text{Concentration of element } i \text{ corrected for spectral interference} =$$

$$\begin{array}{c}\text{Observed}\\ \text{concentration}\\ \text{of } i\end{array} - (K_{ij}) \begin{array}{c}\text{Observed}\\ \text{concentration}\\ \text{of interfering}\\ \text{element } j\end{array} - (K_{ik}) \begin{array}{c}\text{Observed}\\ \text{concentration}\\ \text{of interfering}\\ \text{element } k\end{array}$$

$$- (K_{il}) \begin{array}{c}\text{Observed}\\ \text{concentration}\\ \text{of interfering}\\ \text{element } l\end{array}$$

Interference correction factors may be negative if background correction is used for element i. A negative K_{ij} can result where an interfering line is encountered at the background correction wavelength rather than at the peak wavelength. Determine concentrations of interfering elements j, k, and l within their respective linear ranges. Mutual interferences (i interferes with j and j interferes with i) require iterative or matrix methods for calculation.

d. Correction for nonspectral interference: If nonspectral interference correction is necessary, use the method of standard additions. It is applicable when the chemical and physical form of the element in the standard addition is the same as in the sample, *or* the ICP converts the metal in both sample and addition to the same form; the interference effect is independent of metal concentration over the concentration range of standard additions; and the analytical calibration curve is linear over the concentration range of standard additions.

Use an addition not less than 50% nor more than 100% of the element concentration in the sample so that measurement precision will not be degraded and interferences that depend on element/interferent ratios will not cause erroneous results. Apply the method to all elements in the sample set using background correction at carefully chosen off-line positions. Multielement standard addition can be used if it has been determined that added elements are not interferents.

e. Reporting data: Report analytical data in concentration units of milligrams per liter using up to three significant figures. Report results below the determined detection limit as not detected less than the stated detection limit corrected for sample dilution.

6. Precision and Bias

As a guide to the generally expected precision and bias, see the linear regression equations in Table 3120:II.[9] Additional interlaboratory information is available.[10] **T2A**

7. References

1. Faires, L.M., B.A. Palmer, R. Engleman, Jr. & T.M. Niemczyk. 1984. Temperature determinations in the inductively coupled plasma using a Fourier transform spectrometer. *Spectrochim. Acta* 39B:819.
2. Barnes, R.M. 1978. Recent advances in emission spectroscopy: inductively coupled plasma discharges for spectrochemical analysis. *CRC Crit. Rev. Anal. Chem.* 7:203.
3. Parsons, M.L., S. Major & A.R. Forster. 1983. Trace element determination by atomic spectroscopic methods—State of the art. *Appl. Spectrosc.* 37:411.
4. Larson, G.F., V.A. Fassel, R.K. Winge & R.N. Kniseley. 1976. Ultratrace analysis by optical emission spectroscopy: The stray light problem. *Appl. Spectrosc.* 30:384.
5. Garbarino, J.R. & H.E. Taylor. 1979. A Babington-type nebulizer for use in the analysis of natural water samples by inductively coupled plasma spectrometry. *Appl. Spectrosc.* 34:584.
6. American Society for Testing & Materials. 1988. Standard specification for reagent water; D1193-77 (reapproved 1983). *In* Annual Book of ASTM Standards. Philadelphia, Pa.
7. Botto, R.I. 1984. Quality assurance in operating a multielement ICP emission spectrometer. *Spectrochim. Acta* 39B:95.
8. Botto, R.I. 1982. Long-term stability of spectral interference calibrations for inductively coupled plasma atomic emission spectrometry. *Anal. Chem.* 54:1654.
9. Maxfield, R. & B. Mindak. 1985. EPA Method Study 27, Method 200. 7 (Trace Metals by ICP); EPA-600/S4-85/05. National Technical Information Serv., Springfield, Va.
10. Garbarino, J.R., B.E. Jones, G.P. Stein, W.T. Belser & H.E. Taylor. 1985. Statistical evaluation of an inductively coupled plasma atomic emission spectrometric method for routine water quality testing. *Appl. Spectrosc.* 39:53.

TABLE 3120:II. ICP PRECISION AND BIAS DATA

Element	Concentration Range *μg/L*	Total Digestion* *μg/L*	Recoverable Digestion* *μg/L*
Aluminum	69–4792	$X = 0.9273C + 3.6$	$X = 0.9380C + 22.1$
		$S = 0.0559X + 18.6$	$S = 0.0873X + 31.7$
		$SR = 0.0507X + 3.5$	$SR = 0.0481X + 18.8$
Antimony	77–1406	$X = 0.7940C - 17.0$	$X = 0.8908C + 0.9$
		$S = 0.1556X - 0.6$	$S = 0.0982X + 8.3$
		$SR = 0.1081X + 3.9$	$SR = 0.0682X + 2.5$
Arsenic	69–1887	$X = 1.0437C - 12.2$	$X = 1.0175C + 3.9$
		$S = 0.1239X + 2.4$	$S = 0.1288X + 6.1$
		$SR = 0.0874X + 6.4$	$SR = 0.0643X + 10.3$
Barium	9–377	$X = 0.7683C + 0.47$	$X = 0.8380C + 1.68$
		$S = 0.1819X + 2.78$	$S = 0.2540X + 0.30$
		$SR = 0.1285X + 2.55$	$SR = 0.0826X + 3.54$
Beryllium	3–1906	$X = 0.9629C + 0.05$	$X = 1.0177C - 0.55$
		$S = 0.0136X + 0.95$	$S = 0.0359X + 0.90$
		$SR = 0.0203X - 0.07$	$SR = 0.0445X - 0.10$
Boron	19–5189	$X = 0.8807C + 9.0$	$X = 0.9676C + 18.7$
		$S = 0.1150X + 14.1$	$S = 0.1320X + 16.0$
		$SR = 0.0742X + 23.2$	$SR = 0.0743X + 21.1$
Cadmium	9–1943	$X = 0.9874C - 0.18$	$X = 1.0137C - 0.65$
		$S = 0.0557X + 2.02$	$S = 0.0585X + 1.15$
		$SR = 0.0300X + 0.94$	$SR = 0.0332X + 0.90$
Calcium	17–47 170	$X = 0.9182C - 2.6$	$X = 0.9658C + 0.8$
		$S = 0.1228X + 10.1$	$S = 0.0917X + 6.9$
		$SR = 0.0189X + 3.7$	$SR = 0.0327X + 10.1$
Chromium	13–1406	$X = 0.9544C + 3.1$	$X = 1.0049C - 1.2$
		$S = 0.0499X + 4.4$	$S = 0.0698X + 2.8$
		$SR = 0.0009X + 7.9$	$SR = 0.0571X + 1.0$
Cobalt	17–2340	$X = 0.9209C - 4.5$	$X = 0.9278C - 1.5$
		$S = 0.0436X + 3.8$	$S = 0.0498X + 2.6$
		$SR = 0.0428X + 0.5$	$SR = 0.0407X + 0.4$
Copper	8–1887	$X = 0.9297C - 0.30$	$X = 0.9647C - 3.64$
		$S = 0.0442X + 2.85$	$S = 0.0497X + 2.28$
		$SR = 0.0128X + 2.53$	$SR = 0.0406X + 0.96$
Iron	13–9359	$X = 0.8829C + 7.0$	$X = 0.9830C + 5.7$
		$S = 0.0683X + 11.5$	$S = 0.1024X + 13.0$
		$SR = -0.0046X + 10.0$	$SR = 0.0790X + 11.5$
Lead	42–4717	$X = 0.9699C - 2.2$	$X = 1.0056C + 4.1$
		$S = 0.0558X + 7.0$	$S = 0.0799X + 4.6$
		$SR = 0.0353X + 3.6$	$SR = 0.0448X + 3.5$
Magnesium	34–13 868	$X = 0.9881C - 1.1$	$X = 0.9879C + 2.2$
		$S = 0.0607X + 11.6$	$S = 0.0564X + 13.2$
		$SR = 0.0298X + 0.6$	$SR = 0.0268X + 8.1$
Manganese	4–1887	$X = 0.9417C + 0.13$	$X = 0.9725C + 0.07$
		$S = 0.0324X + 0.88$	$S = 0.0557X + 0.76$
		$SR = 0.0153X + 0.91$	$SR = 0.0400X + 0.82$
Molybdenum	17–1830	$X = 0.9682C + 0.1$	$X = 0.9707C - 2.3$
		$S = 0.0618X + 1.6$	$S = 0.0811X + 3.8$
		$SR = 0.0371X + 2.2$	$SR = 0.0529X + 2.1$
Nickel	17–47 170	$X = 0.9508C + 0.4$	$X = 0.9869C + 1.5$
		$S = 0.0604X + 4.4$	$S = 0.0526X + 5.5$
		$SR = 0.0425X + 3.6$	$SR = 0.0393X + 2.2$
Potassium	347–14 151	$X = 0.8669C - 36.4$	$X = 0.9355C - 183.1$
		$S = 0.0934X + 77.8$	$S = 0.0481X + 177.2$
		$SR = -0.0099X + 144.2$	$SR = 0.0329X + 60.9$
Selenium	69–1415	$X = 0.9363C - 2.5$	$X = 0.9737C - 1.0$
		$S = 0.0855X + 17.8$	$S = 0.1523X + 7.8$
		$SR = 0.0284X + 9.3$	$SR = 0.0443X + 6.6$

TABLE 3120:II, CONT.

Element	Concentration Range µg/L	Total Digestion* µg/L	Recoverable Digestion* µg/L
Silicon	189–9434	$X = 0.5742C - 35.6$	$X = 0.9737C - 60.8$
		$S = 0.4160X + 37.8$	$S = 0.3288X + 46.0$
		$SR = 0.1987X + 8.4$	$SR = 0.2133X + 22.6$
Silver	8–189	$X = 0.4466C + 5.07$	$X = 0.3987C + 8.25$
		$S = 0.5055X - 3.05$	$S = 0.5478X - 3.93$
		$SR = 0.2086X - 1.74$	$SR = 0.1836X - 0.27$
Sodium	35–47 170	$X = 0.9581C + 39.6$	$X = 1.0526C + 26.7$
		$S = 0.2097X + 33.0$	$S = 0.1473X + 27.4$
		$SR = 0.0280X + 105.8$	$SR = 0.0884X + 50.5$
Thallium	79–1434	$X = 0.9020C - 7.3$	$X = 0.9238C + 5.5$
		$S = 0.1004X + 18.3$	$S = 0.2156X + 5.7$
		$SR = 0.0364X + 11.5$	$SR = -0.0106X + 48.0$
Vanadium	13–4698	$X = 0.9615C - 2.0$	$X = 0.9551C + 0.4$
		$S = 0.0618X + 1.7$	$S = 0.0927X + 1.5$
		$SR = 0.0220X + 0.7$	$SR = 0.0472X + 0.5$
Zinc	7–7076	$X = 0.9356C - 0.30$	$X = 0.9500C + 1.22$
		$S = 0.0914X + 3.75$	$S = 0.0597X + 6.50$
		$SR = -0.0130X + 10.07$	$SR = 0.0153X + 7.78$

* X = mean recovery, µg/L,
C = true value, µg/L,
S = multi-laboratory standard deviation, µg/L, and
SR = single-analyst standard deviation, µg/L.

3125 METALS BY INDUCTIVELY COUPLED PLASMA–MASS SPECTROMETRY*

3125 A. Introduction

1. General Discussion

This method is designed to determine trace metals and metalloids in surface, ground, and drinking waters via inductively coupled plasma–mass spectrometry (ICP–MS). Although best suited for ambient or pristine freshwater matrices, this method can also be used to analyze wastewater, soils, sediments, sludge, and biological samples after appropriate digestion followed by dilution and/or cleanup to reduce matrix effects to a manageable level.[1,2] Various cleanup techniques are available to reduce matrix interferences and/or concentrate analytes of interest.[3–7]

For many analytes, the instrument detection limits (IDLs) are between 1 and 100 ng/L. The quadrupole-based ICP–MS may include collision cell technology (CCT) and/or dynamic reaction cell (DRC), which remove the need for mathematical interference correction for many elements. Additional data (Tables 3125:I and 3125:II) demonstrate the performance for elements seriously affected by polyatomic interferences.[8,9]

TABLE 3125:I. METHOD PERFORMANCE WITH CALIBRATION VERIFICATION STANDARDS*†

Element	Mass	Mean Recovery %	Mean *ng/mL*	SD *ng/mL*	RSD %
V	51	100.00	200.0	9.25	4.62
V CCT	51	100.44	200.9	7.30	3.63
Cr	52	99.56	199.1	9.39	4.72
Cr CCT	52	100.56	201.1	7.16	3.56
Mn	55	101.36	1014	54.09	5.34
Mn CCT	55	98.28	982.8	31.95	3.25
Fe	56	101.84	10184	566.43	5.56
Fe CCT	56	100.25	10025	336.29	3.35
Co	59	101.58	20.32	0.89	4.38
Co CCT	59	101.67	20.33	0.64	3.15
Ni	60	101.08	202.2	9.06	4.48
Ni CCT	60	101.90	203.8	6.61	3.24
Cu	63	101.76	1018	62.46	6.14
Cu CCT	63	105.63	1056	36.79	3.48
Cu	65	102.12	1021	56.06	5.49
Zn	66	100.52	1005	47.63	4.74
Zn CCT	66	99.51	995.1	33.94	3.41
As	75	99.54	19.91	1.02	5.14
As CCT	75	98.24	19.65	0.78	3.99
Se	78	102.77	20.55	1.04	5.07
Se CCT	78	104.78	20.96	1.73	8.26

* Single-laboratory, single-operator data acquired 12-2005 using Thermo Electron X Series in Standard and CCT-KED modes.
† Continuing calibration verification standard ($N = 28$).

The method is intended to be performance-based, so the elemental analyte list can be extended, new "clean" preparation techniques can be implemented, and other appropriate modifications can be made as technology evolves. Any modifications to the base method must be validated via suitable quality control standards. More sources of information on quality assurance and other aspects of ICP–MS analysis of metals are available.[10–12]

Ideally, the analysts who use this method will have experience using ICP–MS, interpreting spectral and matrix interferences, and implementing corrective procedures. Before generating data, analysts should demonstrate their proficiency in this method by successfully analyzing a performance evaluation sample for each matrix type.

2. References

1. MONTASER, A. & D.W. GOLIGHTLY, EDS. 1992. Inductively Coupled Plasmas in Analytical Atomic Spectrometry, 2nd ed. VCH Publishers, Inc., New York, N.Y.

TABLE 3125:II. METHOD PERFORMANCE WITH STANDARD REFERENCE WATER*†

Element	Mass	Mean Recovery %	Mean *ng/mL*	SD *ng/mL*	RSD %
V	51	95.49	12.40	0.62	5.01
V CCT	51	101.60	13.20	0.32	2.39
Cr	52	93.34	36.03	0.80	2.21
Cr CCT	52	95.31	36.79	0.89	2.42
Mn	55	99.09	120.40	2.25	1.87
Mn CCT	55	96.99	117.8	2.18	1.85
Fe	56	110.45	37.89	4.32	11.41
Fe CCT	56	102.20	35.06	1.78	5.09
Co	59	98.43	19.96	0.32	1.62
Co CCT	59	99.22	20.12	0.36	1.79
Ni	60	98.78	27.06	0.68	2.51
Ni CCT	60	100.69	27.59	0.50	1.80
Cu†	63	115.36	98.29	3.68	3.74
Cu CCT‡	63	122.91	104.7	2.81	2.68
Cu‡	65	118.83	101.2	2.84	2.80
Zn	66	95.88	51.01	1.36	2.67
Zn CCT	66	97.64	51.95	1.91	3.68
As	75	98.61	26.30	0.48	1.81
As CCT	75	98.38	26.24	0.59	2.26
Se	78	95.83	21.04	0.45	2.15
Se CCT	78	97.58	21.43	1.86	8.66

* Single-laboratory, single-operator data acquired 12-2005 using Thermo Electron X Series in Standard and CCT-KED modes.
† NIST 1640 ($N = 7$).
‡ Copper contamination.

---

* Approved by Standard Methods Committee, 2009. Editorial revisions, 2011.
Joint Task Group: 22nd Edition—Robert Henry (chair), Christopher J. Baggett, Cindy A. Bamfield, Alois F. Clary, William R. Kammin, Gregg Oelker.

2. Date, A.R. & A.L. Gray. 1989. Applications of Inductively Coupled Plasma Mass Spectrometry. Blackie & Son, Ltd., Glasgow, U.K.
3. McLaren, J.W., A.P. Mykytiuk, S.N. Willie & S.S. Berman. 1985. Determination of trace metals in seawater by inductively coupled plasma mass spectrometry with preconcentration on silica-immobilized 8-hydroxyquinoline. *Anal. Chem.* 57: 2907.
4. Burba, P. & P.G. Willmer. 1987. Multielement preconcentration for atomic spectroscopy by sorption of dithiocarbamate metal complexes (e.g., HMDC) on cellulose collectors. *Fresenius Z. Anal. Chem.* 329:539.
5. Wang, X. & R.M. Barnes. 1989. Chelating resins for on-line flow injection preconcentration with inductively coupled plasma atomic emission spectroscopy. *J. Anal. Atom. Spectrom.* 4:509.
6. Siriraks, A., H.M. Kingston & J.M. Riviello. 1990. Chelation ion chromatography as a method for trace elemental analysis in complex environmental and biological samples. *Anal. Chem.* 62:1185.
7. Puget Sound Water Quality Authority. 1996. Recommended Guidelines for Measuring Metals in Puget Sound Marine Water, Sediment and Tissue Samples. Appendix D: Alternate Methods for the Analysis of Marine Water Samples. Puget Sound Water Quality Authority, Olympia, Wash.
8. Nelms, S., ed. 2005. Inductively Coupled Plasma Mass Spectrometry Handbook. Blackwell Science, Cambridge, Mass.
9. Becker, J.S. 2008. Inorganic Mass Spectrometry: Principles and Applications. Wiley Interscience, Malden, Mass.
10. U.S. Environmental Protection Agency. 1994. Determination of trace elements in waters and wastes by inductively coupled plasma–mass spectrometry; Method 200.8. Environmental Monitoring Systems Laboratory, Cincinnati, Ohio.
11. Longbottom, J.E., T.D. Martin, K.W. Edgell, S.E. Long, M.R. Plantz & B.E. Warden. 1994. Determination of trace elements in water by inductively coupled plasma–mass spectrometry: collaborative study. *J. AOAC Internat.* 77:1004.
12. U.S. Environmental Protection Agency. 1995. Method 1638: Determination of trace elements in ambient waters by inductively coupled plasma–mass spectrometry. Off. Water, Washington, D.C.

Table 3125:III. Recommended Analyte Masses, Instrument Detection Limits (IDL), and Internal Standards

Element	Analytical Mass	IDL* *μg/L*	Recommended Internal Standard
Be	9	0.025	Li
Al	27	0.03	Sc
V	51	0.02	Sc
Cr	52	0.04	Sc
Cr	53	0.03	Sc
Mn	55	0.002	Sc
Co	59	0.002	Sc
Ni	60	0.004	Sc
Ni	62	0.025	Sc
Cu	63	0.003	Sc
Cu	65	0.004	Sc
Zn	66	0.017	Ge
Zn	68	0.020	Ge
As	75	0.025	Ge
Se	77	0.093	Ge
Se	82	0.064	Ge
Ag	107	0.003	In
Ag	109	0.002	In
Cd	111	0.006	In
Cd	114	0.003	In
Sb	121	0.07	In
Sb	123	0.07	In
Tl	203	0.03	Th
Tl	205	0.03	Th
Pb	208	0.005	Th
U	235	0.032	Th
U	238	0.001	Th
Mo	98	0.003†	In
Ba	135	0.008†	In
Sr	88	0.001‡	In

* IDLs were determined on a Perkin Elmer Elan 6000 ICP–MS using seven replicate analyses of a 1% nitric acid solution, at Manchester Environmental Laboratory, July 1996.

† From EPA Method 200.8 for the Analysis of Drinking Waters—Application Note, Order No. ENVA-300A, The Perkin Elmer Corporation, 1996.

‡ From Perkin Elmer Technical Summary TSMS-12.

3125 B. Inductively Coupled Plasma–Mass Spectrometry (ICP–MS) Method

1. General Discussion

a. Principle: In this method, analysts introduce sample material to an argon-based, high-temperature radio-frequency plasma, usually via pneumatic nebulization. As energy transfers from the plasma to the sample stream, the target element desolves, atomizes, and ionizes. The resulting ions are extracted from the plasma through a differential vacuum interface and separated based on their mass-to-charge (m/z) ratio by a mass spectrometer. Typically, either a quadrupole (with or without CCT or DRC) or magnetic sector (high-resolution) mass spectrometer is used. An electron multiplier detector counts the separated ions, and a computer-based data-management system processes the resulting information.

b. Applicable elements and analytical limits: This method has been demonstrated to be suitable for aluminum, antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, lead, manganese, molybdenum, nickel, selenium, silver, strontium, thallium, uranium, vanadium, and zinc (see Table 3125:III). It is also acceptable for other elemental analytes as long as the same quality assurance practices are followed, with documented acceptance limits.

Before implementing the method, determine the instrument detection limit (IDL) and method detection limit (MDL) for all analytes (see Section 1030C). Typical IDLs for method analytes are presented in Table 3125:III.[1,2]

Determining the MDL for each element is critical when analyzing complex matrices, such as seawater, brines, and industrial effluents. In these cases, the MDL typically will be higher than

TABLE 3125:IV.A. ELEMENTAL ABUNDANCE EQUATIONS AND COMMON MOLECULAR ION CORRECTION EQUATIONS

Elemental and Molecular Equations*†	
Li 6	$= C\ 6$
Be 9	$= C\ 9$
Al 27	$= C\ 27$
Sc 45	$= C\ 45$
V 51	$= C\ 51 - (3.127)[(C\ 53) - (0.113 \times C\ 52)]$
Cr 52	$= C\ 52$
Cr 53	$= C\ 53$
Mn 55	$= C\ 55$
Co 59	$= C\ 59$
Ni 60	$= C\ 60$
Ni 62	$= C\ 62$
Cu 63	$= C\ 63$
Cu 65	$= C\ 65$
Zn 66	$= C\ 66$
Zn 68	$= C\ 69$
As 75	$= C\ 75 - (3.127)[(C\ 77) - (0.815 \times C\ 82)]$
Se 77	$= C\ 77$
Se 82	$= C\ 82 - (1.008696 \times C\ 83)$
Sr 88	$= C\ 88$
Mo 98	$= C\ 98 - (0.110588 \times C\ 101)$
Rh 103	$= C\ 103$
Ag 107	$= C\ 107$
Ag 109	$= C\ 109$
Cd 111	$= C\ 111 - (1.073)[(C\ 108) - (0.712 \times C\ 106)]$
Cd 114	$= C\ 114 - (0.02686 \times C\ 119)$
Sb 121	$= C\ 121$
Sb 123	$= C\ 123 - (0.127189 \times C\ 125)$
Ba 135	$= C\ 135$
Ho 165	$= C\ 165$
Tl 203	$= C\ 203$
Tl 205	$= C\ 205$
Pb 208	$= C\ 208 + (1 \times C\ 206) + (1 \times C\ 207)$
Th 232	$= C\ 232$
U 238	$= C\ 238$

* C = calibration blank-corrected counts at indicated masses.

† From EPA Method 200.8 for the Analysis of Drinking Water—Application Note, Order No. ENVA-300A, The Perkin Elmer Corporation, 1996.

the IDL because of background levels of analytes introduced during sample preparation, as well as laboratory-derived contamination and matrix-based interferences. Determine both IDL and MDL when first implementing this method, and then repeat yearly or whenever the instrument configuration changes or major maintenance occurs, whichever happens first.

Also, determine the linear dynamic range (LDR) for all method analytes, including multi-element mixtures (to account for possible inter-element effects). *LDR* is the maximum analyte concentration above the highest calibration point at which the analyte response is within ±10% of its theoretical response. When determining LDRs, avoid using unnecessarily high analyte concentrations because they might damage the detector. Determine LDR when first implementing this method, and then repeat yearly.

c. Interferences: ICP–MS is subject to several types of interferences, including the following:

1) Isobars—*Isobars* are isotopes of different elements that form ions with the same nominal atomic mass units/charge number (m/z) ratio that cannot be resolved by a quadrupole or high-resolution mass spectrometer. Typically, ICP–MS operating software includes all known isobaric interferences and will perform the necessary calculations automatically (see Table 3125:IV). Monitor ^{83}Kr, ^{99}Ru, ^{118}Sn, and ^{125}Te to correct for isobaric interference caused by ^{82}Kr on ^{82}Se, by ^{98}Ru on ^{98}Mo, by ^{114}Sn on ^{114}Cd, by ^{115}Sn on ^{115}In, and by ^{123}Te on ^{123}Sb. Monitor ArCl at mass 77 to estimate chloride interferences. Verify that all elemental and molecular correction equations used in this method are correct and appropriate for the mass spectrometer used and the sample matrix.

2) Abundance sensitivity—*Abundance sensitivity* is the possibility that the low and high "wings" of any abundant mass peak will contribute to or obscure adjacent masses. Adjust the mass spectrometer resolution and quadrupole pole bias to minimize these interferences.

3) Polyatomics—*Polyatomics* are (molecular) ion interferences caused by ions with more than one atom that have the same nominal m/z ratio as the isotope of interest. Most of the common molecular ion interferences have been identified (see Table 3125:V). Because of the severity of chloride ion interference on important analytes, particularly vanadium and arsenic, hydrochloric acid is not recommended for use in ICP–MS sample preparation. Because most environmental samples contain some chloride ion, analysts must use chloride-correction equations for affected masses. Collision cell technology and dynamic reaction cell effectively reduce most polyatomic species to analytically negligible levels in quadrupole-based ICP–MS systems, sometimes removing the need for complex correction equations. A high-resolution ICP–MS resolves many—but not all—interferences caused by polyatomic ions. Polyatomic interferences are strongly influenced by instrument design and plasma operating conditions; they sometimes can be reduced by carefully adjusting nebulizer gas flow and other instrument operating parameters.

4) Doubly-charged—Some elements (e.g., barium and strontium) form significant levels of M^{2+} ions under normal plasma conditions. The M^{2+} ions occur in the mass spectrum at M/2 and, in the case of Ba and Sr, will interfere with some isotopes of zinc and calcium, respectively.

5) Physical interferences—These include differences in viscosity, surface tension, and dissolved solids between samples and calibration standards. To minimize these effects, analytical samples should not contain more than 0.5% of dissolved solids. Dilute water and wastewater samples with higher dissolved solids levels before analyzing them. Use internal standards to correct for physical interferences, provided that their analytical behavior is comparable to the elements being determined.

Table 3125:IV.B includes information on each isotope and cautions on using correction equations. Quadrupole ICP–MS with CCT or DRC is recommended for all analytes, except perhaps beryllium (due to lower sensitivity), because it eliminates many of the equations typically needed in the standard operating mode.

6) Memory interferences—These occur when analytes from a previous sample or standard are measured in the current sample. Use a long enough rinse (flush) between samples to minimize such interferences. Persistent memory interferences may indicate problems in the sample-introduction system. Severe memory interferences may require analysts to disassemble and clean the

TABLE 3125:IV.B. ELEMENTS, MASSES, ABUNDANCES, AND CORRECTION EQUATIONS (UPDATED 2008)

Isotope	Mass	Abundance	Interference Calculation (if required)[*]	Comments
Li (IS)[†]	6	7.52	C 6 - 0.08131 × Li^{7}	Corrects for natural lithium in samples (I)[‡]
Be	9	100	C 9	
C	13	1.108	C 13	For ArC^{52} correction
Al	27	100	C 27	
Ca	43	0.13	C 43 - 0.0004 × Sr^{88}	Corrects for Sr^{2+}[§]
Sc (IS)	45	100	C 45	
V	51	99.76	C 51 - 3.1270 × ClO^{53}	Corrects for variable chloride matrix (I) [not normally required in CCT Mode]
Cr	52	83.76	C 52 - 0.0900 × C^{13}	Corrects for variable carbon content (P)[‖] [not normally required in CCT Mode]
ClO (Cr)	53		C 53 - 0.1140 × Cr^{52}	CLO interference corrected for chromium (I)
Mn	55	100	C 55	
Fe	56	91.52	C 56	CCT Mode only (ArO and CaO interferences in Standard Mode)
Co	59	100	C 59	
Ni	60	26.16	C 60 - 0.00150 × Ca^{43}	Corrects for CaO (P) [not normally required in CCT Mode]
Ni	62	3.66	C 62	
Cu	63	69.09	C 63	Possibility of ArNa (P) in high sodium matrix (sea or brackish waters)
Cu	65	30.91	C 65	
Zn	66	27.81	C 66	
Zn	68	18.56	C 68 - 0.0153 × Ba^{135}	Ba^{2+} interferes with Zn^{68}
Ge (IS)	72	27.43	C 72	Possibility of FeO (P) interference in high iron matrix
As	75	100	C 75 - 3.1270 × $ArCl^{77}$	Corrects for variable chloride matrix (I) Correction not required in CCT Mode (I)
ArCl (Se 77)	77		C 77 - 0.8484 × Se^{82}	ArCl interference corrected for Se.
Se	78	23.61	C 78	CCT Mode only due to $ArAr^{78}$ in Standard Mode
Se	82	8.84	C 82 - 1.0009 × Kr^{83}	Corrects for krypton in argon (I)
Kr	83	11.55	C 83	Variable levels in argon
Sr	88	82.56	C 88	Forms Sr^{2+} easily
Mo	95	14.78	C 95	No isobaric correction required (unlike Mo^{98})
Mo	98	24	C 98 - 0.1307 × Ru^{101}	Corrects for variable ruthenium content (I)
Ru	101	16.98	C 101	For Mo^{98} correction
Rh (IS)	103	100	C 103	
Ag	107	51.35	C 107	
Ag	109	48.65	C 109	
Cd	111	12.86	C 111 - 0.0017 × Mo^{95}	Corrects for MoO (P) [not normally required in CCT Mode]
Cd	114	28.81	C 114 - [0.0271 × Sn^{118}] - [0.0028 × Mo^{95}]	Correction for MoO (P) and Sn (I) [MoO correction not normally required in CCT Mode]
In (IS)	115	95.84	C 115 - 0.0142 × Sn^{118}	Corrects for variable tin content (I)
Sn	118	24.01	C 118	For Cd^{114} and In^{115} correction
Sb	121	57.25	C 121	
Sb	123	42.75	C 123 - 0.0449 × Te^{125}	Corrects for variable tellurium content (I)
Te	125	6.99	C 125	For Sb^{123} correction
Ba	135	6.59	C 135	
Tb (IS)	159	100	C 159	
Ho (IS)	165	100	C 165	Ho^{2+} may interfere with Se^{82}
Tl	203	29.5	C 203	
Tl	205	70.5	C 205	
Pb	206	25.15	C 206	
Pb	207	21.11	C 207	
Pb	208	52.38	C 208 + 1 × Pb^{206} + 1 × Pb^{207}	Correction for variable lead abundance (I)
Bi (IS)	209	100	C 209	
U	235	0.715	C 235	
U	238	99.28	C 238	

[*] All corrections should be verified and corrected for mass bias.

[†] IS = internal standard element.

[‡] I = isobaric correction.

[§] Doubly charged corrections may vary with plasma-tuning conditions and should be verified by the user before use.

[‖] P = correction that may vary with plasma-tuning conditions and should be verified by the user before use.

entire sample-introduction system, including the plasma torch and the sampler and skimmer cones.

7) Ionization interferences—These result when moderate (0.1% to 1%) amounts of a matrix ion change the analyte signal. This effect, which usually reduces the analyte signal, also is known as *suppression*. Correct for suppression by using internal standardization techniques.

d. Quality control (QC): The QC practices considered to be an integral part of each method can be found in Section 3020.

TABLE 3125:V. COMMON MOLECULAR ION INTERFERENCES IN ICP–MS[1]

Molecular Ion	Mass	Element Measurement Affected by Interference
Background molecular ions:		
NH^+	15	—
OH^+	17	—
OH_2^+	18	—
C_2^+	24	Mg
CN^+	26	Mg
CO^+	28	Si
N_2^+	28	Si
N_2H^+	29	Si
NO^+	30	—
NOH^+	31	P
O_2^+	32	S
O_2H^+	33	—
$^{36}ArH^+$	37	Cl
$^{38}ArH^+$	39	K
$^{40}ArH^+$	41	—
CO_2^+	44	Ca
CO_2^+H	45	Sc
ArC^+, ArO^+	52	Cr
ArN^+	54	Cr
$ArNH^+$	55	Mn
ArO^+	56	Fe
ArH^+	57	Fe
$^{40}Ar^{36}Ar^+$	76	Se
$^{40}Ar^{38}Ar$	78	Se
$^{40}Ar_2^+$	80	Se
Matrix molecular ions:		
Bromide:		
$^{81}BrH^+$	82	Se
$^{79}BrO^+$	95	Mo
$^{81}BrO^+$	97	Mo
$^{81}BrOH^+$	98	Mo
$Ar^{81}Br^+$	121	Sb
Chloride:		
$^{35}ClO^+$	51	V
$^{35}ClOH^+$	52	Cr
$^{37}ClO^+$	53	Cr
$^{37}ClOH^+$	54	Cr
$Ar^{35}Cl^+$	75	As
$Ar^{37}Cl^+$	77	Se
Sulfate:		
$^{32}SO^+$	48	Ti
$^{32}SOH^+$	49	—
$^{34}SO^+$	50	V, Cr
$^{34}SOH^+$	51	V
SO_2^+, S_2^+	64	Zn
$Ar^{32}S^+$	72	Ge
$Ar^{34}S^+$	74	Ge
Phosphate:		
PO^+	47	Ti
POH^+	48	Ti
PO_2^+	63	Cu
ArP^+	71	Ga
Group I & II metals:		
$ArNa^+$	63	Cu
ArK^+	79	Br
$ArCa^+$	80	Se
Matrix oxides*		
TiO	62–66	Ni, Cu, Zn
ZrO	106–112	Ag, Cd
MoO	108–116	Cd
NbO	109	Ag

* Oxide interferences normally will be tiny and will affect method elements only when oxide-producing elements are present at relatively high concentrations, or when the instrument is improperly tuned or maintained. Preferably monitor Ti and Zr isotopes in soil, sediment, or solid waste samples, because these samples could contain high levels of such interfering elements.

2. Apparatus

a. Inductively coupled plasma–mass spectrometer: Available from several manufacturers, this instrument includes a mass spectrometer, detector, an ICP source, mass flow controllers for regulating ICP gas flows, a peristaltic pump for introducing samples, and a computerized data acquisition and instrument control system. An x-y autosampler also may be used with appropriate control software.

b. Laboratory ware: Use pre-cleaned plastic laboratory ware for standard and sample preparation. Teflon*—either tetrafluoroethylene hexafluoropropylene-copolymer (FEP), polytetrafluoroethylene (PTFE), or perfluoroalkoxy PTFE (PFA)—is preferred for standard preparation and sample digestion, while high-density polyethylene (HDPE) and other dense, metal-free plastics may be acceptable for internal standards, known-addition solutions, etc. Check each new lot of autosampler tubes for suitability, and pre-clean autosampler tubes and pipet tips if certificate of analysis is unavailable (see Section 3010C.2).

c. Air-displacement pipets, sized 10 to 100 μL, 100 to 1000 μL, and 1 to 10 mL.

d. Analytical balance, accurate to 0.1 mg.

e. Sample-preparation apparatus, such as hot plates, microwave digesters, and heated sand baths. Any sample-preparation device could introduce trace levels of target analytes to the sample.

f. Clean hood (optional), Class 100 (certified to contain less than 100 particles/m^3), for sample preparation and manipulation. If possible, perform all sample manipulations, digestions, dilutions, etc. in a certified Class 100 environment. Alternatively, handle samples in glove boxes, plastic fume hoods, or other environments that minimize random contamination by trace metals.

3. Reagents

a. Acids: Use ultra-high-purity grade (or equivalent) acids to prepare standards and process samples. Redistilled acids are acceptable if each batch is demonstrated to be uncontaminated by target analytes. Use extreme care when handling acids in the laboratory to avoid contaminating them with trace levels of metals.

1) *Nitric acid* (HNO_3), conc (specific gravity 1.41).

2) *Nitric acid,* 1 + 1—Add 500 mL conc HNO_3 to 500 mL reagent water.

3) *Nitric acid,* (v/v) 2%—Add 20 mL conc HNO_3 to 100 mL reagent water; dilute to 1000 mL.

---

* Or equivalent.

4) *Nitric acid,* (v/v) 1%—Add 10 mL conc HNO_3 to 100 mL reagent water; dilute to 1000 mL.

b. Reagent water: When preparing blanks, standards, and samples, use metal-free water that was prepared using the methods listed in Section 1080, described below, or provided elsewhere (if they have been proven effective). Use only high-purity water to prepare samples and standards. Reagent water containing trace amounts of analyte elements will skew results.

Analysts can produce suitable reagent water using a multistage system that includes a softener/reverse osmosis unit, a dual-column, strong acid/strong base ion exchange unit; an activated carbon filter; and a UV sterilization process. This will produce a polished water free of metals and organics.

c. Stock, standard, and other required solutions: See Sections 3111B.3*j*, 3111D.3*k*, 3114B.3*j–n*, and 3120B.3*d* on preparing standard stock solutions from elemental materials (pure metals, salts). Preferably, purchase high-purity, commercially prepared stock solutions and dilute to required concentrations. Single- or multi-element stock solutions (1000 mg/L) of the following elements are required: aluminum, antimony, arsenic, barium, beryllium, cadmium, cerium, chromium, cobalt, copper, germanium, indium, lead, magnesium, manganese, molybdenum, nickel, rhodium, scandium, selenium, silver, strontium, terbium, thallium, thorium, uranium, vanadium, and zinc. Prepare internal-standard and target-element stock solutions separately; they could be incompatible and cause precipitation or other solution instability.

1) *Internal standard stock solution*—Germanium, indium, lithium, scandium, and thorium are suggested as internal standards. The following masses are monitored: ^{72}Ge, ^{115}In, ^{6}Li, ^{45}Sc, and ^{232}Th. Add enough internal standard to all samples, standards, and quality control (QC) samples to give a suitable counts/second (cps) signal and stability (100 000 to 300 000 cps for most internal standards). Minimize dilution-related errors by using an appropriately high concentration of internal standard mix solution. Maintain volume ratio for all internal standard additions.

Prepare internal standard mix as follows: Prepare a nominal 50-mg/L solution of ^{6}Li by dissolving 0.15 g $^{6}Li_2CO_3$ [isotopically pure (i.e., 95% or greater purity†)] in a minimal amount of 1:1 HNO_3. Pipet 5.0 mL 1000-mg/L germanium, indium, scandium, and thorium standards into the lithium solution, dilute resulting solution to 500.0 mL, and mix thoroughly. The resultant concentration of Ge, In, Sc, and Th will be 10 mg/L. Determine the internal standard concentrations required to achieve acceptable levels of precision, and dilute the internal standard stock accordingly.

Other internal standards, such as bismuth, holmium, rhodium, terbium, and yttrium, may also be used in this method. Ensure that the internal standard mix used is stable and that there are no undesired interactions among elements.

All new sample matrices should be screened for internal standard elements before analysis. Analyzing a few representative samples for internal standards should be sufficient. Analyze samples "as received" or "as digested" (before adding internal standard), then add internal standard mix and re-analyze. Monitor counts at the internal standard masses. If the "as received" or "as digested" samples show appreciable detector counts (10% or higher of samples with added internal standard), dilute sample or use another internal standard. If the response of a sample containing the internal standard is not within 70 to 125% of the response for a calibration blank with the internal standard, either dilute the sample before analysis or use another internal standard. During actual analysis, monitor internal standard masses and note all internal standard recoveries that are more than 125% of the internal standard response in the calibration blank. Interpret results for these samples with caution.

The internal standard mix may be added to blanks, standards, and samples via a "Y" connector after the peristaltic pump to mix it with the sample stream during sample introduction.

2) *Instrument optimization/tuning solution*—containing beryllium, cadmium, cobalt, copper, germanium, indium, rhodium, scandium, terbium, thallium, (for sensitivity and stability evaluation), barium (for doubly-charged evaluation), cerium (for oxide evaluation), magnesium (mass calibration check), and lead (mass calibration check). Prepare this solution in 2% HNO_3. This mix includes all common elements used to optimize and tune various ICP–MS operating parameters. It may be possible to use fewer elements in this solution, depending on the instrument manufacturer's recommendations.

3) *Calibration standards*—A five standard calibration is recommended, from 0 to 100 μg/L.‡ Other calibration regimes are acceptable if the full suite of quality assurance samples and standards is run to validate any method changes. Fewer standards may be used, and a two-point blank/mid-range calibration technique commonly used in ICP optical methods should also produce acceptable results. Calibrate all analytes using the selected concentrations. Prepare all calibration standards and blanks in a matrix of 2% nitric acid. Add internal standard mix to all calibration standards to provide appropriate count rates for interference correction. NOTE: Add the same ratio of internal standard mix to all standards and blanks used in this method.

4) *Method blank (MB)*—A *method blank* (also known as *reagent blank*) is a portion of reagent water (¶ *b* above) treated exactly as a sample, including exposure to all equipment, glassware, procedures, and reagents. It is used to assess whether analytes or interferences are present in the analytical process or system. No MB should contain a warning level of any analyte of interest (based on the end user's requirements). Undertake immediate corrective action for MB measurements above the minimum reporting level (see Section 3020B.5). Include at least one MB with each batch of samples prepared. For dissolved samples, take reagent water through same filtration and preservation processes used for samples. For samples requiring digestion, process reagent water with the same digestion techniques as samples. Add internal standard mix to method blank.

5) *Calibration verification standard*—Prepare a mid-range standard using a different source than that used for the calibration standards, in 2% HNO_3, with equivalent addition of internal standard.

6) *Calibration verification blank*—Use 2% HNO_3, the same solution as the zero calibration standard.

7) *Laboratory-fortified blank (LFB)*—The *laboratory-fortified blank* (also known as a *blank spike*) is a method blank that has

---

† Cambridge Isotope Laboratories, or equivalent.

‡ Performance data for the method, were obtained with these concentrations.

been fortified with a known concentration of analyte. It is used to evaluate ongoing laboratory performance and analyte recovery in a clean matrix. Prepare fortified concentrations approximating the midpoint of the calibration curve (50 ng/mL) or lower with stock solutions prepared from a different source than that used to develop working standards. Calculate percent recovery, plot control charts, and determine control limits for these measurements. Ensure that the LFB meets the method's performance criteria when such criteria are specified. Establish corrective actions to be taken in case the LFB does not satisfy acceptance criteria. Include at least one LFB with each batch of samples prepared. This standard, sometimes also called a *laboratory control sample* (LCS), is used to validate digestion techniques and known-addition levels.

8) *Reference materials*—Use externally prepared reference material, preferably from National Institute of Standards and Technology§ (NIST) 1643 series or equivalent.

9) *Known-addition solution for samples*—Add stock standard to sample so the volume change is less than 5%. In the absence of information on analyte levels in the sample, prepare known additions at around 50 μg/L or lower. If analyte concentration levels are known, add at 50 to 200% of the sample levels. For samples undergoing digestion, make additions before digestion. For dissolved metals determinations, make additions after filtration, preferably immediately before analysis.

10) *Low-level standards*—Use both a 0.3- and a 1.0-μg/L standard when expected analyte concentration is less than 5 μg/L. Prepare both standards in 2% nitric acid.

Prepare volumetrically a mixed standard containing the method analytes at desired concentration(s) (0.30 μg/L, 1.0 μg/L, or both). Prepare weekly in 100-mL quantities.

d. Argon: Use a prepurified grade of argon unless it can be demonstrated that other grades can be used successfully. Prepurified argon is usually necessary because technical argon often contains significant levels of impurities (e.g., carbon and krypton). ^{82}Kr interferes with the determination of ^{82}Se. Monitor ^{83}Kr at all times.

4. Procedures

a. Sample preparation: See Sections 3010 and 3020 for general guidance and additional specific requirements on sampling and quality control. See Section 3030E for the recommended sample-digestion technique for all analytes except silver and antimony. Use the method in Section 3030F for silver and antimony, paying special attention to chloride ion interferences and using all applicable elemental corrections. Alternative digestion techniques and more guidance on sample preparation are available.[3,4]

Ideally, use a "clean" environment when handling, manipulating, or preparing samples. Preferably perform all sample manipulations in a Class 100 clean hood or room to minimize potential contamination artifacts in digested or filtered samples.

b. Instrument operating conditions: Follow manufacturer's standard operating procedures for initialization, mass calibration, gas flow optimization, and other instrument operating conditions. Maintain complete, detailed information on the instrument's operating status whenever it is used.

TABLE 3125:VI. SUGGESTED ANALYTICAL RUN SEQUENCE

Sample Type	Comments
Tuning/optimization standard	Check mass calibration and resolution
Tuning/optimization standard	Optimize instrument for maximum rhodium counts while keeping oxides, double-charged ions, and background within instrument specifications
Rinse	—
Reagent blank	Check for contamination
Reagent blank	Calibration standard blank
5-μg/L standard	—
10-μg/L standard	—
20-μg/L standard	—
50-μg/L standard	—
100-μg/L standard	—
Rinse	Check for memory
Initial calibration verification, 50 μg/L	Check for calibration accuracy
Initial calibration blank	Check for memory
0.30-μg/L standard	Low-level calibration verification
1.0-μg/L standard	Low-level calibration verification
External reference material	NIST 1643c or equivalent
Continuing calibration verification	Check for calibration stability
Continuing blank calibration	Check for memory
Project sample method blank	Check for contamination
Project sample laboratory-fortified blank	Check for spike recovery
Project sample 1-4	Check for possible interferences
Project sample 5	—
Project sample 5 with known addition	Check for spike recovery
Project sample 5 duplicate with known addition	Check for reproducibility
Continuing calibration verification (every 10 samples)	Check for calibration stability
Continuing calibration blank (every 10 samples)	Check for memory

c. Analytical run sequence: Table 3125:VI outlines a suggested analytical run sequence, including tuning and optimizing the instrument, checking reagent blanks, calibrating the instrument, verifying the calibration, analyzing samples, and analyzing quality control samples and blanks.

d. Instrument tuning and optimization: Follow manufacturer's instructions for optimizing instrument performance. The most important optimization criteria include nebulizer gas flows, detector and lens voltages, radio-frequency forward power, and mass calibration. Periodically check mass calibration and instrument resolution. Ideally, optimize the instrument to minimize the formation of oxide and doubly charged species. Measure CeO^+:Ce^+ and Ba^{2+}:Ba^+ ratios to monitor the formation of oxide and doubly charged species, respectively. Both ratios should meet the manufacturer's criteria before instrument calibration. Moni-

---

§ National Institute of Standards and Technology, www.nist.gov

TABLE 3125:VII. SUMMARY OF PERFORMANCE CRITERIA

Performance Characteristic	Criteria
Mass resolution	Manufacturer's specification
Mass calibration	Manufacturer's specification
Ba^{2+}/Ba^{+}	Manufacturer's specification
CeO/Ce	Manufacturer's specification
Background counts at mass 220	Manufacturer's specification
Correlation coefficient	≥ 0.995
Calibration blanks	< Reporting limit
Calibration verification standards	±10% of true value
Laboratory fortified blank (control sample)	±30% of true value
Precision	±20% relative percent difference for lab duplicates
Known-addition recovery	75–125%
0.3 and 1.0 μg/L standards	Dependent on data quality objectives
Reference materials	Dependent on data quality objectives
Internal standard response	70–125% of response in calibration blank with known addition

tor background counts at mass 220 after optimization, and compare with manufacturer's criteria. (See Table 3125:VII for a summary of method performance criteria related to optimization and tuning, calibration, and analytical performance.)

e. Instrument calibration: After optimization and tuning, calibrate the ICP–MS using an appropriate range of calibration standards. Use appropriate regression techniques to determine calibration responses for each analyte. For acceptable calibrations, the regression curves' correlation coefficients are ideally 0.995 or greater.

Immediately after calibration, run initial calibration verification standard, 3125B.3*c*5); acceptance criteria are ±10% of known analyte concentration. Next, run initial calibration verification blank, 3125B.3*c*6); acceptance criteria are ideally ± the absolute value of the instrument detection limit for each analyte, but in practice, ± the absolute value of the laboratory reporting limit or the laboratory method detection limit for each analyte is acceptable. If analyte concentrations are less than 5 μg/L, verify low-level calibration by using a standard at 40 to 50% of the highest low-level standard.

f. Sample analysis: Ensure that all vessels and reagents are uncontaminated. During the analytical run, include quality-control analyses according to schedule of Table 3125:VIII or follow project-specific QA/QC protocols.

Internal standard recoveries must be between 70 and 125% of internal standard response in the laboratory-fortified blank; otherwise, dilute sample, add internal standard mix, and re-analyze.

Make known-addition analyses for each matrix in a digestion or filtration batch.

5. Calculations and Corrections

Configure instrument software to report internal-standard-corrected results. Water sample results should be reported in micrograms per liter. Report appropriate number of significant figures.

a. Correction for dilutions and solids: Correct all dilution results, and raise the related reporting limits accordingly:

$$R_{Corr} = \frac{R_{Uncorr} \times V}{(V_s/V)}$$

where:

R_{Corr} = diluted corrected results, μg/L,
R_{Uncorr} = uncorrected elemental results, μg/L,
V = volume of digestate (after digestion), L, and
V_s = volume of undiluted sample, L.

Use Method 2540B to determine total solids in solid samples, and report results as micrograms per kilogram, dry weight. Correct all results for solids content of solid samples. Use the following equation to correct solid or sediment sample results for dilution during digestion and moisture content:

TABLE 3125:VIII. QUALITY CONTROL ANALYSES FOR ICP–MS METHOD

Analysis	Frequency	Acceptance Criteria
Reference material [3125B.3*c*9)]	Greater of: once per sample batch, or 5%	Dependent on data quality objectives
Preparatory/method blank [3125B.3*c*4)]	Greater of: once per sample batch, or 5%	± Absolute value of instrument detection limit; absolute value of laboratory reporting limit or MDL is acceptable
Laboratory-fortified blank [3125B.3*c*7)]	Greater of: once per sample batch, or 5%	±30% of true value
Duplicate known-addition samples	Greater of: once per sample batch, or 5%	±20% relative percent difference
Continuing calibration verification standards [3125B.3*c*5)]	10%	±10% of known concentration
Continuing calibration verification blank [3125B.3*c*6)]	10%	± Absolute value of instrument detection limit; absolute value of laboratory reporting limit or MDL is acceptable

TABLE 3125:IX. METHOD PERFORMANCE WITH CALIBRATION VERIFICATION STANDARDS*

		Continuing Calibration Verification Standard ($N = 44$)				Initial Calibration Verification Standard ($N = 12$)			
Element	Mass	Mean Recovery %	Mean $\mu g/L$	Standard Deviation $\mu g/L$	Relative Standard Deviation %	Mean Recovery %	Mean $\mu g/L$	Standard Deviation $\mu g/L$	Relative Standard Deviation %
Be	9	98.71	49.35	3.43	6.94	100.06	50.03	1.90	3.80
Al	27	99.62	49.81	2.99	6.01	98.42	49.21	1.69	3.44
V	51	100.97	50.48	1.36	2.68	99.91	49.96	1.23	2.47
Cr	52	101.39	50.70	1.86	3.66	99.94	49.97	1.47	2.95
Cr	53	100.68	50.34	1.91	3.79	99.13	49.56	1.44	2.90
Mn	55	101.20	50.60	1.98	3.91	99.48	49.74	1.40	2.82
Co	59	101.67	50.83	2.44	4.79	99.44	49.72	1.61	3.24
Ni	60	99.97	49.99	2.14	4.28	97.98	48.99	1.70	3.47
Ni	62	99.79	49.89	2.09	4.18	97.57	48.79	1.32	2.71
Cu	63	100.51	50.25	2.19	4.36	97.87	48.93	1.63	3.33
Cu	65	100.39	50.19	2.26	4.51	98.34	49.17	1.58	3.20
Zn	66	101.07	50.53	1.93	3.82	98.75	49.38	0.87	1.76
Zn	68	100.42	50.21	1.89	3.77	97.75	48.87	0.50	1.02
As	75	100.76	50.38	1.15	2.28	98.83	49.41	0.89	1.80
Se	77	101.71	50.85	1.43	2.81	99.54	49.77	1.01	2.03
Se	82	101.97	50.98	1.50	2.95	99.76	49.88	0.94	1.89
Ag	107	101.50	50.75	1.68	3.30	99.27	49.63	1.17	2.36
Ag	109	101.65	50.83	1.68	3.31	99.66	49.83	1.54	3.08
Cd	111	100.92	50.46	1.94	3.84	98.61	49.30	1.36	2.77
Cd	114	100.90	50.45	2.07	4.10	99.20	49.60	1.41	2.84
Sb	121	100.14	50.07	2.39	4.77	99.38	49.69	1.38	2.78
Sb	123	99.98	49.99	2.48	4.97	99.09	49.54	1.34	2.71
Tl	203	101.36	50.68	1.64	3.23	100.05	50.02	1.01	2.01
Tl	205	102.40	51.20	1.93	3.78	101.23	50.62	1.45	2.87
Pb	208	101.21	50.61	1.65	3.25	99.33	49.67	0.84	1.69
U	238	101.54	50.77	1.93	3.80	99.80	49.90	1.36	2.72

* Single-laboratory, single-operator, single-instrument data, determined using a 50-μg/L standard prepared from sources independent of calibration standard source. Data acquired January–November 1996 during actual sample determinations. Performance of continuing calibration verification standards at different levels may vary. Perkin-Elmer Elan 6000 ICP–MS used for determination.

$$R_{corr} = \frac{R_{uncorr} \times V}{W \times \%\ TS/100}$$

where:

R_{corr} = corrected result, μg/kg,
R_{uncorr} = uncorrected elemental result, μg/L,
V = volume of digestate (after digestion), L,
W = mass of the wet sample, kg, and
$\%\ TS$ = percent total solids determined in the sample.

b. Compensation for interferences: Use instrument software to correct for previously listed interferences. See Table 3125:V for a list of the most common molecular ion interferences.

c. Data reporting: Establish appropriate reporting limits for method analytes based on IDLs and the laboratory blank. For regulatory programs, ensure that reporting limits for method analytes are a factor of three below relevant regulatory criteria whenever possible.

If method blank contamination is typically random, sporadic, or otherwise not statistically controllable, do not correct results for the method blank. Consider correcting blank results only if it can be demonstrated that the blank's analyte concentration is within statistical control over a period of months. Report all method blank data explicitly in a manner identical to sample-reporting procedures.

d. Documentation: Maintain documentation for the following (where applicable): instrument tuning, mass calibration, calibration verification, analyses of blanks (method, field, calibration, and equipment blanks), IDL and MDL studies, analyses of samples and duplicates with known additions, laboratory and field duplicate information, serial dilutions, internal standard recoveries, and any relevant quality control charts.

Also, maintain all raw data generated in support of the method, and keep them available for review.[5]

6. Method Performance

Table 3125:III presents IDL data generated by this method; this represents optimal instrument detection capabilities, not recommended method detection or reporting limits. Tables 3125:I, II, and IX through XI contain single-laboratory, single-operator, single-instrument performance data generated by this method for calibration verification standards, low-level standards, and known-addition recoveries for freshwater matrices, as well as data showing standard and CCT performance data for elements usually affected by polyatomic interferences (Tables 3125:I and II). Section 3125 performance data for some analytes are currently unavailable; however, performance data for similar ICP-MS methods are available in the literature.[1,4]

Table 3125:X. Method Performance for Recovery of Known Addition in Natural Waters*

		Total Recoverable Metals†		Dissolved Metals‡	
Element	Mass	Mean Recovery %	Relative Standard Deviation %	Mean Recovery %	Relative Standard Deviation %
Be	9	89.09	5.77	—	—
V	51	87.00	8.82	—	—
Cr	52	87.33	8.42	88.38	6.43
Cr	53	86.93	7.90	88.52	5.95
Mn	55	91.81	10.12	—	—
Co	59	87.67	8.92	—	—
Ni	60	85.07	8.42	89.31	5.70
Ni	62	84.67	8.21	89.00	5.82
Cu	63	84.13	8.46	88.55	8.33
Cu	65	84.37	8.05	88.26	7.80
Zn	66	86.14	23.01	95.59	13.81
Zn	68	81.95	20.31	91.94	13.27
As	75	90.43	4.46	97.30	8.84
Se	77	83.09	4.76	105.36	10.80
Se	82	83.42	4.73	105.36	10.75
Ag	107	—	—	91.98	5.06
Ag	109	—	—	92.25	4.96
Cd	111	91.37	5.47	96.91	6.03
Cd	114	91.47	6.04	97.03	5.42
Sb	121	94.40	5.24	—	—
Sb	123	94.56	5.36	—	—
Tl	203	97.24	5.42	—	—
Tl	205	98.14	6.21	—	—
Pb	208	96.09	7.08	100.69	7.28

* Single-laboratory, single-operator, single-instrument data. Samples were Washington State surface waters from various locations. Data acquired January–November 1996 during actual sample determinations. Performance of known additions at different levels may vary. Perkin-Elmer Elan 6000 ICP–MS used for determination.

† Known-addition level 20 μg/L. Additions made before preparation according to Section 3030E (modified by clean-hood digestion in TFE beakers). $N = 20$.

‡ Known-addition level for Cd and Pb 1 μg/L; for other analytes 10 μg/L. Additions made after filtration through 1:1 HNO_3 precleaned 0.45-μm filters. $N = 28$.

Table 3125:XI. Method Performance with Calibration Verification Standards*

		1.0-μg/L Standard				0.3-μg/L Standard			
Element	Mass	Mean Recovery %	Mean $\mu g/L$	Standard Deviation $\mu g/L$	Relative Standard Deviation %	Mean Recovery %	Mean $\mu g/L$	Standard Deviation $\mu g/L$	Relative Standard Deviation %
Be	9	97	0.97	0.06	6.24	95	0.284	0.03	12.11
Al	27	121	1.21	0.32	26.49	196	0.588	0.44	74.30
V	51	104	1.04	0.06	5.83	111	0.332	0.10	28.96
Cr	52	119	1.19	0.34	28.62	163	0.490	0.37	75.90
Cr	53	102	1.02	0.36	35.54	113	0.338	0.32	93.70
Mn	55	103	1.03	0.07	6.55	110	0.329	0.08	25.64
Co	59	103	1.03	0.07	6.42	102	0.307	0.04	12.53
Ni	60	101	1.01	0.05	5.24	107	0.321	0.05	14.14
Ni	62	102	1.02	0.06	5.42	109	0.326	0.05	15.94
Cu	63	107	1.07	0.09	8.78	118	0.355	0.06	18.29
Cu	65	107	1.07	0.10	9.05	117	0.352	0.06	17.69
Zn	66	117	1.17	0.51	43.52	182	0.547	0.68	124.13
Zn	68	116	1.16	0.50	42.90	179	0.537	0.66	122.12
As	75	97	0.97	0.05	5.23	101	0.302	0.06	18.29
Se	77	89	0.89	0.08	8.72	88	0.265	0.08	29.07
Se	82	92	0.92	0.14	15.50	106	0.317	0.14	43.91
Ag	107	101	1.01	0.05	4.53	94	0.282	0.04	15.74
Ag	109	103	1.03	0.07	6.57	92	0.277	0.04	13.68
Cd	111	98	0.98	0.04	3.80	96	0.288	0.03	8.74
Cd	114	100	1.00	0.03	3.39	98	0.293	0.03	8.70
Sb	121	94	0.94	0.05	5.28	93	0.280	0.06	21.89
Sb	123	94	0.94	0.05	5.36	93	0.278	0.06	22.39
Tl	203	101	1.01	0.04	3.57	98	0.294	0.03	11.89
Tl	205	104	1.04	0.05	5.15	100	0.300	0.03	10.43
Pb	208	104	1.04	0.04	3.65	104	0.312	0.03	11.13
U	238	106	1.06	0.05	4.64	102	0.307	0.03	9.92

* Single-laboratory, single-operator, single-instrument data. $N = 24$ for both standards.

7. References

1. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1994. Determination of trace elements in waters and wastes by inductively coupled plasma–mass spectrometry; Method 200.8. Environmental Monitoring Systems Lab., Cincinnati, Ohio.
2. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1984. Definition and procedure for the determination of the method detection limit, rev. 1.11. 40 *CFR* 136, Appendix B.
3. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1991. Methods for the Determination of Metals in Environmental Samples. Off. Research & Development, Washington D.C.
4. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1995. Method 1638: Determination of trace elements in ambient waters by inductively coupled plasma mass spectrometry. Off. Water, Washington, D.C.
5. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1995. Guidance on the Documentation and Evaluation of Trace Metals Data Collected for Clean Water Act Compliance Monitoring. Off. Water, Washington, D.C.

8. Bibliography

GRAY, A.L. 1974. A plasma source for mass analysis. *Proc. Soc. Anal. Chem*. 11:182.

HAYHURST, A.N. & N.R. TELFORD. 1977. Mass spectrometric sampling of ions from atmospheric pressure flames. I. Characteristics and calibration of the sampling system. *Combust. Flame*. 67.

HOUK, R.S., V.A. FASSEL, G.D. FLESCH, H.J. SVEC, A.L. GRAY & C.E. TAYLOR. 1980. Inductively coupled argon plasma as an ion source for mass spectrometric determination of trace elements. *Anal. Chem*. 52:2283.

DOUGLAS, D.J. & J.B. FRENCH. 1981. Elemental analysis with a microwave-induced plasma/quadrupole mass spectrometer system. *Anal. Chem*. 53:37.

HOUK, R.S., V.A. FASSEL & H.J. SVEC. 1981. Inductively coupled plasma–mass spectrometry: Sample introduction, ionization, ion extraction, and analytical results. *Dyn. Mass Spectrom*. 6:234.

OLIVARES, J.A. & R.S. HOUK. 1985. Ion sampling for inductively coupled plasma–mass spectrometry. *Anal. Chem*. 57:2674.

HOUK, R.S. 1986. Mass spectrometry of inductively coupled plasmas. *Anal. Chem*. 58:97.

THOMPSON, J.J. & R.S. HOUK. 1986. Inductively coupled plasma–mass spectrometric detection for multi-element flow injection analysis and elemental speciation by reversed-phase liquid chromatography. *Anal. Chem*. 58:2541.

VAUGHAN, M.A. & G. HORLICK. 1986. Oxide, hydroxide, and doubly charged analyte species in inductively coupled plasma/mass spectrometry. *Appl. Spectrosc.* 40:434.

BEAUCHEMIN, D., J.W. MCLAREN, A.P. MYKYTIUK & S.S. BERMAN. 1987. Determination of trace metals in a river water reference material by inductively coupled plasma mass spectrometry. *Anal. Chem*. 59:778.

GARBARINO, J.R. & H.E. TAYLOR. 1987. Stable isotope dilution analysis of hydrologic samples by inductively coupled plasma–mass spectrometry. *Anal. Chem*. 59:1568.

THOMPSON, J.J. & R.S. HOUK. 1987. A study of internal standardization in inductively coupled plasma–mass spectrometry. *Appl. Spectrosc.* 41:801.

JARVIS, K.E., A.L. GRAY & R.S. HOUK. 1992. Inductively Coupled Plasma–Mass Spectrometry. Blackie Academic & Professional, Chapman & Hall, New York, N.Y.

TAYLOR, D.B., H.M. KINGSTON, D.J. NOGAY, D. KOLLER & R. HUTTON. 1996. On-line solid-phase chelation for the determination of eight metals in environmental waters by inductively coupled mass spectrometry. *J. Anal. Atom. Spectrom.* 11:187.

KINGSTON, H.M.S. & S. HASWELL, eds. 1997. Microwave Enhanced Chemistry: Fundamentals, Sample Preparation, and Applications. ACS Professional Reference Book Ser., American Chemical Soc., Washington, D.C.

U.S. ENVIRONMENTAL PROTECTION AGENCY. 1998. Inductively coupled plasma–mass spectrometry; Method 6020. *In* Solid Waste Methods, SW846, Update 4. Environmental Monitoring Systems Lab., Cincinnati, Ohio.

NELMS, S., ed. 2005. Inductively Coupled Plasma–Mass Spectrometry Handbook. Blackwell Science, Cambridge, Mass.

BECKER, J.S. 2008. Inorganic Mass Spectrometry: Principles and Applications. Wiley InterScience, Malden, Mass.