ELEMENTS by ICP 7303
(Hot Block/HCl/HNO_3 Digestion)

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

METHOD: 7303, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 March 2003**

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

PROPERTIES: Table 1

ELEMENTS:

aluminum	cadmium	indium	nickel	strontium	zinc
antimony*	calcium	iron	palladium	tellurium	
arsenic	chromium	lead*	phosphorus	thallium	
barium	cobalt	magnesium	platinum	tin*	
beryllium	copper	manganese	potassium	titanium	
bismuth*	gallium	molybdenum	selenium	vanadium	
boron	gold	neodymium	sodium	yttrium	

* With certain restrictions (see Table 3)

SAMPLING

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

FLOW RATE: 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: 5,000 to 50,000 µg/sample

BIAS: Not determined

OVERALL PRECISION: Not determined

ACCURACY: Not determined

MEASUREMENT

TECHNIQUE: INDUCTIVELY COUPLED ARGON PLASMA, ATOMIC EMISSION SPECTROSCOPY

ANALYTE: See element list above

REAGENTS: Conc. HCl, 1.25 mL; and conc. HNO_3, 1.25 mL

FINAL SOLUTION: 5% HCl and 5% HNO_3, 25 mL

WAVELENGTH: Element and instrument specific

BACKGROUND CORRECTION: Spectral wavelength shift

CALIBRATION: Elements in 5% HCl, 5% HNO_3

RANGE: LOQ to 50,000 µg/sample [1]

ESTIMATED LOD: Varies with element; Table 1

PRECISION (Š): Not evaluated

APPLICABILITY: The working range of this method is up to 100 mg/m^3 for each element in a 500-L sample (the minimum range depends on the LOD for each sample; see Table 1). The analysis is not compound specific. Certain elemental compounds are known to be acceptable or unacceptable by this method (see Table 3). For unverified compounds, a test run should be conducted using a known amount of the compound in question to determine acceptability.

INTERFERENCES: Interferences are spectral in nature and are accounted for by choosing appropriate wavelengths, applying interelement correction factors, and background correction.

OTHER METHODS: Alternative, more sensitive methods exist for some elements by graphite furnace atomic absorption spectroscopy. This method is similar to NIOSH Method 7301, differing only in the use of the hot block for digestion of the sampler.

REAGENTS:

1. Hydrochloric acid,* conc., ultra pure.
2. Nitric acid,* conc., ultra pure.
3. Calibration stock solutions, 50-1000 µg/mL. Commercially available single element solutions or multielement solutions prepared as instructed by the instrument manufacturer.
4. Argon, prepurified.
5. Distilled, deionized, Type II water.
6. Diluting solution: 5% HCl : 5% HNO_3. To about 600 mL of deionized water in a 1-L volumetric flask, slowly add 50 mL conc. HCl and 50 mL conc. HNO3. Dilute to the mark with 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 argon plasma-atomic emission spectrometer, equipped as specified by the manufacturer for analysis of elements of interest.
4. Hot block apparatus at 95 °C.
5. Digestion vessels and caps, 50-mL.
6. Watchglasses.
7. Pipettes, electronic and mechanical.
8. Regulator, two-stage, for argon.
9. Forceps.

SPECIAL PRECAUTIONS: Concentrated acids are powerful oxidizers, toxic, and corrosive liquids. Wear protective clothing and work in a fume 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 for TWA measurements. Do not exceed a filter loading of approximately 2 mg total dust.

SAMPLE PREPARATION:

3. Open the cassette filter holder and with forceps remove the sample filter. Fold the filter into quarters taking care not to lose any sample, and transfer to a clean, 50-mL hot block digestion tube.
4. Add 1.25 mL HCl. Cover with a plastic watchglass. Place in the hot block and heat at an internal temperature of 95 °C for 15 minutes.
   NOTE: The internal temperature may vary from the digital readout. Calibrate the hot block prior to digestion.
5. Remove the sample from the hot block and cool for 5 minutes. Remove watchglass and add 1.25 mL HNO_3. Replace watchglass and return to hot block at 95 °C for 15 minutes.
6. Remove the sample from the hot block and cool for at least 5 minutes. Rinse watchglass into the sample container and discard watchglass.
7. Dilute to 25-mL final volume with distilled, deionized Type II water.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate the spectrometer according to the manufacturer's recommendations. Use standards consisting of the same 5% HCl : 5% HNO_3 matrix as the samples.
9. Analyze a standard every 10 samples.
10. Analyze a media blank every 20 samples, and a reagent blank every 10 samples.
11. Analyze a set of two laboratory control samples every 40 samples of a given matrix for a given analyte.
12. Check recoveries with at least two spiked media blanks per ten samples.
    NOTE: In the determination of lead, there may be a measurement interference (for example, samples with high aluminum levels). More recent instruments have a correction for this.

MEASUREMENT:

13. Set spectrometer to conditions specified by manufacturer.
14. Analyze standards, samples and quality control checks.
    NOTE: If the elemental value for a sample is above the linear range of the element(s) in question, dilute the sample solution with 5% HCl : 5% HNO_3 diluting solution, reanalyze and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

15. Obtain the solution concentrations for the sample, C_s (µg/mL), and the average media blank, C_b (µg/mL), from the instrument.
16. Using the solution volumes of sample, V_s (mL), and media blank, V_b (mL), calculate the concentration, C (mg/m^3), of each element in the air volume sampled, V (L):

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

NOTE: µg/L ≡ mg/m^3

EVALUATION OF METHOD:

The method was evaluated for all elements and compounds listed in Table 1 and Table 2 between 1999 and 2001 using known amounts of bulk material [4]. Evaluation is ongoing for additional elements and compounds. The limits of detection and quantitation were also determined for each element. Two ICP instruments were used in the evaluation, a Thermal Jarrell Ash Model 61E [5] and a TJA IRIS [6], operated according to the manufacturer's instructions.

REFERENCES:

[1] WOHL [2001]. Metals validation using hot block digestion, Unpublished data. Wisconsin Occupational Health Laboratory, Madison, WI.
[2] NIOSH [1994]. Method 7300: Elements by ICP, NIOSH Manual of Analytical Methods, Fourth Edition, Issue 2, Aug. 15, 1994.
[3] WOHL [2001]. Metals Manual 2001, WOHL Internal Document, Updated Apr. 1, 2001. Wisconsin Occupational Health Laboratory, Madison, WI.
[4] WOHL [2001]. WOHL General Operations Procedures Manual, WOHL Internal Document, Updated 2001. Wisconsin Occupational Health Laboratory, Madison, WI.
[5] Thermal Jarrell Ash [1991]. ICAP 61E Plasma Spectrometer Operator's Manual, Thermal Jarrell Ash Corp., Part No. 128832-01, Feb., 1991.
[6] Thermal Jarrell Ash [1997]. IRIS Plasma Spectrometer User's Guide, Thermal Jarrell Ash Corp., Part No. 135811-0, Feb. 4, 1997.

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TABLE 1: ANALYTE INFORMATION FOR VALID ELEMENTS AND COMPOUNDS

Analyte	Properties		LOD (µg/mL)	LOQ (µg/mL)	Estimated LOQ (µg/sample)*	Minimum** air vol. (L)	Maximum*** air vol. (L)
	MW	MP (°C)					
Al	26.98	660	0.111	0.37	9.25	2	10,000
As	74.92	817	0.009	0.03	0.075	8	5,000,000
Au	196.97	10.63	0.015	0.05	1.25	1	3,300
B	10.81	2177	0.0094	0.0283	0.71	1	3,300
Ba	137.34	3.51	0.0018	0.006	0.15	1	100,000
Be	9.01	2178	0.00075	0.0025	0.062	35	25,000,00
Bi	208.98	271	0.025	0.085	2.12	1	10,000
Ca	40.08	842	0.099	0.33	8.25	2	10,000
CaO	56.08	2927	0.139	0.462	11.6	3	10,000
Cd	112.4	321	0.0037	0.012	0.30	3	500,000
Co	58.93	1495	0.003	0.011	0.27	3	500,000
Cr	52.00	1890	0.009	0.03	0.75	8	500,000
Cu	63.54	1083	0.020	0.060	1.50	15	500,000
Fe	55.85	1535	0.070	0.20	5.00	1	5,000
Fe_2O_3 (as Fe)	159.69	1462	0.070	0.20	5.00	1	5,000
Ga	69.72	29.75	0.03	0.09	2.25	1	3,300
In	114.82	156.3	0.015	0.05	1.25	15	500,000
Mg	24.31	651	0.047	0.14	3.50	1	10,000
MgO	40.32	2825	0.078	0.23	5.75	5	33,000
Mn	54.94	1244	0.0012	0.004	0.10	0.05	10,000
Mo	95.94	651	0.0072	0.024	0.60	0.5	10,000
Nd	92.906	2477	0.01	0.03	0.75	0.1	3,300
Ni	58.71	1453	0.012	0.039	0.98	1	50,000
P	30.97	44	0.3	1.0	25	250	500,000
Pb	207.19	328	0.023	0.07	1.75	35	100,000
Pd	106.4	1550	0.009	0.03	0.75	0.1	3,300
Pt	195.09	1769	0.0045	0.015	0.38	200	25,000,000
Sb	121.75	630.5	0.018	0.06	1.50	3	100,000
Se	78.96	217	0.021	0.064	1.60	8	250,000
Sn	118.69	232	0.015	0.05	1.25	1	25,000
Sr	87.62	769	0.002	0.006	0.15	300	100,000,000
Te	127.60	450	0.15	0.5	12.5	125	500,000
Ti	47.90	1675	0.005	0.016	0.40	0.1	10,000
Tl	204.37	304	0.044	0.133	3.32	35	500,000
V	50.94	1890	0.003	0.01	0.25	2.5	500,000
Y	88.91	1495	0.001	0.003	0.075	0.1	50,000
Zn	65.37	419	0.022	0.066	1.65	0.5	10,000
ZnO	81.37	1970	0.027	0.082	2.05	0.5	10,000

* Value based on a 25-mL sample volume.

** The minimum sampling volume needed to obtain the OSHA PEL at the LOQ for the element/compound at a sample digestion volume of 25 mL.

*** The maximum sampling volume for a given sample, calculated by taking 50,000 µg as the limit for the element/compound per sample.

NOTE: The LOD and LOQ values are dependent on the particular analytical instrument used. Also, LOD and LOQ values may vary for a particular element due to certain interelement interferences.

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 dust) 5 (respirable)	10 (total dust) 5 (respirable fume) 2 (salts, alkyls)	10 (dust) 5 (powders, fume) 2 (salts, alkyls)
Arsenic (As)	7440-38-2	CG0525000	varies	C 0.002, Ca	0.01, Ca
Barium (Ba)	7440-39-3	CQ8370000	0.5	0.5	0.5
Beryllium (Be)	7440-41-7	DS1750000	0.002, C 0.005	0.0005, Ca	0.002, Ca
Calcium (Ca)	7440-70-2	--	varies	varies	varies
Cadmium (Cd)	7440-43-9	EU9800000	0.005	lowest feasible, Ca	0.01 (total), Ca 0.002 (respir.), Ca
Cobalt (Co)	7440-48-4	GF8750000	0.1	0.05 (dust, fume)	0.02 (dust, fume)
Chromium (Cr)	7440-47-3	GB4200000	0.5	0.5	0.5
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)	7439-89-6	NO4565500	10 (dust, fume)	5 (dust, fume)	5 (fume)
Potassium (K)	7440-09-7	TS6460000	--	--	--
Lanthanum	7439-91-0	--	–	–	--
Lithium (Li)	7439-93-2	--	--	--	--
Magnesium (Mg)	7439-95-4	OM2100000	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 (soluble) 10 (insoluble)	5 (soluble) 10 (insoluble)
Nickel (Ni)	7440-02-0	QR5950000	1	0.015, Ca	0.1 (soluble) 1 (insoluble, metal)
Phosphorus (P)	7723-14-0	TH3500000	0.1	0.1	0.1
Lead (Pb)	7439-92-1	OF7525000	0.05	0.05	0.05
Antimony (Sb)	7440-36-0	CC4025000	0.5	0.5	0.5
Selenium (Se)	7782-49-2	VS7700000	0.2	0.2	0.2
Tin (Sn)	7440-31-5	XP7320000	2	2	2
Strontium (Sr)	7440-24-6	–	–	–	--
Tellurium (Te)	13494-80-9	WY2625000	0.1	0.1	0.1
Titanium (Ti)	7440-32-6	XR1700000	--	--	--
Thallium (Tl)	7440-28-0	XG3425000	0.1 (skin) (soluble)	0.1 (skin) (soluble)	0.1 (skin)
Vanadium (V)	7440-62-2	YW240000	--	C 0.05	--
Tungsten	7440-33-7	–	5	5 10 (STEL)	5 10 (STEL)
Yttrium (Y)	7440-65-5	ZG2980000	1	N/A	1
Zinc (Zn)	7440-66-6	ZG8600000	–	--	--
Zirconium (Zr)	7440-67-7	ZH7070000	5	5, STEL 10	5, STEL 10

TABLE 3: VALIDATION SUMMARY

Analyte	Status[1]	Analyte	Status	Analyte	Status
Ag	Not Valid	CuO	Valid	S	Not Valid
Al	Valid	Fe	Valid	Sb	Partially Valid[4]
Al_2O_3	Not Valid	Fe_2O_3	Valid	Sb_2O_3	Partially Valid[5]
As	Valid	Ga	Valid	Se	Valid
Au	Valid	In	Valid	Si	Not Valid
B	Valid	KCl	Pending	Sn	Partially Valid[6]
Ba	Pending	Mg	Valid	SnO	Pending
BaO	Pending	MgO	Valid	SnO_2	Pending
BaO_2	Pending	Mn	Valid	Sr	Valid
$BaCl_2$	Valid	MnO	Valid	$SrCrO_4$	Valid (by Cr)
$BaSO_4$	Pending	Mo	Valid	Te	Valid
Be	Valid	NaCl	Pending	Ti	Valid
Bi	Partially Valid[2]	Nd	Valid	Tl	Valid
Ca	Valid	Ni	Valid	V	Valid
$CaCO_3$	Valid	P	Valid	V_2O_5	Valid
CaO	Valid	Pb	Partially Valid[3]	Y	Valid
Cd	Valid	$PbCrO_4$	Valid (by Cr)	Zn	Valid
Co	Valid	PbO	Valid	ZnO	Valid
Cr	Valid	Pd	Valid	Zr	Not Valid
Cu	Valid	Pt	Valid	ZrO	Not Valid

[1] Status definitions

Valid: The method is suitable for samples up to at least 0.0500 g bulk material with recoveries of between 90 and 110 percent. This weight exceeds most expected levels encountered in work environments.

Partially Valid: The method is suitable with bulk-material recoveries of between 90 and 110 percent under certain conditions (as footnoted above).

Not Valid: The method procedure is not suitable for samples at any weight with recoveries of between 90 and 110 percent. An alternative method should be used.

[2] Valid up to 10,000 µg/sample and within 7 days of sample digestion.

[3] Valid up to 50,000 µg/sample and at least 24 hours after sample digestion; Valid up to 15,000 µg/sample within 24 hours of sample digestion.

[4] Valid up to 25,000 µg/sample and within 7 days of sample digestion.

[5] Valid up to 25,000 µg/sample and within 7 days of sample digestion.

[6] Valid up to 30,000 µg/sample and within 7 days of sample digestion.

NOTE: The upper limits of the method can be extended by serial dilution of the samples at the time of analyses.