

## 11.1.26

**AOAC Official Method 974.27**  
**Cadmium, Chromium,**  
**Copper, Iron, Lead, Magnesium,**  
**Manganese, Silver, and Zinc in Water**  
**Atomic Absorption Spectrophotometric Method**  
**First Action 1974**  
**Final Action 1984**

**A. Principle**

Metals in solution are determined directly by atomic absorption (AA) spectrophotometry; suspended metals are separated by membrane filtration, or suspension is dissolved and analyzed; Pb and Cd in low concentration are chelated, concentrated, and then extracted with organic solvent prior to AA determination. Applicable to surface and saline waters, and domestic and industrial wastes. Three synthetic water specimens containing between 0.05 and 1.0 mg each metal/L analyzed by 8–23 laboratories showed results given in Table 974.27A.

**B. Apparatus**

(Use Pyrex, quartz, or Teflon labware exclusively; clean thoroughly with detergent and H<sub>2</sub>O; soak in HNO<sub>3</sub> [1 + 1] for 1 week; rinse with H<sub>2</sub>O, dilute HNO<sub>3</sub>, and H<sub>2</sub>O, in that order. Use deionized, distilled water whenever H<sub>2</sub>O is specified.)

*AA spectrophotometer.*—Spectrophotometer operating at conditions given in Table 974.27B. Operator must become familiar with settings and operations of the instrument, using table only as guide. Use Boling burner for aqueous solutions, and premix burner with solvent.

**C. Reagents**

(a) *Deionized distilled water.*—See 973.48C(a) (see 11.1.11).

(b) *Nitric acid.*—Dilute 500 mL redistilled HNO<sub>3</sub> to 1 L with H<sub>2</sub>O. (*Caution:* Perform distillation in hood with protective sash in place.)

(c) *Hydrochloric acid.*—Dilute 500 mL HCl to 1 L with H<sub>2</sub>O and distil in all-Pyrex apparatus.

(d) *Metal standard solutions.*—(1) *Stock solutions.*—Accurately weigh amount of metal specified in Table 974.27C into beaker and add dissolving medium. When metal is completely dissolved, transfer quantitatively to 1 L volumetric flask and dilute to volume with H<sub>2</sub>O. (2) *Working solutions.*—Prepare daily. Dilute aliquots of stock solutions with H<sub>2</sub>O to make 4 standard solutions of each element within range of determination, Table 974.27B. Add 1.5 mL HNO<sub>3</sub>/L to all working standard solutions before diluting to volume. Add 1 mL LaCl<sub>3</sub>/10 mL Mg working standard solution.

(e) *Lanthanum stock solution.*—50 g La/L ca 5% HCl. Slowly add 250 mL HCl to 58.65 g La<sub>2</sub>O<sub>3</sub> (99.99%, Alfa Aesar, 26 Parkridge Rd, Ward Hill, MA 01835, USA; www.alfa.com; or equivalent), dissolve, and dilute to 1 L.

(f) *Ammonium pyrrolidine dithiocarbamate (APDC) solution.*—Dissolve 1 g APDC in 100 mL H<sub>2</sub>O. Prepare fresh daily.

**D. Preparation of Specimen**

(a) *Dissolved metals.*—As soon as practicable after collection, filter known volume of the specimen through 0.45 μm membrane. Use first 50–100 mL to rinse flask and discard. Collect filtrate and preserve solution by adding 3 mL HNO<sub>3</sub> (1 + 1)/L.

**Table 974.27A. Bias and standard deviations of determination of metals by atomic absorption**

Metal	Added, mg/L	Standard deviation		Bias	
		%	mg/L	%	mg/L
Cd	0.01	53	0.007	+27.5	+0.003
	0.01 (extrn)	61	0.006	0.0	0.0
	0.05	8	0.004	+2.0	+0.001
	0.05 (extrn)	10	0.005	+1.2	+0.001
	0.10	8	0.008	+3.4	+0.003
	0.10 (extrn)	52	0.045	−15.0	−0.015
Cr	0.05	26	0.013	−2.3	−0.001
	0.10	22	0.021	−2.9	−0.003
	0.20	12	0.024	−3.0	−0.006
Cu	0.05	42	0.023	+8.3	+0.004
	0.25	8	0.020	+2.2	+0.006
	1.00	6	0.060	+0.6	+0.006
Fe	0.10	34	0.032	−5.3	−0.005
	0.30	18	0.050	−5.0	−0.015
	0.50	6	0.031	+1.1	+0.006
Pb	0.05	76	0.036	−5.0	−0.002
	0.05 (extrn)	53	0.028	+3.0	+0.002
	0.10	67	0.057	−16.0	−0.016
	0.10 (extrn)	55	0.053	−5.0	−0.005
Mg	0.20	30	0.052	−14.0	−0.028
	0.20 (extrn)	48	0.088	−8.0	−0.017
	0.05	10	0.006	+8.5	+0.004
	0.10	10	0.011	+8.2	+0.008
Mn	0.20	7	0.014	+5.0	+0.010
	0.05	14	0.007	+6.0	+0.003
	0.25	12	0.030	+4.4	+0.011
Ag	0.50	8	0.043	+1.3	+0.007
	0.05	17	0.010	+10.6	+0.005
	0.10	11	0.010	−7.1	−0.007
Zn	0.20	8	0.016	+7.3	+0.015
	0.05	46	0.021	−9.3	−0.005
	0.50	3	0.016	+1.4	+0.007
	1.00	5	0.051	−0.1	−0.001

(b) *Suspended metals.*—Transfer residue and membrane from (a) to 250 mL beaker and add 3 mL HNO<sub>3</sub>. Cover with watch glass and heat gently to dissolve membrane. Increase heat and evaporate to dryness. Cool, and add 3 mL HNO<sub>3</sub>, and heat until digestion is complete, generally indicated by light colored residue. Add 2 mL HCl (1 + 1), and heat gently to dissolve residue. Wash watch glass and beaker with H<sub>2</sub>O and filter. Wash filter and discard. Dilute filtrate with H<sub>2</sub>O to concentration within range of instrument.

(c) *Total metal.*—Transfer aliquot of well mixed specimen to beaker and add 3 mL HNO<sub>3</sub>. Heat, and evaporate to dryness. (Do not boil.) Continue as in (b), beginning “Cool, and add 3 mL HNO<sub>3</sub>, . . .”.  
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**Table 974.27B. Operating parameters**

Metal	Wavelength, nm	Flame	Optimum range, mg/L
Cd	328.1	Oxidizing air-C <sub>2</sub> H <sub>2</sub>	0.1-2
Cr	357.9	Sl. reducing air-C <sub>2</sub> H <sub>2</sub>	1-200
Cu	324.7	Oxidizing air-C <sub>2</sub> H <sub>2</sub>	0.1-10
Fe	248.3	Oxidizing air-C <sub>2</sub> H <sub>2</sub>	0.1-20
Pb	217.0	Sl. oxidizing air-C <sub>2</sub> H <sub>2</sub>	1-10
Mg <sup>a</sup>	285.2	Reducing air-C <sub>2</sub> H <sub>2</sub>	0.01-2
Mn	279.5	Oxidizing air-C <sub>2</sub> H <sub>2</sub>	0.1-20
Ag	328.1	Oxidizing air-C <sub>2</sub> H <sub>2</sub>	0.1-20
Zn	213.9	Oxidizing air-C <sub>2</sub> H <sub>2</sub>	0.1-2

<sup>a</sup> With 1% La solution.

### E. Determination

(P interference in Mg determination is eliminated by adding La stock solution to test portion and working standard solutions so that final dilutions contain 1% La.)

(a) *General method.*—Set up instrument as in Table 974.27B, or previously established optimum settings. Secondary or less sensitive lines [*Spectrochim. Acta* 17, 710(1961)] may be used to reduce necessary dilution, if desired. Read 4 standard solutions within range before and after each group of 6-12 test solutions, and re-establish 0A each time. Prepare calibration curve from average of each standard before and after test group. Read unknown concentration from plot of A against mg/L.

(b) *Special organic extraction method.*—When Pb or Cd concentration is too low for direct AA determination, transfer specimen aliquot to 250 mL beaker and dilute to 100 mL with H<sub>2</sub>O. Prepare blank and standards in same manner. Adjust pH of test and standard solutions to 2.5 with HCl, using pH meter. Transfer quantitatively to 200 mL volumetric flask, add 2.5 mL APDC solution, and mix. Add 10 mL methyl isobutyl ketone and shake vigorously 1 min. Let layers separate; then add H<sub>2</sub>O until ketone layer is in neck of flask. (Centrifugation may be necessary.) Prepare AA for organic analysis. Aspirate ketone layer and record readings of standards and tests against blank. (Fuel-to-air ratio should be adjusted to as blue a flame as possible, since organic solvent adds to fuel supply.) Prepare calibration curve from average of each standard and read unknown concentration from plot (mg/L).

**Table 974.27C. Preparation of metal standard solutions**

Metal <sup>a</sup>	Weight, g	Compound	Dissolving medium (1 L total)
Cd	1.142	CdO	5 mL redistd HNO <sub>3</sub>
Cr	1.923	CrO <sub>3</sub>	H <sub>2</sub> O + 10 mL redistd HNO <sub>3</sub>
Cu	1.000	Cu, electrolytic	5 mL redistd HNO <sub>3</sub>
Fe	1.000	Fe wire	5 mL redistd HNO <sub>3</sub>
Pb	1.599	Pb(NO <sub>3</sub> ) <sub>2</sub>	H <sub>2</sub> O + 10 mL redistd HNO <sub>3</sub>
Mg	0.829	MgO	10 mL redistd HNO <sub>3</sub> <sup>b</sup>
Mn	1.583	MnO <sub>2</sub>	10 mL HCl
Ag	1.575	AgNO <sub>3</sub>	H <sub>2</sub> O + 10 mL redistd HNO <sub>3</sub>
Zn	1.000	Zn	10 mL HNO <sub>3</sub>

<sup>a</sup> Final concentration = 1000 mg/L except for Mg (500 mg/L).

<sup>b</sup> Add 1 mL La stock solution to 10 mL working standard solution.

### F. Calculations

(a) *General method.*—

$$\text{mg Metal/L} = (\text{mg metal in aliquot/L}) \quad F$$

where F = final dilution/mL aliquot.

(b) *Special extraction method.*—

$$\text{mg Metal/L} = \text{mg metal in aliquot/L}$$

References: Water Metals No. 4, Study No. 30 (1968) Analytical Reference Service, Public Health Service (available from National Technical Information Service, 5285 Port Royal Rd, Springfield, VA 22161, USA, NTIS PB215673/BE).

*JAOAC* 67, 421(1984).

CAS-7440-43-9 (cadmium)  
 CAS-7440-47-3 (chromium)  
 CAS-7440-50-8 (copper)  
 CAS-7439-89-6 (iron)  
 CAS-7439-92-1 (lead)  
 CAS-7439-95-4 (magnesium)  
 CAS-7439-96-5 (manganese)  
 CAS-7440-22-4 (silver)  
 CAS-7440-66-6 (zinc)