

# START

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# STANDARD METHODS

## For the Examination of Water and Wastewater

FIFTEENTH EDITION

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note:  
This is the only  
procedure from the Standard  
Methods in Table 1  
(Bismuth - SAP/QAPP-9).

There is a  $\theta$  suppressant  
for 1,1-dichloroethene  
(SAP/QAPP-10) but that  
is wrong - it should be f.

9  
2  
1  
2  
5  
6  
1  
2  
0  
0  
9



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### 303 A. Determination of Antimony, Bismuth, Cadmium\*, Calcium, Cesium, Chromium\*, Cobalt\*, Copper, Gold, Iridium, Iron\*, Lead\*, Lithium, Magnesium, Manganese\*, Nickel\*, Platinum, Potassium, Rhodium, Ruthenium, Silver\*, Sodium, Strontium, Thallium, Tin, and Zinc\* by Direct Aspiration into an Air-Acetylene Flame

#### 1. Apparatus

*Atomic absorption spectrophotometer and associated equipment:* See Section 303.2. Use burner head recommended by the manufacturer.

\*For low concentrations of Cd, Cr, and Pb (<50, 200, and 500  $\mu\text{g/L}$  respectively) and Co, Fe, Mn, Ni, Ag, and Zn, see Section 303B.

#### 2. Reagents

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

b. *Acetylene*, standard commercial grade. Acetone, which always is present in acetylene cylinders, can be prevented

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of Antimony, Bismuth,  
ium, Chromium\*, Cobalt\*,  
Lead\*, Lithium, Magnesium,  
ium, Potassium, Rhodium,  
r, Strontium, Thallium, Tin,  
into an Air-Acetylene Flame

## 2. Reagents

- a. *Air*, cleaned and dried through a suitable filter to remove oil, water, and other foreign substances. The source may be a compressor or commercially bottled gas.
- b. *Acetylene*, standard commercial grade. Acetone, which always is present in acetylene cylinders, can be prevented

from entering and damaging the burner head by replacing a cylinder when its pressure has fallen to 689 kPa acetylene.

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

d. *Calcium solution*: Dissolve 630 mg calcium carbonate,  $\text{CaCO}_3$ , in 50 mL of 1 + 5 HCl. If necessary, heat and boil gently to obtain complete solution. Cool and dilute to 1,000 mL with water.

e. *Hydrochloric acid*, HCl, conc.

f. *Lanthanum solution*: Dissolve 58.65 g lanthanum oxide,  $\text{La}_2\text{O}_3$ , in 250 mL conc HCl. Add acid slowly until the material is dissolved and dilute to 1,000 mL with water.

g. *Hydrogen peroxide*, 30%.

h. *Nitric acid*,  $\text{HNO}_3$ , conc.

i. *Aqua regia*: Add 3 volumes conc HCl to 1 volume conc  $\text{HNO}_3$ .

j. *Iodine solution, 1N*: Dissolve 20 g potassium iodide, KI, in 50 mL water, add 12.7 g iodine, and dilute to 100 mL.

k. *Cyanogen iodide (CNI) solution*: To 50 mL water add 6.5 g potassium cyanide, KCN, 5.0 mL 1N iodine solution, and 4.0 mL conc  $\text{NH}_4\text{OH}$ . Mix and dilute to 100 mL with water. Prepare fresh solution every 2 wk.

l. *Standard metal solutions*: Prepare a series of standard metal solutions in the optimum concentration range by appropriate dilution of the following stock metal

solutions with water containing 1.5 mL conc  $\text{HNO}_3/\text{L}$ . Thoroughly dry reagents before use. In general, use reagents of the highest purity. For hydrates, use fresh reagents.

1) *Antimony*: Dissolve 2.7426 g antimony potassium tartrate hemihydrate (analytical reagent grade),  $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$ , in 1,000 mL water; 1.00 mL = 1.00 mg Sb.

2) *Bismuth*: Dissolve 1.000 g bismuth metal in a minimum volume of 1 + 1  $\text{HNO}_3$ . Dilute to 1,000 mL with 2% (v/v)  $\text{HNO}_3$ ; 1.00 mL = 1.00 mg Bi.

3) *Cadmium*: Dissolve 1.000 g cadmium metal in a minimum volume of 1 + 1 HCl. Dilute to 1,000 mL with water; 1.00 mL = 1.00 mg Cd.

4) *Calcium*: To 2.4972 g  $\text{CaCO}_3$  add 50 mL water and add dropwise a minimum volume of conc HCl (about 10 mL) to complete solution. Dilute to 1,000 mL with water; 1.00 mL = 1.00 mg Ca.

5) *Cesium*: Dissolve 1.267 g cesium chloride, CsCl, in 1,000 mL water; 1.00 mL = 1.00 mg Cs.

6) *Chromium*: Dissolve 2.828 g anhydrous potassium dichromate,  $\text{K}_2\text{Cr}_2\text{O}_7$ , in about 200 mL water, add 1.5 mL conc  $\text{HNO}_3$ , and dilute to 1,000 mL with water; 1.00 mL = 1.00 mg Cr.

7) *Cobalt*: Dissolve 1.407 g cobaltic oxide,  $\text{Co}_2\text{O}_3$ , in 20 mL hot conc HCl. Cool and dilute to 1,000 mL with water; 1.00 mL = 1.00 mg Co.

8) *Copper*: Dissolve 1.000 g copper metal in 15 mL of 1 + 1  $\text{HNO}_3$  and dilute to 1,000 mL with water; 1.00 mL = 1.00 mg Cu.

9) *Gold*: Dissolve 0.1000 g gold metal in a minimum volume of aqua regia. Evaporate to dryness, dissolve residue in 5 mL conc HCl, cool, and dilute to 100 mL with water; 1.00 mL = 1.00 mg Au.

10) *Iridium*: Dissolve 1.147 g ammonium chloroiridate,  $(\text{NH}_4)_2\text{IrCl}_6$ , in a minimum volume of 1% (v/v) HCl and dilute to 100

mL with 1% (v/v) HCl; 1.00 mL = 5.00 mg Ir.

11) *Iron*: Dissolve 1.000 g iron wire in 50 mL of 1 + 1 HNO<sub>3</sub> and dilute to 1,000 mL with water; 1.00 mL = 1.00 mg Fe.

12) *Lead*: Dissolve 1.598 g lead nitrate, Pb(NO<sub>3</sub>)<sub>2</sub>, in about 200 mL water, add 1.5 mL conc HNO<sub>3</sub>, and dilute to 1,000 mL with water; 1.00 mL = 1.00 mg Pb.

13) *Lithium*: Dissolve 5.324 g lithium carbonate, Li<sub>2</sub>CO<sub>3</sub>, in a minimum volume of 1 + 1 HCl and dilute to 1,000 mL with water; 1.00 mL = 1.00 mg Li.

14) *Magnesium*: Dissolve 4.952 g magnesium sulfate, MgSO<sub>4</sub>, in 200 mL water, add 1.5 mL conc HNO<sub>3</sub>, and dilute to 1,000 mL with water; 1.00 mL = 1.00 mg Mg.

15) *Manganese*: Dissolve 3.076 g manganous sulfate, MnSO<sub>4</sub>·H<sub>2</sub>O, in about 200 mL water, add 1.5 mL conc HNO<sub>3</sub>, and dilute to 1,000 mL with water; 1.00 mL = 1.00 mg Mn.

16) *Nickel*: Dissolve 1.273 g nickel oxide, NiO, in a minimum volume of 10% (v/v) HCl and dilute to 1,000 mL with water; 1.00 mL = 1.00 mg Ni.

17) *Platinum*: Dissolve 0.1000 g platinum metal in a minimum volume of aqua regia and evaporate just to dryness. Add 5 mL conc HCl and 0.1 g NaCl and again evaporate just to dryness. Dissolve residue in 20 mL of 1 + 1 HCl and dilute to 100 mL with water; 1.00 mL = 1.00 mg Pt.

18) *Potassium*: Dissolve 1.907 g potassium chloride, KCl, in water and make up to 1,000 mL; 1.00 mL = 1.00 mg K.

19) *Rhodium*: Dissolve 0.412 g ammonium hexachlororhodate, (NH<sub>4</sub>)<sub>3</sub>RhCl<sub>6</sub>·1.5 H<sub>2</sub>O, in a minimum volume of 10% (v/v) HCl and dilute to 100 mL with 10% (v/v) HCl; 1.00 mL = 1.00 mg Rh.

20) *Ruthenium*: Dissolve 0.2052 g ruthenium chloride, RuCl<sub>3</sub>, in a minimum volume of 20% (v/v) HCl and dilute to 100 mL with 20% (v/v) HCl; 1.00 mL = 1.00 mg Ru.

21) *Silver*: Dissolve 1.575 g silver ni-

trate, AgNO<sub>3</sub>, in water, add 1.5 mL conc HNO<sub>3</sub>, and make up to 1,000 mL; 1.00 mL = 1.00 mg Ag.

22) *Sodium*: Dissolve 2.542 g sodium chloride, NaCl, dried at 140 C, in water and make up to 1,000 mL; 1.00 mL = 1.00 mg Na.

23) *Strontium*: Dissolve 2.415 g strontium nitrate, Sr(NO<sub>3</sub>)<sub>2</sub>, in 1,000 mL of 1% (v/v) HNO<sub>3</sub>; 1.00 mL = 1.00 mg Sr.

24) *Thallium*: Dissolve 1.303 g thallium nitrate, TlNO<sub>3</sub>, in water. Add 10 mL conc HNO<sub>3</sub> and dilute to 1,000 mL with water; 1.00 mL = 1.00 mg Tl.

25) *Tin*: Dissolve 1.000 g tin metal in 100 mL conc HCl and dilute to 1,000 mL with water; 1.00 mL = 1.00 mg Sn.

26) *Zinc*: Dissolve 1.000 g zinc metal in 20 mL 1 + 1 HCl and dilute to 1,000 mL with water; 1.00 mL = 1.00 mg Zn.

### 3. Procedure

*a. Instrument operation*: Because of differences between makes and models of atomic absorption spectrophotometers, it is not possible to formulate instructions applicable to every instrument. See manufacturer's operating manual. In general, proceed according to the following: Install a hollow cathode lamp for the desired metal in the instrument and roughly set the wavelength dial according to Table 303-I. Set slit width according to manufacturer's suggested setting for the element being measured. Turn on instrument, apply to the hollow cathode lamp the current suggested by the manufacturer, and let instrument warm up until energy source stabilizes, generally about 10 to 20 min. Re-adjust current as necessary after warmup. Optimize wavelength by adjusting wavelength dial until optimum energy gain is obtained. Align lamp in accordance with manufacturer's instructions.

Install suitable burner head and adjust burner head position. Turn on air and adjust flow rate to that specified by manufacturer to give maximum sensitivity for the

te,  $\text{AgNO}_3$ , in water, add 1.5 mL conc  $\text{HNO}_3$ , and make up to 1,000 mL; 1.00 mL = 1.00 mg Ag.

22) *Sodium*: Dissolve 2.542 g sodium chloride,  $\text{NaCl}$ , dried at 140 C, in water and make up to 1,000 mL; 1.00 mL = 1.00 mg Na.

23) *Strontium*: Dissolve 2.415 g strontium nitrate,  $\text{Sr}(\text{NO}_3)_2$ , in 1,000 mL of 1% (v)  $\text{HNO}_3$ ; 1.00 mL = 1.00 mg Sr.

24) *Thallium*: Dissolve 1.303 g thallium nitrate,  $\text{TlNO}_3$ , in water. Add 10 mL conc  $\text{HNO}_3$  and dilute to 1,000 mL with water; 1.00 mL = 1.00 mg Tl.

25) *Tin*: Dissolve 1.000 g tin metal in 10 mL conc  $\text{HCl}$  and dilute to 1,000 mL with water; 1.00 mL = 1.00 mg Sn.

26) *Zinc*: Dissolve 1.000 g zinc metal in 10 mL 1 + 1  $\text{HCl}$  and dilute to 1,000 mL with water; 1.00 mL = 1.00 mg Zn.

#### Procedure

*Instrument operation*: Because of differences between makes and models of flame atomic absorption spectrophotometers, it is not possible to formulate instructions applicable to every instrument. See manufacturer's operating manual. In general, proceed according to the following: Install hollow cathode lamp for the desired metal in the instrument and roughly set the wavelength dial according to Table 303.1. Adjust slit width according to manufacturer's suggested setting for the element being measured. Turn on instrument, apply to hollow cathode lamp the current suggested by the manufacturer, and let instrument warm up until energy source stabilizes, generally about 10 to 20 min. Reset current as necessary after warmup. Optimize wavelength by adjusting wavelength dial until optimum energy gain is obtained. Align lamp in accordance with manufacturer's instructions.

Install suitable burner head and adjust burner head position. Turn on air and adjust flow rate to that specified by manufacturer to give maximum sensitivity for the

metal being measured. Turn on acetylene, adjust flow rate to value specified, and ignite flame. Aspirate a standard solution and adjust aspiration rate of the nebulizer to obtain maximum sensitivity. Atomize a standard (usually one near the middle of the linear working range) and adjust burner both up and down and sideways to obtain maximum response. Record absorbance of this standard when freshly prepared and with a new hollow cathode lamp. Refer to these data on subsequent determinations of the same element to check consistency of instrument setup and aging of hollow cathode lamp and standard.

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

*b. Standardization*: Select at least three concentrations of each standard metal solution (prepared as in ¶21 above) to bracket the expected metal concentration of a sample. Aspirate each in turn into flame and record absorbance. For calcium and magnesium calibration, mix 100 mL of standard with 10 mL lanthanum solution (see ¶2f above) before aspirating. For chromium calibration mix 1 mL 30%  $\text{H}_2\text{O}_2$  with each 100 mL chromium solution before aspirating. For iron and manganese calibration, mix 100 mL of standard with 25 mL calcium solution (¶2d) before aspirating.

Prepare a calibration curve by plotting on linear graph paper absorbance of standards versus their concentrations. For instruments equipped with direct concentration readout, this step is unnecessary. With some instruments it may be necessary to convert percent absorption to absorbance by using a table generally provided by the manufacturer. Plot calibration

curves for calcium and magnesium based on original concentration of standards before dilution with lanthanum solution. Plot calibration curves for iron and manganese based on original concentration of standards before dilution with calcium solution. Plot calibration curve for chromium based on original concentration of standard before addition of  $\text{H}_2\text{O}_2$ .

Check standards periodically during a run. Recheck calibration curve by aspirating at least one standard after completing analysis of a group of samples. For instruments with built-in memory, enter one to three standards to register a calibration curve for use in subsequent sample analysis.

*c. Analysis of samples*: Rinse nebulizer by aspirating water containing 1.5 mL conc  $\text{HNO}_3/\text{L}$ . Atomize blank and zero instrument. Atomize sample and determine its absorbance.

When determining calcium or magnesium, dilute and mix 100 mL sample with 10 mL lanthanum solution (¶2f) before atomization. When determining iron or manganese, mix 100 mL with 25 mL of calcium solution (¶2d) before aspirating. When determining chromium, mix 1 mL 30%  $\text{H}_2\text{O}_2$  with each 100 mL sample before aspirating.

Analyze standards at the beginning and end of a run and at intervals during longer runs. Run a blank or solvent between each sample or standard to verify baseline stability. Determine metal concentration from calibration curve.

#### 4. Calculations

Calculate concentration of each metal ion, in micrograms per liter, by referring to the appropriate calibration curve prepared according to ¶3b.