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ELEMENTS by ICP (Nitric/Perchloric Acid Ashing) 7300

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

METHOD: 7300, Issue 3 **EVALUATION: PARTIAL** **Issue 1: 15 August 1990**
Issue 3: 15 March 2003

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

PROPERTIES: Table 1

ELEMENTS:

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

*Some compounds of these elements require special sample treatment.

SAMPLING

SAMPLER: FILTER (0.8-µm, cellulose ester membrane, or 5.0-µm, polyvinyl chloride 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 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: conc. HNO_3/ conc. $HClO_4$ (4:1), 5 mL; 2mL increments added as needed

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

FINAL SOLUTION: 4% HNO_3, 1% $HClO_4$, 25 mL

WAVELENGTH: depends upon element; Table 3

BACKGROUND CORRECTION: spectral wavelength shift

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

RANGE: varies with element [1]

ESTIMATED LOD: Tables 3 and 4

PRECISION ($\bar{S}$): 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.

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: This issue updates issues 1 and 2 of Method 7300, which replaced P&CAM 351 [3] 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 (HNO_3), conc., ultra pure.
2. Perchloric acid ($HClO_4$), conc., ultra pure.*
3. Ashing acid: 4:1 (v/v) HNO_3:$HClO_4$. Mix 4 volumes conc. HNO_3 with 1 volume conc. $HClO_4$.
4. Calibration stock solutions, 1000 µg/mL. Commercially available, or prepared per instrument manufacturer's recommendation (see step 12).
5. Dilution acid, 4% HNO_3, 1% $HClO_4$. 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 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: All perchloric acid digestions are required to be done in a perchloric acid hood. When working with concentrated acids, wear protective clothing and gloves.

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, 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 [5-10]. For example, aqua regia may be needed for Mn [6,12].
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 25-mL volumetric flasks.
11. Dilute to volume with dilution acid.
    NOTE: If more sensitivity is required, the final sample volume may be held to 10 mL.

CALIBRATION AND QUALITY CONTROL:

12. Calibrate the spectrometer according to the manufacturers recommendations.
    NOTE: Typically, an acid blank and 1.0 µg/mL multielement working standards are used. The following multielement combinations are chemically compatible in 4% HNO_3/1% $HClO_4$:
    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 blank filters 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, 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:

Issues 1 and 2
Method, 7300 was originally evaluated in 1981 [2,3]. The precision and recovery data were determined at 2.5 and 1000 µg of each element per sample on spiked filters. The measurements used for the method evaluation in Issues 1 and 2 were determined with a Jarrell-Ash Model 1160 Inductively Coupled Plasma Spectrometer operated according to manufacturer's instructions.

Issue 3
In this update of NIOSH Method 7300, 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. Tables 3 and 4 list the precision and recovery data, instrumental detection limits, and analytical wavelengths for mixed cellulose ester (MCE) and polyvinyl chloride (PVC) filters. PVC Filters which can be used for total dust measurements and then digested for metals measurements were tested and found to give good results. The values in Tables 3 and 4 were determined with a Spectro Analytical Instruments Model End On Plasma (EOP)(axial) operated according to manufacturer's instructions.

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METHOD REVISED BY:

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Method originally written by Mark Millson, NIOSH/DART, and R. DeLon Hull, Ph.D., NIOSH/DSHEFS, James B. Perkins, David L. Wheeler, and Keith Nicholson, DataChem Labortories, Salt Lake City, UT.

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	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	5	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 (0.45 µm)

Element (a)	wavelength nm	Est. LOD µg/ Filter	LOD ng/mL	Certified 3x LOD (b)	% Recovery (c)	Percent RSD (N=25)	Certified 10x LOD (b)	% Recovery (c)	Percent RSD (N=25)
Ag	328	0.042	1.7	0.77	102.9	2.64	3.21	98.3	1.53
Al	167	0.115	4.6	1.54	105.4	11.5	6.40	101.5	1.98
As	189	0.140	5.6	3.08	94.9	2.28	12.9	93.9	1.30
Ba	455	0.005	0.2	0.31	101.8	1.72	1.29	97.7	0.69
Be	313	0.005	0.2	0.31	100.0	1.44	1.29	98.4	0.75
Ca	317	0.908	36.3	15.4	98.7	6.65	64.0	100.2	1.30
Cd	226	0.0075	0.3	0.31	99.8	1.99	1.29	97.5	0.88
Co	228	0.012	0.5	0.31	100.8	1.97	1.29	98.4	0.90
Cr	267	0.020	0.8	0.31	93.4	16.3	1.29	101.2	2.79
Cu	324	0.068	2.7	1.54	102.8	1.47	6.40	100.6	0.92
Fe	259	0.095	3.8	1.54	103.3	5.46	6.40	98.0	0.95
K	766	1.73	69.3	23.0	90.8	1.51	96.4	97.6	0.80
La	408	0.048	1.9	0.77	102.8	2.23	3.21	100.1	0.92
Li	670	0.010	0.4	0.31	110.0	1.91	1.29	97.7	0.81
Mg	279	0.098	3.9	1.54	101.1	8.35	6.40	98.0	1.53
Mn	257	0.005	0.2	0.31	101.0	1.77	1.29	94.7	0.73
Mo	202	0.020	0.8	0.31	105.3	2.47	1.29	98.6	1.09
Ni	231	0.020	0.8	0.31	109.6	3.54	1.29	101.2	1.38
P	178	0.092	3.7	1.54	84.4	6.19	6.40	82.5	4.75
Pb	168	0.062	2.5	1.54	109.4	2.41	6.40	101.7	0.88
Sb	206	0.192	7.7	3.08	90.2	11.4	12.9	**41.3**	32.58
Se	196	0.135	5.4	2.3	87.6	11.6	9.64	84.9	4.78
Sn	189	0.040	1.6	0.77	90.2	18.0	3.21	**49**	21.79
Sr	407	0.005	0.2	0.31	101.0	1.55	1.29	97.3	0.65
Te	214	0.078	3.1	1.54	102.0	2.67	6.40	97.4	1.24
Ti	334	0.050	2.0	0.77	98.4	2.04	3.21	93.4	1.08
Tl	190	0.092	3.7	1.54	100.9	2.48	6.40	99.1	0.80
V	292	0.028	1.1	0.77	103.2	1.92	3.21	98.3	0.84
W	207	0.075	3.0	1.54	**72.2**	10.1	6.40	**57.6**	14.72
Y	371	0.012	0.5	0.31	100.5	1.80	1.29	97.4	0.75
Zn	213	0.310	12.4	4.60	102.2	1.87	19.3	95.3	0.90
Zr	339	0.022	0.9	0.31	88.0	19.4	1.29	**25**	57.87

(a) Bold values are qualitative only because of low 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 (c)	wavelength nm	Est. LOD µg per filter	LOD ng/mL	Certified 3x LOD (b)	% Recovery (a)	Percent RSD (N=25)	Certified[17] 10x LOD (b)	% Recovery (a)	Percent RSD (N=25)
Ag	328	0.042	1.7	0.78	104.2	8.20	3.18	81.8	18.9
Al	167	0.115	4.6	1.56	77.4	115.24	6.40	92.9	20.9
As	189	0.140	5.6	3.10	100.7	5.13	12.70	96.9	3.2
Ba	455	0.005	0.2	0.31	102.4	3.89	1.270	99.8	2.0
Be	313	0.005	0.2	0.31	106.8	3.53	1.270	102.8	2.1
Ca	317	0.908	36.3	15.6	**68.1**	12.66	64.00	96.8	5.3
Cd	226	0.0075	0.3	0.31	105.2	5.57	1.27	101.9	2.8
Co	228	0.012	0.5	0.31	109.3	4.67	1.27	102.8	2.8
Cr	267	0.020	0.8	0.31	109.4	5.31	1.27	103.4	4.1
Cu	324	0.068	2.7	1.56	104.9	5.18	6.40	101.8	2.4
Fe	259	0.095	3.8	1.56	88.7	46.82	6.40	99.1	9.7
K	766	1.73	69.3	23.4	96.4	4.70	95.00	99.2	2.2
La	408	0.048	1.9	0.78	**45.5**	4.19	3.18	98.8	2.6
Li	670	0.010	0.4	0.31	107.7	4.80	1.27	110.4	2.7
Mg	279	0.098	3.9	1.56	**54.8**	20.59	6.40	**64.5**	5.7
Mn	257	0.005	0.2	0.31	101.9	4.18	1.27	99.3	2.4
Mo	202	0.020	0.8	0.31	106.6	5.82	1.27	98.1	3.8
Ni	231	0.020	0.8	0.31	111.0	5.89	1.27	103.6	3.2
P	178	0.092	3.7	1.56	101.9	17.82	6.40	86.5	10.4
Pb	168	0.062	2.5	1.56	109.6	6.12	6.40	103.2	2.9
Sb	206	0.192	7.7	3.10	**64.6**	22.54	12.70	**38.1**	30.5
Se	196	0.135	5.4	2.30	83.1	26.23	9.50	76.0	17.2
Sn	189	0.040	1.6	0.78	85.7	27.29	3.18	**52.0**	29.4
Sr	407	0.005	0.2	0.31	**71.8**	4.09	1.27	81.2	2.7
Te	214	0.078	3.1	1.56	109.6	7.49	6.40	97.3	3.8
Ti	334	0.050	2.0	0.78	101.0	9.46	3.18	92.4	5.5
Tl	190	0.092	3.7	1.56	110.3	4.04	6.40	101.9	2.0
V	292	0.028	1.1	0.78	108.3	3.94	3.18	102.5	2.6
W	207	0.075	3.0	1.56	**74.9**	15.79	6.40	**44.7**	19.6
Y	371	0.012	0.5	0.31	101.5	3.63	1.27	101.4	2.5
Zn	213	0.310	12.4	4.70	91.0	68.69	19.1	101.0	9.6
Zr	339	0.022	0.9	0.31	**70.7**	54.20	1.27	**40.4**	42.1

(a) Values reported were obtained with a Spectro Analytical Instruments EOP ICP; performance may vary with instrument and should be independently verified.
(b) Values are certified by Inorganic Ventures INC. at 3x and 10x the approximate instrumental LOD [12].
(c) Bold values are qualitative only because of low recovery. Other digestion techniques may be more appropriate for these elements and their compounds.