



**Techniques of Water-Resources Investigations
of the United States Geological Survey**

Chapter A1

**METHODS FOR DETERMINATION
OF INORGANIC SUBSTANCES
IN WATER
AND FLUVIAL SEDIMENTS**

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Book 5
LABORATORY ANALYSIS

Vanadium, colorimetric, catalytic oxidation

Parameter and Code:

Vanadium, dissolved, I-1880-85 ($\mu\text{g/L}$ as V): 01085

1. Application

This method may be used to analyze most waters containing from 0.5 to 5.0 $\mu\text{g/L}$ of vanadium, provided that the interferences identified below are not exceeded. By reducing the reaction time, concentrations up to 100 $\mu\text{g/L}$ may be determined.

2. Summary of method

2.1 The oxidation of gallic acid by acid-persulfate is catalyzed by the presence of small amounts of vanadium (Jarabin and Szarvas, 1961). Depending on the amount of vanadium present, the reaction produces a yellow-to-red color, the absorbance of which is measured spectrometrically at 415 nm. Under given conditions of reactant concentration, temperature, and reaction time, the extent of oxidation of gallic acid is proportional to the concentration of vanadium present (Fishman and Skougstad, 1964).

2.2 This method is essentially the same as that reported by the American Society for Testing and Materials (1984).

3. Interferences

3.1 Several substances interfere, including chloride above 100 mg/L and bromide and iodide at lower concentrations. Their interference is eliminated or minimized by the addition of mercuric nitrate solution. In the presence of mercuric nitrate, concentrations of 100 mg/L Cl^{-1} , 0.25 mg/L Br^{-1} , and 0.25 mg/L I^{-1} can be tolerated. The following ions interfere when the indicated concentrations are exceeded: silver, 2,000 $\mu\text{g/L}$; cobalt, 1,000 $\mu\text{g/L}$; nickel, 3,000 $\mu\text{g/L}$; copper, 50 $\mu\text{g/L}$; chromium, 1,000 $\mu\text{g/L}$; and ferrous iron, 300 $\mu\text{g/L}$.

3.2 Nitric acid causes erratic and uncertain results.

4. Apparatus

4.1 *Water bath*, regulated to $25 \pm 0.5^\circ\text{C}$.

4.2 *Spectrometer*, for use at 415 nm. Refer to manufacturer's manual for optimizing instrumental parameters.

5. Reagents

5.1 *Ammonium persulfate-phosphoric acid reagent*: Dissolve 2.5 g $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in 25 mL demineralized water. Heat solution to just below boiling, remove from heat, and add an equal volume of concentrated H_3PO_4 (sp gr 1.69). Let stand for approx 24 h before using. Discard after 2 days.

5.2 *Gallic acid solution*, 1 g/100 mL: Dissolve 0.5 g gallic acid in 50 mL hot demineralized water and filter through Whatman No. 42 filter paper. Prepare fresh daily.

5.3 *Mercuric nitrate solution*, 332 mg/L: Dissolve 0.350 g $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ in demineralized water and dilute to 1 L.

5.4 *Vanadium standard solution I*, 1.00 mL = 100 μg V: Dissolve 0.2309 g ammonium metavanadate (NH_4VO_3) in demineralized water and dilute to 1,000 mL.

5.5 *Vanadium standard solution II*, 1.00 mL = 1.0 μg V: Dilute 10.0 mL vanadium standard solution I to 1,000 mL with demineralized water.

5.6 *Vanadium standard solution III*, 1.00 mL = 0.01 μg V: Immediately before use, dilute 10.0 mL vanadium standard solution II to 1,000 mL with demineralized water. This standard is used to prepare working standards at time of analysis.

6. Procedure

6.1 Pipet a volume of sample containing less than 0.05 μg V (10.0 mL max) into a 23-mm

absorbance cell or a 25-mL test tube, and adjust the volume to 10.0 mL.

6.2 Prepare a blank and sufficient standards containing from 0.01 to 0.05 $\mu\text{g V}$ in 23-mm absorbance cells or 25-mL test tubes, and adjust the volume of each to 10.0 mL with demineralized water. (Standards must be included with each set of samples.)

6.3 Add 1.0 mL mercuric nitrate solution to samples, standards, and blank, and place all cells or test tubes in a water bath (25 °C). Allow 30 to 45 min for samples to reach temperature equilibrium.

6.4 Add 1.0 mL ammonium persulfate-phosphoric acid reagent (temperature equilibrated). Mix and return to water bath.

6.5 Add 1.0 mL gallic acid (temperature equilibrated). Mix and return to water bath (NOTE 1).

NOTE 1. Because time and temperature are critical factors, the absorbance of each sample must be measured exactly 60 min after the gallic acid is added. Time the analyses of several samples most easily by starting a stopwatch with the addition of gallic acid to the first sample and by adding the gallic acid to subsequent samples at appropriate intervals.

6.6 After about 58 min, remove all cells or test tubes from the water bath; and at exactly 60 min, measure the absorbance at 415 nm, using demineralized water as a reference (NOTE 2).

NOTE 2. All samples may be removed from the water bath 1 or 2 min before the end of the 60-min period. The samples are then prepared for measurement, and the absorbance of each sample is measured exactly 60 min after the addition of the gallic acid.

7. Calculations

7.1 Determine micrograms of vanadium in each sample from a plot of absorbances of standards.

7.2 Determine the concentration of vanadium in micrograms per liter as follows:

$$V (\mu\text{g/L}) = \frac{1,000}{\text{mL sample}} \times \mu\text{g V in sample}$$

8. Report

Report vanadium, dissolved (01085), concentrations as follows: less than 10 $\mu\text{g/L}$, 1 $\mu\text{g/L}$; 10 $\mu\text{g/L}$ and above, two significant figures.

9. Precision

9.1 Precision for dissolved vanadium within its designated range may be expressed as follows (American Society for Testing and Materials, 1984):

$$S_T = 0.069X + 0.422$$

where

S_T = overall precision, micrograms per liter, and

X = concentration of vanadium, micrograms per liter.

9.2 Precision for dissolved vanadium for four samples expressed in terms of percent relative standard deviation is as follows:

| Number of laboratories | Mean ($\mu\text{g/L}$) | Relative standard deviation (percent) |
|------------------------|--------------------------|---------------------------------------|
| 3 | 1.3 | 46 |
| 3 | 2.3 | 65 |
| 3 | 6.7 | 31 |
| 3 | 12.6 | 57 |

References

- American Society for Testing and Materials, 1984, Annual book of ASTM standards, section 31, water: Philadelphia, v. 1101, p. 676-81.
- Fishman, M. J., and Skougstad, M. W., 1964, Catalytic determination of vanadium in water: Analytical Chemistry, v. 36, p. 1643-6.
- Jarabin, Z., and Szarvas, P., 1961, Detection of small amounts of vanadium by catalytic reaction with the addition of gallic acid: Acta University Debrecen, v. 7, p. 131; Chemical Abstracts, 1962, v. 57, 9192c.

Vanadium, colorimetric, catalytic oxidation, automated-segmented flow

Parameter and Code:

Vanadium, dissolved, I-2880-85 ($\mu\text{g/L}$ as V): 01085

1. Application

This method may be used to analyze most waters containing from 1 to 10 $\mu\text{g/L}$ vanadium, provided that the interferences identified below are not exceeded.

2. Summary of method

Low concentrations of vanadium catalyze the acid-persulfate oxidation of gallic acid. This reaction proceeds rapidly in the presence of vanadium but only very slowly in its absence. The amount of colored oxidation product formed by this reaction is directly proportional to the concentration of vanadium when temperature, reaction time, and concentration of reactants are carefully controlled (Fishman and Skougstad, 1964; Jarabin and Szarvas, 1961).

3. Interferences

3.1 Chloride, bromide, and iodide interfere when their concentrations exceed 100 mg/L, 10 $\mu\text{g/L}$, and 1 $\mu\text{g/L}$, respectively. Iron(II), iron(III), and copper(II) interfere when their concentrations exceed 300 $\mu\text{g/L}$, 500 $\mu\text{g/L}$, and 50 $\mu\text{g/L}$, respectively. The concentrations of other ions are rarely high enough to interfere.

3.2 Nitric acid causes erratic and uncertain results.

4. Apparatus

4.1 *Technicon AutoAnalyzer II*, consisting of sampler, proportioning pump, cartridge manifold, water bath, colorimeter, voltage stabilizer, recorder, and printer.

4.2 With this equipment the following operating conditions have been found satisfactory for the range from 1 to 10 $\mu\text{g/L}$ vanadium.

| | |
|---------------------------|------------|
| Absorption cell ----- | 15 mm |
| Wavelength ----- | 410 nm |
| Cam ----- | 20/h (1/1) |
| Water-bath temperature -- | 60°C |

5. Reagents

5.1 *Ammonium persulfate-phosphoric acid reagent*: Dissolve 2.5 g $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in 25 mL demineralized water. Heat solution to just below boiling, remove from heat, and add an equal volume of concentrated H_3PO_4 (sp gr 1.69). Let stand for approx 24 h before use. Before use, dilute with 50 mL demineralized water. Discard after 2 days.

5.2 *Gallic acid solution*, 20 g/L: Dissolve 5 g gallic acid in 250 mL hot, demineralized water and filter through paper (Whatman No. 42 or equivalent). Prepare fresh daily. Keep the solution warm during analysis to prevent the gallic acid from precipitating.

5.3 *Mercuric nitrate solution*, 332 mg/L: Dissolve 350 mg $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ in demineralized water and dilute to 1 L.

5.4 *Vanadium standard solution I*, 1.00 mL = 100 μg V: Dissolve 0.2309 g ammonium metavanadate (NH_4VO_3) in demineralized water and dilute to 1,000 mL.

5.5 *Vanadium standard solution II*, 1.00 mL = 1.0 μg V: Dilute 10.0 mL vanadium standard solution I to 1,000 mL with demineralized water.

5.6 *Vanadium standard solution III*, 1.00 mL = 0.05 μg V: Dilute 50.0 mL vanadium standard solution II to 1,000 mL with demineralized water.

5.7 *Vanadium working standards*: Prepare a blank and 250 mL each of a series of vanadium working standards by appropriate quantitative

dilution of vanadium standard solution III as follows:

| Vanadium standard solution III (mL) | Vanadium concentration ($\mu\text{g/L}$) |
|-------------------------------------|--|
| 0.0 | 0.0 |
| 5.0 | 1.0 |
| 10.0 | 2.0 |
| 20.0 | 4.0 |
| 30.0 | 6.0 |
| 40.0 | 8.0 |
| 50.0 | 10.0 |

6. Procedure

6.1 Set up manifold (fig. 50).

6.2 Allow colorimeter, recorder, and water bath to warm for at least 30 min or until the temperature of the water bath reaches 60°C.

6.3 Adjust the baseline to read zero scale divisions on the recorder with all reagents, but with demineralized water in the sample line.

6.4 Place a complete set of standards and a blank in the first positions of the first sample

tray, beginning with the most concentrated standard. Place individual standards of differing concentrations in approx every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each tray with unknown samples.

6.5 Begin analysis. When the peak from the most concentrated standard appears on the recorder, adjust the STD CAL. control until the flat portion of the peak reads full scale.

7. Calculations

7.1 Prepare an analytical curve by plotting the height of each standard peak versus its respective vanadium concentration.

7.2 Compute the concentration of vanadium in each sample by comparing its peak height to the analytical curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

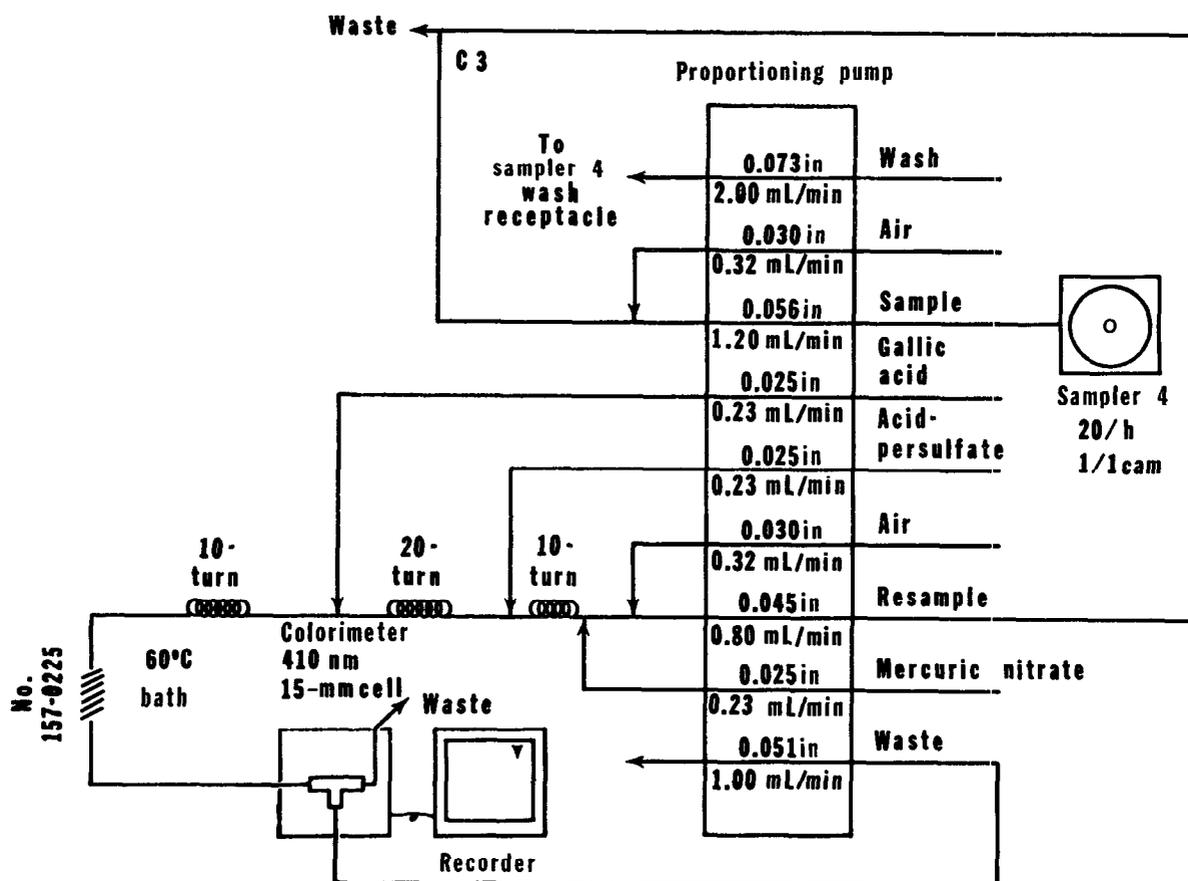


Figure 50.—Vanadium, catalytic oxidation manifold

8. Report

Report vanadium, dissolved (01085), concentrations as follows: less than 10 $\mu\text{g/L}$, nearest 1 $\mu\text{g/L}$; 10 $\mu\text{g/L}$ and above, two significant figures.

9. Precision

Single-operator precision for dissolved vanadium for three samples expressed in terms of percent relative standard deviation is as follows:

| <u>Number of replicates</u> | <u>Mean ($\mu\text{g/L}$)</u> | <u>Relative standard deviation (percent)</u> |
|-----------------------------|--|--|
| 4 | 3.5 | 3 |
| 8 | 8.1 | 1 |
| 8 | 53.9 | 1 |

References

- Fishman, M. J., and Skougstad, M. W., 1964, Catalytic determination of vanadium in water: *Analytical Chemistry*, v. 36, p. 1643-6.
- Jarabin, Z., and Szarvas, P., 1961, Detection of small amounts of vanadium by catalytic reaction with the addition of gallic acid: *Acta University Debrecen*, v. 7, p. 131; *Chemical Abstracts*, 1962, v. 57, 9192c.

Vanadium, atomic emission spectrometric, ICP

Parameter and Code:

Vanadium, dissolved, I-1472-85 ($\mu\text{g/L}$ as V): 01085

2. Summary of method

Vanadium is determined simultaneously with several other constituents on a single sample by a direct-reading emission spectrometric

method utilizing an induction-coupled argon plasma as an excitation source. See method I-1472, metals, atomic emission spectrometric, ICP.

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Zinc, atomic absorption spectrometric, direct

Parameters and Codes:

Zinc, dissolved, I-1900-85 ($\mu\text{g/L}$ as Zn): 01090
Zinc, total recoverable, I-3900-85 ($\mu\text{g/L}$ as Zn): 01092
Zinc, suspended recoverable, I-7900-85 ($\mu\text{g/L}$ as Zn): 01091
Zinc, recoverable-from-bottom-material, dry wt, I-5900-85 ($\mu\text{g/g}$ as Zn): 01093

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing from 10 to 500 $\mu\text{g/L}$ of zinc. Sample solutions containing more than 500 $\mu\text{g/L}$ need to be diluted or to be read on a less expanded scale.

1.2 Suspended-recoverable zinc is calculated by subtracting dissolved zinc from total recoverable zinc.

1.3 This method may be used to analyze bottom material containing at least 1.0 $\mu\text{g/g}$ of zinc. Sample solutions containing more than 500 $\mu\text{g/L}$ of zinc need to be diluted or less scale expansion used.

1.4 Total recoverable zinc in water-suspended sediment needs to undergo preliminary digestion-solubilization by method I-3485, and recoverable zinc in bottom material needs to undergo preliminary digestion-solubilization by method I-5485 before being determined.

2. Summary of method

2.1 Zinc is determined by atomic absorption spectrometry by direct aspiration of the sample into an air-acetylene flame.

2.2 The procedure may be automated by the addition of a sampler and either a strip-chart recorder or a printer or both.

3. Interferences

3.1 Magnesium at concentrations greater than 100 mg/L interferes unless other cations, such as sodium, are present in the sample.

3.2 Individual concentrations of sodium, potassium, sulfate, chloride (9,000 mg/L of each), calcium (4,500 mg/L), nitrate (2,000 mg/L), iron (4×10^6 $\mu\text{g/L}$), and cadmium, nickel,

copper, lead, cobalt, and chromium (10,000 $\mu\text{g/L}$ each) do not interfere. Greater concentrations of each constituent were not investigated.

3.3 Samples containing 100 mg/L of silica cause no interference; however, zinc recovery is approx 10 percent low in samples containing 200 mg/L of silica.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout and automatic zero and concentration controls.

4.2 Refer to the manufacturer's manual to optimize instrument for the following:

| | |
|------------------------------------|-------------|
| Grating ----- | Ultraviolet |
| Wavelength ----- | 213.8 nm |
| Source (hollow-cathode lamp) ----- | Zinc |
| Oxidant ----- | Air |
| Fuel ----- | Acetylene |
| Type of flame ----- | Oxidizing |

4.3 The 50-mm (2-in.) and 100-mm (4-in.) flathead, single-slot burners allow a working range from 10 to 500 $\mu\text{g/L}$ of zinc. Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Zinc standard solution I*, 1.00 mL = 100 μg Zn: Dissolve 0.100 g reagent grade zinc (30-mesh) in a slight excess of concentrated HCl (sp gr 1.19), and dilute to 1,000 mL with demineralized water.

5.2 *Zinc standard solution II*, 1.00 mL = 1.0 μg Zn: Dilute 10.0 mL zinc standard solution I to 1,000 mL with demineralized water containing 1 mL concentrated HNO_3 (sp gr 1.41).

5.3 *Zinc working standards:* Prepare a series of at least six working standards containing from 10 to 500 $\mu\text{g/L}$ of zinc by appropriate dilutions of zinc standard solution II with acidified water.

5.4 *Water, acidified.* Add 1.5 mL concentrated HNO_3 (sp gr 1.41) to 1 L of demineralized water.

6. Procedure

Aspirate the blank (acidified water) to set the automatic zero control. Use the automatic concentration control to set the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check calibration at reasonable intervals.

7. Calculations

7.1 Determine the micrograms per liter of dissolved or total recoverable zinc in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose zinc concentrations exceed the working range of the method and multiply by the proper dilution factors.

7.2 To determine micrograms per liter of suspended recoverable zinc, subtract dissolved-zinc concentration from total-recoverable-zinc concentration.

7.3 To determine micrograms per gram of zinc in bottom-material samples, first determine the micrograms per liter of zinc as in paragraph 7.1, then

$$\text{Zn } (\mu\text{g/g}) = \frac{\mu\text{g/L of Zn} \times \frac{\text{mL of original digest}}{1,000}}{\text{wt of sample (g)}}$$

8. Report

8.1 Report zinc, dissolved (01090), total-recoverable (01092), and suspended-recoverable (01091), concentrations as follows: less than 100 $\mu\text{g/L}$, nearest 10 $\mu\text{g/L}$; 100 $\mu\text{g/L}$ and above, two significant figures.

8.2 Report zinc, recoverable-from-bottom-material (01093), concentrations as follows: less

than 10 $\mu\text{g/g}$, nearest microgram per gram; 10 $\mu\text{g/g}$ and above, two significant figures.

9. Precision

9.1 Precision for dissolved zinc for 30 samples within the range of 14 to 1110 $\mu\text{g/L}$ may be expressed as follows:

$$S_T = 0.070X + 6.51$$

where

S_T = overall precision, micrograms per liter, and

X = concentration of zinc, micrograms per liter.

The correlation coefficient is 0.7967.

9.2 Precision for dissolved zinc for six of the 30 samples expressed in terms of the percent relative standard deviation is as follows:

| Number of laboratories | Mean ($\mu\text{g/L}$) | Relative standard deviation (percent) |
|------------------------|--------------------------|---------------------------------------|
| 33 | 14 | 43 |
| 47 | 104 | 10 |
| 19 | 116 | 22 |
| 41 | 236 | 7 |
| 22 | 520 | 5 |
| 17 | 1110 | 9 |

9.3 It is estimated that the percent relative standard deviation for total recoverable and suspended recoverable zinc and recoverable zinc in bottom material will be greater than that reported for dissolved zinc.

9.4 Precision for total recoverable zinc expressed in terms of the percent relative standard deviation for two water-suspended sediment mixtures is as follows:

| Number of laboratories | Mean ($\mu\text{g/L}$) | Relative standard deviation (percent) |
|------------------------|--------------------------|---------------------------------------|
| 23 | 78.4 | 27 |
| 26 | 172 | 31 |

Reference

Fishman, M. J., and Downs, S. C., 1966, Methods for analysis of selected metals in water by atomic absorption: United States Geological Survey Water-Supply Paper 1540-C., p. 43-5.

Zinc, atomic absorption spectrometric, graphite furnace

Parameter and Code:

Zinc, dissolved, I-1901-85 ($\mu\text{g/L}$ as Zn): 01090

1. Application

1.1 This method may be used to determine zinc in low ionic-strength water and precipitation. With Zeeman background correction and a 20- μL sample, the method is applicable in the range from 0.5 to 40 $\mu\text{g/L}$. Sample solutions that contain zinc concentrations exceeding the upper limits must be diluted or preferably be analyzed by the atomic absorption spectrometric method, or by the atomic emission spectrometry ICP method.

1.2 The analytical range and detection limits can be increased or possibly decreased by varying the volume of sample injected or the instrumental settings. Purification of reagents and use of ASTM Type 1 water (Method D-1193, American Society for Testing and Materials, 1984) may result in lower detection limits.

2. Summary of method

Zinc is determined by atomic absorption spectrometry in conjunction with a graphite furnace containing a graphite platform (Hinderberger and others, 1981). A sample is placed on the graphite platform and a matrix modifier is added. The sample is then evaporated to dryness, charred, and atomized using high-temperature ramping. The absorption signal generated during atomization is recorded and compared with standards.

3. Interferences

3.1 Interferences in low ionic-strength samples, such as precipitation, normally are quite low. In addition, the use of the graphite platform reduces the effects of many interferences. Calcium (25 mg/L), magnesium (8 mg/L), sodium (20 mg/L), sulfate (34 mg/L), and

chloride (25 mg/L) do not interfere. Greater concentrations of these constituents were not investigated.

3.2 Precipitation samples usually contain very low concentrations of zinc. Special precautionary measures must be employed during both sample collection and laboratory determination to prevent contamination.

4. Apparatus

4.1 *Atomic absorption spectrometer*, for use at 213.8 nm and equipped with background correction, digital integrator to quantitate peak areas, graphite furnace with temperature programmer, and automatic sample injector. The programmer must have high-temperature ramping and stopped-flow capabilities.

4.1.1 Refer to the manufacturer's manual to optimize instrumental performance. The analytical ranges reported in paragraph 1.1 are for a 20- μL sample with 5 μL of matrix modifier (NOTE 1).

NOTE 1. A 20- μL sample generally requires 30 s to dry. Samples that have a complex matrix may require a longer drying and charring time.

4.1.2 *Graphite furnace*, capable of reaching temperatures sufficient to atomize the element of interest. Warning: dial settings frequently are inaccurate and newly conditioned furnaces require temperature calibration.

4.1.3 *Graphite tubes and platforms*. Pyrolytically coated graphite tubes and solid pyrolytic graphite platforms are recommended.

4.2 *Labware*. Many trace metals at very low concentrations have been found to sorb very rapidly to glassware. To preclude this, fluorinated ethylene propylene (FEP) or Teflon labware may be used. Alternately, glassware, particularly flasks and pipets, may be treated

with silicone anti-wetting agent such as Surfal (Pierce Chemical Co., Rockford, IL, 61105) according to the manufacturer's instructions. Autosampler cups must be checked for contamination. Lancer (1831 Olive St., St. Louis, MO, 63103) polystyrene disposable cups have been found to be satisfactory after acid rinsing. Alternately, re-useable Teflon or FEP cups may be used.

4.3 *Argon*, standard, welder's grade, commercially available. Nitrogen may also be used if recommended by the instrument manufacturer.

5. Reagents

5.1 *Matrix modifier solution*, 40g $\text{NH}_4\text{H}_2\text{PO}_4/\text{L}$: Add 40.0 g $\text{NH}_4\text{H}_2\text{PO}_4$ to 950 mL Type 1 water, mix, and dilute to 1,000 mL. Analyze 20 μL of matrix modifier for zinc contamination. If the zinc reading is more than 0.005 absorbance-seconds, purify the solution by chelation with ammonium pyrrolidine dithiocarbamate (APDC) and extraction with methyl isobutyl ketone (MIBK, NOTE 2). Analyze 20 μL of the purified solution. Repeat extractions until the zinc level is reduced to the acceptable level. **DO NOT ADD ACID TO THE PURIFIED MATRIX MODIFIER SOLUTION.**

NOTE 2. To purify matrix modifier solution, pour the solution into a Teflon or FEP container. Add 0.25 g APDC for each liter of solution. While stirring, adjust the solution to pH 2.9 by dropwise addition of concentrated HNO_3 (sp gr 1.41). Transfer portions of the solution to a separatory funnel, add 100 mL MIBK/liter of solution, and shake vigorously for at least 5 min. Frequently, vent the funnel in a hood. Collect the extracted solution in the FEP container. Repeat the extraction with 50 mL MIBK/liter of solution. Because MIBK can dissolve some plastic autosampler cups, boil the solution for at least 10 min in a silicone-treated or acid-rinsed container covered with a watchglass to remove MIBK.

5.2 *Nitric acid, concentrated, high-purity*, (sp gr 1.41): J. T. Baker "Ultrex" brand HN_3 has been found to be adequately pure; however, each lot must be checked for contamination. Analyze acidified Type 1 water for zinc. Add an additional 1.5 mL of concentrated HNO_3 /liter of water, and repeat analysis. The integrated

signal should not increase by more than 0.001 absorbance-seconds.

5.3 *Water, acidified, Type 1*: Add 1.5 mL high-purity, concentrated HNO_3 (sp gr 1.41) to each liter of water.

5.4 *Water, Type 1*.

5.5 *Zinc standard solution I*, 1.00 mL = 1,000 μg Zn: Dissolve 1.0000 g Zn powder in a minimum of dilute HNO_3 . Heat to increase rate of dissolution. Add 10 mL high-purity, concentrated HNO_3 (sp gr 1.41) Ultrex or equivalent and dilute to 1,000 mL with Type 1 water. Alternatively, a certified standard solution at this concentration may be purchased.

5.6 *Zinc standard solution II*, 1.00 mL = 10.0 μg Zn: Dilute 10.0 mL zinc standard solution I to 1,000 mL (NOTE 3).

NOTE 3. Use acidified, Type 1 water (paragraph 5.3) to make dilutions. All standards must be stored in sealed Teflon or FEP containers. Each container must be rinsed twice with a small volume of standard before being filled. Standards stored for 6 months in FEP containers yielded values equal to those of freshly prepared standards.

5.7 *Zinc standard solution III*, 1.00 mL = 1.00 μg Zn: Dilute 100.0 mL zinc standard solution II to 1,000 mL. This standard is used to prepare working standards serially at time of analysis.

5.8 *Zinc standard solution IV*, 1.00 mL = 0.010 μg Zn: Dilute 10.0 mL zinc standard solution III to 1,000 mL. This standard also is used to prepare working standards serially at time of analysis.

6. Procedure

6.1 Systematically clean and rinse work areas with deionized water on a regular schedule. Use a laminar flow hood or a "clean room" environment during sample transfers. Ideally, the autosampler and the graphite furnace should be in a clean environment.

6.2 Soak autosampler cups at least overnight in a 1 + 1 solution of Type 1 water and high-purity nitric acid.

6.3 Rinse the sample cups twice with sample before filling. Place cups in sample tray and cover. Adjust sampler so that only the injection tip contacts the sample.

6.4 In sequence, inject 20- μL aliquots of

blank and working standards plus 5 μL of modifier each and analyze. Analyze the blank and working standards twice. Construct the analytical curve from the integrated peak areas (absorbance-seconds). Generally, the curve should be linear up to a peak-absorbance (peak-height) value of 0.40 absorbance units.

6.5 Similarly, inject and analyze the samples twice. Every tenth sample cup should contain either a standard or a reference material.

6.6 Restandardize as required. Minor changes of values for known samples usually indicate deterioration of the furnace tube, contact rings, and/or platform. A major variation usually indicates either autosampler malfunction or residue buildup from a complex matrix in a previous sample.

7. Calculations

Determine the micrograms per liter of zinc in each sample from the digital display or printer output. Dilute those samples containing concentrations of zinc that exceed the working range of the method; repeat the analysis, and multiply by the proper dilution factors.

8. Report

Report zinc, dissolved (01090), concentrations as follows: less than 10.0 $\mu\text{g/L}$, nearest 0.1 $\mu\text{g/L}$; 10 $\mu\text{g/L}$ and above, two significant figures.

9. Precision

9.1 Analysis of four samples by a single operator using Zeeman background correction is as follows:

| Number of replicates | Mean ($\mu\text{g/L}$) | Standard deviation ($\mu\text{g/L}$) | Relative standard deviation (percent) |
|----------------------|--------------------------|--|---------------------------------------|
| 6 | 5.92 | 0.24 | 4.1 |
| 4 | 16.02 | .26 | 1.6 |
| 6 | 19.70 | 1.29 | 6.5 |
| 12 | 40.21 | 3.18 | 7.9 |

9.2 The precision and bias for the Zeeman background correction were tested on deionized water and tap water (specific conductance 280

$\mu\text{S/cm}$). A known amount of zinc was added to each sample, and single-operator precision and bias for six replicates are as follows:

| Amount added ($\mu\text{g/L}$) | Amount found ($\mu\text{g/L}$) | Standard deviation ($\mu\text{g/L}$) | Relative standard deviation (percent) | Recovery (percent) |
|----------------------------------|----------------------------------|--|---------------------------------------|--------------------|
| Deionized water | | | | |
| 3.05 | 4.20 | 1.16 | 27.6 | 138 |
| 5.5 | 5.53 | .86 | 15.6 | 101 |
| 6.1 | 6.13 | .83 | 10.3 | 100 |
| 11 | 11.30 | .62 | 5.5 | 103 |
| 36 | 39.95 | 4.51 | 11.3 | 111 |
| Tap water (NOTE 4) | | | | |
| 3.05 | 2.17 | .73 | 7.2 | 71 |
| 5.5 | 4.27 | .65 | 5.3 | 78 |
| 6.1 | 6.38 | 1.44 | 10.1 | 105 |
| 11 | 8.85 | .92 | 5.5 | 80 |
| 36 | 42.93 | 4.67 | 10.0 | 119 |

NOTE 4. The tap water contained 8 $\mu\text{g/L}$ of zinc, and the standard deviation and percent relative standard deviation were calculated prior to subtraction of zinc originally present.

References

- American Society for Testing and Materials, 1984, Annual book of ASTM Standards, section 11, water: Philadelphia, v. 11.01, p. 39-42.
- Cooksey, M., and Barnett, W. B., 1979, Matrix modification and the method of additions in flameless atomic absorption: Atomic Absorption Newsletter, v. 18, p. 101-5.
- Fernandez, F. J., Beatty, M. M., and Barnett, W. B., 1981, Use of the L'vov platform for furnace atomic absorption applications: Atomic Spectroscopy, v. 2, p. 16-21.
- Hinderberger, E. J., Kaiser, M. L., and Koirtyohann, S. R., 1981, Furnace atomic absorption analysis of biological samples using the L'vov platform and matrix modification: Atomic Spectroscopy, v. 2, p. 1-11.
- Manning, D. C., and Slavin, W., 1983, The determination of trace elements in natural waters using the stabilized temperature platform furnace: Applied Spectroscopy, v. 37, p. 1-11.
- Ottaway, J. M., 1982, A revolutionary development in graphite furnace atomic absorption: Atomic Spectroscopy, v. 3, p. 89-92.
- Slavin, W., Carnrick, G. R., and Manning, D. C., 1982, Magnesium nitrate as a matrix modifier in the stabilized temperature platform furnace: Analytical Chemistry, v. 54, p. 621-4.

Zinc, atomic emission spectrometric, ICP

Parameter and Code:

Zinc, dissolved, I-1472-85 ($\mu\text{g/L}$ as Zn): 01090

2. Summary of method

Zinc is determined simultaneously with several other constituents on a single sample by a direct-reading emission spectrometric

method utilizing an induction-coupled argon plasma as an excitation source. See method I-1472, metals, atomic emission spectrometric, ICP.

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Zinc, total-in-sediment, atomic absorption spectrometric, direct

Parameter and Code:

Zinc, total, I-5474-85 (mg/kg as Zn): none assigned

2. Summary of method

A sediment sample is dried, ground, and homogenized. The sample is digested with a combination of nitric, hydrofluoric, and perchloric acids in a Teflon beaker heated on a

hotplate at 200°C. Zinc is determined on the resulting solution by atomic absorption spectrometry. See method I-5474, metals, major and minor, total-in-sediment, atomic absorption spectrometric, direct.

Metals, atomic emission spectrometric, ICP

Parameters and Codes: Metals, dissolved, I-1472-85 (see below)

| <u>Parameter</u> | <u>Code</u> | <u>Parameter</u> | <u>Code</u> |
|------------------------------------|-------------|--|-------------|
| Barium ($\mu\text{g/L}$ as Ba) | 01005 | Magnesium (mg/L as Mg) | 00925 |
| Beryllium ($\mu\text{g/L}$ as Be) | 01010 | Manganese ($\mu\text{g/L}$ as Mn) | 01056 |
| Cadmium ($\mu\text{g/L}$ as Cd) | 01025 | Molybdenum ($\mu\text{g/L}$ as Mo) | 01060 |
| Calcium (mg/L as Ca) | 00915 | Silica (mg/L as SiO_2) | 00955 |
| Cobalt ($\mu\text{g/L}$ as Co) | 01035 | Sodium (mg/L as Na) | 00930 |
| Copper ($\mu\text{g/L}$ as Cu) | 01040 | Strontium ($\mu\text{g/L}$ as Sr) | 01080 |
| Iron ($\mu\text{g/L}$ as Fe) | 01046 | Vanadium ($\mu\text{g/L}$ as V) | 01085 |
| Lead ($\mu\text{g/L}$ as Pb) | 01049 | Zinc ($\mu\text{g/L}$ as Zn) | 01090 |
| Lithium ($\mu\text{g/L}$ as Li) | 01130 | | |

1. Application

1.1 This method may be used only for the determination of dissolved constituents in water that have a measured specific conductance of less than $2,000 \mu\text{S/cm}$ at 25°C . Table 8 specifies the upper and lower concentration limits. Samples containing analyte concentrations greater than the upper concentration limit may be analyzed for calcium, magnesium, silica, and sodium if the sample is diluted and if, after dilution, the specific conductance is below $2,000 \mu\text{S/cm}$. Trace metals can also be determined in samples that have a measured specific conductance greater than $2,000 \mu\text{S/cm}$ by dilution; however, detection levels and sensitivity will change proportionally.

1.2 Analyses must be performed on filtered and acidified samples. Water-suspended sediment and bottom material cannot be analyzed.

1.3 The induction-coupled argon plasma (ICP) technology is so new that instruments and associated data-processing equipment and software available on the commercial market are not standardized and operating conditions vary. Until operating conditions of various manufacturers' instruments become more comparable and the equivalency of methods using those instruments are established by extensive testing, the ICP methods approved for U.S. Geological Survey use will specify instrument and associated software brands. This does not imply en-

dorsement of one product over another, but rather, acknowledges that ICP technology is rapidly changing and developing.

2. Summary of method

All parameters are determined simultaneously on a single sample by a direct-reading emission spectrometric method utilizing an induction-coupled argon plasma as an excitation source. Samples are pumped into a pneumatic nebulizer, atomized, and introduced into the plasma via a spray chamber and torch assembly. Each analysis is determined on the basis of the average of two replicate exposures, each of which is background-corrected by a spectrum-shifting technique. Calibration is performed by standardizing with a series of four mixed-element standards and a blank.

3. Interferences

3.1 Several interelement-interference effects have been evaluated. Interelement-correction factors have been programmed into the proprietary-data-system software and corrections are automatically applied, internally, to the data before they are printed as output.

3.2 Samples containing high dissolved solids exhibit a variety of unidentified interference effects. Therefore, analyses must be limited to samples with a specific conductance of $2,000 \mu\text{S/cm}$ or less.

Table 8.—Working ranges of constituents for ICP

| Constituent | Lower limit ($\mu\text{g/L}$ except where noted) | Upper limit ($\mu\text{g/L}$ except where noted) | Wavelength (nm) |
|---------------------------|--|--|-----------------|
| Barium | 2 | 10,000 | 455.5 |
| Beryllium | .5 | 10,000 | 313.0 |
| Cadmium | 1 | 10,000 | 214.4 |
| Calcium (1) | .02 mg/L | 100 mg/L | 396.8 |
| Calcium (2) | 100 mg/L | 1,000 mg/L | 315.8 |
| Cobalt | 3 | 10,000 | 238.8 |
| Copper | 10 | 10,000 | 324.7 |
| Iron | 3 | 10,000 | 259.9 |
| Lead | 10 | 10,000 | 220.3 |
| Lithium | 4 | 100,000 | 670.7 |
| Magnesium (1) | .001 mg/L | 5 mg/L | 279.5 |
| Magnesium (2) | 5 mg/L | 100 mg/L | 382.9 |
| Manganese | 1 | 10,000 | 257.6 |
| Molybdenum | 10 | 10,000 | 203.8 |
| Silica (SiO_2) | .009 mg/L | 100 mg/L | 288.1 |
| Sodium (1) | .2 mg/L | 100 mg/L | 589.0 |
| Sodium (2) | 100 mg/L | 1,000 mg/L | 330.2 |
| Strontium | .5 | 10,000 | 421.5 |
| Vanadium | 6 | 10,000 | 292.4 |
| Zinc | 3 | 10,000 | 206.0* |

*Second order.

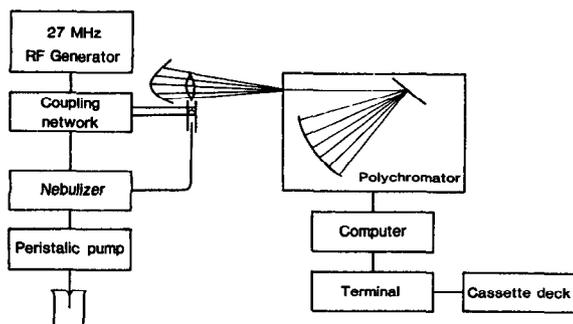


Figure 51.—Block diagram of spectrometer system

4. Apparatus (do not substitute)

4.1 *Emission Spectrometry System* (fig. 51) consisting of _____

4.1.1 *Spectrometer*, Jarrell-Ash Plasma Atom Comp, 0.75-meter focal curve with spectrum-shifter background correction and crossflow pneumatic nebulizer or Babington-type nebulizer as described by Garbarino and Taylor (1980). (See table 8 for element wavelengths.)

4.1.2 *Computer*, Digital Equipment Co., PDP8e.

4.1.3 *Quartz Torch* (fig. 52).

4.1.4 *Radio Frequency Generator*, Plasma-Therm Inc., Model HFS-2000D, 27.1-MHz.

4.1.5 *Peristaltic Pump*, Gilson, Model HP4 (fig. 53).

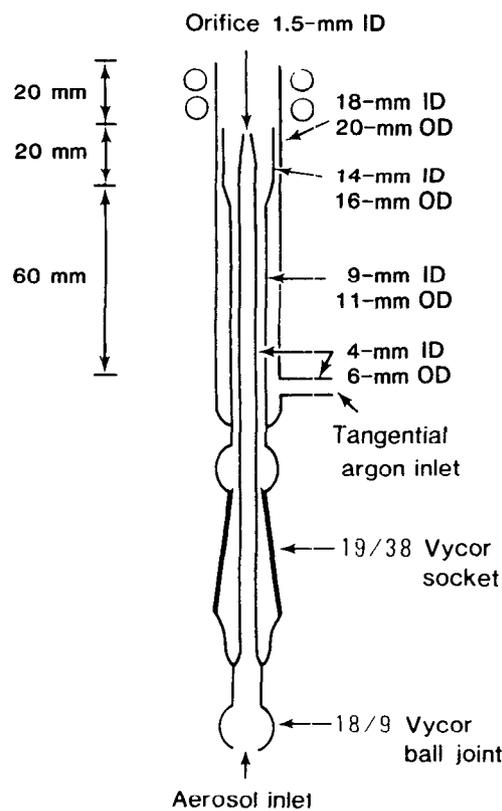
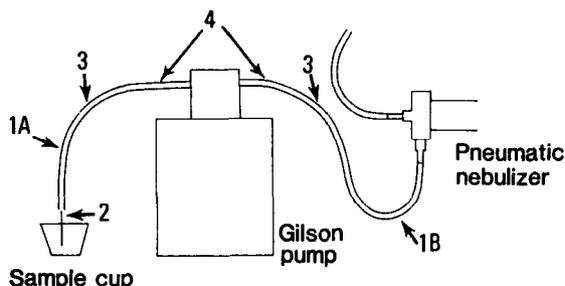


Figure 52.—Quartz torch

4.2 Refer to the Jarrell-Ash Instruction Manual, Atom Comp 750, for operating techniques.



- 1 Technicon tubing SMATM, flow rate 0.42 mL/min part 116-0549PO8, collar color-orange (1A-4 inches, 1B-6 inches)
- 2 Teflon tubing 26TW NAT: 4 inches
- 3 Tube connector part 116-0003-0
- 4 Technicon tubing SMATM, flow rate 0.80 mL/min part 116-0549P10 collar color-red-standard

Figure 53.—Pump system

4.2.1

Operating conditions:

| | |
|---|-----------------------------|
| Incident RF power ----- | 1.25 kW |
| Reflected RF power ---- | <10 W |
| Vertical observation position ----- | 16 mm (above load coil) |
| Horizontal observation position ----- | Center |
| Argon head pressure -- | 40 lb/in. ² |
| Sample argon pressure for crossflow nebulizer -- | 17 lb/in. ² |
| Sample argon pressure for Babington nebulizer - | 30 lb/in. ² |
| Sample argon flow rate for crossflow nebulizer -- | 0.9 L/min |
| Sample argon flow rate for Babington nebulizer (approx) ----- | 0.6 L/min |
| Plasma argon flow rate (for both nebulizers) - | 0 L/min |
| Coolant argon flow rate | 18 L/min |
| Sample pumping rate for crossflow nebulizer -- | 10 percent above aspiration |
| Sample pumping rate for Babington nebulizer - | 3 to 5 mL/min |
| Refractor plate position | Optimized for Hg profile |
| Spectrum shifter ----- | Full shift |

4.2.2 The software matrix containing all the required parameters for data acquisition is shown in table 9. Only three of these parameters ever require an update. The background constants should be updated wherever the plasma torch position has been changed. Background constants are obtained by setting them equal to 1.000, except for Li-channel 24 and Na-channel 23, by aspirating the blank solution, and then by making several measurements in intensities. From these intensity measurements new background constants are calculated using the formula:

$$B = \frac{I_N + I_B}{I_B}$$

where

B = new background constant, I_N = net intensity and I_B = background intensity. The new background constants are then entered into the matrix.

When background constants are updated the interelement-correction factors must be updated. Interelement-correction factors are obtained by setting them equal to zero, standardizing the instrument, analyzing each interfering-element standard stock solution, and printing the results in concentration units. These results are used to calculate the interelement-correction factors for each element using the formula:

$$I_e = A_e/C_i$$

where

I_e = interelement correction factor for element e, A_i = the apparent concentration of element e, and C_i = concentration of the interfering element i. The units of I_e are milligrams per liter of element e per milligrams per liter of interfering element i. New interelement correction factors are then entered into the matrix.

Finally, in some cases it is impractical to make standard stock solutions at concentrations of exactly 100.0 mg/L. Therefore, the concentration for each element should be entered into the matrix.

5. Reagents

5.1 Acids used in the preparation of standards must be Ultrex grade or equivalent.

5.1.1 *Aqua regia*: *Cautiously* mix 3 parts concentrated HCl (sp gr 1.19) and 1 part concentrated HNO₃ (sp gr 1.41) just before use.

5.1.2 *Hydrochloric acid, 6M*: Add 500 mL concentrated HCl (sp gr 1.19) to 400 mL demineralized water and dilute to 1 L.

5.2 Prepare standard stock solutions from Spex HiPure-grade chemicals or equivalent. Dry all salts for 1 h at 105°C unless otherwise specified. Do not dry hydrated salts. Clean all metals thoroughly with the appropriate acid and dry prior to weighing.

5.2.1 *Barium standard solution I, 1.00 mL = 100 µg Ba*: Dissolve 0.1516 g BaCl₂ dried at 180°C for 1 h in 10 mL demineralized water with 1 mL 6M HCl. Add 10.0 mL 6M HCl and dilute to 1,000 mL with demineralized water.

5.2.2 *Beryllium standard solution I, 1.00 mL = 100 µg Be*: Dissolve 0.1000 g beryllium flakes—**CAUTION: deadly poison**—in a minimum of aqua regia. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO₃ (sp gr 1.41) and dilute to 1,000 mL with demineralized water (NOTE 1). **NOTE 1. Beryllium is extremely toxic and may be fatal if swallowed or inhaled.**

5.2.3 *Calcium standard solution I, 1.00 mL = 100 µg Ca*: Suspend 0.2498 g CaCO₃ dried at 180°C for 1 h before weighing, in demineralized water and dissolve *cautiously* with a minimum amount of dilute HNO₃. Add 10.0 mL concentrated HNO₃ (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.2.4 *Cadmium standard solution I, 1.00 mL = 100 µg Cd*: Dissolve 0.1000 g cadmium splatters in a minimum of dilute HNO₃. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO₃ (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.2.5 *Cobalt standard solution I, 1.00 mL = 100 µg Co*: Dissolve 0.4939 g cobalt nitrate, Co(NO₃)₂·6H₂O, in demineralized water. Add 10.0 mL concentrated HNO₃ (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.2.6 *Copper standard solution I, 1.00 mL = 100 µg Cu*: Dissolve 0.1000 g copper shot in a minimum of dilute HNO₃. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO₃ (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.2.7 *Iron standard solution I, 1.00 mL = 100 µg Fe*: Dissolve 0.1000 g iron wire in a minimum of dilute HNO₃. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO₃ (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.2.8 *Lead standard solution I, 1.00 mL = 100 µg Pb*: Dissolve 0.1000 g lead shot in a minimum of dilute HNO₃. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO₃ (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.2.9 *Lithium standard solution I, 1.00 mL = 100 µg Li*: Dissolve 0.5323 g Li₂CO₃, slowly, in a minimum amount of dilute HNO₃. Add 10.0 mL concentrated HNO₃ (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.2.10 *Magnesium standard solution I, 1.00 mL = 100 µg Mg*: Dissolve 0.1000 g magnesium rod in a minimum of dilute HNO₃. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO₃ (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.2.11 *Manganese standard solution I, 1.00 mL = 100 µg Mn*: Dissolve 0.1000 g manganese flakes in a minimum of dilute HNO₃. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO₃ (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.2.12 *Molybdenum standard solution I, 1.00 mL = 100 µg Mo*: Dissolve 0.2043 g (NH₄)₂MoO₄ in demineralized water. Dilute to 1,000 mL with demineralized water.

5.2.13 *Silica standard solution I, 1.00 mL = 100 µg SiO₂*: Dissolve 0.3531 g Na₂SiO₃·5H₂O in demineralized water. Add 10.0 mL concentrated HNO₃ (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.2.14 *Sodium standard solution I, 1.00 mL = 500 µg Na*: Dissolve 1.271 g NaCl in demineralized water. Add 10.0 mL concentrated HNO₃ (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.2.15 *Strontium standard solution I, 1.00 mL = 100 µg Sr*: Dissolve 0.2416 g Sr(NO₃)₂ in demineralized water. Add 10.0 mL concentrated HNO₃ (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.2.16 *Vanadium standard solution I, 1.00 mL = 100 µg V*: Dissolve 0.2297 g NH₄VO₃ in a minimum amount of concentrated HNO₃. Heat to increase rate of dissolution. Add 10.0 mL

concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 with demineralized water.

5.2.17 *Zinc standard solution I*, 1.00 mL = 100 μg Zn: Dissolve 0.1000 g zinc powder in a minimum of dilute HNO_3 . Heat to increase rate of dissolution. Add 10.0 mL of concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.3 Mixed working-standard solutions.

5.3.1 Prepare four mixed standard solutions as follows: Pipet 50.0 mL of each appropriate standard stock solution into a 500-mL volumetric flask. Dilute with demineralized water. Transfer to acid-rinsed PTFE bottle for storage. Freshly mixed standards should be prepared weekly. Final concentration will be 1.00 mL = 10.0 μg for all parameters exception sodium, which will be 1.00 mL = 50.0 μg . Composition for mixed standards should be as follows:

5.3.2 *Mixed standard solution I*: Iron, cadmium, lead, and zinc.

5.3.3 *Mixed standard solution II*: Beryllium, copper, strontium, vanadium, and cobalt.

5.3.4 *Mixed standard solution III*: Molybdenum, silica, lithium, and barium.

5.3.5 *Mixed standard solution IV*: Calcium, magnesium, manganese, and sodium.

5.3.6 *Reagent blank*: Dilute 1 mL concentration HNO_3 (sp gr 1.41) to 1,000 mL with demineralized water.

5.4 *Check standard solution*: Pipet 5.00 mL of each standard stock solution into a 100-mL volumetric flask. Dilute with demineralized water. Transfer to PTFE bottle for storage. Fresh check standard solution should be prepared weekly. Final concentration will be 1.00 mL = 5.00 μg for all parameters except Na, which will be 1.00 mL = 28.83 μg (due to the Na in the SiO_2 standard).

6. Procedure

6.1 Set up instrument with proper operating parameters (paragraph 4.2) and ignite plasma. Instrument must warm for 30 min prior to standardization.

6.2 Retrieve the appropriate proprietary software matrix from memory. Set the Time and Date. Set number of cycles for spectrum shifter to 5. Enter the following "coded string" for standardization: (QEGGAIN).

6.3 Position the mercury pen lamp in front of the entrance slit. Initiate the "profile" computer

command, and profile the instrument by averaging the micrometer settings obtained at identical intensity positions on each side of the mercury spectral line. Position the micrometer to the average setting.

6.4 Standardize the data system by running a blank and the series of four mixed standard solutions using an "O" command to initiate each run. Identify the standard at the end of each run when demanded by the computer. Pump blank solution for 30 s between standards. Allow 30 s for equilibration each time a new solution is introduced.

6.5 Change the "coded string" to the following: (QEGGAC). Analyze the check standard described in paragraph 5.4. Concentration values obtained should not deviate from the actual values by more than 2 percent. If values do deviate more than 2 percent, inspect nebulizer for malfunction.

6.6 Check standardization by running secondary reference samples or equivalent certified reference samples in natural matrix materials. The determined concentration must be within one standard deviation of the elemental mean given for the reference material.

6.7 Analyze samples allowing 30 s for equilibration. Pump blank solution for 30 s between samples. Check calibration after analyzing 10 samples by rerunning a reference sample and the check standard. The results for the reference sample and check standard must be within one-standard-deviation of the elemental mean given for the reference material and less than ± 2 percent for each element respectively. If not, the data system *must* be restandardized as described starting at paragraph 6.3.

6.8 Reprofile instrument (paragraph 6.3) as necessary. If profile position changes by more than 4 micrometer units, the instrument must be restandardized (starting with paragraph 6.2).

7. Calculations

7.1 All calculations are performed internally by the computer data system. SiO_2 will be labeled Si if headings are used to identify the results.

7.2 If dilutions were performed, multiply the results by the appropriate dilution factor.

8. Report

8.1 All results are printed directly in milligrams per liter (NOTE 2).

Table 9.—Single-operator precision data for ICP

| Constituent | Slope | Intercept | Units |
|----------------------------|--------|-----------|-------|
| Barium | 0.0061 | 0.83 | µg/L |
| Beryllium | .0061 | .06 | Do. |
| Cadmium | .0203 | .30 | Do. |
| Cobalt | .0650 | .40 | Do. |
| Copper | .0039 | 1.32 | Do. |
| Iron | .0071 | .059 | Do. |
| Lead | .1210 | 5.0 | Do. |
| Lithium | .0240 | .076 | Do. |
| Manganese | .0042 | .30 | Do. |
| Molybdenum | .1220 | .18 | Do. |
| Strontium | .0089 | .076 | Do. |
| Zinc | .0059 | 1.24 | Do. |
| Calcium | .0044 | .30 | mg/L |
| Magnesium | .0060 | .018 | Do. |
| Silica (SiO ₂) | .0040 | .019 | Do. |
| Sodium | .0077 | .26 | Do. |

Standard deviation, S_o , is calculated by $S_o = mx + b$, where m is slope of line, x is concentration of constituent in units specified, and b is intercept.

NOTE 2. If either the reported calcium or sodium concentration is greater than 100 mg/L or the magnesium concentration is greater than 5.0 mg/L, report the second value given, otherwise report only the first value. Trace-metal results must be converted to micrograms per liter.

8.2 Report the dissolved constituent concentrations as follows:

8.2.1 Calcium (00915), magnesium (00925), silica (00955), and sodium (00930): less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

8.2.2 Beryllium (01010), cadmium (01025), manganese (01056), and strontium (01080): less than 10 µg/L, nearest µg/L; 10 µg/L and above, two significant figures.

8.2.3 Barium (01005), cobalt (01035), iron (01046), lithium (01130), and zinc (01090): less than 10 µg/L, nearest µg/L to the lower limit of detection as specified in table 8; 10 µg/L and above, two significant figures.

8.2.4 Copper (01040), lead (01049), molybdenum (01060), and vanadium (01085): less than 100 µg/L, nearest 10 µg/L; 100 µg/L and above, two significant figures.

9. Precision

9.1 Within its designated range, single-operator precision of the method for each metal may be expressed as described in table 9. A minimum of 10 replicate analyses were performed to obtain each regression equation shown.

9.2 Interlaboratory precision data obtained on standard reference water samples are shown in table 10. The specific instrument described in this method may not have been used. Laboratories were not asked to provide this information.

Reference

Garbarino, J. R., and Taylor, H. E., 1980, A Babington-type nebulizer for use in the analysis of natural water samples by inductively coupled plasma spectrometry: Applied Spectroscopy, v. 34, p. 584-90.

Table 10.—Interlaboratory precision data for ICP

[S_T = overall precision, in units specified and X = concentration of constituent, in units specified; SD_p = average standard deviation, in units specified and CI = 95 percent confidence intervals for the average standard deviation, in units specified.]

| Constituent | Number of samples | Range (µg/L except where noted) | Precision | Correlation coefficient |
|----------------------------|-------------------|---------------------------------|--------------------------------------|-------------------------|
| Barium | 6 | 18 to 240 | $S_T = 0.055 X + 1.68$ | 0.9448 |
| Beryllium | 6 | 4.0 to 47 | $S_T = 0.056 X + 0.836$ | .8442 |
| Cadmium | 6 | 4.0 to 15 | $S_T = 0.396 X - 1.50$ | .8992 |
| Calcium | 7 | .77 to 186 mg/L | $S_T = 0.067 X - 0.433$ | .9907 |
| Cobalt | 6 | 3.5 to 14 | $SD_p = 3.3$ $CI = 2.6$ to 4.6 | -- |
| Copper | 6 | 22 to 470 | $S_T = 0.065 X + 2.97$ | .9915 |
| Iron | 7 | 100 to 770 | $SD_p = 24.1$ $CI = 20.1$ to 29.8 | -- |
| Lithium | 6 | 43 to 650 | $S_T = 0.092 X + 3.59$ | .8337 |
| Magnesium | 7 | .10 to 120 mg/L | $S_T = 0.044 X + 0.072$ | .9985 |
| Manganese | 6 | 38 to 570 | $SD_p = 23.1$ $CI = 18.8$ to 28.5 | -- |
| Molybdenum | 5 | 12 to 36 | $SD_p = 5.7$ $CI = 4.5$ to 8.1 | -- |
| Silica (SiO ₂) | 5 | 5.2 to 11 mg/L | $SD_p = 0.78$ $CI = 0.62$ to 1.06 | -- |
| Sodium | 7 | .33 to 160 mg/L | $S_T = 0.027 X + 0.763$ | .9215 |
| Strontium | 12 | 57 to 2700 | $S_T = 0.042 X + 3.73$ | .9345 |
| Vanadium | 5 | 6.0 to 10 | $S_T = 0.879 X - 4.72$ | .9557 |
| Zinc | 6 | 15 to 570 | $SD_p = 14.0$ $CI = 11.6$ to 17.8 | -- |