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ELEMENTS BY ICP ON PVC FILTERS USING MICROWAVE DIGESTION

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BACKUP DATA REPORT

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INTRODUCTION

This method incorporates the speed of Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) multi-element analysis along with the simplicity of microwave single acid digestion. Prior to the development of the procedure reported herein, digestions of filter media for elements involved the use of perchloric acid on hotplates. This new procedure eliminates the danger that is associated with the use of perchloric acid. It also cuts the digestion time from days to a matter of hours using microwave digestion.

This method also demonstrates that PVC filters can be used for most of the elements studied, thereby allowing both gravimetric measurements and ICP multi-element analyses to be performed on the same sample. The polyvinyl chloride (PVC) filters used in this method can be digested in nitric acid if a high-pressure microwave is employed. Single acid microwave digestion greatly simplifies the sample preparation. These filters have little affinity for water absorption and are therefore suitable for gravimetric analysis.

Of the elements studied, antimony, silver, and tin had low and extremely variable recoveries from PVC filters. This is possibly due to the interference of chlorine from the digested PVC filters. The analysis of these elements is more successful if they are collected on MCE filters (See Method NMAM 730x).

REAGENTS AND STANDARDS

Presented in Tables 1 and 2 are the lists of reagents and standards used for this method evaluation. All of the standards were made up in 20% nitric acid by the vendors.

Table 1. List of Chemicals

Chemical	Vendor	CAS#	Purity	Lot#
Nitric Acid	J. T. Baker	7697-37-2	70%	9598-34
Water	Data Chem Laboratories	7732-18-5	ASTM Type ll [1]	--

Table 2. List of Standards

Analyte	Primary ID#	Primary Conc.	Vendor	Lot#
Al	IP-PS-02-012	1000 ug/mL	CPI	2AF233
As	IP-PS-02-012	500 ug/mL	CPI	2AF233
Ba	IP-PS-02-012	200 ug/mL	CPI	2AF233
Be	IP-PS-02-012	200 ug/mL	CPI	2AF233
Ca	IP-PS-02-012	1000 ug/mL	CPI	2AF233
Co	IP-PS-02-012	200 ug/mL	CPI	2AF233
Cr	IP-PS-02-012	200 ug/mL	CPI	2AF233
Cu	IP-PS-02-012	200 ug/mL	CPI	2AF233
Fe	IP-PS-02-012	500 ug/mL	CPI	2AF233
Li	IP-PS-02-012	200 ug/mL	CPI	2AF233
Mg	IP-PS-02-012	500 ug/mL	CPI	2AF233
Mn	IP-PS-02-012	200 ug/mL	CPI	2AF233
Mo	IP-PS-02-012	200 ug/mL	CPI	2AF233
Na	IP-PS-02-012	500 ug/mL	CPI	2AF233
Ni	IP-PS-02-012	500 ug/mL	CPI	2AF233
Pb	IP-PS-02-012	500 ug/mL	CPI	2AF233
Se	IP-PS-02-012	1000 ug/mL	CPI	2AF233
Sr	IP-PS-02-012	200 ug/mL	CPI	2AF233
Ti	IP-PS-02-012	200 ug/mL	CPI	2AF233
V	IP-PS-02-012	200 ug/mL	CPI	2AF233
Y	IP-PS-02-012	200 ug/mL	CPI	2AF233
Zn	IP-PS-02-012	200 ug/mL	CPI	2AF233
Zr	IP-PS-02-012	200 ug/mL	CPI	2AF233
B	IP-PS-02-026	10000 ug/mL	EM Science	B1065147
K	IP-PS-02-068	10000 ug/mL	EM Science	B2025030
P	IP-PS-02-035	10000 ug/mL	EM Science	B2025035
Si	IP-PS-02-026	10000 ug/mL	EM Science	B1125060
Te	IP-PS-02-040	1000 ug/mL	EM Science	B1125041
Tl	IP-PS-02-046	10000 ug/mL	EM Science	A8075015
Cd	IP-PS-02-028	10000 ug/mL	EM Science	B1025044
Pt	IP-PS-02-123	10000 ug/mL	EM Science	B0125146

SAMPLE PREPARATION AND INSTRUMENT CONDITIONS

Air Sampling

The scope of this evaluation did not include the collection of any generated atmospheres. It is assumed that previous method evaluations have sufficiently evaluated this aspect of the analysis of the elements. A summary of the pertinent exposure limits is given in Table 3.

The normal sampling procedure is as follows, although it was not applicable to this evaluation. Calibrated personal sampling pumps equipped with PVC filters are used to monitor work place exposure conditions for airborne inorganic contaminants. The pumps are set at a flow rate of between 1 and 4 L/min. For total sample volume, see Table 4. Sample loading limits can be estimated from TWA values (see Table 3), instrument sensitivity, and sampling flow rate [2]. A filter loading of approximately 2

mg of dust should not be exceeded. Once collected the sample cassette filter holders are removed from the personal sampling pumps, the ends capped, and sent in for ICP-AES analysis.

Table 3. EXPOSURE LIMITS, CAS #, RTECS [5][6]

Exposure Limits, mg/m^3 (Ca=carcinogen; C=ceiling limit; *not adopted due to adverse effects at this level

Element (Symbol)	CAS #	RTECS	OSHA	NIOSH	ACGIH
Aluminum (Al)	7429-90-5	BD0330000	15 (total dust) 5 (respirable)	10 (total dust) 5 (respirable, fume) 2 (salt, alkyls)	10 (dust) 5 (powder, fume) 2 (salt, alkyls)
Arsenic (As)	7440-38-2	CG0525000	0.010 (inorganic)	C 0.002, Ca	0.01, Ca
Barium (Ba)	7440-39-3	CQ8370000	0.5 [5]		
Boron (B) (1)	7440-42-8				
Beryllium (Be)	7440-41-7	DS1750000	0.002, C 0.005	Not to exceed 0.0005, Ca	0.002, Ca
Calcium (Ca) (1)	7440-70-2		Varies	Varies	varies
Cadmium (Cd)	7440-43-9	EU9800000	0.2, C 0.6 (dust) 0.1, C 0.3 (fume)	lowest feasible conc., Ca	0.01 (total), Ca 0.002 (respirable), Ca
Cobalt (Co)	7440-48-4	GF8750000	0.1	0.05 (dust, fume)	0.05 (dust, fume)
Chromium (II) (Cr)	22541-79-3	GB6260000	0.5	0.5	Not given
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, mists) 0.1 (fume)	1 (dust, mists) 0.2 (fume)
Iron (Fe)	1309-37-1	NO7400000	10 (fume) as oxide	5 (dust, fume) as oxide	5 (fume) as oxide
Potassium (K) (1)	7440-09-7				
Lithium (Li) (1)	7439-93-2				
Magnesium (Mg)	1309-48-4	OM3850000	15 (dust) as oxide	10 (fume) as oxide*	10 (fume) as oxide
Manganese (Mn)	7439-96-5	OO9275000	C 5	1; STEL 3	0.2
Molybdenum (Mo)	7439-98-7	QA4680000	5 (soluble) 15 (total insoluble)	5 (soluble)* 10 (insoluble)*	5 (soluble) 10 (insoluble)
Sodium (Na) (1)	7440-23-5				
Nickel (Ni)	7440-02-0	QR5950000	1	0.015, Ca	1.5 (metal) (soluble) 0.2 (insoluble), Ca
Phosphorus (P)	7723-14-0	TH3500000	0.1	0.1	
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
Strontium (Sr) (1)	7440-24-6	WK7849000			
Tellurium (Te)	13494-80-9	WY2625000	0.1	0.1	0.1
Titanium (Ti)	7440-32-6	XR1700000	As TiO_2, 15	lowest feasible, Ca	10
TiO_2	13463-67-7	XR2275000	as TiO_2, 5 (respirable)		
Thallium (Tl)	7440-28-0	XG3425000	0.1 (skin) (soluble)	0.1 (skin) (soluble)	0.1 (skin)
Vanadium (V)	7440-62-2	YW240000	C 0.5 (respirable) as V_2O_5	C 0.05	0.05 (respir.) as V_2O_5
V_2O_5	1314-62-1	YW1355000	C 0.1 (fume) 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

(1) No PEL, REL, STEL data found [5][6].

Table 4. PROPERTIES AND SAMPLING VOLUMES

	Properties [3]		Air Volume, L @ OSHA PEL [4]	
Element (Symbol)	Atomic Weight	MP, °C	MIN	MAX
Aluminum (Al)	26.98	660	5	100
Arsenic (As)	74.92	817	5	2000
Barium (Ba)	137.3	727	5(2)	200(2)
Boron (B) (1)	10.81	2300	5	2000
Beryllium (Be)	9.01	1278	1250	2000
Calcium (Ca) (1)	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) (1)	39.10	63	5	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
Sodium (Na) (1)	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
Strontium (Sr) (1)	87.62	769	5	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

(1) No PEL, REL, STEL data found [5][6].
(2) Air Volumes Estimated from TWA and LOQs (see Tables 3 and 7) [2].

Sample Preparation

For all the studies in this method evaluation, blank PVC filters were spiked with the elements of interest and transferred to clean PTFE XP-1500 digestion vessels. To each vessel was added 10 mL of nitric acid and 2 mL of ASTM Type II water. Where applicable the blanks and QC filters were also prepared in this same manner. The digestion vessels were then placed into a MARS 5 programmable microwave and digested using the following conditions:

MICROWAVE CONDITIONS:

METHOD	Ramp to Temperature (215 °C)	
POWER	1,200W	100%
PRESSURE MAX	625 psi	
RAMP TIME	20 min.	
HOLD TIME	10 min.	
COOL DOWN	Auto	

NUMBER OF VESSELS: 6 to12

NOTE: For this digestion procedure to be successful on PVC filters it is important that a programmable high-pressure microwave digestion apparatus be used.

After digestion was complete the vessels were allowed to cool. The lids were then removed and the contents of the vessels were rinsed into 50 mL volumetric flasks with ASTM type II water and diluted to the mark. The samples were then submitted for ICP-AES analysis.

**ICP Instrument Conditions and Calibration **

The ICP spectrometer was setup and calibrated according to the manufacturers recommendations. An acid blank and a multi-element working standard were used for calibration. The two point curves obtained covered the linear working range of the analytes of interest. Listed in Table 5 are the concentrations of the standards that make up the top end of the curves produced for this method development and evaluation.

The following multi-element combinations are chemically compatible in 20% HNO3.

1. Al, As, Ba, Be, Ca, Co, Cr, Cu, Fe, Li, Mg, Mn, Mo, Na, Ni, Pb, Se, Sr, Ti, V, Y, Zn, and Zr;
2. B, K, P, Si, Te, and Tl;
3. Cd;
4. Pt.

Mixture number 1 above was obtained from CPI and was used as-is. The others were obtained as individual solutions from EM Science.

A Continuing Calibration Verification Standard (CCV) or standards that contain the analytes of interest are analyzed after every ten analyses (minimum frequency), and recoveries are checked with media blanks and spikes every twenty samples.

The concentration of the standards that gives a linear calibration on the instruments involved in this evaluation are given in Table 5 below.

Table 5. Calibration Standard Concentrations

Analyte	Primary ID#	Primary Conc.	Volume of Primary	Final Volume	Final Concentration
Al	IP-PS-02-012	1000 ug/mL	20 mL	2000 mL	10 ug/mL
As	IP-PS-02-012	500 ug/mL	20 mL	2000 mL	5 ug/mL
Ba	IP-PS-02-012	200 ug/mL	20 mL	2000 mL	2 ug/mL
Be	IP-PS-02-012	200 ug/mL	20 mL	2000 mL	2 ug/mL
Ca	IP-PS-02-012	1000 ug/mL	20 mL	2000 mL	10 ug/mL
Co	IP-PS-02-012	200 ug/mL	20 mL	2000 mL	2 ug/mL
Cr	IP-PS-02-012	200 ug/mL	20 mL	2000 mL	2 ug/mL
Cu	IP-PS-02-012	200 ug/mL	20 mL	2000 mL	2 ug/mL
Fe	IP-PS-02-012	500 ug/mL	20 mL	2000 mL	5 ug/mL
Li	IP-PS-02-012	200 ug/mL	20 mL	2000 mL	2 ug/mL
Mg	IP-PS-02-012	500 ug/mL	20 mL	2000 mL	5 ug/mL
Mn	IP-PS-02-012	200 ug/mL	20 mL	2000 mL	2 ug/mL
Mo	IP-PS-02-012	200 ug/mL	20 mL	2000 mL	2 ug/mL
Na	IP-PS-02-012	500 ug/mL	20 mL	2000 mL	5 ug/mL
Ni	IP-PS-02-012	500 ug/mL	20 mL	2000 mL	5 ug/mL
Pb	IP-PS-02-012	500 ug/mL	20 mL	2000 mL	5 ug/mL
Se	IP-PS-02-012	1000 ug/mL	20 mL	2000 mL	10 ug/mL
Sr	IP-PS-02-012	200 ug/mL	20 mL	2000 mL	2 ug/mL
Ti	IP-PS-02-012	200 ug/mL	20 mL	2000 mL	2 ug/mL
V	IP-PS-02-012	200 ug/mL	20 mL	2000 mL	2 ug/mL
Y	IP-PS-02-012	200 ug/mL	20 mL	2000 mL	2 ug/mL
Zn	IP-PS-02-012	200 ug/mL	20 mL	2000 mL	2 ug/mL
Zr	IP-PS-02-012	200 ug/mL	20 mL	2000 mL	2 ug/mL
B	IP-PS-02-026	10000 ug/mL	1 mL	1000 mL	10 ug/mL
K	IP-PS-02-068	10000 ug/mL	5 mL	1000 mL	50 ug/mL
P	IP-PS-02-035	10000 ug/mL	2 mL	1000 mL	20 ug/mL
Te	IP-PS-02-040	1000 ug/mL	10 mL	1000 mL	10 ug/mL
Tl	IP-PS-02-046	10000 ug/mL	2 mL	1000 mL	20 ug/mL
Cd	IP-PS-02-028	10000 ug/mL	0.2 mL	1000 mL	2 ug/mL
Pt	IP-PS-02-123	10000 ug/mL	2 mL	2000 mL	10 ug/mL

LIMITS OF DETECTION

The limit of detection (LOD) was determined according to the protocol given in the Environmental Protection Agency's 40 CFR[7] for the determination of the minimum detectable limit (MDL). In this procedure, seven or more replicates are analyzed. The MDL for each element is then calculated. The calculated MDL must be equal to or less than the TC by no more than a factor of 0.1. In other words, the MDL is acceptable if the MDL and the TC have the following relationship: 1#TC/MDL#10. Otherwise, a new TC must be selected and the MDL estimated again. The MDLs determined in this manner are given in Table 6 for both instruments involved in this evaluation. For the balance of this evaluation, the term LOD (limit of detection) is used in place of MDL. The term LOQ (limit of quantitation) is then calculated as 10/3 times the LOD.

The LOD is also a function of the wavelength. The wavelength at which an analyte is measured is generally the most sensitive available. Where there are spectral

interferences from other elements in a sample, it may be necessary to use an alternate wavelength. With a fixed wavelength instrument this is not always possible. In this method evaluation two different ICP instruments were used. Most of the data for this method evaluation was generated using a fixed channel Fisons ARL Accuris ICP-AES. For those analytes where there were possible interference or other problems on the Fisons, a Perkin Elmer Optima 3000 DV ICP-AES was employed.

The replicates along with filter blanks and quality control (QC) samples for this LOD study were prepared and processed through the sample digestion procedure as given in the section on Sample Preparation.

Table 6. WAVELENGTHS AND DETECTON LIMITS

	Wavelength (nm)[8]		LOD (ug/sample)		LOQ (ug/sample)	
Element[a]	Fisons[b]	P-E[c]	Fisons[b]	P-E[c]	Fisons[b]	P-E[c]
Ag	328.07	328.068*	0.1	0.2*	0.5	0.5*
Al	308.22	308.214	2	0.5	6	2
As	193.76	193.695*	2	0.9*	6	3*
Ba	493.41	233.529*	0.2	*	0.6	*
B	249.68	249.772*	0.4	*	1	*
Be	313.04	313.103*	0.008	0.007*	0.03	0.02*
Ca	315.89	315.886	2	2	7	8
Cd	228.80	226.501*	0.2	0.1*	0.7	0.4*
Co	228.62	228.615*	0.7	0.4*	2	1*
Cr	267.72	267.712	0.7	0.3	2	0.9
Cu	324.75	324.753	0.08	0.08	0.3	0.3
Fe	259.94	259.939	14.7	5	49	16
K	766.49	766.496	3		9	
Li	670.78	610.364*	0.06	0.07*	0.2	0.2*
Mg	279.08	279.078	0.9	0.4	3	1
Mn	257.61	257.609*	0.09	0.05*	0.3	0.2*
Mo	202.03	202.029	0.4	0.3	1	0.9
Na	589.00	589.596*	5	7*	17	22*
Ni	231.60	231.603	0.3	0.2	1	0.6
P	214.92	214.916	2	2	6	7
Pb	220.35	220.350*	1	0.7*	3	2*
Pt	203.659	265.944*	9	6*	30	21*
Sb	206.84	206.837*	0.7	*	2	*
Se	196.09	196.025	5	2	16	6
Sr	421.55	421.545*	0.04	*	0.1	*
Te	214.27	214.287	4	2	12	5
Ti	337.28	334.942	0.2	0.1	0.6	0.4
Tl	190.86	190.794	2	1	6	4
V	292.40	292.403	0.1	0.09	0.4	0.3
Y	371.03	371.030*	0.07	0.02*	0.2	0.06*
Zn	213.85	213.855	0.2	0.4	0.8	1
Zr	339.20	343.823*	0.2	0.03*	0.6	0.1*

* These elements were not analyzed using the Perkin-Elmer in any of the subsequent studies.

(a) Performance may vary with instrument and should be independently verified.

(b) Fisons ICP-AES .

(c) Perkin-Elmer (PE) Optima 3000 DV ICP-AES

The two instruments were comparable in LODs within at least one order of magnitude and more commonly within a factor of 2.

PRECISION and ACCURACY STUDY

To determine the precision and accuracy for this method, six concentrations for each element ranging from 1 x LOQ to 300 x LOQ were prepared on the PVC filters. Table 7 gives the concentration of the analytes in ug/filter used for the study based on an approximation of the previously determined LOQs (ug/filter is equivalent to ug/sample).

Table 7. CONCENTRATION OF ANALYTES in ug/sample

Element	LOQ[(a)]		1xLOQ	3xLOQ	10xLOQ	30xLOQ	100xLOQ	300xLOQ
	Fisons	P-E						
Aluminum	6	2	5.025	15	50.25	150	500.25	1500
Antimony	2		5.025	15	50.25	150	500.25	1500
Arsenic	6	3	5.025	15	50.25	150	500.25	1500
Barium	0.6		0.50384	1.504	5.0384	15.04	50.1584	150.4
Berylium	0.03	0.02	0.05092	0.152	0.5092	1.52	5.0692	15.2
Boron	1		2.51384	7.504	25.1384	75.04	250.2584	750.4
Cadmium	0.7	0.4	1.005	3	10.05	30	100.05	300
Calcium	7	8	15.075	45	150.75	450	1500.75	4500
Chromium	2	0.9	2.51384	7.504	25.1384	75.04	250.2584	750.4
Cobalt	2	1	2.51384	7.504	25.1384	75.04	250.2584	750.4
Copper	0.3	0.3	0.50384	1.504	5.0384	15.04	50.1584	150.4
Iron	49	16	10.05	30	100.5	300	1000.5	3000
Lead	3	2	5.025	15	50.25	150	500.25	1500
Lithium	0.2	0.2	0.50384	1.504	5.0384	15.04	50.1584	150.4
Magnesium	3	1	5.025	15	50.25	150	500.25	1500
Manganese	0.3	0.2	0.50384	1.504	5.0384	15.04	50.1584	150.4
Molybdenum	1	0.9	1.50884	4.504	15.0884	45.04	150.2084	450.4
Nickel	1	0.6	1.50884	4.504	15.0884	45.04	150.2084	450.4
Phosphorus	6	47	10.05	30	100.5	300	1000.5	3000
Platinum	30	21	50	150	500	1500	5000	15000
Potassium	9		10.05	30	100.5	300	1000.5	3000
Selenium	16	6	25.125	75	251.25	750	2501.25	7500
Silver	0.5	0.5	1.005	3	10.05	30	100.05	300
Sodium	17	22	25.125	75	251.25	750	2501.25	7500
Strontium	0.1		2.51384	7.504	25.1384	75.04	250.2584	750.4
Tellurium	12	5	10.05	30	100.5	300	1000.5	3000
Thallium	6	4	5.025	15	50.25	150	500.25	1500
Tin		1	25.125	75	251.25	750	2501.25	7500
Titanium	0.6	0.4	1.005	3	10.05	30	100.05	300
Vanadium	0.4	0.3	0.50384	1.504	5.0384	15.04	50.1584	150.4
Yttrium	0.2	0.6	0.25192	0.752	2.5192	7.52	25.0792	75.2
Zinc	0.8	0.4	1.005	3	10.05	30	100.05	300
Zirconium	0.6	0.03	0.5025	1.5	5.025	15	50.025	150

(a) LOQs are those given in Table 6.

At each level, six blank filters were spiked with certified standards and digested following the procedure outlined in the section on sample preparation. After digestion the samples were analyzed on the Fisons instrument, the raw data collected, and precision and accuracy calculated. Whenever it looked like the Fisons' data might not pass the criteria the solutions were reanalyzed on the Perkin-Elmer instrument.

PROCEDURE FOR PROCESSING THE DATA:

The resulting data was entered into spreadsheets that calculated percent recovery and precision at each level (See Tables 8 and 9). Each set of six replicates was tested for Grubbs outliers at the 1% risk of false rejection level. No more than one Grubbs outlier was removed from any set of six replicates. No more than 2 Grubbs outliers were removed from any set of 18. However, up to 3 Grubbs outliers were removed from sets of 24 or more.

Where the Precision and Accuracy criteria were met for all 6 levels, no other processing was necessary. Where the criteria could not be met with 6 levels, the CV for the lowest level was omitted to see if the criteria could be met. Where this was not sufficient, the CVs at each level for each analyte were entered into a second spreadsheet that performed a Bartlett's test for all possible combinations of CVs for 5 and 4 concentration levels, and in some cases for all possible combinations of CVs for 3 concentration levels after the lowest level was omitted. Of those combinations that passed the Bartlett's test, using a Chi squared for a 97.5% distribution for each respective number of levels considered, the combination that gave the largest Chi squared was accepted for calculation of the pooled precision, which is the overall precision of the method, Srt.

The weighted average of the bias was calculated on those levels that passed the Bartlett's test for homogeneity of precision, although the bias itself was not tested for homogeneity. (See Table 10 for the average bias at each individual concentration level.) From the pooled precision and the weighted average of the bias for each element, the accuracy of the method for each element was estimated from the Nomogram given in the Guidelines manual. This was accomplished by making an enlargement of the nomogram on the copier for easier estimation. The resulting final data is given in Table 11.

Table 8. PERCENT RECOVERY at each CONCENTRATION LEVEL

Element[(a)]	Instrument	1xLOQ	3xLOQ	10xLOQ	30xLOQ	100xLOQ	300xLOQ
Aluminum	Fisons Perkin-Elmer	***-48.16*** ***129.79***	***53.19*** 115.05	89.78 105.67	98.28 107.04	102.41 106.66	100.71 105.17
Antimony	Fisons	108.29	***25.29***	***14.72***	***55.94***	***75.79***	111.95
Arsenic	Fisons	***61.79***	93.29	101.45	107.27	114.24	115.84
Barium	Fisons	106.90	107.16	104.11	103.53	105.83	102.22
Beryllium	Fisons	110.79	102.38	104.61	103.66	109.80	107.71
Boron	Fisons	***57.13***	86.38	95.98	99.33	103.33	101.19
Cadmium	Fisons	***120.89***	109.65	108.47	107.18	113.46	111.68
Calcium	Fisons Perkin-Elmer	***-24.83*** 109.63	***62.06*** 104.82	92.68 103.49	105.04 103.77	115.26 100.99	116.25 98.13
Chromium	Fisons Perkin-Elmer	117.88 112.45	112.65 102.60	111.36 98.55	109.74 97.31	117.11 95.51	118.65 92.98
Cobalt	Fisons	***70.01***	89.87	103.04	105.86	115.08	114.15
Copper	Fisons Perkin-Elmer	111.94 **123.45**	106.84 117.16	104.73 110.48	102.72 106.95	105.04 105.18	100.42 103.13
Iron	Fisons Perkin-Elmer	***175.94*** ***157.16***	***120.58*** 112.55	109.04 104.26	106.30 104.41	109.74 97.95	112.41 97.20
Lead	Fisons	91.37	95.85	96.72	93.31	100.12	100.54
Lithium	Fisons	101.32	97.51	95.12	93.53	89.85	81.96
Magnesium	Fisons Perkin-Elmer	109.80 113.71	105.25 107.33	102.92 104.21	100.75 106.03	102.92 104.65	97.47 101.75
Manganese	Fisons	117.56	110.24	110.05	110.52	116.95	115.56
Molybdenum	Fisons Perkin-Elmer	90.94 109.69	87.79 89.75	84.03 ***79.67***	102.92 90.83	113.53 95.71	***120.57*** 100.44
Nickel	Fisons Perkin-Elmer	106.41 114.06	102.93 109.91	106.96 107.23	108.02 103.48	112.74 102.86	110.59 101.77
Phosphorus	Fisons Perkin-Elmer	83.33 89.63	81.82 86.36	99.56 99.87	100.11 100.18	106.36 102.25	107.20 103.33
Platinum	Fisons	99.90	104.67	103.69	100.97	106.71	105.19
Potassium	Fisons Perkin-Elmer	***25.38*** ***159.42***	66.32 107.88	85.57 99.40	96.84 96.84	94.76 93.77	86.46 90.02
Selenium	Fisons Perkin-Elmer	104.59 100.69	102.05 99.93	106.75 100.88	108.05 99.78	111.50 101.15	111.35 99.72
Silver	Fisons	104.71	***63.01***	***31.29***	***9.50***	***6.19***	***3.92***
Sodium	Fisons	***211.30***	***124.56***	107.19	97.61	92.43	83.07
Strontium	Fisons	96.29	100.00	101.09	101.79	103.73	99.54
Tellurium	Fisons Perkin-Elmer	102.53 101.63	95.80 97.18	***76.24**** ***74.98****	102.33 98.36	110.37 100.62	110.81 99.64
Thallium	Fisons Perkin-Elmer	80.03 99.51	96.38 97.75	101.31 96.33	101.48 93.12	103.34 93.75	97.25 92.04
Tin	Fisons Perkin-Elmer	***54.57*** ***73.72***	***30.82*** ***37.87***	***33.41*** ***40.81***	***63.30*** 80.54	***75.80*** 93.63	***79.56*** 92.34
Titanium	Fisons Perkin-Elmer	94.16 88.92	81.66 82.68	88.42 88.22	91.04 85.91	88.52 85.88	103.42 96.13
Vanadium	Fisons Perkin-Elmer	110.02 100.26	104.54 100.99	104.38 98.64	105.60 97.82	111.95 99.37	111.15 99.38
Yttrium	Fisons	105.18	105.98	106.31	104.66	107.96	105.03
Zinc	Fisons Perkin-Elmer	***129.76*** 88.29	110.76 93.45	110.01 96.12	106.30 94.60	115.38 95.09	116.84 94.01
Zirconium	Fisons	106.48	102.61	101.96	99.04	103.51	101.56

* Average recovery is 101.27% when the 3 replicates are removed having about 50% recovery.
** Average recovery is 98.06% when the 3 replicates are removed having about 50% recovery.
Bold numbers in Table 7 are recoveries greater than 120% or less than 80%.

ANALYSIS OF RECOVERY (Refer to Table 8)

With 3 exceptions, recoveries were very good, meaning that the recoveries were between 80 to 125% on at least 5 of the six levels for at least one of the instruments. The exceptions were antimony, silver, and tin. Recoveries for Antimony and silver were so bad that no attempt was made to reanalyze them on the Perkin-Elmer. Recoveries for tin were poor on the Fisons, but improved at the upper 3 concentration levels on the Perkin-Elmer. Excluding those 3 elements, of the remaining 276 data points only 23 were either above 120% or below 80% recovery. If the 1xLOQ level is omitted, then only 6 of 230 data points were below 80% and 3 just barely above 120%. This signals very good recoveries in general. However, recoveries were not constant across the concentration range. Nearly a third of the elements were generally decreasing in recovery and a third were generally increasing in recoveries. This has an affect on the homogeneity of the bias, to be discussed later in this report.

Of the 6 low recoveries, excluding antimony, silver, and tin, 2 of them were at the 10xLOQ level for tellurium, one for the Fisons and the other for the Perkin-Elmer. This set of replicates had 3 of 6 that were about 50% (43-57%) of what they were supposed to be while the other 3 were 97-107% of target. This suggests that they were either miss-spiked or losses occurred during sample processing. Because there were 3 apparent outliers, they could not be removed by the Grubbs test which allows for only one outlier to be removed. Nevertheless, they probably were outliers because it was obvious that they were out of character with both the levels immediately above and below where the recoveries ranged from 90 to 106%. However, in obtaining the pooled CV and the weighted averaged bias it was convenient to remove this level entirely.

A similar situation existed within the 100xLOQ level for titanium where one replicate had a low recovery which just barely could not pass the Grubbs test. The CVs for titanium were able to pass the Bartlett's test when the 100xLOQ level was omitted entirely.

Table 9. PRECISION at each CONCENTRATION LEVEL

Element[(a)]	Instrument	1xLOQ	3xLOQ	10xLOQ	30xLOQ	100xLOQ	300xLOQ
Aluminum	Fisons Perkin-Elmer	***-0.13135*** 0.6222	0.07108 0.01990	0.05647 0.04329	0.04193 0.05515	0.01844 0.01494	0.00550 0.00557
Antimony	Fisons	0.06795	***0.58611***	***0.39811***	***0.55483***	***0.45773***	0.00860
Arsenic	Fisons	***0.21277***	0.05706	0.05106	0.03121	0.06093	0.01743
Barium	Fisons	0.05702	0.02945	0.01755	0.01417	0.01656	0.01043
Berylium	Fisons	***0.10771***	0.08614	0.01305	0.01979	0.02007	0.00905
Boron	Fisons	***0.11443***	0.02770	0.01042	0.01551	0.00373	0.00817
Cadmium	Fisons	0.09103	0.03163	0.04098	0.02950	0.00667	0.01523
Calcium	Fisons Perkin-Elmer	***-0.15397*** 0.02403	0.02410 0.00897	0.05120 0.02745	0.02741 0.03656	0.01766 0.01264	0.01527 0.00657
Chromium	Fisons Perkin-Elmer	0.06810 0.01590	0.02329 0.00480	0.01986 0.01625	0.03299 0.01830	0.00997 0.00946	0.01363 0.00666
Cobalt	Fisons	***0.17799***	0.03377	0.03639	0.02700	0.01319	0.01405
Copper	Fisons Perkin-Elmer	0.06594 0.07000	0.03639 0.03613	0.01512 0.01726	0.01352 0.01874	0.02691 0.01855	0.00585 0.01497
Iron	Fisons Perkin-Elmer	***0.37295*** ***0.43215***	0.04050 0.04896	0.03240 0.03163	0.05388 0.05141	0.02737 0.02537	0.00833 0.00845
Lead	Fisons	***0.10415***	0.03086	0.03825	0.02318	0.02716	0.01542
Lithium	Fisons	0.03530	0.02527	0.01304	0.01536	0.02854	0.03781
Magnesium	Fisons Perkin-Elmer	0.04184 0.03663	0.00880 0.00430	0.02285 0.02661	0.01271 0.01516	0.02430 0.01408	0.00769 0.00586
Manganese	Fisons	0.02435	0.01504	0.02429	0.02707	0.01257	0.00901
Molybdenum	Fisons Perkin-Elmer	***0.10744*** 0.01606	0.04332 0.02152	0.04907 0.01888	***0.10487*** 0.08228	0.06227 0.06060	0.00930 0.01543
Nickel	Fisons Perkin-Elmer	***0.14563*** 0.01629	0.04750 0.00471	0.03754 0.02347	0.02807 0.00907	0.01884 0.01906	0.00808 0.01389
Phosphorus	Fisons Perkin-Elmer	***0.14554*** 0.04185	0.05116 0.00770	0.04639 0.03744	0.02499 0.00982	0.00813 0.01195	0.01029 0.01739
Platinum	Fisons	***0.12157***	0.01817	0.03058	0.03082	0.01509	0.00879
Potassium	Fisons Perkin-Elmer	***0.29584*** ***0.24737***	0.08464 ***0.16547***	0.02537 0.03008	0.01260 0.02889	0.03674 0.01779	0.02597 0.02053
Selenium	Fisons Perkin-Elmer	0.07610 0.01446	0.05316 0.00510	0.02358 0.03620	0.01488 0.01009	0.00923 0.01951	0.00633 0.00819
Silver	Fisons	0.06792	0.07391	***1.16058***	***0.19928***	0.82078	0.08656
Sodium	Fisons	***0.19601***	0.08589	0.02622	0.01229	0.03116	0.02477
Strontium	Fisons	0.00314	0.00491	0.02057	0.01488	0.01505	0.00545
Tellurium	Fisons Perkin-Elmer	***0.17814*** 0.02015	0.06240 0.01000	***0.36530**** ***0.34382****	0.03211 0.02299	0.01286 0.00940	0.00944 0.00743
Thallium	Fisons Perkin-Elmer	***0.28641*** 0.03295	0.06058 0.00328	0.04364 0.03679	0.01677 0.01020	0.03432 0.02093	0.01488 0.01195
Tin	Fisons Perkin-Elmer	0.03626 0.02704	0.05026 0.08164	***0.10670*** ***0.11068***	***0.15248*** ***0.16060***	0.03928 0.03434	0.01240 0.01289
Titanium	Fisons Perkin-Elmer	***0.19395*** 0.04812	0.03928 0.03737	0.02617 0.02429	***0.10189*** 0.08879	***0.26058*** ***0.16405***	0.01016 0.01213
Vanadium	Fisons Perkin-Elmer	***0.11184*** 0.03255	0.05286 0.01468	0.01095 0.01410	0.02773 0.00894	0.00671 0.01546	0.01602 0.02320
Yttrium	Fisons	0.07897	0.02445	0.01503	0.02044	0.01088	0.00727
Zinc	Fisons Perkin-Elmer	0.05967 ***0.12053***	0.03269 0.03505	0.05931 0.02424	0.03132 0.00650	0.02247 0.02950	0.01525 0.00556
Zirconium	Fisons	0.07239	0.02424	0.01245	0.02384	0.00405	0.01439

* CV is 0.04778 when the 3 replicates are removed having about 50% recovery.

** CV is 0.02073 when the 3 replicates are removed having about 50% recovery.

Bold numbers are those that exceed 0.1000 (10%RSD) or are negative in sign.
Numbers that are shaded are less than 0.0200 (2%RSD).

ANALYSIS OF PRECISION: (Refer to Table 9.

Only a few elements analyzed were able to pass the Precision and Accuracy criteria with all 6 levels considered on either the Fisons or the Perkin-Elmer. On the Fisons these were Lithium, Manganese, and Zinc. On the Perkin-Elmer only Chromium, Selenium, and Vanadium were able to pass all criteria with all 6 levels considered.

When the 1xLOQ level was omitted from consideration several additional metals were able to meet all the criteria. On the Fisons these were Calcium, Chromium, Platinum, Yttrium, and Zirconium, and on the Perkin-Elmer they were Copper and Nickel.

The primary reason for the elements not meeting the Precision and Accuracy criteria was the non-homogeneity of precision. The homogeneity of precision was tested using the Bartlett's test. The homogeneity of the bias was not tested, but it was apparent from looking at the data that the bias (percent recoveries) were, as were the precisions, a function of concentration. At the higher levels the precisions were very small compared to the lower levels. This is observable in Table 9 where all CVs that were less than 0.02000 are shaded. Most of the shaded entries are at the right side in the table. These values might be considered "inliers".

At the 300xLOQ level the precisions were almost without exception below 2%RSD. If the CVs for antimony, silver, and tin are excluded, the average of all the CVs at the 100xLOQ level is about twice the average of those at the 300xLOQ level. At the 30xLOQ level, the average is about 3 times that at 300x LOQ. At the 10x and 3xLOQ level, the average is about 4 times that at 300x LOQ, and at the 1xLOQ level, the average CV is about 7.4 times that at 300xLOQ. From experience it has been observed that, roughly speaking, when any CV is more than about twice its neighbors, it usually doesn't pass the Bartlett's test. Since on average so many CVs are 3 and 4 times greater than those at 300 or 100xLOQ, either the 100x and 300xLOQ level data has to be excluded in spite of its excellent precision, or some of the data at the lower levels has to be excluded, even though the precisions at these levels often only range from 3-9%RSD, which is certainly not very bad.

By selectively removing data it is possible to get a set of CVs that satisfy Bartlett's test. But often this creates what might be regarded as an artificial pooled precision. If apparent inliers are removed, then the precision appears to be worse than it really is at the higher concentrations. But if the lower level CVs are removed, then the precision appears to be much better than it really is at the low levels. The situation is simply this: For most of the elements the precision and bias cannot be predicted for concentration levels not studied. But it might be safe to say that since the precision and recovery generally improve with increasing concentration, that the accuracy of the method for higher concentrations is at least as good or better than that for the highest level tested, the 300xLOQ level.

The values at the 3xLOQ level will be generally indicative of conditions at the lower concentration levels, while those at the 300xLOQ level will be indicative of the expectations for levels above the 300xLOQ level.

Because the spiked PVC filters were not weathered, nor were atmospheres generated, the Precision and Accuracy study is essentially a Desorption Efficiency study. The precision values obtained in this study are in effect Sr1 for analytical samples and not Sr2 for generated samples, according to the Guidelines manual (page 60).

Table 10. AVERAGE BIAS at each CONCENTRATION LEVEL

Element[(a)]	Instrument	1xLOQ	3xLOQ	10xLOQ	30xLOQ	100xLOQ	300xLOQ
Aluminum	Fisons Perkin-Elmer	**-1.4816** **0.2979**	**-0.4681** 0.1505	-0.1022 0.0567	-0.0172 0.0704	0.0241 0.0666	0.0071 0.0517
Antimony	Fisons	0.0829	**-0.7471**	**-0.8528**	**-0.4406**	**-0.2421**	0.1195
Arsenic	Fisons	**-0.3821**	-0.0671	0.0145	0.0727	0.1148	0.1584
Barium	Fisons	0.0690	0.0716	0.0411	0.0353	0.0513	0.0222
Beryllium	Fisons	0.1079	0.0238	0.0461	0.0366	0.0980	0.0771
Boron	Fisons	**-0.4287**	-0.1362	-0.0402	-0.0067	0.0333	0.0119
Cadmium	Fisons	**0.2089**	0.0965	0.0847	0.0718	0.1346	0.1168
Calcium	Fisons Perkin-Elmer	**-1.2483** 0.0963	**-0.3794** 0.0482	-0.0732 0.0349	0.0504 0.0377	0.1526 0.0099	0.1625 -0.0187
Chromium	Fisons Perkin-Elmer	0.1788 0.1245	0.1265 0.0260	0.1136 -0.0145	0.0974 -0.0269	0.1711 -0.0449	0.1865 -0.0702
Cobalt	Fisons	**-0.2999**	-0.1013	0.0304	0.0586	0.1508	0.1415
Copper	Fisons Perkin-Elmer	0.1194 **0.2345**	0.0684 0.1716	0.0473 0.1048	0.0272 0.0695	0.0504 0.0518	0.0042 0.0313
Iron	Fisons Perkin-Elmer	**0.7594** **0.5716**	**0.2058** 0.1255	0.0904 0.0426	0.0630 0.0441	0.0974 -0.0205	0.1241 -0.0280
Lead	Fisons	-0.0863	-0.0415	-0.0328	-0.0669	0.0124	0.0054
Lithium	Fisons	0.0132	-0.0249	-0.0488	-0.0647	-0.1015	-0.1804
Magnesium	Fisons Perkin-Elmer	0.0980 0.1371	0.0525 0.0733	0.0292 0.0421	0.0075 0.0603	0.0203 0.0465	-0.0253 0.0175
Manganese	Fisons	0.1756	0.1024	0.1005	0.1052	0.1695	0.1556
Molybdenum	Fisons Perkin-Elmer	-0.0906 0.0969	-0.1221 -0.1025	-0.1597 -0.2033	0.0292 -0.0917	0.1353 -0.0429	**0.2057** 0.0044
Nickel	Fisons Perkin-Elmer	0.0641 0.1406	0.0293 0.0991	0.0696 0.0723	0.0802 0.0348	0.1274 0.0286	0.1059 0.0177
Phosphorus	Fisons Perkin-Elmer	-0.1667 -0.1037	-0.1818 -0.1364	-0.0044 -0.0013	0.0011 0.0018	0.0636 0.0225	0.0720 0.0333
Platinum	Fisons	-0.0010	0.0467	0.0369	0.0097	0.0671	0.0519
Potassium	Fisons Perkin-Elmer	**-0.7462** **0.5942**	**-0.3368** 0.0788	-0.1443 -0.0060	-0.0316 -0.0316	-0.0524 -0.0623	-0.1354 -0.0998
Selenium	Fisons Perkin-Elmer	0.0459 0.0069	0.0205 -0.0007	0.0675 -0.0088	0.0805 -0.0022	0.1150 0.0115	0.1135 -0.0028
Silver	Fisons	0.0471	**-0.3699**	**-0.6871**	**-0.9050**	**-0.9381**	**-0.9608**
Sodium	Fisons	**1.1130**	**0.2456**	0.0719	-0.0239	-0.0757	-0.1693
Strontium	Fisons	-0.0371	-0.0000	0.0109	0.0179	0.0373	-0.0046
Tellurium	Fisons Perkin-Elmer	0.0253 0.0163	-0.0420 -0.0282	**-0.2376*** **-0.2502****	0.0233 -0.0164	0.1037 0.0062	0.1081 -0.0036
Thallium	Fisons Perkin-Elmer	-0.1997 -0.0049	-0.0362 -0.0225	0.0131 -0.0367	0.0148 -0.0688	0.0334 -0.0625	-0.0275 -0.0796
Tin	Fisons Perkin-Elmer	**-0.4543** **-0.2628**	**-0.6918** **-0.6213**	**-0.6659** **-0.5919**	**-0.3670** -0.1946	**-0.2420** -0.0637	**-0.2044** -0.0766
Titanium	Fisons Perkin-Elmer	-0.0584 0.1108	-0.1834 -0.1732	-0.1158 -0.1178	-0.0896 -0.1409	-0.1148 -0.1412	0.0342 -0.0387
Vanadium	Fisons Perkin-Elmer	0.1002 0.0026	0.0454 0.0099	0.0438 -0.0136	0.0560 -0.0218	0.1195 -0.0063	0.1115 -0.0062
Yttrium	Fisons	0.0518	0.0598	0.0631	0.0466	0.0796	0.0503
Zinc	Fisons Perkin-Elmer	**0.2976** -0.1171	0.1076 -0.0655	0.1001 -0.0388	0.0630 -0.0540	0.1538 -0.0491	0.1684 -0.0599
Zirconium	Fisons	0.0648	0.0261	0.0196	-0.0096	0.0351	0.0156

* Bias is 0.0126 if three replicates around 50% recovery are removed.

** Bias is -0.0194 if three replicates around 50% recovery are removed.

Bold numbers are Bias values greater than plus or minus 0.2000.
Shaded numbers are Bias values greater than plus or minus 0.1000.

ANALYSIS OF BIAS: (Refer to Table 10.)

The comments made in reference to the percent recoveries are applicable to the bias as well. Table 10 reflects the same information as is given in Table 8. Also, the fact that this precision and accuracy study is based upon analytical samples and not generated samples might affect the interpretation of the extent of bias. Because the definition of the method bias excludes correctable bias, which is bias that can be explained as a desorption efficiency, and since this precision and accuracy study is essentially a desorption efficiency study, therefore biases of greater than plus or minus 10% must be allowed. Therefore, the 10% cut-off rule was not followed. In Table 10, biases that are greater than an absolute value of 10% are shaded.

The biases were not tested for homogeneity. It is apparent that there was a lot of dependency upon concentration in over half of the analyses independent of which instrument was used.

FINAL POOLED PRECISION, BIAS, AND ACCUARCY: (Refer to Table 11.)

Using the concentration levels that passed Bartlett's test on either instrument, the following data was determined. In the far right hand column of Table 11 the concentration levels are listed that had to be omitted in order to make the data pass the Bartlett's test. This included some very good data that were either inliers, or data that would not pool because the remaining data contained inlier CVs.

In Table 12 are listed the recoveries and precision for the 3xLOQ and 300xLOQ levels in consolidated form. Data from both the Fisons and the Perkin-Elmer are included for comparison and to show that the data is fairly comparable in most cases. In several cases with the Fisons data the 3xLOQ data is substituted with the 10xLOQ data because of low recoveries at the 3xLOQ level. Where recoveries were also low at the 10xLOQ level, the 3xLOQ level data was retained and no was substitution made. From this table it is apparent that even though much of the data was not poolable across all concentration levels, the recoveries and precision still appeared to be good.

Table 11. POOLED PRECISION, BIAS, and ACCURACY

Element	Instrument	Bias	Range of Bias		Precision S_{rT}	Accuracy	xLOQ Conc. Levels Omitted [a]
			From	To			
Aluminum	Fisons Perkin-Elmer	-0.03179 0.08325	-0.10224 0.05672	0.02406 0.15047	0.04198 0.03789	9.9 15.1	1,3,300 [b] 1,300 [b]
Antimony	Fisons	Poor and variable recoveries across study range.					
Arsenic	Fisons	0.06299	-0.06705	0.15837	0.04610	14.3	1
Barium	Fisons	0.04336	0.02221	0.07163	0.01817	7.6	1
Beryllium	Fisons	0.06524	0.03661	0.09799	0.01633	9.5	1,3
Boron	Fisons	-0.03874	-0.13619	0.01188	0.01646	6.4	1,100 [b]
Cadmium	Fisons	0.09227	0.07181	0.11676	0.03070	14.8	1,100 [b]
Calcium	Fisons Perkin-Elmer	0.07796 0.04530	-0.05363 0.00988	0.16246 0.09630	0.03130 0.02454	13.4 8.8	1,3 300 [b]
Chromium	Fisons Perkin-Elmer	**0.13945** -0.00175	0.09742 -0.07016	0.18650 0.12454	0.02142 0.01316	18 <5	1 none
Cobalt	Fisons	0.05924	-0.10130	0.15079	0.02635	10.4	1
Copper	Fisons Perkin-Elmer	0.04745 0.08287	0.02721 0.03131	0.06841 0.17161	0.02403 0.02171	8.9 12.1	1,300 [b] 1
Iron	Fisons Fisons Perkin-Elmer	**0.11018** 0.08362 0.04456	0.06302 0.06302 -0.02049	0.20578 0.09742 0.12547	0.03978 0.03959 0.04041	18.6 15.4 11.4	1,300 [b] 1,3,300 [b] 1,300 [b]
Lead	Fisons	-0.02409	-0.06686	0.01240	0.02791	6.9	1
Lithium	Fisons	-0.06908	-0.18040	0.01319	0.02757	11.1	none
Magnesium	Fisons Perkin-Elmer	0.01560 0.07151	-0.02530 0.04212	0.05246 0.13715	0.01705 0.02489	<5 11.5	1 3,300 [b]
Manganese	Fisons	**0.13571**	0.10053	0.17556	0.02007	17.3	none
Molybdenum	Fisons Perkin-Elmer	-0.03878 -0.04891	-0.15965 -0.20331	0.13527 0.09687	0.07949 0.01794	16.7 7.7	300 [b] 30,100
Nickel	Fisons Perkin-Elmer	0.07873 0.06456	0.02934 0.01765	0.12744 0.14061	0.03386 0.01593	13.8 9.2	1,300 [b] none
Phosphorus	Fisons Perkin-Elmer	-0.05463 -0.01630	-0.18183 -0.13640	0.00114 0.03333	0.04170 0.01248	12 <5	1,100 [b],300 [b] 1,10
Platinum	Fisons	0.04232	0.00971	0.06712	0.02261	8.2	1
Potassium	Fisons Perkin-Elmer	-0.09093 -0.04992	-0.14431 -0.09983	-0.03164 -0.00597	0.02658 0.02489	13.1 8.8	1,3 1,3
Selenium	Fisons Perkin-Elmer	0.09414 0.00266	0.06753 -0.00278	0.11497 0.01149	0.01502 0.01274	12.1 <5	1,3 10
Silver	Fisons	Poor and variable recoveries across study range.					
Sodium	Fisons	-0.04926	-0.16935	0.07188	0.02461	8.8	1,3
Strontium	Fisons	0.01722	-0.00002	0.03731	0.01531	<5	1,300 [b]
Tellurium	Fisons Perkin-Elmer	0.02949 -0.00436	-0.04203 -0.02823	0.10369 0.01625	0.04041 0.01553	9.8 <5	1,300 [b] 10
Thallium	Fisons Perkin-Elmer	-0.00811 -0.05050	-0.03622 -0.06883	0.03339 -0.00486	0.04072 0.02500	8.2 9	1,300 [b] 3 [b]
Tin	Fisons Perkin-Elmer	Poor and variable recoveries across study range.					
Titanium	Fisons Perkin-Elmer	-0.08272 **-0.10724**	-0.18337 -0.17323	0.03424 -0.03867	0.02687 0.03209	12.3 15.3	1,30,100 30,100
Vanadium	Fisons Perkin-Elmer	0.07042 -0.00634	0.04384 -0.02178	0.11148 0.00991	0.01954 0.01986	10.5 <5	1,3,100 [b] none
Yttrium	Fisons	0.05988	0.04659	0.07958	0.01641	8.9	1
Zinc	Fisons Fisons Perkin-Elmer	**0.14522** **0.11895** -0.05028	0.06299 0.06299 -0.06550	0.29755 0.16838 -0.03881	0.03995 0.03562 0.02952	22 18.7 9.6	None 1 1,30 [b],300 [b]
Zirconium	Fisons	0.01639	-0.00963	0.03508	0.01753	<5	1

[a] Concentration levels that were omitted to permit CVs to pass Bartlett's test for homogeneity.
[b] These levels had CVs that were inliers.

Table 12. RECOVERIES AND PRECISION AT 3xLOQ AND 300xLOQ

Element[a]	Wavelength (nm)	LOD (ug/sample)	30xLOQ				300xLOQ			
			ug/sample	N =	Percent Recovery	Precision (S_r)	ug/sample	N =	Percent Recovery	Precision (S_r)
Ag	328.07	0.1	3.00	5	63.01	0.07391	300	6	3.92	0.08656
Al	308.22	2	50.25 [d]	6	89.78	0.05647	1500	6	100.71	0.00550
Al[b]	308.214	0.5	15.0	5	115.05	0.01990	1500	6	105.17	0.00557
As	193.76	2	15.0	5	93.29	0.05706	1500	6	115.84	0.01743
Ba	493.41	0.2	1.50	5	107.16	0.02945	150	6	102.22	0.01043
B	249.68	0.4	7.50	5	86.38	0.02770	750	6	101.19	0.00817
Be	313.04	0.008	0.152	6	102.38	0.08614	15.2	6	107.71	0.00905
Ca	315.89		151 [d]	6	94.64	0.05120	4500	6	116.25	0.01527
Ca[b]	315.886	2	45.0	5	104.82	0.00897	4500	6	98.13	0.00657
Cd	228.80	0.2	3.00	5	109.65	0.03163	300	6	111.68	0.01523
Co	228.62	0.7	7.50	5	89.87	0.03377	750	6	114.15	0.01405
Cr	267.72	0.7	7.50	5	112.65	0.02329	750	6	118.65	0.01363
Cr[b]	267.712	0.3	7.50	5	102.60	0.00480	750	6	92.98	0.00666
Cu	324.75	0.08	1.50	5	106.84	0.03639	150	6	100.42	0.00585
Cu[b]	324.753	0.08	1.50	5	117.16	0.03613	150	6	103.13	0.01497
Fe	259.94	15	30	5	120.58	0.04050	3000	6	112.41	0.00833
Fe[b]	259.939	5	30	5	112.55	0.04896	3000	6	97.20	0.00845
K	766.49	3	100 [d]	6	85.57	0.02537	3000	6	86.46	0.02597
K[b]	766.496		100 [d]	6	99.40	0.03008	3000	6	90.02	0.02053
Li	670.78	0.06	1.50	5	97.51	0.02527	150	6	81.96	0.03781
Mg	279.08	0.9	15.0	5	105.25	0.00880	1500	6	97.47	0.00769
Mg[b]	279.078	0.4	15.0	5	107.33	0.00430	1500	6	101.75	0.00586
Mn	257.61	0.09	1.50	5	110.24	0.01504	150	6	115.56	0.00901
Mo	202.03	0.4	4.50	5	87.79	0.04332	450	6	120.57	0.00930
Mo[b]	202.029	0.3	4.50	5	89.75	0.02152	450	6	100.44	0.01543
Na	589.00	5	75.0	6	124.56	0.08589	7500	6	83.07	0.02477
Ni	231.60	0.3	4.50	5	102.93	0.04750	450	6	110.59	0.00808
Ni[b]	231.603	0.2	4.50	5	109.91	0.00471	450	6	101.77	0.01389
P	214.92	2	30.0	5	81.82	0.05116	3000	6	107.20	0.01029
P[b]	214.916	2	30.0	5	86.36	0.00770	3000	6	103.33	0.01739
Pb	220.35	1	15.0	5	95.85	0.03086	1500	6	100.54	0.01542
Pt	203.65	9	150	5	104.67	0.01817	15000	6	105.19	0.00879
Sb[c]	206.84	0.7	15.0	6	25.29	0.58611	1500	6	111.95	0.00860
Se	196.09	5	75.0	5	102.05	0.05316	7500	6	111.35	0.00633
Se[b]	196.025	2	75.0	5	99.93	0.00510	7500	6	99.72	0.00819
Sn	189.9		75.0	5	30.82	0.05026	7500	6	79.56	0.01240
Sn[b,c]	189.9	0.4	75.0	5	37.87	0.08164	7500	6	92.34	0.01289
Sr	421.55	0.04	7.50	5	100.00	0.00491	750	6	99.54	0.00545
Te	214.27	4	30.0	5	95.80	0.06240	3000	6	110.81	0.00944
Te[b]	214.287	2	30.0	5	97.18	0.01000	3000	6	99.64	0.00743
Ti	337.28	0.2	3.00	5	81.66	0.03928	300	6	103.42	0.01016
Ti[c]	334.942	0.1	3.00	5	82.68	0.03737	300	6	96.13	0.01213
Tl	190.86	2	15.0	5	96.38	0.06058	1500	6	97.25	0.01488
Tl[c]	190.794	1	15.0	5	97.75	0.00328	1500	6	92.04	0.01195
V	292.40	0.1	1.50	5	104.54	0.05286	150	6	111.15	0.01602
V[b]	292.403	0.09	1.50	5	100.99	0.01468	150	6	99.38	0.02320
Y	371.03	0.07	0.752	5	105.98	0.02445	75.2	6	105.03	0.00727
Zn	213.85	0.2	3.00	5	110.76	0.03269	300	6	116.84	0.01525
Zn[b]	213.855	0.4	3.00	5	93.45	0.03505	300	6	94.01	0.00556
Zr	339.20	0.2	1.50	5	102.61	0.02424	150	6	101.56	0.01439

(a) Values reported were obtained with a Fisons ARL Accuris ICP-AES unless otherwise noted; performance may vary with instrument and should be independently verified.
(b) Values reported were obtained with a Perkin Elmer Optima 3000 DV ICP-AES.
(c) Elements that were evaluated and found not suitable for analysis by this method.
(d) Values given are for the 10xLOQ level due to low recoveries at the 3xLOQ level.

Media Background

Media blank results for PVC filters showed only the calcium, boron and aluminum blanks to be higher than there LOQ's, but less than the operating range. Thus, with the practical operating range being from 3xLOQ to 300xLOQ, subtraction of the media blank from the spiked filter results was not found to be necessary.

Table 13: MEDIA BACKGROUND RESULTS[(a)]

Element[(a)]	Average (N=6) (ug/sample)	LOQ (ug/sample)
Al	8.72	7
As	-1.44	7
Ba	0.0546	0.7
B	1.81	1
Be	-0.0026	0.03
Ca	20.3	7
Cd	0.242	0.7
Co	-0.674	2
Cr	0.105	2
Cu	0.0210	0.3
Fe	2.71	50
K	-4.07	10
Li	0.0530	0.2
Mg	0.534	3
Mn	0.0312	0.3
Mo	-0.323	1
Na	12.5	20
Ni	-0.0312	1
P	0.109	7
Pb	-0.383	3
Pt	3.13	30
Se	0.677	20
Sr	0.173	0.1
Te	-1.31	10
Ti	0.191	0.7
Tl	-0.690	7
V	-0.0291	0.3
Y	-0.0126	0.2
Zn	0.283	0.7
Zr	0.0314	0.7

(a) Values and LOQs reported were obtained with a Fisons ARL Accuris ICP-AES and Perkin Elmer Optima 3000 DV ICP-AES; performance may vary with instrument and should be independently verified.

SUMMARY AND COMMENTS

The method evaluated herein passes the NIOSH criteria with the special exceptions noted because of the inliers and the fact that the precision and accuracy determinations were made on analytical samples and not on generated samples. The exceptional precision generally at the higher concentration levels in many of the metals makes it difficult for the CVs to pass Bartlett's test for homogeneity.

Only three metals failed on PVC filters in the range studied. These were silver, antimony, and tin. This is believed to be due to the presence of chorine from the PVC filters from digestion.

One metal, tellurium, had 3 replicates of 6 at the 10xLOQ level that were about 50% recovery. With the Perkin-Elmer results that entire level was omitted to permit the remaining CVs to pass Bartlett's test. But with the Fisons data, no combination of CVs from three or more levels would pass Bartlett's test. This is because two CVs were inliers and two others were mid range and the two remaining were very large. Any of these pairs would pass but not any combination of three or more. But if the three low recovery replicates at the 10xLOQ level were omitted, then four concentration levels did pass Bartlett's test. But a statistical justification for removing those three replicates is unknown, except that they were definitely out of character with the levels at either higher or lower concentrations. This set was an extreme example of the problem with inliers making it difficult to find enough levels to pool when something happens to one set of replicates.

If each level is taken by itself without having to pool with its neighboring concentration levels, the data seems adequate in both recovery and precision (recoveries 81-121% and relative standard deviations less than 0.1100 in the worst cases, and most of them better than these values).

With most of the metals the CV appeared to be a function of concentration. The smallest CVs were at the highest concentrations. Omitting the CV at the highest concentration level has the consequence of creating overall precisions that are larger than what would probably be encountered at concentrations above the range studied.

When the data was initially processed, all Grubbs outliers with a 1% risk of false rejection or less were removed. This had the unintended consequence of creating inlier CVs from the remaining 5 replicates in a large number of cases. It was decided that returning these data points was the wise and conservative thing to do even though their removal might be justified simply on the setting of a 1% threshold limit. By returning these values the resulting CVs were often raised from less than 1% to a more reasonable 3 or 4%, making it easier for the Bartlett's test to pass more levels. By lowering the Grubbs outlier threshold to 0.1%, or in worse case to 0.5%, much more data was able to pass the Bartlett's test. This was probably the right thing to do since it is better to give conservative precision estimates than those which are overly small. Even so, many of the metals still have very small overall precisions.

This method is for the analysis of metal and nonmetal dust collected on PVC filters in the workplace and environment in general. This method increases the applicability of NMAM 7300 [4]. Using a microwave digestion approach simplifies and expedites the analysis. The elimination of perchloric acid [9] in the sample digestion helps to improve the safety of the method.

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