Methods for Analysis of Selected Metals in Water by Atomic Absorption

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GEOLOGICAL SURVEY WATER-SUPPLY PAPER 1540-C

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By MARVIN J. FISHMAN *and* SANFORD C. DOWNS

SPECTROGRAPHIC ANALYSIS OF NATURAL WATER

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A manual of procedures for determining calcium, copper, lithium, magnesium, manganese, potassium, sodium, strontium, and zinc in atmospheric precipitation, fresh waters, and brines by atomic absorption spectroscopy

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METHODS FOR ANALYSIS OF SELECTED METALS IN WATER BY ATOMIC ABSORPTION

By Marvin J. Fishman and Sanford C. Downs

ABSTRACT

This manual describes atomic-absorption-spectroscopy methods for determining calcium, copper, lithium, magnesium, manganese, postassium, sodium, strontium, and zinc in atmospheric precipitation, fresh waters, and brines. The procedures are intended to be used by water quality laboratories of the Water Resources Division of the U.S. Geological Survey. Detailed procedures, calculations, and methods for the preparation of reagents are given for each element along with data on accuracy, precision, and sensitivity. Other topics discussed briefly are the principle of atomic absorption, instrumentation used, and special analytical techniques.

INTRODUCTION

The purpose of this manual is to describe atomic-absorption methods of water analysis to be used by water quality laboratories of the Water Resources Division of the U.S. Geological Survey and to standardize procedures by serving as a guide for laboratory personnel. The procedures in this manual are applicable to the analysis of most natural waters, and some of them are applicable to the analysis of brines. If a particular element can be determined in a brine and if sufficient data to support this determination are available, the individual procedure is discussed. Determinations of other elements that cannot be supported by current data are not discussed. Because atomic absorption permits very low detection limits, precipitation waters can be analyzed readily by the procedures presented. Most of the procedures in this manual were adapted from the Perkin-Elmer instruction manual (1964). Modifications have been made where necessary to adapt the procedures to water analysis. Additional information may be obtained from the manufacturer's manual.

The use of trade names of equipment, supplies, and reagents in this manual does not constitute endorsement. It is done only in the interest of standardization.

PRINCIPLE OF ATOMIC ABSORPTION

It has been known for more than a hundred years that atoms of some elements are excited when vaporized and fed into a flame. As these atoms return to their ground state, they emit radiation of characteristic measurable wavelengths. This principle is the basis for flame-emission photometry.

Most elements are not easily excited in a flame, and most of the atoms remain in the ground state. These unexcited atoms can absorb energy from a beam of light of the same characteristic wavelength. The beam of light from a hollow-cathode lamp made of the metal being determined was used by Walsh (1955) to develop atomic-absorption instrumentation. He found that a source of radiation of the same wavelength as that of the absorption line puts less demand upon the resolution of the monochromator than a source of broadband radiation. Since the wavelength of the light beam is characteristic of only the metal being determined, the light energy absorbed by the flame is a measure of the concentration of that metal in the sample. This principle is the basis of atomic absorption spectroscopy.

INSTRUMENTATION

Several manufacturers currently supply atomic-absorption equipment. Among them are Jarrell-Ash, Beckman, Aztec, Hilger and Watts, Unicam, and Perkin-Elmer. Instruments offered by these manufacturers differ in design.

The selection of a given commercial product is based largely upon its design, durability, cost, and maintenance requirements, but also on standardization of equipment in all water quality laboratories of the Water Resources Division of the U.S. Geological Survey. Experience gained in individual laboratories, is evaluated, and the results are used by other laboratories.

A schematic diagram of the Perkin-Elmer optical system is shown in figure 3. The energy or light beam from the source, either a hollow-cathode or vapor-discharge lamp, is divided by a rotating chopper into a reference beam and a sample beam. The water sample is aspirated into an atomizer-burner, and part of the sample beam passing through the flame is absorbed, the amount depending upon the concentration of the metal being determined. The remainder of the sample beam is recombined with the reference beam by a semitransparent mirror. The analytical wavelength of the metal being analyzed is isolated from all other energy in the light beam by a grating monochromator. Two gratings are mounted back to back—one for the ultraviolent region and the other for the visible region. The extent to which the energy of the characteristic emission wavelength of the source lamp is

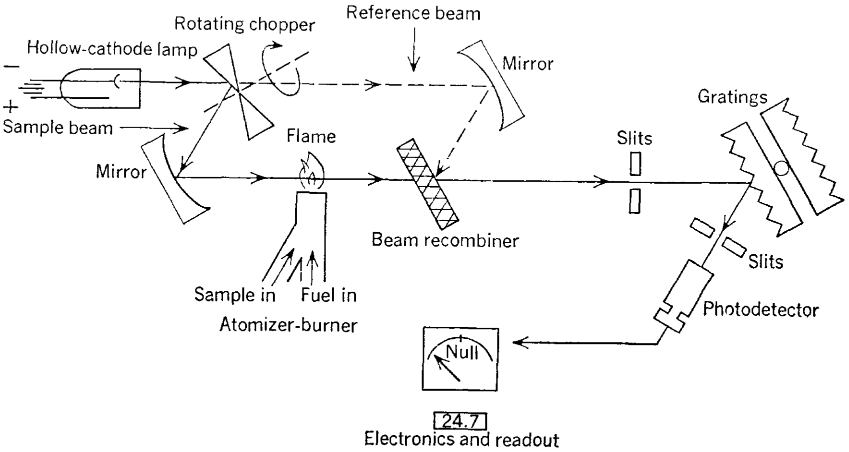

FIGURE 3.—Perkin-Elmer Model 303 atomic absorption spectrophotometer optical system. Reprinted by permission of Perkin-Elmer Corp.

absorbed in the flame is measured by a photodetector. The signal from the photodetector is amplified and fed into circuitry that produces a manual electronic null in combination with a digital readout which corresponds to the concentration of the metal being determined.

By varying the relative proportions of fuel and air in the atomizer-burner, an oxidizing (air-rich) or a reducing (fuel-rich) flame is produced. The type of flame to be used depends upon the metal being analyzed. An oxidizing flame is preferable because of its greater stability. However, some metals tend to form refractory oxides in an oxidizing flame, and a reducing flame is necessary to increase the number of atoms available for absorption. The type of flame to be used is stated in each procedure under the operating conditions.

SPECIAL ANALYTICAL TECHNIQUES—STANDARD-ADDITION METHOD

The standard-addition technique is used when the solids content of the sample is so high that its affect on absorption is difficult to duplicate with the aqueous standards or when an interference is present which cannot be corrected.

Equal volumes of the sample are added to a blank (distilled water) and to three standards containing different known quantities of the test element. The blank and standards must first be diluted to the same volume. The percentage of absorption of each solution is determined and converted to the corresponding absorbance unit. Absorbance is then plotted against concentration on a graph, and the resulting line is extended back through zero absorbance. The intercept on the concentration axis is the concentration of the metal in the original sample.

The line should preferably be straight to insure accurate analyses. An example of the standard-addition technique is shown in figure 4.

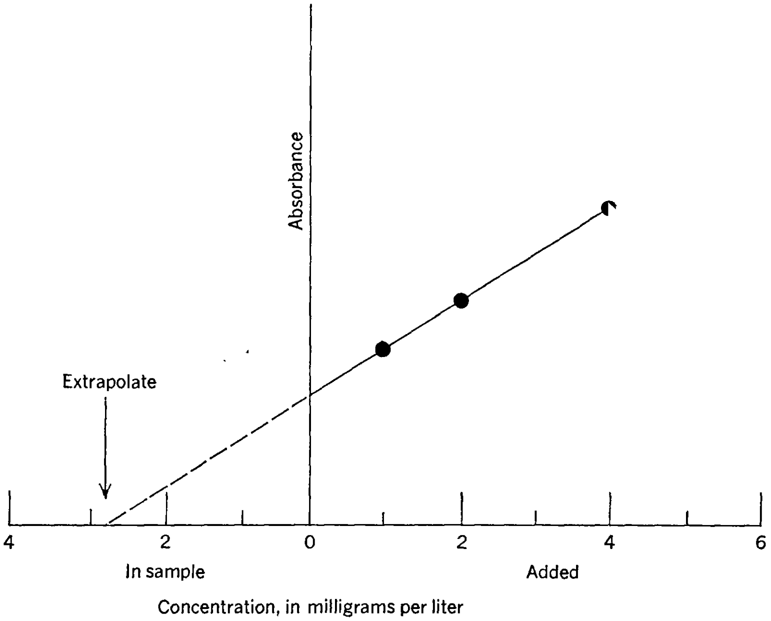

FIGURE 4.—Example of standard-addition method.

ANALYTICAL PROCEDURES

A Perkin-Elmer Model 303 atomic absorption spectrophotometer was used to determine each metal.

CALCIUM

DISCUSSION OF METHOD

A hollow-cathode lamp and a reducing flame are used to determine calcium. Phosphate, sulfate, and aluminum interfere but are masked by the addition of a 1-percent lanthanum solution to the sample. Low calcium values result if the pH of the sample is above 7; therefore, both standards and samples are prepared in 5-percent hydrochloric acid solution. Magnesium in concentrations higher than 1,000 ppm (parts per million) also causes low calcium values. Concentrations of up to 500 ppm each of sodium, potassium, and nitrate show no interference.

The 4227 A (angstrom) line is used to determine concentrations of calcium less than 20 mg per l (milligrams per liter). For concentrations of calcium greater than 20 mg per l, dilution is required. The calcium lamp is extremely quiet, and the results of the method are accurate and reproducible to ±0.1 mg per l for concentrations of calcium less than 20 mg per l and to ±0.2—±1.0 mg per l for concentrations of calcium from 20 to 200 mg per l. When excessive dilution is required, the accuracy and reproducibility are decreased. There is excellent agreement between results obtained by atomic absorption and by EDTA [1] titration.

The sensitivity for calcium concentrations of less than 20 mg per l ranges from 0.15 to 0.30 mg per l per 1 percent absorption. With scale expansion concentrations of calcium less than 1 mg per l can be determined with an accuracy of ±0.01 mg per l.

APPARATUS

Grating: Visible
Wavelength counter: 211.4 (4227 A)
Scale: 1 ×
Slit: 5 (3 mm, 40 A)
Source: Calcium hollow-cathode lamp
Lamp current: 10 ma (milliampere)
Air pressure: 28 psi (pounds per square inch); 8.0 on flowmeter
Fuel: Acetylene. Pressure: 8 psi; 9.0 on flowmeter initially (use a 10 mg calcium per liter standard solution and adjust acetylene flow rate to obtain maximum absorption)
Flame: Reducing
Sample uptake: About 4 ml per min (milliliters per minute)

The following absorption readings have been observed:

Calcium concentration, mg per l	*Absorption, percent*
5.0	26.4
10	43.6
15	54.4
20	61.8

REAGENTS

Calcium chloride standard stock solution, 1.00 ml=0.50 mg calcium: Suspend 1.250 g $CaCO_3$, dried at 180°C for 1.0 hour before weighing, in distilled water and dissolve cautiously with a minimum of dilute HCl. Dilute to 1,000 ml with distilled water.

Calcium chloride standard working solutions: Prepare a series of standard solutions containing from 0 to 20 mg calcium per liter by diluting the $CaCl_2$ standard stock solution. Add 1.0 ml of $LaCl_3$–HCl solution to each 10.0 ml working standards prepared. For example, to 500 ml of a working standard, add 50 ml $LaCl_3$–HCl solution.

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[1] Ethylenediaminetetraacetic acid.

Lanthanum chloride–hydrochloric acid solution: Dissolve 58.65 g of La_2O_3, slowly and in small portions, in 250 ml concentrated HCl (CAUTION! Reaction is violent) and dilute to 500 ml with distilled water.

PROCEDURE

1. Filter the sample (0.45μ (micron) micropore membrane filter) when necessary to avoid clogging the atomizer-burner.
2. Add 1.0 ml of $LaCl_3$–HCl solution to 10.0 ml of sample.
3. Atomize each sample and standard, and record the percent absorption observed. Repeat, and average the two values. If the calcium concentration is greater than 20 mg per l, the sample must be diluted. Be sure that the diluted sample contains the proper amount of $LaCl_3$–HCl solution.

CALCULATIONS

1. Convert percent absorption to absorbance and determine the calcium concentration in the sample from a plot of absorbances of standards. For samples containing more than 20 mg calcium per liter, multiply by the proper dilution factor. Exact reproducibility is not obtained, and a working curve must be prepared with each set of samples.
2. $\text{ppm calcium} = \frac{1}{\text{density}} \times \text{mg calcium per liter.}$

   Report calcium concentrations less than 10 ppm to the nearest 0.1 ppm, those between 10 and 200 ppm to the nearest whole number, and those greater than 200 ppm to two significant figures.

COPPER

DISCUSSION OF METHOD

A hollow-cathode lamp operating at 3247 A is used to determine copper. Allow the lamp to warm up for about 30 minutes at a current of 15 ma before use.

Cations and anions normally found in water do not interfere. To determine copper concentrations less than 1.0 mg per l, 10 × scale expansion is used, and the results are accurate and reproducible to approximately ± 0.02 mg of copper per liter. Concentrations of copper greater than 1.0 mg per l can be determined by using less scale expansion. The maximum copper concentration that can be determined at the 3247 A line without dilution is approximately 20 mg per l.

The sensitivity for copper concentrations of less than 1.0 mg per l is approximately 0.02 mg per l for each scale division.

APPARATUS

Grating: Ultraviolet
Wavelength counter: 324.7 (3247 A)
Scale: 10 ×
Slit: 4 (1 mm, 6.5 A)
Source: Copper hollow-cathode lamp
Lamp current: 15 ma, or optimum operating current
Air pressure: 28–30 psi; 9.0 on flowmeter (varies with different flowmeters and burners)
Fuel: Acetylene. Pressure: 8 psi; 9.0 on flowmeter
Flame: Oxidizing
Sample uptake: 2–5 ml per min
Response-time control: 1
The following readings have been observed:

Copper concentration, mg per l	*Scale reading*
0.10	5.8
.20	11.8
.50	31.9
.80	50.9
1.00	63.7

REAGENTS

Copper nitrate standard solution I, 1.00 ml = 1.00 mg copper: Dissolve 1.00 g metallic copper in a slight excess of dilute HNO_3, and dilute to 1,000 ml with metal-free water.

Copper nitrate standard solution II, 1.00 ml = 0.005 mg copper: Dilute 5.00 ml $Cu(NO_3)_2$ standard solution I to 1,000 ml with metal-free water containing one or two drops of concentrated HNO_3.

Copper nitrate standard working solutions: Prepare a series of standard solutions containing from 0.00 to 1.0 mg copper per liter by diluting the $Cu(NO_3)_2$ standard solution II.

PROCEDURE

1. Filter the sample (0.45μ micropore membrane filter) when necessary to avoid clogging the atomizer-burner.
2. Atomize each sample and standard, and record the scale readings observed. Repeat, and average the two values.

CALCULATIONS

1. Determine the copper concentration in the sample from a plot of scale readings of standards. Because a scale expansion of 10 × is used, scale readings need not be converted to absorbance. Exact reproducibility is not obtained, and a working curve must be prepared with each set of samples.

2. $\text{ppm copper} = \frac{1}{\text{density}} \times \text{mg copper per liter.}$

Report copper concentrations less than 1.0 ppm to the nearest 0.01 ppm, and those greater than 1.0 ppm to two signficant figures.

LITHIUM

DISCUSSION OF METHOD

A hollow-cathode lamp is used to determine lithium. The lamp current must be high enough to prevent excessive noise; 20 ma is suggested, although some lamps may require less. Higher currents are not recommended because the cathode will begin to melt at about 25–28 ma.

Concentrations of up to 1,000 ppm sodium, 100 ppm potassium, 200 ppm magnesium, 200 ppm calcium, 1,500 ppm chloride, 2,000 ppm sulfate, and 100 ppm nitrate do not interfere. Strontium, at concentrations greater than 5 ppm, interferes.

The 6708 A line is used to determine lithium. Since the detection limit is 0.005 mg per 1 or less, three working curves are recommended to cover the concentration range 0–10 mg lithium per liter. For the working curve 0.00–0.10 mg lithium per liter, results are accurate and reproducible to approximately ±0.002 mg per 1; between 0.1 and 1.0 mg lithium per liter to ±0.01 mg per 1; and between 1.0 and 10 mg lithium per liter, to ±0.1 mg per 1. There is excellent agreement between lithium concentrations determined by both the atomic-absorption and the flame-photometric methods (Beckman DU flame photometer).

The sensitivity for lithium concentrations of less than 0.1 mg per 1 is approximately 0.005 mg per 1 for each scale division; for those between 0.1 and 1.0 mg lithium per liter, approximately 0.01 mg per 1 for each scale division; and for those greater than 1.0 mg per 1, approximately 0.1 mg per 1 per 1 percent absorption. The method is applicable to both fresh waters and brines. Brines must be diluted to concentrations of 15,000 ppm or less total dissolved solids.

APPARATUS

Concentration range: 1.0–10 mg lithium per liter
  Grating: Visible
  Wavelength counter: 335.4 (6708 A)
  Scale: 1 ×
  Slit: 5 (3 mm, 40 A)
  Source: Lithium hollow-cathode lamp
  Lamp current: 20 ma maximum
  Air pressure: 28 psi; 9.0 on flowmeter (varies with different flowmeters and burners)
  Fuel: Acetylene. Pressure: 8 psi; 9.0 on flowmeter

Flame: Oxidizing
Sample uptake: About 4 ml per min
Response-time control: 1

The following absorption readings have been observed:

Lithium concentration, mg per l	*Absorption, percent*
2.0	28.0
4.0	47.8
6.0	59.6
8.0	67.4
10	73.5

Concentration range: 0.1–1.0 mg lithium per liter.

Scale: 5 ×

All other operating conditions the same as used for concentration range from 1.0 to 10 mg lithium per liter.

The following readings have been observed:

Lithium concentration, mg per l	*Scale reading*
0.25	18.5
.50	37.2
.75	54.0
1.0	74.2

Concentration range: 0.00–0.10 mg lithium per liter.

Scale: 10 ×

All other operating conditions the same as used for concentration range from 1.0 to 10 mg lithium per liter.

The following readings have been observed:

Lithium concentration, mg per l	*Scale reading*
0.01	2.0
.05	9.4
.10	18.7

REAGENTS

Lithium nitrate standard stock solution, 1.00 ml = 1.00 mg lithium: Dissolve 9.9357 g $LiNO_3$ in demineralized water and dilute to 1,000 ml.

Lithium nitrate standard working solutions: Prepare a series of standard solutions containing from 0 to 10 mg lithium per liter by diluting the $LiNO_3$ standard stock solution.

PROCEDURE

1. Filter the sample (0.45μ micropore membrane filter) when necessary to avoid clogging the atomizer-burner.
2. Atomize each sample and standard, and record the percent absorption or scale reading observed. Repeat, and average the two values. If the lithium concentration is greater than 10 mg per l, the sample must be diluted.

CALCULATIONS

1. Concentration range 1.0–10 mg lithium per liter: Convert percent absorption to absorbance, and determine the lithium concentration in the sample from a plot of absorbances of standards. For samples containing more than 10 mg lithium per liter, multiply by proper dilution factor.
2. Concentration ranges 0.10–1.0 mg lithium per liter and 0.00–0.10 mg lithium per liter: Determine the lithium concentration in the sample from a plot of scale readings of standards. Because scale expansion's of 5 × and 10 × are used, scale readings need not be converted to absorbance.
3. ppm lithium $=\frac{1}{\text{density}} \times$ mg lithium per liter.

Report lithium concentrations less than 0.10 ppm to the nearest 0.005 ppm, those between 0.10 and 1.0 ppm to the nearest 0.01 ppm, those between 1.0 and 10 ppm to the nearest 0.1 ppm, and those greater than 10 ppm to whole numbers.

MAGNESIUM

DISCUSSION OF METHOD

A hollow-cathode lamp and a reducing flame are used to determine magnesium. Two magnesium lines—one at 2852 A, and the ground-state line at 2025 A—are employed to avoid excessive dilution of samples. Aluminum, in concentrations greater than 2 ppm, interferes at both lines; sulfate and phosphate interfere at the 2025 A line. These interferences, however, are masked by the addition of approximately 1 percent lanthanum. Low magnesium values result if the pH of the sample is above 7; therefore, both standards and samples are prepared in 5-percent hydrochloric acid solution. Sodium, potassium, and calcium, in concentrations less than 400 ppm, show no interference. There is also a zinc line at 2025 A, but 2 ppm zinc shows no interference.

The 2852 A line is used to determine concentrations of magnesium less than 2 mg per l. Magnesium concentrations of 2–10 mg per l are determined using the same line by dilution of the sample. The 2025 A line is used to determine magnesium concentrations between 10 and 50 mg per l. To determine magnesium concentrations greater than 50 mg per l, dilution is required.

For magnesium concentrations of less than 10 mg per l, results are accurate and reproducible to ±0.1 mg per l, and with extreme care the results are accurate and reproducible to ±0.02 mg per l at concentrations less than 2 mg per l without scale expansion. The results are accurate and reproducible to ±1 mg per l for concentrations of magnesium between 10 and 50 mg per l. When dilution is required, for samples containing more than 50 mg per l, the accuracy and reproducibility are decreased. There is excellent agreement between results obtained by atomic absorption and those obtained by EDTA titration for samples containing 10–50 mg magnesium per liter.

The sensitivity for magnesium concentrations of less than 2 mg per l is approximately 0.03 mg per l per 1 percent absorption. For the 10–50 mg magnesium per liter range, the sensitivity is approximately 1 mg per l per 1 percent absorption.

APPARATUS

Concentration range: 0–10 mg magnesium per liter (samples containing more than 2 mg magnesium per liter must be diluted)
Grating: Ultraviolet
Wavelength counter: 285.2 (2852 A)
Scale: 1 ×
Slit: 5 (3 mm, 20 A)
Source: Magnesium hollow-cathode lamp
Lamp current: 10 ma
Air pressure: 28 psi; 8.0 on flowmeter
Fuel: Acetylene. Pressure: 8 psi; 9.0 on flowmeter initially (use a 1 mg magnesium per liter standard solution and adjust acetylene flow rate to obtain maximum absorption)
Flame: Reducing
Sample uptake: About 4 ml per min

The following absorption readings have been observed:

Magnesium concentration, mg per l	*Absorption, percent*
0.5	20.2
1.0	35.6
1.5	48.3
2.0	58.8

Concentration range: 10–50 mg magnesium per liter
Wavelength counter: 202.5 (2025 A)
Response-time control: 1
All other operating conditions same as used for concentration range 0–10 mg magnesium per liter.

The following absorption readings have been observed:

Magnesium concentration, mg per l	*Absorption, percent*
10	14.0
25	29.8
50	46.0

REAGENTS

Lanthanum chloride–hydrochloric acid solution: Dissolve 58.65 g of La_2O_3, slowly and in small portions, in 250 ml concentrated HCl (CAUTION! Reaction is violent) and dilute to 500 ml with distilled water.

Magnesium chloride standard stock solution, 1.00 ml=0.50 mg magnesium: Dissolve 0.500 mg pure metallic magnesium in a minimum amount of dilute HCl and dilute to 1,000 ml with distilled water.

Magnesium chloride standard working solutions: Prepare a series of standard solutions containing from 0 to 50 mg magnesium per liter by diluting the $MgCl_2$ standard stock solution. Add 1.0 ml $LaCl_3$–HCl solution to each 10.0 ml of the working standards prepared. For example, to 500 ml of a working standard, add 50 ml $LaCl_3$–HCl solution.

PROCEDURE

1. Filter the sample (0.45 μ micropore membrane filter) when necessary to avoid clogging the atomizer-burner.
2. Add 1.0 ml of $LaCl_3$–HCl solution to 10.0 ml of sample.
3. Atomize each sample and standard, and record the percent absorption observed. Repeat, and average the two values. If the magnesium concentration is greater than 50 mg per l, the sample must be diluted. Be sure that the diluted sample contains the proper amount of $LaCl_3$–HCl solution.

CALCULATIONS

1. Convert percent absorption to absorbance, and determine the magnesium concentration in the sample from a plot of absorbances of standards. For samples containing more than 2 mg magnesium per liter (0–2 mg magnesium per liter working curve) or more than 50 mg magnesium per liter (10–50 mg magnesium per liter working curve) multiply by the proper dilution factor. Exact reproducibility is not obtained, and working curves must be prepared with each set of samples.
2. $\text{ppm magnesium} = \frac{1}{\text{density}} \times \text{mg magnesium per liter.}$

   Report magnesium concentrations less than 10 ppm to the nearest 0.1 ppm, those between 10 and 200 ppm to the nearest whole number, and those greater than 200 ppm to two significant figures.

MANGANESE

DISCUSSION OF METHOD

A hollow-cathode lamp is used to determine manganese, and the lamp should be allowed to warm up for about 30 minutes before use. The optimum current may differ slightly for different lamps. However, currents greater than the maximum stated on the lamp should not be used because the cathode may melt.

The 2795 A line is used to determine manganese. Although there are two iron lines and a magnesium line near this line, concentrations of up to 25 ppm iron, 100 ppm magnesium show no interference. Magnesium in concentrations greater than 100 ppm interferes when the manganese concentration exceeds 0.50 ppm. However, magnesium does not interfere when other cations, such as sodium, are present in the sample. Other cations and anions normally found in water do not interfere.

To determine manganese concentrations of less than 1.0 mg per l, 10 × scale expansion is used. Results are accurate and reproducible to approximately ±0.02 mg manganese per liter. Concentrations greater than 1.0 mg per l are determined directly by using less scale expansion. The maximum concentration that can be determined at the 2795 A line without dilution is about 25 mg manganese per liter.

The sensitivity for manganese concentrations of less than 1.0 mg per l is approximately 0.02 mg per l for each scale division.

APPARATUS

Grating: Ultraviolet
Wavelength counter: 279.5 (2795 A)
Scale: 10 ×
Slit: 4 (1 mm, 6.5 A)
Source: Manganese hollow cathode lamp
Lamp current: 10–15 ma
Air pressure: 28 psi; 9.0 on flowmeter (varies with different flowmeters and burners)
Fuel: Acetylene. Pressure: 8 psi, 9.0 on flowmeter
Flame: Oxidizing
Sample uptake: 3–5 ml per min
Response-time control: 1

The following readings have been observed:

Manganese concentration, mg per l	*Scale reading*
0.25	17.3
.50	33.7
.75	49.5
1.00	66.9

REAGENTS

Manganous sulfate standard solution I, 1.00 ml = 0.100 mg manganese: Heat 0.5 g $MnSO_4 \cdot H_2O$ for 1 hour at 180° C. Dissolve 0.2749 g in demineralized water containing 1 ml concentrated H_2SO_4 (specific gravity 1.84). Add 2.0 ml formalin to inhibit mold growth, and dilute to 1,000 ml with demineralized water.

Manganous sulfate standard solution II, 1.00 ml = 0.010 mg manganese: Immediately before use, dilute 10 ml of $MnSO_4$ standard solution I to 100 ml with demineralized water.

Manganous sulfate standard working solutions: Prepare a series of standard solutions containing from 0.00 to 1.0 mg manganese per liter by diluting the $MnSO_4$ standard solution II.

PROCEDURE

1. Filter the sample (0.45 μ micropore membrane filter) when necessary to avoid clogging the atomizer burner.
2. Atomize each sample and standard, and record the scale reading observed. Repeat, and average the two values.

CALCULATIONS

1. Determine the manganese concentration in the sample from a plot of scale readings of standards. Because a scale expansion of 10 × is used, the scale readings need not be converted to absorbance. Exact reproducibility is not obtained, and a working curve must be prepared with each set of samples.
2. $$\text{ppm manganese} = \frac{1}{\text{density}} \times \text{mg manganese per liter.}$$

   Report manganese concentrations less than 1.0 ppm to the nearest 0.01 ppm and those greater than 1.0 ppm to two significant figures.

POTASSIUM

DISCUSSION OF METHOD

A vapor-discharge lamp operating at 350 ma is used to determine potassium. Some lamps may require a source current of 500 ma if the potassium arc is unstable, if absorption values are low, or if there is excessive noise. Additional current often produces considerably more light, and a smaller slit width may be required.

The 7665 A line is used to determine potassium. Only sodium interferes, and approximately equivalent amounts of sodium must be present in both standards and samples. At any given sodium concentration up to 1,000 mg per l, the actual sodium concentration may vary by as much as ±50 mg per l without a significant effect on the amount of potassium observed. Therefore, 200 mg sodium per liter is added to each standard, and each sample is so prepared that its sodium concentration is between 150 and 250 mg per l. Results are accurate and reproducible to ±0.1 mg per l for potassium concentrations of less than 10 mg potassium per liter, and to ±0.1–±1.0 mg per l for concentrations of potassium from 10 to 100 mg per l. When excessive dilution is required, the accuracy and reproducibility are decreased. With scale expansion, results are accurate and reproducible to ±0.01 mg per l for potassium concentrations of less than 1 mg per l.

The sensitivity for potassium concentrations of less than 10 mg per l is approximately 0.1 mg per l per 1 percent absorption.

The atomic absorption method is applicable to a wide range of potassium concentrations, such as traces in rainwater and as much as 7,000 mg per l in brines. For samples containing concentrations of potassium greater than 10 mg per l, dilution is required.

APPARATUS

Grating: Visible
Wavelength counter: 383.2 (7665 A)
Scale: 1 ×
Slit: 5 (3 mm, 40 A)
Source: Osram potassium-vapor-discharge lamp
Lamp current: 350 ma, or optimum operating current
Air pressure: 28 psi; 9.0 on flowmeter (varies with different flowmeters and burners)
Fuel: Acetylene. Pressure: 8 psi; 9.0 on flowmeter
Flame: Oxidizing
Sample uptake: About 4 ml per min
The following absorption readings have been observed:

Potassium concentration, mg per l	*Absorption, percent*
2.0	21.5
4.0	37.2
6.0	48.7
8.0	57.3
10	63.3

REAGENTS

Potassium chloride standard stock solution, 1.00 ml=0.10 mg potassium: Dissolve 0.1907 g KCl in demineralized water and dilute to 1,000 ml.

Potassium chloride standard working solutions: Prepare a series of standard solutions containing from 0 to 10 mg potassium and 200 mg sodium per liter by diluting the potassium standard stock solution and the NaCl standard stock solution.

Sodium chloride standard stock solution, 1.00 ml=1.00 mg sodium: Dissolve 2.542 g NaCl in demineralized water and dilute to 1,000 ml.

PROCEDURE

1. Filter the sample (0.45 μ micropore membrane filter) when necessary to avoid clogging the atomizer-burner.
2. Adjust the sodium concentration of each sample to between 150 and 250 mg per l by adding the calculated volume of the NaCl standard stock solution.
3. Atomize each sample and standard, and record the percent absorption observed. Repeat, and average the two values. If the concentration is greater than 10 mg per l, the sample must be diluted. Be sure that the diluted sample contains between 150 and 250 mg sodium per liter.

CALCULATIONS

1. Convert percent absorption to absorbance, and determine the potassium concentration in the sample from a plot of absorbances of standards. For samples containing more than 10 mg potassium per liter, multiply by the proper dilution factor. Also, if the sample was adjusted to contain between 150 and 250 mg sodium per liter, multiply by the proper dilution factor. Exact reproducibility is not obtained, and a working curve must be prepared with each set of samples.
2. $\text{ppm potassium} = \frac{1}{\text{density}} \times \text{mg potassium per liter}$.

Report potassium concentrations less than 10 ppm to the nearest 0.1 ppm, those between 10 and 1,000 ppm to the nearest whole number, and those greater than 1,000 ppm to three significant figures.

SODIUM

DISCUSSION OF METHOD

A vapor-discharge lamp is used to determine sodium. The exact slit width and lamp current differs with the lamp used. The lamp current should be increased until the color of the arc is the characteristic yellow orange of the sodium discharge. Additional current often produces considerably more light and a smaller slit width may be required; a decrease in current has the opposite effect.

To avoid excessive dilution of the sample, two sodium lines are used. For waters containing less than 10 mg sodium per liter, the 5890 A line is used, and for those containing more than 10 mg per l, the weaker resonance line at 3302 A is used. Two working curves are prepared for the 3302 A line: one for the sodium concentration range 6–60 mg per l, and another for the range 40–200 mg sodium per liter.

Other elements found in water do not interfere, and the results are accurate and reproducible to ±0.1 mg per l for sodium concentrations of less than 10 mg per l, and to ±1–±2 mg per l for sodium concentrations between 10 and 200 mg per l.

The sensitivity for sodium concentrations of less than 10 mg per l is approximately 0.05 mg per l per 1 percent absorption; for concentrations between 10 and 40 mg per l, approximately 1 mg per l for each scale division; and concentrations greater than 40 mg per l, about 3 mg per l for each scale division.

The atomic absorption method is applicable to a wide range of sodium concentrations—from traces in rainwater and to 100,000 mg per l in brines. For samples containing more than 200 mg per l, dilution is required.

APPARATUS

Concentration range: 0.0–10 mg sodium per liter
Grating: Visible
Wavelength counter: 294.4 (5888 A)
Scale: 1 ×
Slit: 3 (0.3 mm, 4.0 A)
Source: Osram sodium-vapor discharge lamp
Lamp current: 900 ma, or optimum operating current
Air pressure: 28 psi; 9.0 on flowmeter (varies with different flowmeters and burners)
Fuel: Acetylene. Pressure: 8 psi; 9.0 on flowmeter
Flame: Oxidizing
Sample uptake: About 4 ml per min

The following absorption readings have been observed:

Sodium concentration, mg per l	*Absorption, percent*
2.0	40.2
4.0	63.3
6.0	76.8
8.0	84.7
10	89.4

Concentration range: 6–60 mg sodium per liter
Grating: Ultraviolet
Wavelength counter: 330.2 (3302 A)
Scale: 5 ×
Slit: 4 (1 mm, 13 A)
All other operating conditions same as used for concentration range 0.0–10 mg sodium per liter.

The following readings have been observed:

Sodium concentration, mg per l	*Scale reading*
6.0	7.3
10	11.4
20	21.0
40	38.4
60	56.6

Concentration range: 40–200 mg sodium per liter

Grating: Ultraviolet

Wavelength counter: 330.2 (3302 A)

Scale: 2×

Slit: 4 (1 mm, 13 A)

All other operating conditions same as used for concentration range 0.0 – 10 mg sodium per liter.

The following absorption readings have been observed:

Sodium concentration, mg per l	*Scale reading*	*Absorption, percent*
40	16.0	8.0
60	23.6	11.8
80	29.8	14.9
100	36.6	18.3
150	52.2	26.1
200	65.6	32.8

REAGENTS

Sodium chloride standard stock solution, 1.00 ml = 1.00 mg sodium: Dissolve 2.542 g NaCl in demineralized water and dilute to 1,000 ml.

Sodium chloride standard working solutions: Prepare a series of standard solutions containing from 0 to 200 mg sodium per liter by diluting the NaCl standard stock solution.

PROCEDURE

1. Filter the sample (0.45 μ micropore membrane filter) when necessary to avoid clogging the atomizer-burner.
2. Atomize each sample and standard, and record the percent absorption or scale reading observed. Repeat, and average the two values. If the sodium concentration is greater than 200 mg per l, the sample must be diluted.

CALCULATIONS

1. Concentration range 0.0–10 mg sodium per liter: Convert percent absorption to absorbance, and determine the sodium concentration in the sample from a plot of absorbances of standards.
2. Concentration range 6–60 mg sodium per liter: Determine the sodium concentration in the sample from a plot of scale readings

of standards. Because a scale expansion of 5 × is used, scale readings need not be converted to absorbance.

3. Concentration range 40–200 mg sodium per liter: Divide the scale reading by 2 to obtain percent absorption. Convert to absorbance, and determine the sodium concentration in the sample from a plot of absorbances of standards. For samples containing more than 200 mg sodium per liter, multiply by the proper dilution factor. Exact reproducibility is not obtained, and working curves must be prepared with each set of samples.
4. $\text{ppm sodium} = \frac{1}{\text{density}} \times \text{mg sodium per liter.}$

   Report sodium concentrations less than 10 ppm to the nearest 0.1 ppm, those between 10 and 1,000 ppm to the nearest whole number, and those greater than 1,000 ppm to three significant figures.

STRONTIUM

DISCUSSION OF METHOD

A hollow-cathode lamp and a reducing flame are used to determine strontium. Sodium and potassium decrease the strontium ionization in the flame. This effect levels off above concentrations of 100 ppm of either sodium or potassium. To control the ionization, 1,000 ppm of potassium is added to both standards and samples. Aluminum, phosphate, and silica interfere but are masked by the addition of lanthanum. No interferences occur for concentrations of up to 50 ppm nitrate and 2,000 ppm each of sulfate, magnesium, and calcium. Above 2,500 ppm total dissolved solids, and depending upon the ratio of strontium to total dissolved solids present, low strontium values result even in the presence of potassium and lanthanum. Therefore, the standard-addition technique must be used for highly mineralized waters or for brines containing more than 2,500 ppm total dissolved solids.

The 4607 A line is used to determine concentrations of strontium less than 20 mg per l. Two working curves are required. Results are accurate and reproducible to approximately ±0.02 mg per l for the concentration range 0.00–1.0 mg strontium per liter. For the concentration range 1.0–20 mg per l, results are accurate and reproducible to approximately ±0.1 mg per l for concentrations less than 10 mg per l, and to approximately ±0.5 mg per l for concentrations greater than 10 mg per l.

The sensitivity for strontium concentrations of less than 1.0 mg per l is approximately 0.02 mg per l for each scale division, and for concentrations between 1 and 20 mg per l, approximately 0.2–0.3 mg per l per 1 percent absorption.

APPARATUS

Concentration range: 1.0–20 mg strontium per liter
Grating: Visible
Wavelength counter: 230.4 (4607 A)
Scale: 1 ×
Slit: 4 (1 mm, 13 A)
Source: Strontium hollow-cathode lamp
Lamp current: 15 ma
Air pressure: 28 psi; 8.0 on flowmeter
Fuel: Acetylene. Pressure: 8 psi, 9.0 on flowmeter initially (use a 10 mg strontium per liter standard solution and adjust acetylene flow rate to obtain maximum absorption)
Flame: Reducing
Sample uptake: About 4 ml per min

The following absorption readings have been observed:

Strontium concentration, mg per l	*Absorption, percent*
1.0	5.6
5.0	24.5
10	41.5
15	53.0
20	62.6

Concentration range: 0.00–1.0 mg strontium per liter
Scale: 10 ×
Response-time control: 1
All other operating conditions same as used for concentration range 1.0–20 mg strontium per liter.

The following readings have been observed:

Strontium concentration, mg per l	*Scale reading*
0.10	5.3
.50	26.2
1.0	52.4

REAGENTS

Lanthanum chloride–potassium chloride solution: Dissolve 117.3 g La_2O_3 in a minimum amount of dilute HCl. Add 19.1 g KCl, and dilute to 1,000 ml with distilled water.

Strontium chloride standard stock solution, 1.00 ml=0.10 mg strontium: Dissolve 0.1684 g of $SrCO_3$ in a minimum amount of dilute HCl, and dilute to 1,000 ml.

Strontium chloride standard working solutions: Prepare a series of solutions containing from 0 to 20 mg strontium per liter by diluting the $SrCl_2$ standard stock solution. Add 1.0 ml of $LaCl_3$–KCl solution to each 10.0 ml of the working standards prepared. For example, to 500 ml of a working standard, add 50 ml $LaCl_3$–KCl solution.

PROCEDURE

1. Filter the sample (0.45 μ micropore membrane filter) when necessary to avoid clogging the atomizer-burner.
2. Add 1.0 ml $LaCl_3$–KCl solution to 10.0 ml of sample.
3. Atomize each sample and standard, and record the percent absorption or scale reading observed. Repeat, and average the two values. If the strontium concentration is greater than 20 mg per l, the sample must be diluted. Be sure that the diluted sample contains the proper amount of $LaCl_3$–KCl solution.

CALCULATIONS

1. Concentration range 1.0–20 mg strontium per liter: Convert percent absorption to absorbance, and determine the strontium concentration in the sample from a plot of absorbances of standards. For samples containing more than 20 mg per l, multiply by proper dilution factor.
2. Concentration range 0.00–1.0 mg strontium per liter: Determine the strontium concentration in the sample from a plot of scale readings of standards. Because a scale expansion of 10 × is used, scale readings need not be converted to absorbance. Exact reproducibility is not obtained, and working curves must be prepared with each set of samples.
3. $\text{ppm strontium} = \frac{1}{\text{density}} \times \text{mg strontium per liter.}$

   Report strontium concentrations less than 1.0 ppm to the nearest 0.01 ppm, those between 1.0 and 10 ppm to the nearest 0.1 ppm, and those greater than 10 ppm to the nearest whole number.

ZINC

DISCUSSION OF METHOD

A hollow-cathode lamp is used to determine zinc. The lamp should be allowed to warm up for about 30 minutes at a current of 12 ma before use. The lamp current is then optimized by adjusting the source control to obtain a minimum noise level (not more than one or two divisions on the null meter). The final setting should be between 10 and 15 ma and should not exceed the maximum stated on the lamp because the cathode will begin to melt.

The 2138 A line is used to determine zinc. Of the cations and anions normally found in water, only magnesium interferes. Magnesium concentrations greater than 100 ppm interfere unless other cations, such as sodium, are present in the sample. There is currently no explanation for this phenomenon.

To determine zinc at concentrations of less than 0.4 mg per l, 10 × scale expansion is used, and results are accurate and reproducible to approximately ±0.02 mg per l. Concentrations of zinc greater than 0.4 mg per l can be determined by using less scale expansion. The maximum concentration that can be determined at the 2138 A line without dilution is 10 mg zinc per liter.

The sensitivity for concentrations of zinc of less than 0.4 mg per l is approximately 0.005 mg per l for each scale division.

APPARATUS

Grating: Ultraviolet
Wavelength counter: 213.8 (2138 A)
Scale: 10 ×
Slit: 5 (3 mm, 20 A)
Source: Zinc hollow-cathode lamp
Lamp current: 12 ma, or optimum operating current
Air pressure: 30 psi; 9.0 on flowmeter (varies with different flowmeters and burners)
Fuel: Acetylene. Pressure: 8 psi, 9.0 on flowmeter
Flame: Oxidizing
Sample uptake: 2–5 ml per min
Response-time control: 1 or 2

The following readings have been observed:

Zinc concentration, mg per l	*Scale reading*
0.10	18.2
.20	35.6
.30	50.5
.40	68.2

REAGENTS

Zinc chloride standard solution I, 1.00 ml=0.100 mg zinc: Dissolve 0.100 mg reagent-grade zinc (30-mesh) in a slight excess of HCl, and dilute to 1,000 ml with demineralized water.

Zinc chloride standard solution II, 1.00 ml=0.100 mg zinc: Immediately before use, dilute 10 ml of $ZnCl_2$ standard solution I to 100 ml with demineralized water.

Zinc chloride standard working solutions: Prepare a series of standard solutions containing from 0.00 to 0.40 mg zinc per liter by diluting the $ZnCl_2$ standard solution II.

PROCEDURE

1. Filter the sample (0.45μ micropore membrane filter) when necessary to avoid clogging the atomizer-burner.

2. Atomize each sample and standard, and record the scale reading observed. Repeat, and average the two values.

CALCULATIONS

1. Determine the zinc concentration in the sample from a plot of scale readings of standards. Because a scale expansion of 10 × is used, scale readings need not be converted to absorbance. Exact reproducibility is not obtained, and a working curve must be prepared with each set of samples.
2. $\text{ppm zinc} = \frac{1}{\text{density}} \times \text{mg zinc per liter}$.

   Report zinc concentrations less than 1.0 ppm to the nearest 0.01 ppm and those greater than 1.0 ppm to two significant figures.

REFERENCES

Perkin-Elmer Corp., 1964, Analytical methods for atomic absorption spectrophotometry: Norwalk, Conn.

Walsh, Allan, 1955, The application of atomic absorption spectra to chemical analysis: Spectrochim. Acta, v. 7, p. 108–117.