ELEMENTS by ICP 7300

MW: Table 1 CAS: Table 2 RTECS: Table 2

METHOD: 7300, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 August 1990**
Issue 2: 15 August 1994

OSHA: Table 2
NIOSH: Table 2
ACGIH: Table 2

PROPERTIES: Table 1

ELEMENTS:

aluminum*	chromium*	lithium*	phosphorus	tellurium	zinc
aresenic	cobalt*	magnesium	platinum*	thallium	zirconium*
beryllium*	copper	manganese*	selenium	titanium	
Cadmium	iron	molybdenum*	silver	vanadium	
calcium	lead* nickel	sodium	yittrium		

*Some compounds of these elements require special sample treatment.

SAMPLING

SAMPLER: FILTER (0.8-µm, cellulose ester membrane)

FLOWRATE: 1 to 4 L/min

VOL-MIN: Table 1
-MAX: Table 1

SHIPMENT: routine

SAMPLE STABILITY: stable

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: not studied

BIAS: none identified

OVERALL PRECISION ($\hat{S}$): not evaluated

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: INDUCTIVELY COUPLED ARGON PLASMA, ATOMIC EMISSION SPECTROSCOPY

ANALYTE: elements above

ASHING REAGENTS: conc. HNO_3, 4 mL; and conc. $HClO_4$, 1 mL

CONDITIONS: room temperature, 30 min; 150 °C to near dryness

FINAL SOLUTION: 4% HNO_3, 1% $HClO_4$, 10 mL

WAVELENGTH: depends upon element; Table 3

BACKGROUND CORRECTION: spectral wavelength shift

CALIBRATION: elements in 4% HNO_3, 1% $HClO_4$

RANGE: 2.5 to 1000 µg per sample [1]

ESTIMATED LOD: 1 µg per sample [1]

PRECISION ($\bar{S}$): Table 3

APPLICABILITY: The working range of this method is 0.005 to 2.0 mg/m^3 for each element in a 500-L air sample. This is simultaneous elemental analysis, not compound specific. An alternative microwave digestion procedure is included. Verify that the types of compounds in the samples are soluble with the ashing procedure selected.

INTERFERENCES: Spectral interferences are the primary interferences encountered in ICP-AES analysis. These are minimized by judicious wavelength selection, interelement correction factors and background correction [1,2].

OTHER METHODS: This method replaces P&CAM 351 [2] for trace elements. Flame atomic absorption spectroscopy (e.g., Methods 70XX) is an alternate analytical technique for many of these elements. Graphite furnace AAS (e.g., 7102 for Be, 7105 for Pb) is more sensitive.

REAGENTS:

1. Nitric acid, conc., ultra pure.
2. Perchloric acid, conc., ultra pure.*
3. Ashing acid: 4:1 (v/v) HNO3:HClO4. Mix 4 volumes conc. HNO3 with 1 volume conc. HClO4.
4. Calibration stock solutions, 1000 µg/mL. Commercially available, or prepared per instrument manufacturer's recommendation (see step 12).
5. Dilution acid, 4% HNO3, 1% HClO4. Add 50 mL ashing acid to 600 mL water; dilute to 1 L.
6. Argon.
7. Distilled,deionized water.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: cellulose ester membrane filter, 0.8-µm pore size, 37-mm diameter; in cassette filter holder.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. Inductively coupled plasma-atomic emission spectrometer, equipped as specified by the manufacturer for analysis of elements of interest.
4. Regulator, two-stage, for argon.
5. Beakers, Phillips, 125-mL, or Griffin, 50-mL, with watchglass covers.**
6. Volumetric flasks, 10- and 100- mL.**
7. Assorted volumetric pipets as needed.**
8. Hotplate, surface temperature 150°C.

** Clean all glassware with conc. nitric acid and rinse thoroughly in distilled water before use.

SPECIAL PRECAUTIONS: Perform all perchloric acid digestions in a perchloric acid hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 4 L/min for a total sample size of 200 to 2000 L (see Table 1) for TWA measurements. Do not exceed a filter loading of approximately 2 mg total dust.

SAMPLE PREPARATION:

3. Open the cassette filter holders and transfer the samples and blanks to clean beakers.
4. Add 5 mL ashing acid. Cover with a watchglass. Let stand 30 min at room temperature.
   NOTE: Start a reagent blank at this step.
5. Heat on hotplate (120°C) until ca. 0.5 mL remains.
   NOTE 1: Recovery of lead from some paint matrices may require other digestion techniques. See Method 7082 (Lead by Flame AAS) for an alternative hotplate digestion procedure or the Appendix for a microwave digestion procedure [8].
   NOTE 2: Some species of Al, Be, Co, Cr, Li, Mn, Mo, V, and Zr will not be completely solubilized by this procedure. Alternative solubilization techniques for most of these elements can be found elsewhere [2-7]. For example, aqua regia may be needed for Mn [4,9].
6. Add 2 mL ashing acid and repeat step 5. Repeat this step until the solution is clear.
7. Remove watchglass and rinse into the beaker with distilled water.
8. Increase the temperature to 150°C and take the sample to near dryness (ca. 0.5 mL).
9. Dissolve the residue in 2 to 3 mL dilution acid.
10. Transfer the solutions quantitatively to 10-mL volumetric flasks.
11. Dilute to volume with dilution acid.

CALIBRATION AND QUALITY CONTROL:

12. Calibrate the spectrometer according to the manufacturers recommendations.
    NOTE: Typically, an acid blank and 10 µg/mL multielement working standards are used. The following multielement combinations are chemically compatible in 4% HNO3/1%

HClO4:

a. Ag, Ca, Co, Mn, Pb, V, Zn;
b. Al, Be, Cd, La, Li, Ni, Tl;
c. As, B, Ba, Mg, Mo, P;
d. Cu, Fe, Na, Pt, Sr, Te, Y;
e. Cr, K, Se, Ti, Zr; and
f. Si, W (distilled water only)

13. Analyze a standard for every ten samples.
14. Check recoveries with at least two spiked media blanks per ten samples.

MEASUREMENT:

15. Set spectrometer to conditions specified by manufacturer.
16. Analyze standards and samples.

NOTE: If the values for the samples are above the range of the standards, dilute the solutions with dilution acid, reanalyze and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

17. Obtain the solution concentrations for the sample, Cs (µg/mL), and the average media blank, Cb (µg/mL), from the instrument.
18. Using the solution volumes of sample, Vs (mL), and media blank, Vb (mL), calculate the concentration, C (mg/m3), of each element in the air volume sampled, V (L):

$$C = \frac{C_s V_s - C_b V_b}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Method P&CAM 351 was evaluated in 1981 [1,2]. The precision and recovery data were determined at 2.5 and 1000 µg of each element per sample on spiked filters. The precision and recovery data, instrumental detection limits, sensitivity, and analytical wavelengths are listed in Table 3. The values in Table 3 were determined with a Jarrell-Ash Model 1160 ICP operated according to manufacturer's instructions.

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[3] Ibid, S341 (Lead).
[4] Ibid, V. 2, S5 (Manganese), U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
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METHOD WRITTEN BY:

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James B. Perkins, David L. Wheeler, and Keith Nicholson, DataChem Labortories, Salt Lake City, UT, prepared the microwave digestion procedure in the Appendix.

TABLE 1. PROPERTIES AND SAMPLING VOLUMES

Element (Symbol)	Properties: Atomic Weight	Properties: MP,°C	Air Volume, L @ OSHA PEL: MIN	Air Volume, L @ OSHA PEL: MAX
Silver (Ag)	107.87	961	250	2000
Aluminum (Al)	26.98	660	5	100
Arsenic (As)	74.92	817	5	2000
Beryllium (Be)	9.01	1278	1250	2000
Calcium (Ca)	40.08	842	5	200
Cadmium (Cd)	112.40	321	13	2000
Cobalt (Co)	58.93	1495	25	2000
Chromium (Cr)	52.00	1890	5	1000
Copper (Cu)	63.54	1083	5	1000
Iron (Fe)	55.85	1535	5	100
Lithium (Li)	6.94	179	100	2000
Magnesium (Mg)	24.31	651	5	67
Manganese (Mn)	54.94	1244	5	200
Molybdenum (Mo)	95.94	651	5	67
Sodium (Na)	22.99	98	13	2000
Nickel (Ni)	58.71	1453	5	1000
Phosphorus (P)	30.97	44	25	2000
Lead (Pb)	207.19	328	50	2000
Platinum (Pt)	195.09	1769	1250	2000
Selenium (Se)	78.96	217	13	2000
Tellurium (Te)	127.60	450	25	2000
Titanium (Ti)	47.90	1675	5	100
Thallium (Tl)	204.37	304	25	2000
Vanadium (V)	50.94	1890	5	2000
Yttrium (Y)	88.91	1495	5	1000
Zinc (Zn)	65.37	419	5	200
Zirconium (Zr)	91.22	1852	5	200

TABLE 2. EXPOSURE LIMITS, CAS #, RTECS

Element (Symbol)	CAS #	RTECS	Exposure Limits, mg/m^3 (Ca = carcinogen) OSHA	NIOSH	ACGIH
Silver (Ag)	7440-22-4	VW3500000	0.01 (dust, fume, metal)	0.01 (metal, soluble)	0.1 (metal) 0.01 (soluble)
Aluminum (Al)	7429-90-5	BD0330000	15 (total) 5 (respirable)	5	10 (dust) 5 (fume)
Arsenic (As)	7440-38-2	CG0525000	varies	C 0.002, Ca	0.01, Ca
Beryllium (Be)	7440-41-7	DS1750000	0.002, C 0.005	0.0005, Ca	0.002, Ca
Calcium (Ca)	--	--	varies	varies	varies
Cadmium (Cd)	7440-43-9	EU9800000	0.2, C 0.6 (dust) 0.1, C 0.3 (fume)	lowest feasible, Ca	0.01 (total), Ca 0.002 (respir.), Ca
Cobalt (Co)	7440-48-4	GF8750000	0.1	0.05	0.05 (dust, fume)
Chromium (II) (Cr)	22541-79-3	GB6260000	0.5	0.5	0.5
Chromium (III) (Cr)	16065-83-1	GB6261000	0.5	0.5	0.5
Chromium (VI) (Cr)	18540-29-9	GB6262000	C 0.1	0.001 (dust)	0.05 (soluble) 0.05 (insoluble), Ca
Copper (Cu)	7440-50-8	GL5325000	1 (dust, mists) 0.1 (fume)	1 (dust) 0.1 (fume)	1 (dust, mists) 0.2 (fume)
Iron (Fe)	1309-37-1	NO7400000	10 (dust, fume)	5 (dust, fume)	5 (fume)
Lithium (Li)	--	--	--	--	--
Magnesium (Mg)	1309-48-4	OM3850000	15 (dust) as oxide 5 (respirable)	10 (fume) as oxide	10 (fume) as oxide
Manganese (Mn)	7439-96-5	OO9275000	C 5	1; STEL 3	5 (dust) 1; STEL 3 (fume)
Molybdenum (Mo)	7439-98-7	QA4680000	5 (soluble) 15 (total insoluble) 5 (respirable insol.)	5 (soluble) 10 (insoluble)	5 (soluble) 10 (insoluble)
Nickel (Ni)	7440-02-0	QR5950000	1	0.015, Ca	0.05, Ca
Lead (Pb)	7439-92-1	OF7525000	0.05	<0.1	0.05
Platinum (Pt)	7440-06-4	TP2160000	0.002	1 (metal)	1 (metal)
Selenium (Se)	7782-49-2	VS7700000	0.2	0.2	0.2
Tellurium (Te)	13494-80-9	WY2625000	0.1	0.1	0.1
Titanium (Ti) TiO_2	7440-32-6 13463-67-7	XR1700000 XR2275000	as TiO_2, 15 as TiO_2, 5 (respirable)	lowest feasible, Ca	10
Thallium (Tl)	7440-28-0	XG3425000	0.1 (skin) (soluble)	0.1 (skin) (soluble)	0.1 (skin)
Vanadium (V) V_2O_5	7440-62-2 1314-62-1	YW240000 YW1355000	C 0.5 (respirable) as V_2O_5 C 0.1 (fume) as V_2O_5	C 0.05	0.05 (respir.) as V_2O_5
Yttrium (Y)	7440-65-5	ZG2980000	1	1	1
Zinc (Zn)	1314-13-2	ZH4810000	5 (ZnO fume) 15 (ZnO dust) 5 (ZnO respirable)	5; STEL 10 (ZnO fume) 5; C 15 (ZnO dust)	5; STEL 10 (ZnO fume) 10 (ZnO dust)
Zirconium (Zr)	7440-67-7	ZH7070000	5	5, STEL 10	5, STEL 10

TABLE 3. MEASUREMENT PROCEDURES AND DATA[a]

Element	Wavelength (nm)	Instrumental LOD (ng/mL)	Sensitivity (Intensity/ µg/mL)	Recovery @ 2.5 µg/ filter [b]	Recovery @ 1000 µg/ filter	Precision ($\bar{S}_r$) (N = 3) @ 2.5 µg/ filter	Precision ($\bar{S}_r$) (N = 3) @ 1000 µg/ filter
Ag	328.3	26	0.65	111	91	0.02	0.075
Al	308.2	14	0.23	93	100	0.092	0.023
As	193.7	13	0.57	103	99	0.062	0.026
Be	313.0	1.5	1.29	107	90	0.040	0.034
Ca	315.9	10	0.49	99	95	0.036	0.014
Cd	226.5	1.6	0.83	107	99	0.032	0.020
Co	231.2	7.4	0.38	101	95	0.040	0.005
Cr	205.6	1.3	0.50	98	106	0.053	0.016
Cu	324.8	2.1	0.72	98	99	0.036	0.022
Fe	259.9	3.9	0.13	94	97	0.068	0.016
Li	670.8	2.8	0.48	89	95	0.171	0.043
Mg	279.6	24	0.22	105	106	0.084	0.027
Mn	257.6	0.4	0.74	84	93	0.062	0.035
Mo	281.6	7.0	0.18	94	88	0.023	0.049
Na	589.0	10	0.76	(c)	101	(c)	0.045
Ni	231.6	3.4	0.41	105	97	0.027	0.020
P	214.9	22	0.17	(c)	91	(c)	0.056
Pb	220.4	17	0.42	105	95	0.060	0.011
Pt	203.7	15	0.69	106	91	0.041	0.075
Se	190.6	21	0.28	105	97	0.068	0.049
Sn[d]	190.0	64	0.49	74	67	0.33	0.16
Te	214.3	29	0.41	102	94	0.050	0.063
Ti	334.9	1.2	0.55	96	108	0.051	0.029
Tl	190.9	17	0.22	103	99	0.043	0.017
V	310.2	3.2	0.88	99	94	0.043	0.014
W[d]	207.9	13	2.58	35	23	0.053	0.60
Y	371.0	0.8	2.35	99	100	0.015	0.013
Zn	213.9	0.6	0.60	101	94	0.013	0.013
Zr	339.2	1.9	0.88	75	98	0.049	0.008

(a) Values reported were obtained with a Jarrell-Ash Model 1160 ICP; performance may vary with instrument and should be independently verified.
(b) 2.5 µg/filter corresponds to 5 µg/m^3 for a 500-L air sample.
(c) Blank levels too high to make accurate determinations.
(d) Qualitative only because of low recovery.

APPENDIX - MICROWAVE DIGESTION FOR LEAD IN PAINT CHIPS (AND OTHER MATRICES)

This procedure is an alternative to the procedure presented in the Sample Preparation section of this method. It provides a rapid, complete acid digestion prior to analysis by flame atomic absorption (FAA), heated graphite furnace atomic absorption (HGFAA), and inductively coupled plasma spectroscopy (ICP) [10].

Apparatus and Material[11-16]

1. Microwave apparatus requirements:
   a. The microwave unit provides programmable power with a minimum of 574 W and can be programmed to within ± 10 W of the required power.
   b. The microwave unit cavity is corrosion resistant as well as ventilated. All electronics are protected against corrosion for safe operation.
   c. The system requires Teflon PFA digestion vessels (120-mL capacity) capable of withstanding pressures up to 7.5 ± 0.7 atm (110 ± 10 psi) and capable of controlled pressure relief at pressures exceeding 7.5 ± 0.7 atm (110 ± 10 psi).
   d. A rotating turntable is employed to ensure homogeneous distribution of microwave radiation within the unit. The speed of the turntable should be a minimum of 3 rpm.
   e. A safety concern relates to the use of sealed containers without pressure relief valves in the unit. Temperature is the important variable controlling the reaction. Pressure is needed to attain elevated temperatures but must be safely contained [12].
   f. Polymeric volumetric ware in plastic (Teflon or polyethylene), 50- or 100-mL capacity.
   g. Disposable polypropylene filter funnel.
   h. Analytical balance, 300-g capacity, and minimum ± 0.001 g.

Reagents

1. Nitric acid, concentrated, spectroscopy grade.
2. Reagent Water. Reagent water shall be interference free. All references to water in the method refer to reagent water that meets the ASTM Type 2 standard.

Procedure

1. Calibration of Microwave Equipment.
   Calibrate microwave equipment in accordance with manufacturer's instructions. If calibration instructions are not available, see EPA Method 3051 [11].
2. All digestion vessels and volumetric ware must be carefully acid washed and rinsed with reagent water. All digestion vessels should be cleaned by leaching with hot (1:1) nitric acid for a minimum of fifteen minutes, rinsed with reagent water, and dried in a clean environment.
3. Sample Digestion
   a. Tare the Teflon PFA digestion vessel.
   b. Weigh out 0.1 g paint chip sample to the nearest 0.001 g into the tared Teflon PFA sample vessel. With large paint chip samples, measure out a 2 cm^2 piece, weigh to the nearest 0.001 g, and quantitatively transfer it to the vessel.
   c. Add 5.0 ± 0.1 mL concentrated nitric acid to the sample vessel in a fume hood. If a vigorous reaction occurs, allow the reaction to stop before capping the vessel. Cap the vessel and torque the cap to 12 ft-lb (16 N-m) according to the manufacturer's directions. The sample vessel may be connected to an overflow vessel using Teflon PFA connecting tubes. Place the vessels in the microwave carrousel. Connect the overflow vessels to the center well of the unit.
   d. Place the vessels evenly distributed in the turntable of the microwave unit using groups of two, six, or 12 sample vessels. Any vessels containing 5 mL of nitric acid for reagent blank purposes are counted as sample vessels. When fewer than the recommended number of samples are to be digested, i.e., three samples plus one blank, the remaining vessels should be filled with 5 mL of nitric acid to achieve the full complement of vessels. This provides an energy balance since the microwave power absorbed is proportional to the total mass in the cavity [14]. Irradiate each group of samples to achieve a temperature of 180°C in five minutes at a pressure of 50 psi. Continue to irradiate to achieve a temperature of 180°C at 100 psi after 25 minutes. Continue

digestion for five minutes. A sample digestion program for 12 samples is presented in the following table.

PROGRAM VARIABLES FOR PAINT CHIPS SAMPLE DIGESTION WITH NITRIC ACID

Stage	(1)	(2)	(3)
Power	90%	90%	0%
Pressure, psi	50	100	0
Run Time, min	10:00	20:00	05:00
Time @ P, min	05:00	15:00	00:00
Temperature	180°C	180°C	0°C
Fan Speed	100%	100%	100%
Number of Vessels:	12		
Liquid Volume per Vessel:	5 mL		
Sample Weight:	0.1 g		

If the analyst wishes to digest other than two, six, or 12 samples at a time, use different values of power as long as they result in the same time and temperature conditions.

e. At the end of the microwave program, allow the vessels to cool for a minimum of five minutes before removing them from the microwave unit. If a loss of sample is detected (e.g., material in overflow collection vessel, liquid outside liner), determine the reason for the loss (e.g., loss of vessel seal integrity, use of a digestion time longer than 30 minutes, too large a sample, or improper heating conditions). Once the source of the loss has been corrected, prepare a new sample beginning at Section 2. If insufficient material is available for reanalysis, dilute remaining digestate and note that some sample loss may have occurred.

f. Uncap and vent each vessel in a fume hood. Add 20 mL reagent water, then reseal vessels and shake to mix thoroughly. Transfer the sample to an acid-cleaned polyethylene bottle. If the digested sample contains particulates which may clog nebulizers or interfere with injection of the sample into the instrument, allow the sample to settle or filter it:

Settling: Allow the sample to stand until the supernatant is clear (usually, overnight is sufficient). If it does not clear, filter the sample.

Filtering: The filtering apparatus must be thoroughly precleaned and rinsed with dilute nitric acid. Filter the sample through quantitative filter paper into a second acid-cleaned container.

The digestate is now ready for analysis for elements of interest using the appropriate method.

4. Calculations: Report the concentrations based on the actual weight of the original sample.