ELEMENTS by ICP (Microwave Digestion) 7302

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

METHOD: 7302, Issue 1 | **EVALUATION: FULL** | **Issue 1: 21 July 2014**

OSHA: Table 2
NIOSH: Table 2
Other OELs: [1,2]*

PROPERTIES: Table 1

ELEMENTS:

aluminum	cadmium	lead	phosphorus	strontium	yttrium
antimony	calcium	lithium	platinum	tellurium	zinc
arsenic	chromium	magnesium	potassium	thallium	zirconium
barium	cobalt	manganese	selenium	tin	
beryllium	copper	molybdenum	silver	titanium	
boron	iron	nickel	sodium	vanadium	

SAMPLING

SAMPLER: FILTER (mixed cellulose ester membrane (MCE), 37-mm diameter, 0.8-µm pore size)

FLOW RATE: 1 to 4 L/min

VOL-MIN:
-MAX: Table 1

SHIPMENT: Routine

SAMPLE STABILITY: Stable

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: See Table 4

ACCURACY: See Table 4

BIAS: See Table 4

OVERALL PRECISION ($\hat{S}_{rT}$): See Table 4

MEASUREMENT

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

ANALYTE: Elements listed above

REAGENTS: 10.0 mL of 1:1 nitric (HNO_3) and ASTM Type II water

FINAL SOLUTION: 20% HNO_3, 25 mL

WAVELENGTH: Depends upon element (see Table 3)

BACKGROUND CORRECTION: Spectral wavelength shift

CALIBRATION: Elements in 20% HNO_3

RANGE: See Table 4

ESTIMATED LOD: Table 3

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

APPLICABILITY: This method is for the analysis of metal and nonmetal dust collected on MCE filters in the workplace. The working range varies from element to element. The method entails simultaneous elemental analysis using a microwave digestion approach to simplify and expedite the analysis.

INTERFERENCES: Spectral interferences are the primary interferences encountered in ICP-AES analysis. These are minimized by judicious wavelength selection, inter-element correction factors and background correction [3].

OTHER METHODS: This method complements NIOSH hotplate digestion methods 7300 and 7301 for trace elements. Flame atomic absorption spectroscopy (e.g., Methods 7013 through 7082) is an alternative analytical technique for many of these elements [4]. Graphite furnace AAS (e.g., 7102 for Be, 7105 for Pb) is usually more sensitive [4]. NMAM 7301 and 7303 contain alternative extraction procedures.

REAGENTS:

1. Nitric acid, conc., trace metal grade*
2. Calibration stock solutions, 1000 µg/mL and 10,000 µg/mL commercially available, or prepared per instrument manufacturer's recommendation (see step10)
3. Digestion acid*. 1:1 water, ASTM type II, and nitric acid*, trace metal grade
4. Argon, liquid
5. De-ionized Water, ASTM Type II [5]
6. Dilution acid*, 20% nitric acid in ASTM Type II water

* See Special Precautions

EQUIPMENT:

1. Sampler: mixed cellulose ester membrane (MCE) filter, 0.8-µm pore size, 37-mm diameter; in 2-piece 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. Microwave, programmable power, active temperature control, minimum of 574 W, corrosion resistant ventilated oven and turntable
6. Microwave digestion vessels, high pressure, closed PTFE, 100-mL capacity
7. Volumetric flasks, 25 mL**
8. Assorted volumetric pipettes as needed**

** Acid wash all glassware and vessels before using.

SPECIAL PRECAUTIONS: Wear gloves, lab coat, and safety glasses while handling all chemicals. All work should be performed with adequate ventilation to personnel and equipment. Because this method involves the use of capped digestion containers, avoid the use of other acids such as perchloric acid in combination with nitric acid that could cause a violent reaction [6,7]. In the preparation of the digestion and dilution acids, it is imperative that acid be added to water in order to avoid a violent exothermic reaction.

SAMPLING

1. Calibrate each personal sampling pump with a representative sampler connected to the pump (in line).
2. Sample at an accurately known flow rate between 1 and 4 L/min. For estimated sampling volumes see Table 1. For TWA measurements see Table 2. Do not exceed a filter loading of approximately 2 mg total dust.
   NOTE: Filter overloading can be assessed by periodic visual checks. See NMAM Chapter O, "Factors Affecting Aerosol Sampling," for additional discussion on filter capacity. [http://www.cdc.gov/niosh/docs/2003-154/pdfs/chapter-o.pdf.]

SAMPLE PREPARATION

NOTE: If total weights are desired, weighing should be done at this step. Follow NIOSH method 0500 for gravimetric analysis [11].

3. Open the cassette filter holders and transfer the samples, blanks, and Quality Control (QC) filters to clean PTFE digestion vessels. Wipe the internal cassette surfaces with a 37-mm MCE filter, polyvinyl alcohol wipe or cellulosic wipe wetted with deionized water, and add to the digestion vessel to transfer non-filter aerosol deposits into the digestion vessels.
4. Add digestion acid up to 10 mL, and cap the vessels.

NOTE: In order to avoid a violent exothermic reaction, do not add water to concentrated nitric acid. Acid should be added after the water has been placed in the vessel.

5. Place digestion vessels in microwave, and run the preprogrammed digestion procedure for 12-vessel digestion: 1200 W power, ramp to 150 °C over 20 min, hold for 10 min at 215 °C followed by at least a 5 min cool down (power will be adjusted lower for fewer vessels).
6. Allow the samples to cool to room temperature.
7. Remove vessel lids and rinse contents into 25-ml volumetric flasks with ASTM Type II water.
8. Dilute to the mark with ASTM Type II water and mix.
9. Submit extracted and diluted samples for analysis.

CALIBRATION AND QUALITY CONTROL

10. Calibrate the spectrometer according to the manufacturer recommendations.
    NOTE: Typically an acid blank and multi-element working standards are used. The following multi-element combinations are chemically compatible in 20% HNO_3.
    a. Al, As, Ba, Be, Ca, Co, Cr, Cu, Fe, Li, Mg, Mn, Mo, Na, Ni, Pb, Se, Sr, Ti, V, Y, Zn, Zr;
    b. B, K, P, Sn, Te, Tl;
    c. Ag, Cd, Sb;
    d. Pt.
11. Analyze all applicable standards at least once every twenty (20) analyses (minimum frequency 5%).
12. Check recoveries with at least one media blank and two spiked media blanks per twenty samples. Use a spike level that is within the range of 10 to 20 times the LOQ.
    NOTE: Whenever possible, QA/QC samples should be prepared from certified reference materials in a matrix similar to the bulk material sampled. Liquid spiked filters are only surrogates for real world samples and QC data based upon certified samples are preferred.

MEASUREMENT

13. Set ICP-AES spectrometer to conditions specified by manufacturer.
14. Analyze standards and samples at applicable wavelengths for each element (target analytes are in Table 3).
    NOTE: If the values for the samples are above the linear range of the instrument, dilute the solutions with dilution acid, reanalyze, and apply the appropriate dilution factor in 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 volume of sample, V_s (mL), and media blank, V_b (mL), calculate the concentration for the sample, C (mg/m^3), of each element in the air volume sampled, V (L), as follows:

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

NOTE: µg/Liter air is equivalent to mg/m^3.

EVALUATION OF METHOD

Method 7302 was evaluated using multi-element filter spikes at six spiking levels, based on the estimated LOQ for each element [8]. Using microwave digestion is less time consuming and more

convenient than using the traditional mixed acid hot plate approach. The elimination of perchloric acid in the sample digestion procedure helps to improve the safety of the method. [7]

Summary data are presented in Table 3 for levels 3X LOQ (lower level in Table 3) and 300X LOQ (higher level in Table 3) and for the ranges of loadings given in Table 4. Samples were subjected to microwave digestion using a CEM MDS-2100 device according to the conditions specified in the "sample preparation" section above (see Note of step #5). The values in Tables 3 and 4 were determined using several different ICP-AES instruments which were operated according to manufacturer's instructions. The precision and recovery data, instrumental detection limits, sensitivity, and analytical wavelengths are listed in Table 3 and Table 4. All of the precision data were evaluated for homogeneity for all six concentration levels tested using the Bartlett's test and the results are listed in the method backup data report [8] and summarized in Tables 3 and 4. A statistical analysis found that the data were poolable and all elements had calculated method precision accuracies of less than 25%. This overall precision ($\hat{S}_{rT}$) and accuracy as given in Table 4 is an upper limit predictor of precision. Accuracy data (Table 4) demonstrate the utility of the method for all of the elements listed.

A discussion of metals and metalloid analysis by ICP-AES is presented in an international voluntary consensus standard [3] and the microwave digestion procedure has been evaluated against other digestion procedures through an interlaboratory trial [10].

REFERENCES

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[10] Butler OT, Howe AM [1999]. Development of an international standard for the determination of metals and metalloids in workplace air using ICP-AES: Evaluation of sample dissolution procedures through an interlaboratory trial. J. Environ. Monit. 1: 23-32.

[11] Code of Federal Regulations, 29 CFR Part 1910.1000 (Table Z-1) [https://www.osha.gov/pls/oshaweb/owadisp.show_document?p_table=STANDARDS&p_id=9992]. Website accessed on December 13, 2013.

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* Other OELs: Because exposure limits and guidelines may change over time, NIOSH recommends referring to the following sources for updated limits and guidelines on the use of this compound.

TABLE 1. PROPERTIES AND SAMPLING VOLUMES

	Properties [9]		Air Volume, L @ OSHA PEL [11]	
Element (Symbol)	**Atomic Weight**	**MP, °C**	**MIN**	**MAX**
Aluminum (Al)	26.98	660	5	100
Antimony (Sb)	121.76	630	10[2]	2000[2]
Arsenic (As)	74.92	817	5	2000
Barium (Ba)	137.3	727	5[2]	200[2]
Beryllium (Be)	9.01	1278	1250	2000
Boron (B)[1]	10.81	2300	5	2000
Cadmium	112.40	321	12	2000
Calcium (Ca)[1]	40.08	842	5	200
Chromium (Cr)	52.00	1890	5	1000
Cobalt (Co)	58.93	1495	25	2000
Copper (Cu)	63.54	1083	5	1000
Iron (Fe)	55.85	1535	5	100
Lead (Pb)	207.19	328	50	2000
Lithium (Li)[1]	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
Platinum (Pt)	195.09	1769	1250	2000
Potassium (K)[1]	39.10	63	5	2000
Selenium (Se)	78.96	217	13	2000
Silver (Ag)	107.87	961	250	2000
Sodium (Na)[1]	22.99	98	13	2000
Strontium (Sr)[1]	87.62	769	5	2000
Tellurium (Te)	127.60	450	25	2000
Tin (Sn)	118.69	232	20[2]	2000[2]
Thallium (Tl)	204.37	304	25	2000
Titanium (Ti)	47.90	1675	5	100
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

[1] No PEL, REL, or STEL data found [1,6,11].
[2] Air volumes estimated from TWAs and LOQs (see Tables 2, 3) [1].

TABLE 2. EXPOSURE LIMITS, CAS #, RTECS [1,6,11]

Element (Symbol)	CAS #	RTECS	Exposure Limits in mg/m³ (C = ceiling limit)	
			OSHA	NIOSH
Aluminum (Al)	7429-90-5	BD0330000	15 (total dust) 5 (respirable)	10 (total dust) 5 (respirable, fume)
Arsenic (As)	7440-38-2	CG0525000	0.010 (inorganic)	C 0.002(1)
Arsenic (As)	7440-38-2	CG0525000	0.010 (inorganic)	C 0.002(1)
Barium (Ba)	7440-39-3		0.5 (Soluble compounds, as Ba)	0.5 (Soluble compounds, as Ba)
Beryllium (Be)	7440-41-7	DS1750000	0.002, C 0.005	C 0.0005(1)
Cadmium (Cd)	7440-43-9	EU9800000	0.005	lowest feasible conc.(1)
Calcium (Ca)	7440-70-2		No OELs	No OELs
Chromium (II) (Cr)	22541-79-3	GB6260000	0.5	0.5
Chromium (III) (Cr)	16065-83-1	GB6261000	0.5	0.5
Chromium (VI) (Cr)	18540-29-9	GB6262000	0.005	0.0002
Cobalt (Co)	7440-48-4	GF8750000	0.1	0.05 (dust, fume)
Copper (Cu)	7440-50-8	GL5325000	1(dust, mists) 0.1 (fume)	1 (dust, mists) 0.1 (fume)
Iron (Fe)	1309-37-1	NO7400000	10 (fume) as oxide	5 (dust, fume) as oxide
Lead (Pb)	7439-92-1	OF7525000	0.05	0.05
Magnesium (Mg)	1309-48-4	OM3850000	15 (dust) as oxide	--
Manganese (Mn)	7439-96-5	OO9275000	C 5	1; STEL 3
Molybdenum (Mo)	7439-98-7	QA4680000	5 (soluble) 15 (total insoluble)	
Nickel (Ni)	7440-02-0	QR5950000	1	0.015, Ca
Phosphorus (P)	7723-14-0	TH3500000	0.1	0.1
Platinum (Pt)	7440-06-4	TP2160000	0.002 (soluble)	1 (metal)
Antimony (Sb)	7440-36-0	CC4025000	0.5	0.5
Selenium (Se)	7782-49-2	VS7700000	0.2	0.2
Silver (Ag)	7440-22-4	VW3500000	0.01 (soluble, metal)	0.01 (soluble, metal)
Tellurium (Te)	13494-80-9	WY2625000	0.1	0.1
Tin (Sn)	7440-31-5	XP7320000	2	2
Titanium (Ti)	7440-32-6	XR1700000	15 (as TiO_2)	lowest feasible(1)
Thallium (Tl)	7440-28-0	XG3425000	0.1 (soluble)	0.1 (soluble)
Uranium (U)	7440-61-1	YR3490000	0.25 (insoluble) 0.05 (soluble)	0.2; STEL 0.6 (insoluble)
Vanadium (V)	7440-62-2	YW240000	C 0.5 (respirable) as V_2O_5 C 0.1 (fume) as V_2O_5	C 0.05
Yttrium (Y)	7440-65-5	ZG2980000	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)
Zirconium (Zr)	7440-67-7	ZH7070000	5	5, STEL 10

(1) Carcinogen

TABLE 3. MEASUREMENT WAVELENGTHS AND RECOVERY DATA [8]

			Lower Level			Higher Level		
Element[1]	Wavelength (nm)[6]	LOD (µg/sample)	µg/sample	% Recovery N=6)	% RSD	µg/sample	% Recovery (N=6)	% RSD
Ag	328.1	0.1	1.50	95.5	1.01	150	99.0	0.497
Al	308.2	1	7.50	92.7	0.981	750	98.7	0.462
As	193.8	1	7.50	101	2.22	750	107	0.340
B	249.7	0.5	3.75	112	2.96	375	99.5	0.454
Ba	493.4	0.06	0.752	104	3.09	75.2	101	0.438
Be	313.0	0.009	0.076	95.8	2.36	7.60	103	0.714
Ca	315.9	2	22.5	107	2.87	2250	99.0	0.620
Cd	228.8	0.1	1.50	98.8	3.46	150	104	0.701
Co	228.6	0.3	3.75	99.7	1.72	375	104	0.566
Cr[2]	267.7	0.4	3.75	103	7.87	375	103	3.36
Cu	324.8	0.07	0.752	98.8	3.47	75.2	94.2	0.371
Fe	259.9	2	15.0	112	2.43	1500	101	0.263
K	766.5	2	15.0	98.3	5.70	1500	103	0.472
Li	670.8	0.03	0.752	92.4	2.98	75.2	98.8	0.749
Mg	279.1	0.5	7.50	89.3	3.52	750	95.1	0.309
Mn	257.6	0.02	0.752	86.2	2.38	75.2	98.2	0.389
Mo	202.0	0.2	2.25	96.8	5.41	225	103	0.373
Na	589.0	4	37.5	100	0.823	3750	110	0.457
Ni	231.6	0.2	2.25	98.3	5.21	225	97.7	0.592
P	214.9	2	15.0	100	5.67	1500	104	0.315
Pb	220.4	0.6	7.50	98.9	3.94	750	104	0.570
Pt[2]	265.9	8	75.0	98.3	0.282	10000	95.7	1.49
Sb	206.8	0.4	7.50	94.4	3.21	750	103	0.255
Se	196.1	3	37.5	104	3.21	3750	106	0.270
Sn[2]	189.9	0.8	37.5	105	5.04	3750	90.3	3.23
Sr	421.6	0.02	3.75	92.6	2.36	375	97.5	0.553
Te[2]	214.3	2	15.0	90.1	21.8	1500	103	0.614
Ti	337.3	0.2	1.50	101	1.70	150	98.8	0.575
Tl	190.9	0.9	7.5	103	4.14	750	99.3	0.352
V	292.4	0.1	0.752	93.7	4.74	75.2	103	0.341
Y[2]	371.0	0.02	0.376	107	4.44	37.6	102	3.33
Zn[2]	213.9	0.1	1.50	106	13.1	150	97.4	3.42
Zr	339.2	0.06	0.750	93.1	5.35	75.0	95.4	0.971

(1) Values reported were obtained with a Fisons ARL Accuris ICP-AES; performance may vary with instrument and should be independently verified.

(2) Values reported were obtained with a Perkin Elmer Optima 3000 DV ICP-AES. Sample concentration was based on Fisons ICP LOD data.

TABLE 4. PRECISION AND ACCURACY DATA BY ELEMENT [8]

Element (µg/sample)	Range (µg/sample)	Bias	$\hat{S}_{rt}$ (%)	Accuracy
Ag	0.5 to 150	-0.0175	0.668	2.85
Al	2.5 to 750	0.0505	1.455	7.41
As	2.5 to 750	-0.2249	0.554	23.40
Ba	0.25 to 75.2	-0.0330	0.920	4.82
Be	0.025 to 7.60	0.0297	0.863	4.39
Ca	7.43 to 2250	-0.0081	0.836	2.18
Cd	0.50 to 150	-0.0082	0.729	2.02
Co	1.24 to 375	-0.0161	0.574	2.56
Cr	1.24 to 375	-0.0204	0.655	3.12
Cu	0.248 to 75.2	0.0160	0.984	3.21
Fe	5.00 to 1500	-0.0039	1.637	3.30
K	5.00 to 1500	0.1487	1.665	17.61
La	12.6 to 50.1	-0.0136	0.920	2.87
Li	0.25 to 75.2	0.2241	1.209	24.40
Mg	2.5 to 750	0.0180	0.844	3.19
Mn	0.25 to 75.2	-0.0348	0.865	4.91
Mo	0.75 to 225	0.0140	1.469	3.82
Ni	0.75 to 225	-0.0063	0.672	1.73
P	5.0 to 1500	0.0669	1.212	8.69
Pb	2.5 to 750	-0.0246	0.544	3.36
Sb	2.5 to 750	0.0172	0.722	2.91
Se	12.4 to 3750	0.0538	0.758	6.63
Sn	12.4 to 3750	0.0561	0.936	7.15
Sr	1.24 to 375	-0.0074	0.710	1.90
Te	5.0 to 1500	0.0161	0.892	3.08
Ti	0.5 to 150	0.0212	1.043	3.84
Tl	2.5 to 750	-0.0293	0.602	3.92
V	0.25 to 75.2	0.0175	1.223	3.76
Y	0.12 to 37.6	-0.0179	1.115	3.62
Zn	0.5 to 150	0.0075	1.343	3.02
Zr	0.25 to 75.0	0.0314	0.980	4.76