ELEMENTS by ICP (Aqua Regia Ashing) 7301

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

METHOD: 7301, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 March 2003**

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

PROPERTIES: Table 1

ELEMENTS:						
	aluminum*	calcium	lead*	phosphorus	thallium	zinc
	antimony*	chromium*	lithium	potassium	tin	zirconium*
	arsenic	cobalt	magnesium	selenium	titanium	
	barium	copper	manganese	silver	tungsten*	
	beryllium	iron*	molybdenum	strontium	vanadium	
	cadmium	lanthanum	nickel	tellurium	yttrium	

* Some compounds of those elements require special sample treatment.

SAMPLING

SAMPLER: FILTER (0.8-µm, cellulose ester membrane, or 5.0-µm, polyvinyl chloride 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: Not determined

BIAS: Not determined

OVERALL PRECISION ($\hat{S}_{rT}$): Not determined

ACCURACY: Not determined

MEASUREMENT

TECHNIQUE: INDUCTIVELY COUPLED ARGON PLASMA, ATOMIC EMISSION SPECTROSCOPY (ICP-AES)

ANALYTE: Elements above

ASHING REAGENTS: Aqua regia (1 HNO_3: 3 HCl)

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

FINAL SOLUTION: 5% aqua regia, 25 mL

WAVELENGTH: Depends upon element, Table 3

BACKGROUND CORRECTION: Spectral wavelength shift

CALIBRATION: Elements in 5% aqua regia

RANGE: Varies with element [1]

ESTIMATED LOD: Tables 3 and 4

PRECISION ($\hat{S}_r$): Tables 3 and 4

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. Verify that the types of compounds in the samples are soluble with the ashing procedure selected. This method does not digest PVC filters completely.

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 [1-4].

OTHER METHODS: 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. NIOSH Methods 7300 & 7302 are alternative digestion procedures.

REAGENTS:

1. Nitric acid (HNO_3), conc.*, ultra pure.
2. Hydrochloric acid (HCl), conc.*, ultra pure.
3. Ashing acid (Aqua Regia): 1:3 (v/v) HNO_3:HCl. Mix 1 volume conc. HNO_3 with 3 volumes conc. HCl.
4. Calibration stock solutions, 1000 µg/mL. Commercially available, or prepared per instrument manufacturer's recommendation (see step 12).
5. Dilution acid, 1% HNO_3, 3% HCl. 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; or polyvinyl chloride (PVC) membrane, 5.0-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-, 25-,100-mL., and 1-L**
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: 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 (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 Method 7302 for a microwave digestion procedure.
   NOTE 2: Some species of Al, Be, Co, Cr, Li, Mo, Sb, W, and Zr will not be completely solubilized by this procedure. Alternative solubilization techniques for most of these elements can be found elsewhere [5-10].
6. Add 2 mL ashing acid and repeat step 5. Repeat this step until the solution is clear.
   NOTE: PVC filters will not completely dissolve after repeated additions of ashing acid.
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 25-mL volumetric flasks.
11. Dilute to volume with dilution acid.

CALIBRATION AND QUALITY CONTROL:

12. Calibrate the spectrometer according to the manufacturer's recommendations.
    NOTE: Typically, an acid blank and 1.0 µg/mL multielement working standards are used. The following multielement combinations are chemically compatible in 5% Aqua Regia:
    a. Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, La, In, Na
    b. Ag, K, Li, Mg, Mn, Ni, P, Pb, Se, Sr, Tl, V, Y, Zn, Sc
    c. Mo, Sb, Sn, Te, Ti, W, Zr
    d. Acid blank
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, samples, and blanks.
    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. If more sensitivity is required, the final sample volume may be held to 10.0 mL.

CALCULATIONS:

17. Obtain the solution concentrations for the sample, C_s (µg/mL), and the average media blank, C_b (µg/mL), from the instrument.
18. 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):

$$C = \frac{CsVs - CbVb}{V}, mg/m^3$$

NOTE: µg/L ≡ mg/m^3

EVALUATION OF METHOD:

The precision and recovery data were determined at approximately 3x and 10x the instrumental detection limits on commercially prepared spiked filters [12] using 25.0 mL as the final sample volume. The precision and recovery data, instrumental detection limits, and analytical wavelengths are listed in Tables 3 and 4. In general, better recoveries were obtained from MCE filters than from PVC filters. The values in Tables 3 and 4 were determined with a Spectro Analytical Instruments model EOP operated according to manufacturer's instructions.

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[12] Certification Inorganic Ventures for spikes.

METHOD WRITTEN BY:

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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
Barium (Ba)	137.34	710	50	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
Potassium (K)	39.10	63.65	5	1000
Lanthanum (La)	138.91	920	5	1000
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
Nickel (Ni)	58.71	1453	5	1000
Phosphorus (P)	30.97	44	25	2000
Lead (Pb)	207.19	328	50	2000
Antimony (Sb)	121.75	630.5	50	2000
Selenium (Se)	78.96	217	13	2000
Tin (Sn)	118.69	231.9	5	1000
Strontium (Sr)	87.62	769	10	1000
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
Tungsten (W)	183.85	3410	50	1000
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/m³ (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. MEASUREMENT PROCEDURES AND DATA [1].
Mixed Cellulose Ester Filters (0.45µm)

Element (a)	wavelength (nm)	Est.LOD (µg/ Filter)	LOD (ng/mL)	Certified 3x LOD (µg/filter) (b)	% Recovery (c)	Percent RSD (N=25)	Certified 10x LOD (µg/filter) (b)	% Recovery (c)	Percent RSD (N=25)
Ag	328	0.042	1.7	0.77	100.3	2.39	3.21	93.4	4.95
Al	167	0.115	4.6	1.54	**208.1**	42.4	6.40	99.6	9.43
As	189	0.140	5.6	3.08	97.6	4.71	12.90	95.1	1.14
Ba	455	0.005	0.2	0.31	104.3	1.65	1.29	100.8	1.54
Be	313	0.005	0.2	0.31	99.6	1.42	1.29	100.6	0.68
Ca	317	0.908	36.3	15.4	101.6	5.01	64.00	101.6	1.42
Cd	226	0.0075	0.3	0.31	106.8	2.60	1.29	99.2	0.76
Co	228	0.012	0.5	0.31	105.6	1.64	1.29	100.4	0.87
Cr	267	0.020	0.8	0.31	97.0	27.0	1.29	88.0	5.38
Cu	324	0.068	2.7	1.54	118.9	65.2	6.40	102.0	0.68
Fe	259	0.095	3.8	1.54	114.9	43.0	6.40	82.7	7.81
K	766	1.73	69.3	23.00	94.7	2.60	96.40	95.8	0.98
La	408	0.048	1.9	0.77	105.7	1.80	3.21	101.3	0.84
Li	670	0.010	0.4	0.31	104.3	2.37	1.29	99.3	0.89
Mg	279	0.098	3.9	1.54	105.2	4.23	6.40	99.2	1.24
Mn	257	0.005	0.2	0.31	103.5	1.64	1.29	91.2	2.01
Mo	202	0.020	0.8	0.31	108.9	2.70	1.29	97.4	1.25
Ni	231	0.020	0.8	0.31	112.2	2.28	1.29	94.2	1.73
P	178	0.092	3.7	1.54	93.2	10.9	6.40	97.1	5.93
Pb	168	0.062	2.5	1.54	88.0	6.52	6.40	102.2	1.06
Sb	206	0.192	7.7	3.08	**50.1**	54.7	12.90	80.0	19.46
Se	196	0.135	5.4	2.30	93.2	8.38	9.64	89.1	7.23
Sn	189	0.040	1.6	0.77	**25.8**	81.9	3.21	91.7	16.39
Sr	407	0.005	0.2	0.31	100.8	1.27	1.29	99.3	0.66
Te	214	0.078	3.1	1.54	103.1	1.88	6.40	95.0	1.31
Ti	334	0.050	2.0	0.77	98.3	1.88	3.21	96.0	1.06
Tl	190	0.092	3.7	1.54	101.3	3.57	6.40	98.2	0.71
V	292	0.028	1.1	0.77	106.0	1.38	3.21	101.3	0.81
W	207	0.075	3.0	1.54	**64.9**	21.8	6.40	**74.1**	11.34
Y	371	0.012	0.5	0.31	104.3	1.55	1.29	99.3	0.72
Zn	213	0.310	12.4	4.60	99.8	9.73	19.30	98.0	0.86
Zr	339	0.022	0.9	0.31	**52.5**	71.2	1.29	**76.6**	18.19

(a) Bold values are qualitative only, because of poor recovery.
(b) Values are certified by Inorganic Ventures INC. at 3x and 10x the approximate instrumental LOD.
(c) Values reported were obtained with a Spectro Analytical Instruments EOP ICP; performance may vary with instrument and should be independently verified.

TABLE 4. MEASUREMENT PROCEDURES AND DATA [1].
Polyvinyl Chloride Filter (5.0 µm)

Element (a)	wavelength (nm)	Est. LOD (µg/ Filter)	LOD (ng/mL)	Certified 3x LOD (µg/filter) (b)	% Recovery (c)	Percent RSD (N=25)	Certified 10x LOD (µg/ filter) (b)	% Recovery (c)	Percent RSD (N=25)
Ag	328	0.042	1.7	0.78	**57.9**	0.2	3.18	**55.0**	21.7
Al	167	0.115	4.6	1.56	**-1.9**		6.40	112.1	59.6
As	189	0.140	5.6	3.10	78.2	1.6	12.70	80.2	7.9
Ba	455	0.005	0.2	0.31	**73.0**	0.1	1.27	95.7	3.7
Be	313	0.005	0.2	0.31	81.1	0.1	1.27	97.2	4.3
Ca	317	0.908	36.3	15.60	**68.2**	4.9	64.00	97.7	4.5
Cd	226	0.0075	0.3	0.31	86.7	0.1	1.27	97.4	4.3
Co	228	0.012	0.5	0.31	83.8	0.1	1.27	99.2	4.4
Cr	267	0.020	0.8	0.31	80.1	0.1	1.27	94.1	6.8
Cu	324	0.068	2.7	1.56	75.9	0.5	6.40	96.1	4.3
Fe	259	0.095	3.8	1.56	78.4	0.6	6.40	88.4	9.0
K	766	1.73	69.3	23.40	**61.4**	3.1	95.00	91.6	5.7
La	408	0.048	1.9	1.78	**34.4**	0.4	3.18	95.3	3.8
Li	670	0.010	0.4	0.31	76.3	0.0	1.27	96.0	4.7
Mg	279	0.098	3.9	1.56	77.5	0.6	6.40	94.0	4.6
Mn	257	0.005	0.2	0.31	77.4	0.1	1.27	93.4	4.2
Mo	202	0.020	0.8	0.31	79.7	0.2	1.27	89.2	9.8
Ni	231	0.020	0.8	0.31	86.2	0.1	1.27	100.8	4.8
P	178	0.092	3.7	1.56	76.9	0.9	6.40	**69.0**	14.5
Pb	168	0.062	2.5	1.56	82.0	0.9	6.40	99.4	4.4
Sb	206	0.192	7.7	3.10	**40.3**	1.5	12.70	**23.0**	76.5
Se	196	0.135	5.4	2.30	89.4	1.2	9.50	87.5	9.9
Sn	189	0.040	1.6	0.78	101.1	0.4	3.18	**21.1**	124.0
Sr	407	0.005	0.2	0.31	**73.4**	0.1	1.27	95.2	3.9
Te	214	0.078	3.1	1.56	91.8	0.7	6.40	85.3	7.5
Ti	334	0.050	2.0	0.78	**53.4**	0.2	3.18	**46.3**	39.9
Tl	190	0.092	3.7	1.56	**71.6**	0.8	6.40	86.1	9.3
V	292	0.028	1.1	0.78	77.8	0.3	3.18	96.1	4.6
W	207	0.075	3.0	1.56	**51.3**	0.8	6.40	**29.8**	47.0
Y	371	0.012	0.5	0.31	79.6	0.1	1.27	95.8	4.4
Zn	213	0.310	12.4	4.70	80.9	2.2	19.10	94.7	4.2
Zr	339	0.022	0.9	0.31	**46.2**	0.1	1.27	**39.2**	112.7

(a) Bold values are qualitative only because of poor recovery.
(b) Values are certified by Inorganic Ventures INC. at 3x and 10x the approximate instrumental LOD.
(c) Values reported were obtained with a Spectro Analytical Instruments EOP ICP; performance may vary with instrument and should be independently verified.