

9.2.39

AOAC Official Method 990.08 Metals in Solid Wastes

Inductively Coupled Plasma Atomic Emission Spectrometric Method First Action 1990 Final Action 1993

(Applicable to determination of Al, Sb, As, Ba, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Se, Ag, Na, Tl, V, and Zn in coal fly ash, industrial and electroplating sludges, mine tailings, river sediments, and soils.)

Results of interlaboratory study:

See Table 990.08A for the results of the interlaboratory study.

A. Principle

Method measures element-emitted light by optical spectrometry. Digested materials are nebulized into radio-frequency inductively coupled plasma. Spectra of elements are dispersed by grating spectrometer, and intensities are measured by photomultiplier tubes. Correction for background and interferences is required.

B. Labware Cleaning

Labware can be acid-cleaned by soaking detergent-cleaned ware 2 h in 50% HNO₃, rinsing in water, soaking 2 h in 50% HCl, and rinsing in water. Any alternative procedure shown to minimize blank levels is acceptable. Avoid use of chromic acid for cleaning plastic and when Cr is an analyte.

C. Apparatus

(a) *Inductively coupled plasma emission spectrometer*.—Computer-controlled, with background-correction capacity and radio-frequency generator. Operating conditions: Follow instrument manufacturer's instructions for general guidance. Establish instrument sensitivity, detection limit, precision, linear range, and interference effects for each wavelength used in analysis. Verify that operating conditions satisfy analytical requirements. Record quality control data to confirm instrument performance.

(b) *Conical beakers*.—250 mL.

(c) *Watch glasses*.—To fit 250 mL beakers.

(d) *Filter paper*.—Whatman No. 41, or equivalent.

(e) *Hot plate or steam bath*.

(f) *Centrifuge*.—Optional. Capable of 200 rpm.

D. Reagents

(a) *Water*.—Deionized. Use throughout.

(b) *Nitric acid*.—Concentrated, reagent grade or better, as needs dictate.

(c) *Nitric acid, 50% (v/v)*.—Add 500 mL concentrated HNO₃ to 400 mL water and dilute to 1 L with water.

(d) *Hydrochloric acid*.—Concentrated, reagent grade or better, as needs dictate.

(e) *Hydrochloric acid, 50% (v/v)*.—Add 500 mL concentrated HCl to 400 mL water and dilute to 1 L with water.

(f) *Hydrogen peroxide*.—30%.

(g) *Argon gas*.—Welding grade or better.

(h) *Calibration blank*.—Prepare 1 L by diluting 20 mL 50% HNO₃, (c), and 100 mL 50% HCl, (e), with water, (a).

(i) *Reagent blank*.—Prepare and process the same as for samples, except exclude waste material.

E. Preparation of Standards

(a) *Standard reference solutions*.—Certified mixed-element standards can be purchased from National Institute of Standards and Technology (NIST) or other sources. If mixed-element standards are prepared from single-element solutions, the latter should be analyzed separately to determine contribution of any relevant contaminants or interferences. When mixed standards are prepared, compatibility of cations and anions must be considered in order to produce stable solutions. Prepare concentrations in calibration ranges by diluting portions of mixed standards to 100 mL with 2 mL 50% HNO₃, D(c), 10 mL 50% HCl, D(e), and water, D(a). For Ag concentrations above 2 mg/L, use more than 10 mL 50% HCl per 100 mL. Store diluted standard solutions in acid-cleaned FEP fluorocarbon bottles, unused acid-cleaned polyethylene bottles, or unused acid-cleaned polypropylene bottles.

(b) *Instrument check standard solution*.—Prepare by diluting mixed standards near midpoint of calibrated ranges to 100 mL with 2 mL 50% HNO₃, 10 mL 50% HCl, and water.

(c) *Interference check standard solution*.—Prepare 100 mL of an aqueous solution that contains 2 mL 50% HNO₃ and 10 mL 50% HCl, and (per liter) 500 mg Al, Ca, and Mg, 200 mg Fe, 5 mg Pb, and 1 mg Ba, Be, Cd, Cr, Co, Cu, Mn, Ni, Ag, Tl, V, and Zn. Use to test that interference correction factors yield data within ± 3 standard deviations of calibration means.

(d) *Quality control standard solutions*.—Prepare from reference sources with analyte concentrations near 10 \times instrument detection limits (Table 990.08B), 2 mL 50% HNO₃, 10 mL HCl, and water to 100 mL.

F. Preparation of Samples

Weigh 1–2 g test portion of well-mixed material to nearest 0.01 g (wet weight basis), and transfer to 250 mL beaker. (Performance data provided are based on 2 g portions to assess behavior at upper limit.) To express results on dry weight basis, dry another portion of material to constant weight to determine wet/dry weight ratio, but do not digest and analyze this portion because dried portion could lose analytes during drying, or extractability of analytes could be altered. Add 10 mL 50% HNO₃ to undried test portion and mix. Cover beaker with watch glass, heat to 95°C, and let solution reflux 10–15 min. Let digest cool, add 5 mL concentrated HNO₃, D(b), replace watch glass, and let solution reflux 30 min at 95°C. Let digest cool, add 5 mL concentrated HNO₃, replace watch glass, and let solution reflux another 30 min at 95°C.

Evaporate solution to ca 5 mL without letting any section of beaker bottom go dry (ribbed watch glass allows evaporation and protects beaker contents from dust.) Let solution cool, add 2 mL water and 3 mL 30% H₂O₂, D(f), cover with watch glass, and heat slowly (to avoid losses by excessive reaction) to initiate peroxide reaction. Continue heating beaker until effervescence subsides. Let solution cool, and add 7 mL 30% H₂O₂ in 1 mL portions with warming (so that all samples will receive 10 mL 30% H₂O₂ and reagent blank contribution from H₂O₂ will be constant). Let solution cool, add 5 mL concentrated HCl, D(d), and 10 mL water, cover with watch glass, and let solution reflux additional 15 min without boiling. Let solution cool, dilute to 100 mL with water, and mix. Remove any particulate matter in digest by filtration, centrifugation, or settling. If any analyte level exceeds linear range, dilute digest further with calibration blank solution.

Table 990.08A Interlaboratory study results for extractable metals in wastes [except where “(s)” signifies data for spiked materials]^a

National Institute of Standards and Technology Standard Reference Materials River Sediment 1645 and Estuarine Sediment 1646, and EPA test materials industrial sludge, electroplating sludge, and soil					
Element	Concentration, mg/kg	s _r	s _R	RSD _r , %	RSD _R , %
Al	5057–15590	91–1400	1200–3600	6.1–18	15–32
Sb	70–461(s)	5.0–36	28–260	3.3–21	27–62
As	232.2–285(s)	6.0–23	30–74	2.6–9.0	13–26
Ba	33.3–5130	1.8–520	4.8–1200	3.9–20	7.8–37
Be	42.43–48.1(s)	0.96–5.7	3.0–7.8	2.3–12	7.1–18
Cd	2.52–106	0.38–15	1.1–24	6.7–42	18–53
Ca	3590–73700	150–13000	400–17000	4.2–21	7.7–27
Cr	36.4–30200	2.8–2900	6.4–5800	4.6–9.6	11–22
Co	5.6–16.8	0.29–8.4	1.0–13	3.5–50	12–79
Cu	12.70–708	0.52–52	2.2–91	2.1–7.4	9.4–17
Fe	16000–81000	940–13000	2400–19000	4.3–16	9.9–24
Pb	29.9–12790	4.1–760	12–2100	5.9–14	8.0–39
Mg	1650–26300	120–2200	260–2700	4.1–11	9.7–17
Mn	209.3–697	7.0–88	23–120	3.3–14	8.7–24
Mo	43.6–61.6(s)	1.1–6.5	7.6–21	2.5–10	18–34
Ni	18.1–441	1.0–13	3.0–57	2.9–21	13–29
K	426–3330	31–200	130–580	6.1–15	11–34
Se	348–389(s)	2.5–21	41–68	1.8–6.5	10–18
Ag	39.9–43.4(s)	2.6–14	8.3–15	6.0–34	19–37
Na	311–73700	23–4600	160–12000	3.0–18	9.1–52
Tl	183–229(s)	10–74	39–77	4.6–40	17–42
V	11.50–38.6	0.82–5.4	3.2–12	3.8–32	17–73
Zn	98.8–12990	4.3–820	8.4–1200	2.5–6.3	8.6–14
NIST SRM Coal Fly Ash 1633a					
Al	15000	1100	2800	7.2	19
Sb	154(s)	13	39	8.3	26
As	135.8	7.5	44	5.5	32
Ba	661	18	32	2.8	4.8
Be	2.94	0.25	0.81	8.4	28
Cd	2.36	0.38	1.3	16	55
Ca	4670	130	450	2.8	9.7
Cr	24.2	2.8	6.7	12	28
Co	10.9	1.8	2.6	17	24
Cu	30.3	1.9	4.7	6.2	16
Fe	18100	4400	9400	25	52
Pb	27.9	6.3	9.8	22	35
Mg	772	51	160	6.6	21
Mn	45.1	1.9	8.9	4.2	20
Mo	25.6	2.2	5.0	8.8	20
Ni	25.5	4.8	8.7	19	34
K	1850	240	380	13	20
Se	391(s)	13	40	3.3	10
Ag	40.6(s)	4.2	20	10	50
Na	260.3	8.5	31	3.3	12
Tl	181.4(s)	4.8	62	2.6	34
V	75.6	3.4	12	4.4	15
Zn	52.7	5.8	11	11	20

Table 990.08A (continued)

Element	Concentration, mg/kg	s _r	s _R	RSD _r , %	RSD _R , %
University of Nevada reference material mine tailings					
Al	14100	1000	2500	7.2	18
Sb	39.8(s)	5.7	24	14	61
As	627	76	170	12	28
Ba	405	14	37	3.5	9.2
Be	0.52	0.04	0.21	8.6	41
Cd	45.5(s)	1.4	8.8	3.1	19
Ca	9760	250	850	2.6	8.7
Cr	13.31	0.86	12	6.5	91
Co	7.5	1.4	2.4	19	31
Cu	234.7	4.9	27	2.1	11
Fe	10070	940	1800	9.4	18
Pb	5740	370	770	6.4	13
Mg	14230	610	1300	4.3	9.2
Mn	92500	2000	10000	2.2	11
Mo	55.1	2.5	15	4.5	27
Ni	20.7	3.0	8.3	14	40
K	7330	260	1000	3.6	14
Se	378(s)	13	48	3.4	13
Ag	9.9	1.0	6.0	10	60
Na	3370	140	430	4.3	13
Tl	235(s)	13	110	5.4	45
V	14.7	1.9	6.8	13	46
Zn	360	16	70	4.3	20

^a Average concentrations (column 2) are reported to significant figures consistent with repeatability standard deviations (s_r). Precision data (columns 3 and 6) are reported to 2 significant figures as recommended in the *Statistical Manual of the AOAC* (1975) AOAC, Arlington, VA, p. 59.

G. Determination

After instrument response is stable (usually 30 min after plasma is started), profile and calibrate instrument according to manufacturer's instructions. Flush system for ≥1 min with calibration blank solution before introducing standards or sample solutions. Verify calibration accuracy (±10%) by analysis of certified reference solutions as quality control standards before any test samples are analyzed. Analyze instrument check standards and calibration blank before each 10 test samples to confirm that calibration is still acceptable. Verify inter-element and background corrections (±3 standard deviations of mean) by analysis of interference check standard at beginning and end of analysis session and at least twice in each 8 h period. Recommended quality control includes at least one reagent blank for each batch of test samples, and one duplicate digest for each 20 test samples. For new or unusual matrixes, absence of significant interference is indicated by 5-fold dilution that is within 10% of expected value (provided concentrations are not near detection limit) and/or by spike added to digest that is recovered with 10% of expected value (spike level should be 2–4 times unspiked concentration). When matrix interference is indicated, dilution or the method of standard additions can usually compensate for the effect.

Recommended wavelengths and typical instrumental detection limits are given in Table 990.08B. Other wavelengths may be used if they provide the needed sensitivity and are treated with the same correction techniques for spectral interferences.

The method is suitable for determining many elements but only those elements for which interlaboratory performance data are available are listed.

H. Calculations

Calculations involve subtraction of reagent blank values, adjustment for wet weight of test portions (multiply by wet/dry weight fraction), and for the digest volume and any additional dilutions.

$$C_s = (I_C - B) \times D \times R$$

where B = reagent blank concentration, mg/L; C_s = concentration of element in test portion, mg/kg; D = dilution factor (= 50 when preparation of 2 g test portion results in 100 mL solution and no extra dilution is required); I_C = test solution digest concentration from instrument, mg/L; and R = wet weight/dry weight ratio for test portion.

References: An Interlaboratory Study of Inductively Coupled Plasma Atomic Emission Spectroscopy Method 6010 and Digest Method 3050, NTIS No. PB88-124318, National Technical Information Service, 5285 Port Royal Rd, Springfield, VA 22161. *JAOAC* 73, 404(1990).

Table 990.08B Recommended wavelengths and estimated instrumental detection limits

Analyte	Chemical Abstracts Registry No.	Interfering elements ^a	Recommended wavelength, nm	Estimated instrumental detection limit, µg/L
Aluminum	7429-90-5	Mn, <u>V</u>	308.215	45
Antimony	7440-36-0	Al, <u>Cr</u> ,Fe,Tl,V	206.833	32
Arsenic	7440-38-2	<u>Al</u> ,Cr, <u>V</u>	193.696	53
Barium	7440-39-3		455.403	2
Beryllium	7440-41-7	Tl,V	313.042	0.3
Cadmium	7440-43-9	Fe,Ni	226.502	4
Calcium	7440-70-2	Cr,Fe,Mg,Mn,Tl,V	317.933	10
Chromium	7440-47-3	Fe,Mn,V	267.716	7
Cobalt	7440-48-4	Cr,Fe,Ni,Tl	228.616	7
Copper	7440-50-8	Fe,Tl,V	324.754	6
Iron	7439-89-6	Mn	259.940	7
Lead	7439-92-1	Al	220.353	42
Magnesium	7439-95-4	Ca,Cr,Fe,Mn,Tl,V	279.079	30
Manganese	7439-96-5	Al,Cr,Fe,Mg	257.610	2
Molybdenum	7439-98-7	Al,Fe	202.030	8
Nickel	7440-02-0		231.604	15
Potassium	7440-09-7	Mg	766.491	500
Selenium	7782-49-2	Al,Fe	196.026	75
Silver	7440-22-4		328.068	7
Sodium	7440-23-5	Tl	588.995	29
Thallium	7440-28-0	Al	190.864	40
Vanadium	7440-62-2	Cr,Fe,Tl	292.402	8
Zinc	7440-66-6	Cu,Ni	213.856	2

^a Underlined elements indicate apparent (false) analyte concentrations exceeding 1 µg/L caused by 100 mg/L of the interfering element.