Arsenic, Cadmium, Cobalt, Copper, Lead, and Nickel
(Open Vessel Microwave Digestion/ICP-MS Analysis)

Method number: 1006

Control number: T-1006-FV-01-0502-M

Analyte (isotope)	Target Concn (mg/m^3)	OSHA PEL (mg/m^3)*	ACGIH TLV (mg/m^3)	RQL ($\mu g/m^3$)	Standard Error of Estimate (%)
As (75)	0.01	0.01**	0.01	0.34	±5.75
Cd (114)	0.005	0.005**	0.01	0.013	±5.43
Co (59)	0.1	0.1	0.02	0.0064	±5.29
Cu (63)	0.1	0.1	0.2	0.30	±5.27
Ni (60)	1.0	1.0	1.5	0.25	±5.37
Pb (208)	0.05	0.05**	0.05	0.029	±5.26

* PELs are from Table Z-1 & Table Z-2 of 29 CFR , 1910.1000. PELs are time-weighted averages (TWA).

** Arsenic, cadmium and lead have expanded standards requiring biological monitoring and/or medical examinations (29 CFR 1910.1018, 29 CFR 1910.1025, 29 CFR 1910.1027 and 29 CFR 1926.62).

Procedure: A calibrated personal sampling pump is used to draw a known volume of air through a mixed-cellulose ester (MCE) membrane filter with back-up pad (BUP) contained in a polystyrene cassette. The inside walls of the cassette are wiped with a cellulose nitrate filter. The filter and accompanying cassette wipe are digested in a microwave oven with nitric acid and hydrogen peroxide. The BUP, if visibly contaminated, is analyzed separately following microwave digestion. After cooling, hydrochloric acid is added and the sample is microwaved again. Analysis is done by Inductively-Coupled Plasma/Mass Spectrometry (ICP/MS). Other analytical techniques may be used after compatibility with the digestate of this method is demonstrated for the analytes of interest. These techniques include, but are not limited to, Flame Atomic Absorption Spectrometry (FAAS), Graphite Furnace Atomic Absorption Spectrometry (GFAAS) and Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES). Those using a different analytical technique must consider the detection limit, precision, and sensitivity of the technique as it relates to each particular analyte. Digestates from other methods (e.g. ID-105, ID-121, ID-125G, ID-206) can be analyzed by ICP/MS after compatibility with the ICP/MS instrumentation is evaluated and equivalent analytical results are demonstrated.

Recommended sampling time and sampling rate: 240 min at 2.0 L/min (480L) TWA

Special requirement: The industrial hygienist (IH) must use an MCE filter in conjunction with a sodium carbonate-impregnated BUP when sampling for volatile arsenic compounds.

Status of method: Evaluated method. This method has been subjected to the established procedures of the Methods Development Team.

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1. General Discussion

For assistance with accessibility problems in using figures and illustrations presented in this method, please contact the SLTC at (801) 233-4900. These procedures were designed and tested for internal use by OSHA personnel. Mention of any company name or commercial product does not constitute endorsement by OSHA.

1.1 Background

1.1.1 History

This method describes the collection and subsequent analysis of airborne metal and metalloid particulates by ICP-MS. It provides rapid preparation of samples collected on MCE filters, and simultaneous analysis and data reduction for a wide range of elements, eliminating the necessity of separate analyses by conventional atomic absorption techniques. Air samples should be collected on an MCE filter with included cellulose BUP. This method was not evaluated for its application to surface sampling wipes or bulks collected in the workplace. For samples where volatile arsenic is considered likely to be present (e.g., As_2O_3, $AsCl_3$, AsF_3, AsI_3, AsP, As_2S_3, and H_3AsO_4), use both an MCE filter and a sodium carbonate-impregnated BUP.

Previous to the introduction of Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES), samples containing metallic particulates were digested in several ways and analyzed by Atomic Absorption Spectroscopy (AAS). While that technique is still used today at the OSHA Salt Lake Technical Center (SLTC), several generations of ICP instruments, with their ability to analyze many elements simultaneously, have tended to shift the analysis of samples toward the ICP. In recent years a new, more sensitive, technique has arisen which combines the generation of a hot plasma, containing many ions (via ICP), with a detector which differentiates those ions based on their mass/charge ratio (using a Mass Spectrometer or MS), rather than their optical emission spectra. One of the primary reasons for choosing ICP-MS is its improved sensitivity for arsenic analysis compared to that found using ICP-AES. The presence of carbon in the matrix enhances the signal of certain elements such as arsenic and selenium. Carbon has this effect because it is better than argon at ionizing atoms such as arsenic and selenium that have ionization potentials between 9-11 electron volts (eV).[1] To make this enhancement uniform, all standards and samples are prepared in a solution containing 1% ethanol.

A microwave oven is used to digest the samples in disposable centrifuge tubes. The use of such tubes saves time ordinarily spent on cleaning glassware. It also eliminates the possibility of losing sample when transferring between glass containers, because the sample remains in the centrifuge tube, even during analysis. A comparison of the microwave digestion to a hotplate digestion can be found in Section 4.9. The Standard Reference Material (SRM) used was Urban Particulate Matter, SRM 1648. Overall, the results are fairly similar for the elements tested in this method.

Closed-vessel, high pressure microwave digestion has been used for several years for the preparation of various environmental and industrial hygiene samples. Specialized digestion vessels are employed that have a high initial cost and require cleaning between uses. Due to these factors, a lower cost, less labor intensive digestion

[1] Allain, P.; Jaunault, L.; Mauras, Y.; Mermet, J-P.; Delaporte, T. Signal Enhancement of Elements Due to the Presence of Carbon-Containing Compounds in Inductively Coupled Plasma Mass Spectrometry. *Anal. Chem.* **1991,** 63, 1497-1498.

procedure using open vessels was chosen as having the potential to decrease sample preparation times for routine samples.

This method was fully validated for six elements (As, Cd, Co, Cu, Ni, and Pb). Other elements can be added to the method, depending on their solubility and stability in the acid matrix used in this method, 4% HNO_3 + 1% HCl. Some compounds, such as Cr_2O_3, BeO, Co_3O_4 and certain oxides of iron and nickel, are not very soluble in this acid matrix. To completely solubilize all compounds, more rigorous digestion procedures must be employed. Digestion in a sulfuric acid matrix can improve the solubility for some compounds (Section 4.8.4), but volatile arsenic compounds may be lost in the process.

1.1.2 Toxic effects (This section is for information only and should not be taken as the basis of OSHA policy.)

Ingestion of arsenic can produce fever, anorexia, hepatomegaly, melanosis, cardiac arrhythmia, and death.[2] Neurologic effects include neuropathy, paresthesia, and motor dysfunction. Effects on the liver include jaundice, cirrhosis, and ascites. Cardiovascular problems include acrocyanosis, Raynaud's phenomenon, and gangrene of the lower extremities. The Environmental Protection Agency (EPA) and the International Agency for Research on Cancer (IARC) classify arsenic as a carcinogen of the skin.

Ingestion of cadmium can cause nausea, vomiting, and abdominal pain. Pulmonary effects include pneumonitis, edema, and obstructive pulmonary disease. In the kidneys, it causes tubular dysfunction. Skeletal effects include calcium loss, bone pain, and osteoporosis. The main cardiovascular effect is essential hypertension. IARC classifies cadmium as a human carcinogen based on its relationship to pulmonary tumors.

Ingestion of cobalt can cause vomiting, diarrhea, polycythemia, and goiter. Neurologic effects include tinnitus and deafness due to nerve damage. Cardiovascular effects include giddiness, increased blood pressure, slowed respiration, and cardiomyopathy. Pulmonary effects include respiratory irritation and pneumoconiosis. On the skin, cobalt can cause allergic dermatitis.

Ingestion of copper has been shown to cause vomiting, anemia, hypotension, melena, jaundice, hepatic necrosis, coma, and death.

Ingestion of lead can cause anemia. In the cardiovascular system, it increases blood pressure. Neurologic effects include loss of IQ, neuropathy, convulsions, coma, and death. In the kidneys, it causes tubular necrosis. Reproductive problems involve sterility and neonatal death.

Nickel causes allergic dermatitis. Suspicion of nickel carcinogenicity has focused primarily on respirable particles of nickel subsulfide and nickel oxide.[3]

1.1.3 Workplace exposure[4]

Arsenic is a common by-product in ores containing copper, lead, cobalt, and gold. The smelting and refining of these ores can produce arsenic fumes. Arsenic compounds are used in herbicides, insecticides, glassmaking, and wood preservation. The metal is used in alloys in combination with lead and copper in batteries, bearings, electrotype metal, ammunition, automobile body solder, and corrosion resistance. The highly

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[2] *Casarett and Doull's Toxicology,* 5th ed.; Klaassen, C.D., Amdur, M.O., Doull, J., Eds.; McGraw Hill: New York, 1996.

[3] National Academy of Sciences, Committee on Medical and Biological Effects of Environmental Pollutants. *Nickel* ; Washington, DC, 1975.

[4] *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th ed.; Kroschwitz,J.I., Ex. Ed., John Wiley: New York, 1991.

purified metal is useful in semiconductor applications. Arsenicals are still important for the treatment of African trypanosomiasis. Arsenamide is used to kill adult heartworms in dogs.

Cadmium occurs primarily as sulfide minerals in zinc ores, which also may contain lead and copper. In the smelting and refining of these ores, cadmium fumes may be present. The principal uses of cadmium are in batteries, as a coating and plating agent for inhibiting corrosion, in pigments, as a heat stabilizer in plastics and synthetic products, and as a component in brazing and low melting alloys.

Cobalt occurs in minerals associated with ores of nickel, iron, silver, bismuth, copper, manganese, antimony, and zinc. The greatest uses of cobalt are in metallic form in magnetic alloys, cutting and wear-resistant alloys, and high temperature superalloys. Cobalt salts are useful in electroplating, as a catalyst for hardening paints, and as a pigment for glass and ceramics.

Copper fumes are usually present during the smelting and refining of copper ores. The uses of copper metal are very extensive. They include building wiring, plumbing, heating, air conditioning, refrigeration, architectural materials, electrical and electronic products, industrial machinery, valves and fittings, heat exchangers, automobiles, trucks, railroads, aircraft, appliances, ordnance, fasteners, coinage, and utensils and cutlery. Copper compounds are used in fungicides, algicides, insecticides, bactericides, pigments, wood preservatives, electroplating, animal feeds, dietary supplements, antifouling paints, and as heat and light stabilizers in polymers.

Nickel ores come in the form of sulfides, oxides, and silicates, usually in combination with iron. The main uses for the metal are in stainless steels and alloy steels, nonferrous and high temperature alloys, electroplating, magnets, and as a catalyst. Nickel compounds are used in ceramics, thermisters, varistors, electroplating, batteries, colored glass, and in various catalytic reactions.

Lead ranks fifth in the modern industrial world production of metals, behind iron, copper, aluminum, and zinc. Galena is the main lead mineral in ores. Care must be taken during the smelting and refining of the ore to prevent lead inhalation. The principal uses of lead and its compounds are storage batteries, pigments, ammunition, solders, plumbing, cable covering, bearings, and caulking. It is also used to attenuate soundwaves, atomic radiation, and mechanical vibration.

1.1.4 Physical properties

Physical properties of the six metals and their many inorganic compounds can be found in a variety of sources.[5,6]

This method was evaluated according to the OSHA SLTC "Evaluation Guidelines for Air Sampling Methods Utilizing Spectroscopic Analysis".[7] The Guidelines define analytical parameters, specify required laboratory tests, statistical calculations and acceptance criteria. The analyte air concentrations throughout this method are based on the recommended sampling and analytical parameters.

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[5] *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th ed.; Kroschwitz,J.I., Ex. Ed., John Wiley: New York, 1991.
[6] *The Merck Index*, 12th ed.; Budavari, S., Ed., Merck & Co. Inc.: Whitehouse Station, NJ, 1996.
[7] OSHA SLTC, Sandy, UT. Evaluation Guidelines For Air Sampling Methods Utilizing Spectrometric Analysis, unpublished, 2005.

1.2 Limit defining parameters

1.2.1 Detection limit of the analytical procedure (DLAP)

The DLAP for each of the elements is the response of the reagent blank plus three times the standard deviation (SD) of that reagent blank. It is calculated after doing 10 analyses of the reagent blank. (Sections 1.2.3 and 4.1)

1.2.2 Detection limit of the overall procedure (DLOP)

The DLOP is that amount of analyte spiked on sample media that will give a detector response significantly different from the response of a sampler blank. Eight to twelve spikes in incremental amounts were used to determine the DLOPs. (Sections 1.2.3 and 4.1)

1.2.3 Reliable quantitation limit (RQL)

The RQL is that amount of analyte spiked on a sampler which will give a detector response that is considered to be the lower limit for a precise quantitative measurement. Eight to twelve spikes in incremental amounts were used to determine the RQLs. (Section 4.2)

Table 1.2.3
Detection Limits (DLAPs and DLOPs) and Reliable Quantitation Limits (RQLs)

analyte (isotope)	*DLAP (µg)	*DLOP (µg)	*RQL (µg)	*RQL ($\mu g/m^3$)
As (75)	0.0074	0.049	0.16	0.34
Cd (114)	0.00072	0.0019	0.0063	0.013
Co (59)	0.00041	0.00091	0.0030	0.0064
Cu (63)	0.0044	0.043	0.14	0.30
Ni (60)	0.0034	0.037	0.12	0.25
Pb (208)	0.0024	0.0042	0.014	0.029

*The values above are given as micrograms per 50-mL solution volume.

1.2.4 Instrument calibration

The ICP-MS instrument used in this evaluation, the Perkin-Elmer Elan 6100, employs a single detector with two stages. The lower pulse counting stage is most useful for low intensity signals, while the upper analog stage is most useful for high intensity signals. Both pulse and analog signals are measured simultaneously. A “dual detector calibration” is run routinely to join the two stages together into one straight-line curve, which plots intensity on the same scale from zero to ~ 1×10^9 counts per second (cps). This instrument has shown linearity over 7-8 orders of magnitude for most elements, including the six elements in this method.

The standard error of estimate (S_{EE}) from the linear regression of data points was determined from four separate analyses of analytical standards prepared from soluble salts at masses corresponding to 0.1, 0.5, 1, and 2 times the target mass. The standard error of estimate measures the variation or scatter about the line of regression. (An example is shown in Section 3.5.2.)

Table 1.2.4
Standard Error of Estimate for Instrument Calibration

analyte	S_{EE} (µg)	analyte	S_{EE} (µg)	analyte	S_{EE} (µg)	analyte	S_{EE} (µg)	analyte	S_{EE} (µg)	analyte	S_{EE} (µg)
As	0.083	Cd	0.051	Co	1.0	Cu	0.93	Ni	10	Pb	0.78

1.2.5 Precision

The precision of the overall procedure at the 95% confidence level for the six validated elements was obtained from the ambient temperature 17-day storage test done at the target concentrations. This includes an additional 5% error for sampling pump variability. Precision ranged from 10.3 - 11.3%. (Section 4.4)

1.2.6 Recovery

The recovery of arsenic trioxide remained above 95% in the 17-day storage test done at ambient temperature. The recoveries of the other five analytes remained above 98% in the 17-day storage test done at ambient temperature. (Section 4.5)

1.2.7 Reproducibility

Using soluble salts of the analytes, six samples were prepared and submitted to the OSHA Salt Lake Technical Center (SLTC) for analysis. A draft copy of the analytical procedure was given to the analyst. No individual analytical result deviated from the theoretical value by more than the overall precision for the analyte (Section 4.4). Recoveries ranged from 91.9 - 108% (Section 4.6).

2. Sampling procedure

All safety practices that apply to the work area being sampled should be followed. The sampling equipment should be attached to the worker in a manner that will not interfere with work performance or safety.

2.1 Apparatus

2.1.1 MCE filters. Mixed cellulose ester (MCE) membrane filters (0.8 µm pore size) with cellulose backup pads (BUPs), 37 mm diameter, are used to collect air samples. Millipore filters (Cat. no. AAWP03700) were used in this evaluation. These are not to be used for arsenic samples.

2.1.2 Cassettes, 37-mm. Clear, polystyrene cassettes, either 2-section or 3-section can be used for air sampling. SKC cassettes (Cat. No. 225-2 and Cat. no. 225-3) were used in this evaluation.

2.1.3 Pre-assembled 37-mm polystyrene cassettes must be used when arsenic compounds are present. In front is an MCE filter, 0.8 µm pore size, and directly behind it is the sodium carbonate-impregnated BUP. SKC (Cat. no. 225-9001) cassettes were used in this evaluation.

2.1.4 Pre-assembled cassettes, 25-mm. Black, carbon-filled polypropylene cassettes with included MCE filter, 0.8 µm pore size, and BUP can also be used for air sampling. SKC (Cat. no. 225-321) cassettes were used in this evaluation. These are not to be used for arsenic samples.

Air samples are collected using a personal sampling pump attached to the polystyrene cassette and calibrated to within ±5% of the recommended flow rate.

2.2 Reagents

None required

2.3 Technique

Remove the two end plugs from the cassette. Attach the cassette to the sampling pump with plastic tubing and position the components so they do not impede work performance or safety. Draw the atmosphere to be sampled directly into the inlet of the cassette. The atmosphere being sampled should not be passed through any hose or tubing before entering the sampling cassette.

After sampling for an appropriate time, turn off the pump, remove the cassette and replace the two end plugs. Seal each sample end-to-end with a Form OSHA-21.

Submit at least one blank sample with each set of samples. Handle the blank sampler in the same manner as the other samples except draw no air through it.

Record sample air volume (liters), sampling time (minutes) and sampling rate (L/min) for each sample, along with any potential interferences known to be present on the Form OSHA-91A. Submit the samples to the laboratory for analysis as soon as possible after sampling.

2.4 Sampler capacity (Section 4.7)

SLTC does not currently have the capability of generating aerosols of metal particulates. For this reason, sampler capacity was tested using retention efficiency tests. Four samplers, each containing an MCE filter in front spiked with soluble salts of the six analytes, separated by a spacer from a sodium carbonate-impregnated BUP in back, had humid air drawn through them for five hours at 2.0 L/min. The MCE filter and the BUP were analyzed separately, both by ICP-MS. No analyte was detected on any BUP. The average recovery was 99.0% for arsenic, 99.6% for cadmium, 97.9% for cobalt, 99.0% for copper, 101% for lead, and 98.9% for nickel (Section 4.7).

2.5 Digestion efficiency (Section 4.8)

Digestion efficiencies for the six analytes were determined at five different concentrations. Four MCE filters were spiked with soluble salts of the analytes at each concentration. The average digestion efficiency was 97.6% for arsenic, 103% for cadmium, 97.4% for cobalt, 99.1% for copper, 104% for lead, and 99.4% for nickel. (Section 4.8.1)

2.6 Recommended sampling time and sampling rate

Sample for a minimum of 240 min at 2.0 L/min (480 L) to collect long-term time weighted average (TWA) samples. If needed, short-term samples can be taken for 15 min at 2.0 L/min (30 L).

2.7 Interferences (sampling)

None are known

3. Analytical Procedure

Adhere to the rules set down in your Chemical Hygiene Plan.[8] Avoid skin contact and inhalation of all chemicals. Review all appropriate MSDSs before beginning work. Follow any SOP or accreditation protocol necessary for proper instrument optimization and analysis.

3.1 Apparatus

[8] Occupational Exposure to Hazardous Chemicals in Laboratories. *Code of Federal Regulations*, Part 1910.1450, Title 29, 1998.

3.1.1 Inductively coupled plasma - mass spectrometer (ICP-MS). A Perkin-Elmer Elan 6100 was used in this evaluation. It came with its own accessories, including auto-sampler, peristaltic pump, mass flow controller and water chiller. The Elan software controls the instrument and provides the analytical results.

3.1.2 Laboratory quality microwave. A CEM MARS-5 with accessories, including temperature probe and high throughput accessory set, was used in this evaluation.

3.1.3 Centrifuge. A Thermo IEC Centra CL3 centrifuge with accessories was used in this evaluation.

3.1.4 Plastic graduated centrifuge tubes, 50-mL, accuracy of ±2% or better at the 50-mL mark. Corning polypropylene tubes used in this evaluation had an accuracy of ±2%.[9]

3.1.5 Cellulose nitrate filters. Whatman filters (Cat. no. 7184-004), 0.45 µm pore size, 47 mm diameter, were used in this evaluation to wipe-out the inside of the cassette.

3.2 Reagents

3.2.1 Nitric acid, [CAS no. 7697-37-2], for trace metal analysis. Nitric acid, 'Baker Instra-Analyzed', 69.0-70.0%, (lot V17032) purchased from JT Baker was used in this evaluation.

3.2.2 Hydrochloric acid, [CAS no. 7647-01-0], for trace metal analysis. Hydrochloric acid, 'Baker Instra-Analyzed', 36.5-38.0%, (lot T45036) purchased from JT Baker was used in this evaluation.

3.2.3 Calibration standards

3.2.3.1 Arsenic standard, [CAS no. 7440-38-2], 1000 µg/mL, in 2% HNO_3, (lot 3AD064) purchased from CPI International (CPI) was used in this evaluation.

3.2.3.2 Cadmium standard, [CAS no. 7440-43-9], 1000 µg/mL, in 2% HNO_3, (lot 1LM044) purchased from CPI was used in this evaluation.

3.2.3.3 Cobalt standard, [CAS no. 7440-48-4], 1000 µg/mL, in 2% HNO_3, (lot 2JT116) purchased from CPI was used in this evaluation.

3.2.3.4 Copper standard, [CAS no. 7440-50-8], 1000 µg/mL, in 2% HNO_3, (lot 3AM188) purchased from CPI was used in this evaluation.

3.2.3.5 Lead standard, [CAS no. 7439-92-1], 1000 µg/mL, in 2% HNO_3, (lot 2LF025) purchased from CPI was used in this evaluation.

3.2.3.6 Nickel standard, [CAS no. 7440-02-0], 1000 µg/mL, in 2% HNO_3, (lot PLNI2-2Y) purchased from SPEX CertiPrep, Inc. was used in this evaluation.

3.2.4 Internal standards (IS). Internal standards are used to correct for matrix interferences, instrument drift and short-term noise. The following were used for the evaluation of this method.

3.2.4.1 Germanium standard, [CAS no. 7440-56-4], 1000 µg/mL, in 2% HNO_3, (lot OBF145) purchased from CPI was used in this evaluation. Germanium is used as an internal standard for arsenic, cobalt, copper, and nickel.

[9] Personal communication from Connie MacDonald, Corning Life Sciences, 10/20/2004.

3.2.4.2 Indium standard, [CAS no. 7440-74-6], 1000 µg/mL, in 2% HNO_3, (lot OBF173) purchased from CPI was used in this evaluation. Indium is used as an internal standard for cadmium.

3.2.4.3 Lutetium standard, [CAS no. 7439-94-3], 1000 µg/mL, in 2% HNO_3, (lot 1IF013) purchased from CPI was used in this evaluation. Lutetium is used as an internal standard for lead.

3.2.5 De-ionized water (DIW), 18 megaohm. A Barnstead Model D11901 NANOpure DIamond water purifier was used in this evaluation.

3.2.6 Hydrogen peroxide, [CAS no. 7722-84-1], 30%. Hydrogen peroxide solution, 30%, (lot 5240 T45A05) purchased from Mallinckrodt was used in this evaluation.

3.2.7 Ethanol, [CAS no. 64-17-5], 95%. Ethanol, 95%, (lot 98G23BB) purchased from AAPER Alcohol and Chemical Co. was used in this evaluation.

3.3 Standard preparation

3.3.1 Match the matrix of the standards to the final digested sample matrix of 4% nitric acid, 1% hydrochloric acid, 1% internal standard (IS) mix, and 1% ethanol. For the evaluation of this method, the IS and ethanol were added during preparation of the samples and standards. Alternatively, they may be added at the time of introduction into the instrument (e.g., using a mixing block just prior to the nebulizer).

3.3.2 Bracket sample concentrations with standard concentrations. If, upon analysis, sample concentrations are above the range of prepared standards, dilute the high samples and re-analyze.

3.3.3 Prepare a calibration standard at the target concentrations of the six elements in this method using a 480-L air volume and a final solution volume of 50 mL. This results in the following concentrations: 50 ppb Cd, 100 ppb As, 500 ppb Pb, 1000 ppb Co and Cu, and 10 ppm Ni. The IS mix is prepared at the following concentrations: 2 ppm In, 3 ppm Lu, and 9 ppm Ge.

3.4 Sample preparation

3.4.1 Transfer the MCE filter from the 37 mm cassette to the bottom of the plastic centrifuge tube. Wipe the inside walls of the cassette with a cellulose nitrate filter (Section 3.1.5) moistened with 2-3 drops of DIW. (Table 4.8.3 shows recoveries of spikes on these filters.) Place the wipe at the bottom of the centrifuge tube with the MCE filter. If the BUP is visibly contaminated, digest it (see Section 3.4.2) and analyze it separately (see Table 4.8.2 for recoveries). Add 2 mL of concentrated nitric acid and 0.2 mL of 30% hydrogen peroxide. Cap the tube loosely (no more than ¼ turn), allowing any excess pressure to vent around the cap. Swirl the acid to wet the contents. Place the tube in the fast throughput carousel in the microwave oven. Samples are microwaved using these parameters:

Maximum power = 600 W
Ramp temperature to 104 ºC over 9 min
Hold temperature at 104 ºC for 3 min

Allow the samples to cool at least 10 min before removing from the microwave. Add 0.5 mL of concentrated hydrochloric acid. Recap the samples and return them to the microwave. Reheat using the following parameters:

Maximum power = 600 W
Ramp temperature to 86 ºC over 5 min
Hold temperature at 86 ºC for 1 min

Allow the samples at least 10 minutes to cool before removing from the microwave. Add 0.5 mL of IS solution and 0.5 mL of 95% ethanol (see Section 3.3.1). Fill the tube to the 50-mL mark with DIW. If solid particles remain after diluting to volume, filter the sample and digest the filter and particles in the microwave using the same technique. Sample results should be added together after both solutions have been analyzed separately. For this evaluation, the final matrix contains 4% nitric acid, 1% hydrochloric acid, 1% IS, and 1% ethanol.

Note: If volumes other than 50 mL are used, the amounts of acids should be adjusted to keep the matrix approximately the same for samples and standards.

3.4.2 Analyze a contaminated BUP, identified by a discoloration on the white pad, separately using a modification of the above microwave procedure. Instead of using 2 mL of nitric acid, use 4 mL of nitric acid and 0.3 mL of 30% hydrogen peroxide. In the second step, use 1 mL of concentrated hydrochloric acid. In the final step, transfer the contents of the centrifuge tube to a 100-mL volumetric flask, add 1 mL of IS solution and 1 mL of 95% ethanol (see Section 3.3.1), and dilute to volume with DIW. Although the procedure may not completely digest all of the fibers present, a study was done to show that analytes spiked on the BUP do go into solution (Section 4.8.2). If needed, centrifuge tubes for 10 min @ 2000 rpm to compact the fibers.

3.5 Analysis

3.5.1 Follow the manufacturer's standard operating procedures for the particular ICP-MS instrument. Calibrate with the appropriate standards. The parameters that were used in developing this method for the PE Elan 6100 were:

Number of replicates:	3	Integration time:	1 sec
Readings/Replicate:	1	Detector Mode:	Dual
Auto Lens:	On	Dwell time:	20 msec
Sweeps/Reading:	50	Scan Mode:	Peak Hopping

3.5.2 Instrument calibration example

The following calibration curve, using an internal standard, is an example of a curve constructed for arsenic analysis. It is also representative of the calibration curves of the other five analytes. Four spikes of a soluble salt are added to volumetrics at four different concentrations that covers a range 0.1 to 2 times the target concentration for arsenic. The standard error of estimate for this curve is 0.083 µg of arsenic.

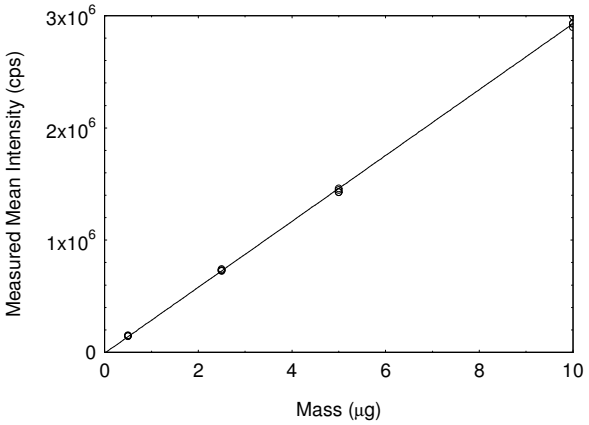

Figure 3.5.2. Plot of calibration curve for arsenic.

3.6 Interferences (analytical)

The following interferences, typically encountered with ICP-MS techniques, were addressed during the evaluation of this method:

Table 3.6
ICP-MS Analytical Interferences

analyte	interference	corrective measures
^{75}As	$^{40}Ar^{35}Cl$	Mathematical correction factor
^{75}As	C	Add ethanol to standards and samples
^{114}Cd	$^{98}Mo^{16}O$	Adjust nebulizer flow to minimize oxides
^{114}Cd	^{114}Sn	Mathematical correction factor
^{63}Cu	$^{31}P^{16}O_2$, $^{47}Ti^{16}O$	Adjust nebulizer flow to minimize oxides
^{115}In	^{115}Sn	Mathematical correction factor
^{60}Ni	$^{44}Ca^{16}O$	Adjust nebulizer flow to minimize oxides
^{208}Pb	^{206}Pb, ^{207}Pb	Mathematically combine all 3 isotopes*

*These three stable isotopes of lead are the endpoint of the radiologic decay of ^{232}Th, ^{235}U, and ^{238}U. The abundance ratio of these lead isotopes to each other may change slightly depending on the source of origin, but together they constitute 98.6% of all stable lead found. Summing the isotopes together cancels out ratio differences.

Although ICP-MS analysis has been found by analysts working in the field to be definitive for most of the elements evaluated in this method. Other analytical techniques can be used if interferences are large and/or additional confirmation is needed. These techniques include, but are not limited to: FAAS, GFAAS, and ICP-AES.

3.7 Calculations

Air sample results are reported in units of mg/m^3. For analytes having a PEL listed as a compound, results are reported as mg/m^3 of that compound by using gravimetric factors. If it is necessary to analyze the BUP, it is analyzed separately from the combined MCE filter + cellulose nitrate wipe, and the results for each analyte are combined.

The concentration of analyte in the digestate is calculated from the appropriate calibration curve. The concentration (ng/mL) of an analyte in solution multiplied by its volume (mL) results in the mass per sample (ng). The final result, in mg/m^3, is calculated using the following formulas:

$A = G[(C \times D \times H) - (E \times F \times I)]$ where

- A is combined mass of analytes on sample MCE filter + cellulose nitrate wipe (µg)
- C is combined concn of analytes on sample MCE + cellulose nitrate wipe (ng/mL)
- D is sample solution volume (mL)
- E is concn of analytes on blank MCE filter + blank cellulose nitrate wipe (ng/mL)
- F is blank solution volume (mL)
- G is 1000 ng/µg conversion factor
- H is dilution factor (if any) for sample filters
- I is dilution factor (if any) for blank filters

$$B = G[(J \times K \times L) - (M \times N \times O)]$$

where B is mass of analyte on sample BUP (µg)
J is concn of analyte on sample BUP (ng/mL)
K is sample BUP solution volume (mL)
L is dilution factor (if any) for sample BUP
M is concn of analyte on blank BUP (ng/mL)
N is blank BUP solution volume (mL)
O is dilution factor (if any) for blank BUP

$$X = \frac{A + B}{V}$$

where X is concn by weight (mg/m^3)
V is liters of air sampled

4. Backup data

General background information about the determination of detection limits and precision of the overall procedure is found in the "Evaluation Guidelines for Air Sampling Methods Utilizing Spectroscopic Analysis".[10] The Guidelines define analytical parameters, specific laboratory tests, statistical calculations and acceptance criteria.

This evaluation examined samples collected on MCE filters, cellulose BUPs, and cellulose nitrate filters. Other sample matricies that are digested and/or diluted into the same digestate matrix may be analyzed by this method, but acceptable digestion and instrument performance must be demonstrated.

ICP-MS was the analytical technique used for the evaluation of this method. One of the primary reasons for choosing ICP-MS was its ability to analyze for arsenic, cadmium, and lead simultaneously. Other techniques may be applicable to the analysis of the digestate. Compatibility of the digestate with alternate analytical techniques must be demonstrated for each analyte of interest.

4.1 Detection limit of the analytical procedure (DLAP)

The DLAP is the response of the reagent blank (Y_{BR}) plus three times the standard deviation of that reagent blank (S_{BR}), DLAP = $Y_{BR} + 3 \times S_{BR}$. It is calculated after doing 10 analyses of the reagent blank.

Table 4.1
Detection Limit of the Analytical Procedure

analyte	Y_{BR} (ppb)	S_{BR} (ppb)	solution volume (mL)	DLAP (µg)
As	0.0003	0.049	50	0.0074
Cd	0.0067	0.0026	50	0.00072
Co	0.0037	0.0015	50	0.00041
Cu	0.0605	0.0092	50	0.0044
Ni	0.0318	0.0121	50	0.0034
Pb	0.0353	0.0042	50	0.0024

[10] OSHA SLTC, Sandy, UT. Evaluation Guidelines For Air Sampling Methods Utilizing Spectrometric Analysis, unpublished, 2005.

4.2 Detection limit of the overall procedure (DLOP) and reliable quantitation limit (RQL)

The DLOP is the amount of analyte spiked on a sampler that will give a detector response significantly different from the response of a sampler blank. The RQL is that amount of analyte spiked on a sampler which will give a detector response that is considered to be the lower limit for a precise quantitative measurement.

The DLOPs and RQLs for the six analytes were determined from the same set of data. The results of the analysis of a blank filter and eleven spiked filters in incremental amounts near these values were plotted to give linear regression lines for each analyte with its own slope and standard error of estimate about the line.

Table 4.2.1
Arsenic Detection Limits
DLOP = 0.049 µg; RQL = 0.16 µg

ng	intensity (cps)	ng	intensity (cps)
0	785.8	150	24886
20	2833	180	41002
40	5466	210	47760
60	7454	240	55743
90	9744	270	62519
120	22662	300	68962

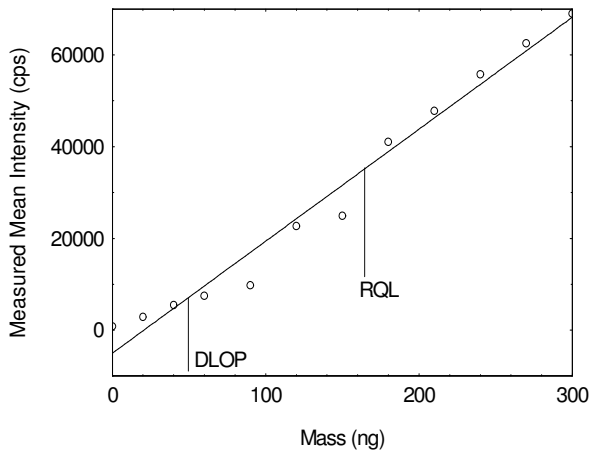

Figure 4.2.1. Plot of data to determine the DLOP/RQL for arsenic ($y = 244.1x - 5020$; $S_{EE} = 4024$).

Table 4.2.2
Cadmium Detection Limits
DLOP = 0.0019 µg; RQL = 0.0063 µg

ng	intensity (cps)	ng	intensity (cps)
0	39.8	30	3821
4	559.7	36	4809
8	1022	42	5367
12	1531	48	6269
18	2249	54	7126
24	3205	60	7953

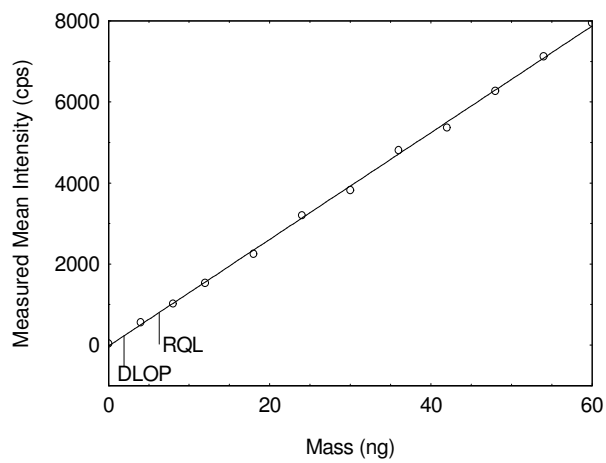

Figure 4.2.2. Plot of data to determine the DLOP/RQL for cadmium ($y = 131.6x - 21.8$; $S_{EE} = 83.3$).

Table 4.2.3
Cobalt Detection Limits
DLOP = 0.00091 µg; RQL = 0.0030 µg

ng	intensity (cps)	ng	intensity (cps)
0	286.0	6.0	2572
0.8	545.0	7.2	3312
1.6	763.7	8.4	3647
2.4	1024	9.6	4354
3.6	1443	10.8	4954
4.8	2237	12.0	5375

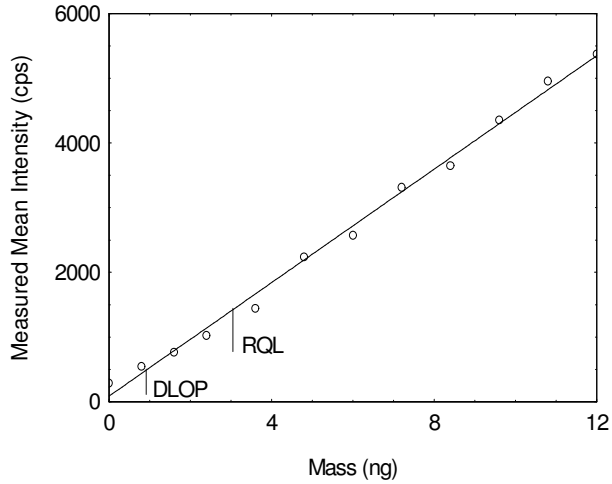

Figure 4.2.3. Plot of data to determine the DLOP/RQL for cobalt ($y = 438.7x + 86.1$; $S_{EE} = 133.8$).

Table 4.2.4
Copper Detection Limits
DLOP = 0.043 µg; RQL = 0.14 µg

ng	intensity (cps)	ng	intensity (cps)
0	5945	150	35884
20	11573	180	49825
40	15000	210	52885
60	16628	240	61327
90	21072	270	77093
120	32400	300	76775

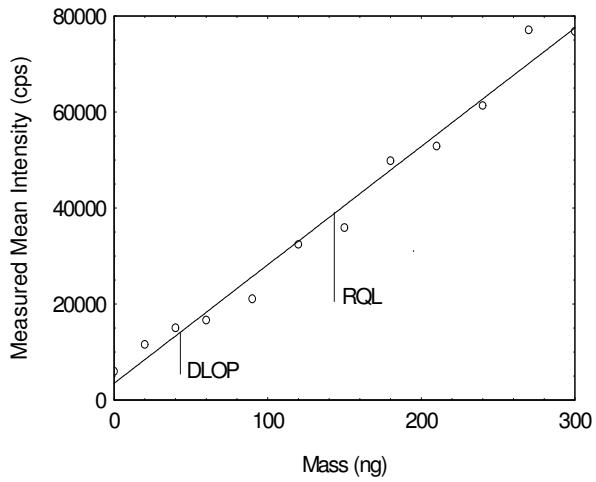

Figure 4.2.4. Plot of data to determine the DLOP/RQL for copper ($y = 246.8x + 3483$; $S_{EE} = 3541$).

Table 4.2.5
Nickel Detection Limits
DLOP = 0.037 µg; RQL = 0.12 µg

ng	intensity (cps)	ng	intensity (cps)
0	3252	150	14889
20	4215	180	20023
40	5027	210	21892
60	6162	240	26033
90	7982	270	28898
120	13343	300	31541

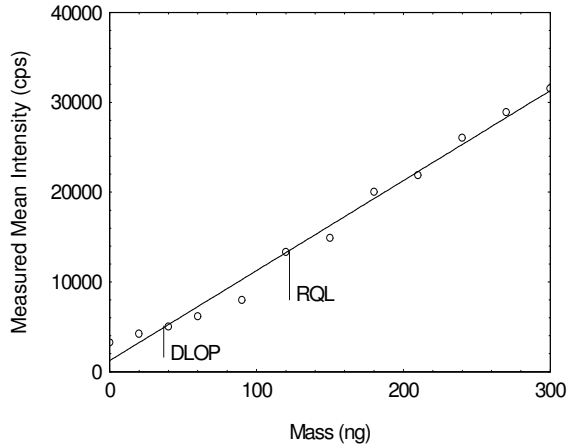

Figure 4.2.5. Plot of data to determine the DLOP/RQL for nickel ($y = 100.2x + 1239$; $S_{EE} = 1225$).

Table 4.2.6
Lead Detection Limits
DLOP = 0.0042 µg; RQL = 0.014 µg

ng	intensity (cps)	ng	intensity (cps)
0	2733	15	9664
2	3579	18	13911
4	4091	21	16548
6	5414	24	18536
9	6599	27	20580
12	9474	30	23069

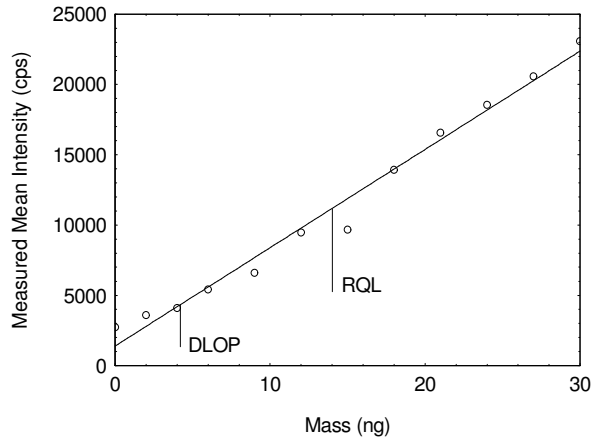

Figure 4.2.6. Plot of data to determine the DLOP/RQL for lead ($y = 699.1x + 1396$; $S_{EE} = 979.4$).

4.3 Instrument calibration

The standard error of estimate from the linear regression of data points was determined from four separate analyses of analytical standards at the following levels: 0.1, 0.5, 1, and 2 times the target mass, prepared from soluble salts. The standard error of estimate (S_{EE}) measures the variation or scatter about the line of regression.

Table 4.3
Instrument Calibration, Average Intensity (cps)

analyte	mass (µg)	0.1 × targ. concn (SD)	mass (µg)	0.5 × targ. concn (SD)	mass (µg)	1 × targ. concn (SD)	mass (µg)	2 × targ. concn (SD)	S_{EE} (µg)	upper limit (µg)
As	0.5	1.47×10^5 (2.97×10^3)	2.5	7.33×10^5 (6.98×10^3)	5	1.44×10^6 (1.62×10^4)	10	2.94×10^6 (4.07×10^4)	0.083	1000
Cd	0.25	4.50×10^4 (7.54×10^2)	1.25	2.21×10^5 (1.21×10^3)	2.5	4.30×10^5 (6.66×10^3)	5	8.36×10^5 (1.21×10^4)	0.051	500
Co	5	2.80×10^6 (3.66×10^4)	25	1.40×10^7 (7.15×10^4)	50	2.77×10^7 (1.68×10^5)	100	5.54×10^7 (1.23×10^6)	1.0	250
Cu	5	1.50×10^6 (1.94×10^4)	25	7.37×10^6 (4.45×10^4)	50	1.47×10^7 (1.05×10^5)	100	2.91×10^7 (5.62×10^5)	0.93	1000
Ni	50	6.39×10^6 (1.17×10^5)	250	3.21×10^7 (1.52×10^5)	500	6.39×10^7 (3.73×10^5)	1000	1.28×10^8 (2.81×10^6)	10	1500
Pb	2.5	1.71×10^6 (2.37×10^4)	12.5	7.81×10^6 (8.89×10^4)	25	1.51×10^7 (3.53×10^5)	50	2.91×10^7 (8.13×10^5)	0.78	1000

4.4 Precision (overall procedure)

The precision at the 95% confidence level is obtained by multiplying the standard error of estimate from the storage test (Section 4.5) by 1.96 (the z-statistic from the standard normal distribution at the 95% confidence level). In Section 4.5, 95% confidence intervals are drawn about their respective regression lines for the six analytes in the ambient storage graph figures. Precisions are summarized below:

Table 4.4
Overall Precision of Analytes

analyte	precision	analyte	precision
As	±11.3	Cu	±10.3
Cd	±10.6	Ni	±10.5
Co	±10.4	Pb	±10.3

4.5 Effects of storage

One of the most common compounds of arsenic is arsenic trioxide, As_2O_3. This compound is known to sublime at 135 ºC. To test the storage stability of this compound, 52.34 mg of the pure compound was weighed out and transferred to a 100-mL volumetric flask. The flask was brought to volume with DIW. At room temperature, the As_2O_3 was observed to take 6 days to completely dissolve in solution. Six 50-µL spikes of this solution were pipetted into separate 200-mL volumetric flasks, which were then brought to volume with the standard acid matrix solution. The average recovery of arsenic from the six spikes was 99.8% of the theoretical value (19.82 µg). Eighteen pre-assembled cassettes (Section 2.1.3) were each spiked with 50 µL of the As_2O_3 solution. Humid air containing approximately 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2 ºC) was drawn through the samplers for 4 hours at 2 L/min. Three of these filters were analyzed immediately by ICP-MS. The other 15 were stored at ambient temperature (~23 ºC) and analyzed in sets of 3 over the course of 17 days. It was decided to look first at the more rugged ambient test before doing a refrigerated test. A regression curve for arsenic trioxide was obtained by plotting percent recovery versus days of storage. The recovery of arsenic trioxide at ambient temperature remained above 95% at day 17 (Table 4.5.1). The results of this ambient storage test demonstrated that no refrigerated storage test was needed.

Table 4.5.1
Ambient Storage Test for Arsenic Trioxide

time (days)	recovery (%)		
0	97.7	98.1	101
3	101	96.4	97.3
7	93.6	97.6	97.8
10	104	99.4	102
14	92.9	96.9	96.7
17	96.8	95.2	96.4

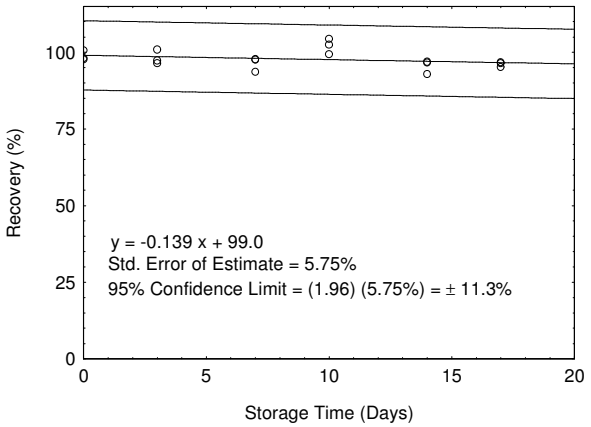

Figure 4.5.1. Ambient storage test for arsenic trioxide on MCE filters.

Eighteen MCE filters placed in 37-mm cassettes (Section 2.1.4) were each spiked with a solution containing soluble salts equivalent to the target concentration of the other five analytes. Humid air containing approximately 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2 ºC) was drawn through the samplers for 4 hours at 2 L/min. Three filters were analyzed immediately by ICP-MS. The other 15 were analyzed in sets of 3 over the course of 17 days. All filters were kept at ambient temperature (~23 ºC) in an undisturbed location. A refrigerated storage test was not done. A regression curve measuring the storage stability for each analyte was obtained by plotting percent recovery versus days of storage. All five analytes had recoveries above 95% after 17 days.

Table 4.5.2
Ambient Storage Test for Cadmium

time (days)	recovery (%)		
0	99.8	100	101
3	102	104	105
6	98.4	99.7	99.1
10	100	101	101
13	98.7	96.6	98.3
17	103	101	98.3

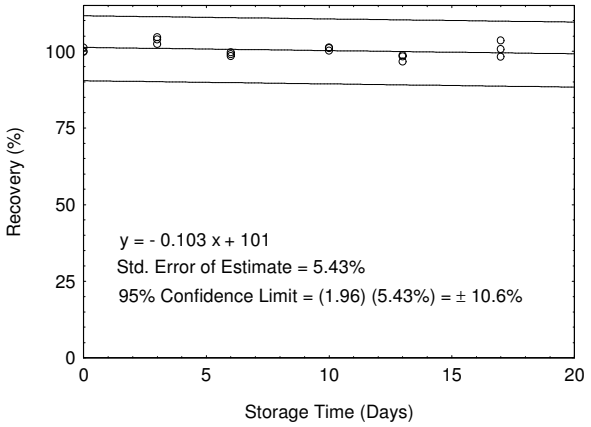

Figure 4.5.2. Ambient storage test for cadmium on MCE filters.

Table 4.5.3
Ambient Storage Test for Cobalt

time (days)	recovery (%)		
0	97.2	98.6	99.5
3	98.8	97.6	98.5
6	102	103	102
10	103	102	102
13	99.8	101	99.9
17	99.4	100	101

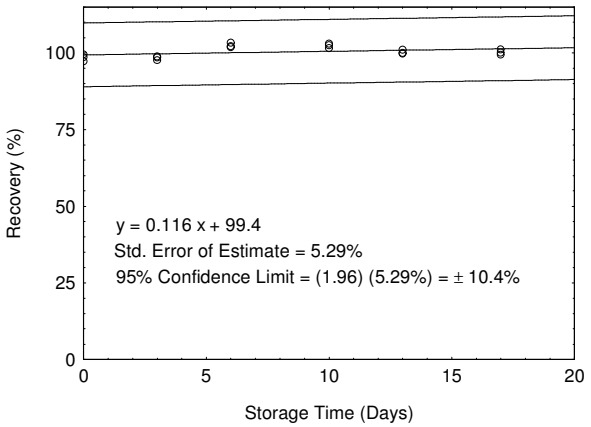

Figure 4.5.3. Ambient storage test for cobalt on MCE filters.

Table 4.5.4
Ambient Storage Test for Copper

time (days)	recovery (%)		
0	98.5	98.8	99.8
3	99.7	99.0	99.7
6	102	104	102
10	96.8	102	102
13	103	102	101
17	102	101	102

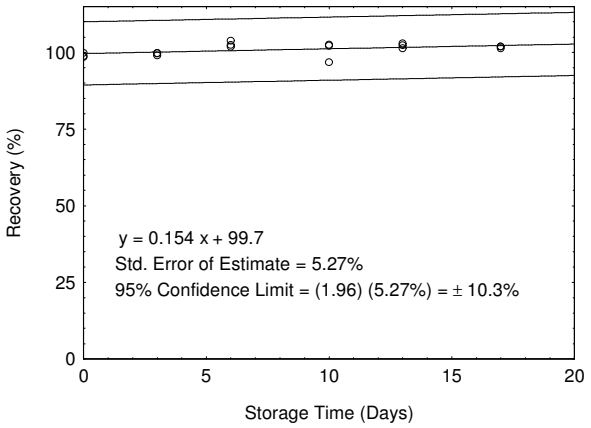

Figure 4.5.4. Ambient storage test for copper on MCE filters.

Table 4.5.5
Ambient Storage Test for Nickel

time (days)	recovery (%)		
0	98.3	99.1	100
3	99.7	98.0	99.7
6	103	105	103
10	106	102	103
13	102	102	102
17	101	101	102

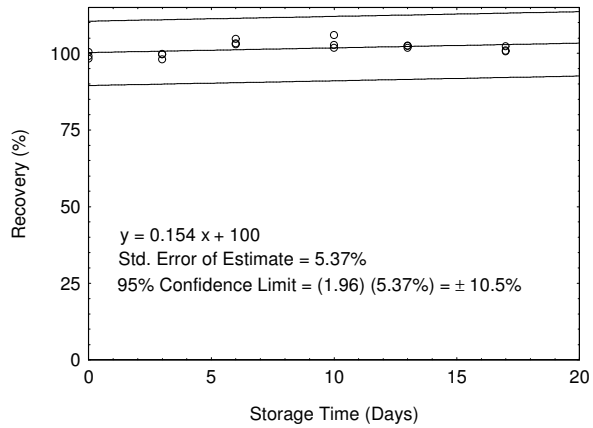

Figure 4.5.5. Ambient storage test for nickel on MCE filters.

Table 4.5.6
Ambient Storage Test for Lead

time (days)	recovery (%)		
0	97.5	97.5	99.2
3	99.0	99.6	99.6
6	100	102	101
10	104	101	102
13	99.3	98.7	98.6
17	100	99.3	99.3

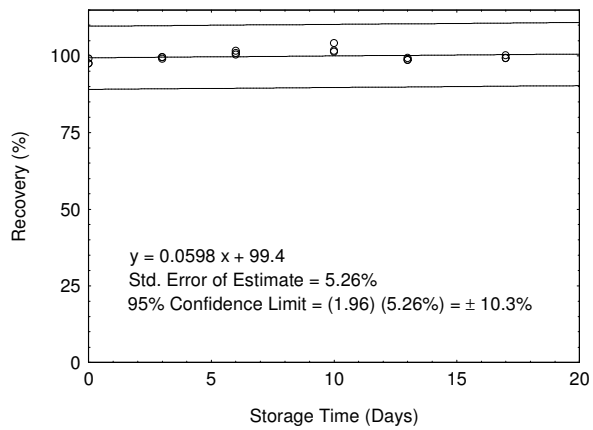

Figure 4.5.6. Ambient storage test for lead on MCE filters.

4.6 Reproducibility

Six filters were spiked with a mixture containing the six elements at the target concentration. This set was submitted to the OSHA SLTC for analysis by ICP-MS. Recoveries for the six analytes ranged from 91.9 - 108% (Tables 4.6.1 - 4.6.6). No spike result for any of the six analytes had a deviation greater than the precision of the overall procedure (see Section 4.4).

Table 4.6.1
Arsenic Reproducibility

theoretical (µg/sample)	recovered (µg/sample)	recovery (%)	deviation (%)
5.00	4.60	91.9	-8.1
5.00	4.90	97.9	-2.1
5.00	4.85	96.9	-3.1
5.00	4.99	99.9	-0.1
5.00	4.97	99.4	-0.6
5.00	4.69	93.6	-6.2

Table 4.6.2
Cadmium Reproducibility

theoretical (µg/sample)	recovered (µg/sample)	recovery (%)	deviation (%)
2.50	2.42	96.9	-3.1
2.50	2.56	102	2.4
2.50	2.55	102	2.0
2.50	2.59	104	3.6
2.50	2.57	103	2.8
2.50	2.45	98.0	-2.0

Table 4.6.3
Cobalt Reproducibility

theoretical (µg/sample)	recovered (µg/sample)	recovery (%)	deviation (%)
50.0	47.2	94.4	-5.6
50.0	49.1	98.2	-1.8
50.0	49.1	98.2	-1.8
50.0	50.6	101	1.2
50.0	51.0	102	2.0
50.0	48.0	96.1	-3.9

Table 4.6.4
Copper Reproducibility

theoretical (µg/sample)	recovered (µg/sample)	recovery (%)	deviation (%)
50.0	49.2	98.3	-1.7
50.0	51.5	103	3.0
50.0	51.0	102	2.0
50.0	52.8	106	5.6
50.0	52.6	105	5.2
50.0	49.3	98.7	-1.3

Table 4.6.5
Nickel Reproducibility

theoretical (µg/sample)	recovered (µg/sample)	recovery (%)	deviation (%)
500	501	100	0.2
500	524	105	4.8
500	520	104	4.0
500	537	108	7.4
500	540	108	8.0
500	510	102	2.0

Table 4.6.6
Lead Reproducibility

theoretical (µg/sample)	recovered (µg/sample)	recovery (%)	deviation (%)
25.0	23.5	94.1	-5.9
25.0	24.8	99.2	-0.8
25.0	24.8	99.4	-0.6
25.0	24.9	99.5	-0.5
25.0	25.1	100	0.4
25.0	23.4	93.7	-6.3

4.7 Sampler capacity

Four samplers, each containing a 0.8-µm MCE filter and a sodium carbonate-impregnated back-up pad (BUP) separated from the filter by a spacer, were spiked with an amount of soluble salt of the analyte equivalent to approximately the target concentration based on an air volume of 480 L. Humid air containing approximately 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2 ºC) was drawn through the samplers for five hours at 2 L/min. The MCE filter and the BUP were digested separately, both by microwave digestion. Samples were analyzed by ICP-MS.

Table 4.7
Retention Efficiency

analyte	amount spiked (µg)	average recovery on MCE filter (µg)	SD on MCE filter (µg)	amount found on BUP	% average total recovery
As	5.00	4.95	0.03	ND	99.0
Cd	2.50	2.49	0.02	ND	99.6
Co	50.0	49.0	0.81	ND	97.9
Cu	50.0	49.5	0.13	ND	99.0
Ni	500	494	8.0	ND	98.9
Pb	25.0	25.3	0.72	ND	101

4.8 Digestion efficiency

4.8.1 Recoveries from MCE filters

Digestion efficiencies (DE) for the six analytes were obtained at five different levels (near the RQL and at 0.1, 0.5, 1, and 2 times the target concentration). Six MCE filters were spiked at each mass. The filters were digested in the microwave and diluted to a 50-mL volume. The final matrix was 4% HNO_3, 1% HCl, 1% IS, and 1% ethanol. Average digestion efficiencies range from 97.4% to 104%.

Table 4.8.1.1
Average % DE for Arsenic on MCE Filters

×target concn	mass (µg)	average recovery (%)	SD (%)
RQL	0.150	90.1	1.8
0.1	0.500	101	1.3
0.5	2.50	100	1.6
1.0	5.00	97.9	1.6
2.0	10.0	99.2	1.9
All 5 levels		97.6	

Table 4.8.1.2
Average % DE for Cadmium on MCE Filters

×target concn	mass (µg)	average recovery (%)	SD (%)
RQL	0.02	102	0.74
0.1	0.25	103	1.2
0.5	1.25	104	1.9
1.0	2.50	103	0.90
2.0	5.00	102	1.7
All 5 levels		103	

Table 4.8.1.3
Average % DE for Cobalt on MCE Filters

×target concn	mass (µg)	average recovery (%)	SD (%)
RQL	0.0100	104	2.0
0.1	5.00	96.5	0.42
0.5	25.0	95.8	1.7
1.0	50.0	93.8	0.69
2.0	100	96.6	2.2
All 5 levels		97.4	

Table 4.8.1.4
Average % DE for Copper on MCE Filters

×target concn	mass (µg)	average recovery (%)	SD (%)
RQL	0.200	98.4	3.0
0.1	5.00	105	1.2
0.5	25.0	97.7	1.5
1.0	50.0	95.4	0.88
2.0	100	98.9	1.9
All 5 levels		99.1	

Table 4.8.1.5
Average % DE for Nickel on MCE Filters

×target concn	mass (µg)	average recovery (%)	SD (%)
RQL	0.200	104	3.1
0.1	50.0	99.2	0.88
0.5	250	98.1	1.5
1.0	500	95.7	1.0
2.0	1000	99.4	2.2
All 5 levels		99.4	

Table 4.8.1.6
Average % DE for Lead on MCE Filters

×target concn	mass (µg)	average recovery (%)	SD (%)
RQL	0.0500	108	1.9
0.1	2.50	103	0.99
0.5	12.5	103	0.85
1.0	25.0	101	1.4
2.0	50.0	106	1.7
All 5 levels		104	

4.8.2 Recoveries from back-up pads

Six BUPs were spiked with the six analytes at the target concentration. After drying, they were each placed in separate 50-mL centrifuge tubes and taken through a slightly modified version of the microwave digestion procedure described in Section 3.4.2. Four milliliters of concentrated nitric acid and 0.3 mL of 30% hydrogen peroxide were added to each tube. Following the first digestion step, the tubes were cooled and 1 mL of concentrated hydrochloric acid was added to each. After the second digestion step, it could be seen that some fibers remained undigested. Each tube was filled to the 50-mL mark with DIW and centrifuged for 10 minutes @ 2000 rpm. This resulted in the fibers being compacted into the bottom of the tube. The clear solution on top was poured into 100-mL volumetrics. Another 30 mL of DIW were added to each tube and they were centrifuged again. The clear solutions were added to their appropriate volumetric. One milliliter of IS solution and 1 mL of ethanol were added and the volumetrics were brought to volume with DIW. They were analyzed by ICP-MS and the recoveries, which range from 97.6 - 101%, are shown in Table 4.8.2.

Table 4.8.2
Spike Recoveries (%) from Microwaved Back-up Pads

analyte	1	2	3	4	5	6	average recovery	SD
As	102	102	101	98.7	101	99.6	101	1.4
Cd	99.4	100	98.9	97.0	99.3	97.0	98.6	1.3
Co	96.3	97.1	98.9	96.1	99.8	97.4	97.6	1.5
Cu	101	100	102	99.6	103	100	101	1.3
Ni	98.8	99.9	101	98.9	103	100	100	1.5
Pb	102	102	101	99.4	103	101	102	1.2

4.8.3 Recoveries from cellulose nitrate filters (used to wipe out insides of cassettes)

Six cellulose nitrate filters were spiked with the six analytes at the target concentration. They were digested using the normal microwave procedure (Section 3.4.1). They were analyzed by ICP-MS and the recoveries, which range from 99.8 - 103%, are shown in Table 4.8.3.

Table 4.8.3
Spike Recoveries (%) from Cellulose Nitrate Filters

analyte	1	2	3	4	5	6	average recovery	SD
As	103	102	103	104	102	101	103	1.1
Cd	103	100	99.6	99.4	101	99.5	100	1.4
Co	108	97.9	98.2	99.6	97.8	97.1	99.8	4.1
Cu	111	100	100	102	100	99.2	102	4.6
Ni	111	99.7	100	102	100	99.2	102	4.5
Pb	100	101	102	103	102	103	102	1.2

4.8.4 Recoveries from MCE filters digested on the hotplate using sulfuric acid

When MCE filters that have been spiked with solutions containing arsenic are digested on the hotplate using sulfuric acid, most of the arsenic is lost. Six MCE filters were spiked with the six analytes, three at half the target concentration and three at the target concentration. They were digested on the hotplate with four mL of H_2SO_4:H_2O (1:1). Several drops of 30% hydrogen peroxide were added to facilitate the digestion. After cooling, 0.5 mL of concentrated HCl and 0.5 mL of IS solution were added to each. The contents were transferred to 50-mL volumetrics and brought to volume with DIW. They were analyzed by ICP-MS using calibration standards with the same matrix. The recoveries, which range from 11.2 - 101%, are shown in Table 4.8.4.

Table 4.8.4
Spike Recoveries (%) from MCE Filters Digested on the Hotplate using H_2SO_4

analyte	spiked at 0.5 × target concn			spiked at 1 × target concn			average recovery (SD)
As	12.7	9.4	11.1	13.5	9.4	10.9	11.2 (1.7)
Cd	98.3	98.3	98.9	96.0	95.6	96.7	97.3 (1.4)
Co	93.8	92.7	92.1	89.8	87.7	89.2	90.9 (2.3)
Cu	99.6	98.7	98.5	94.2	92.2	93.9	96.2 (3.1)
Ni	95.3	94.4	93.9	91.8	90.0	91.5	92.8 (2.0)
Pb	100	100	101	101	102	104	101 (1.5)

4.9 Comparison of Microwave Digestion and Hotplate Digestion Using SRM 1648*

In the following microwave digestion, different conditions were used as compared to those in Section 3.4.1. The differences are not judged to constitute a significant change in the procedure. Approximately 100 mg each of SRM 1648 were weighed out on each of six MCE filters and carefully placed into 50-mL centrifuge tubes. Two milliliters of concentrated HNO_3 and 0.2 mL of 30% H_2O_2 were added to each. Samples were then digested in a microwave for 15 min (max T = 110 ºC). Samples were cooled for an hour and another 2 mL of concentrated HNO_3 were added, whereupon they were digested for a second time in the microwave under the same conditions. After cooling for an hour, 1 mL of concentrated HCl was added to each and they were re-heated for 6 minutes (max T = 86 ºC). Samples were transferred to 100-mL volumetrics, 1 mL of IS solution was added, and they were brought to a final volume with DIW. The final acid matrix was 4% HNO_3 + 1% HCl + 1% IS. Samples were analyzed by ICP-MS.

OSHA ID-121, Metal & Metalloid Particulates in Workplace Atmospheres (Atomic Absorption), is the method commonly used to analyze for various metals by atomic absorption. The final acid matrix for many of these metals, including cadmium, cobalt, copper, and nickel is 4% HNO_3, plus 1-2 drops of HCl to facilitate particulate dissolution. A hotplate is used for these digestions.

For the hotplate digestion, approximately 100 mg of SRM 1648 were weighed out on MCE filters and placed in 250-mL Phillips beakers. Eight milliliters of concentrated HNO_3 were added to each. The beakers were heated on the hotplate and drops of 30% H_2O_2 were added until the solution turned clear or no further lightening of color was observed. Samples were heated until approximately half of the HNO_3 had boiled off, leaving about 4 mL of HNO_3. After cooling, 1 mL of concentrated HCl was added and the beakers heated again on the hotplate until boiling began, at which point they were removed and cooled. Samples were transferred to 100-mL volumetrics, 1 mL of IS solution was added, and they were brought to a final volume with DIW. The final matrix was 4% HNO_3 + 1% HCl + 1% IS. Samples were analyzed by ICP-MS.

For the six elements in this method, only cobalt is not included in the results, because it is present at very low levels in the SRM and has a non-certified value. For the other five elements tested, the results are quite comparable, indicating that the two digestion techniques produce similar results.

Table 4.9
Comparison of Microwave Digestion vs. Hotplate Digestion of SRM 1648*

	As						Cd					
	microwave			hotplate			microwave			hotplate		
	expected (µg)	found (µg)	found (%)	expected (µg)	found (µg)	found (%)	expected (µg)	found (µg)	found (%)	expected (µg)	found (µg)	found (%)
	11.75	12.14	103	11.67	12.01	103	7.66	6.91	90.2	7.61	6.92	90.9
	11.65	12.24	105	11.65	11.87	102	7.60	6.96	91.6	7.60	6.82	89.8
	11.82	12.37	105	11.62	12.00	103	7.71	7.06	91.5	7.58	6.86	90.6
	11.67	12.35	105	11.93	11.81	99.0	7.61	7.04	92.5	7.78	6.74	86.7
	11.57	12.47	108	11.75	11.68	99.4	7.55	7.02	93.0	7.66	6.66	86.9
	11.92	12.37	104	11.72	12.32	105	7.78	7.08	91.0	7.64	6.92	90.5
$\bar{x}$	11.73	12.32	105	11.72	11.95	102	7.65	7.01	91.6	7.65	6.82	89.2
SD			1.7			2.3			1.0			1.9

Table 4.9
Comparison of Microwave Digestion vs. Hotplate Digestion of SRM 1648*

	Cu						Ni					
	microwave			hotplate			microwave			hotplate		
	expected (µg)	found (µg)	found (%)	expected (µg)	found (µg)	found (%)	expected (µg)	found (µg)	found (%)	expected (µg)	found (µg)	found (%)
	62.23	56.24	90.4	61.81	61.28	99.1	8.38	6.05	72.2	8.32	6.54	78.6
	61.71	58.86	95.4	61.71	60.81	98.5	8.31	6.20	74.6	8.31	6.49	78.1
	62.60	58.90	94.1	61.51	62.00	101	8.43	6.30	74.7	8.28	6.45	77.9
	61.80	59.18	95.8	63.17	60.66	96.0	8.32	6.30	75.7	8.50	6.34	74.6
	61.27	58.86	96.1	62.21	61.57	99.0	8.25	6.31	76.5	8.38	6.41	76.5
	63.15	59.97	95.0	62.06	64.18	103	8.50	6.50	76.5	8.36	6.75	80.8
$\bar{x}$	62.13	58.67	94.5	62.08	61.75	99.5	8.37	6.28	75.0	8.36	6.50	77.7
SD			2.1			2.4			1.6			2.1

Table 4.9
Comparison of Microwave Digestion vs. Hotplate Digestion of SRM 1648*

	Pb					
	microwave			hotplate		
	expected (µg)	found (µg)	found (%)	expected (µg)	found (µg)	found (%)
	669.3	640.7	95.7	664.8	632.6	95.2
	663.7	636.7	95.9	663.7	626.7	94.4
	673.3	636.5	94.5	661.6	632.1	95.5
	664.7	658.9	99.1	679.4	620.3	91.3
	659.0	647.8	98.3	669.1	622.2	93.0
	679.2	643.8	94.8	667.4	647.4	97.0
$\bar{x}$	668.2	644.1	96.4	667.7	630.2	94.4
SD			1.9			2.0

*Urban Particulate Matter (Standard Reference Material 1648) was purchased from National Institute of Standards & Technology (NIST) in April, 1998. It consists of natural atmospheric particulate material collected in an urban location. Original certification date: 11/16/78. Additional certification update: 5/11/82. This SRM may not be representative of air samples collected for OSHA compliance purposes.

4.10 Qualitative analysis

The Elan ICP-MS can also be used to obtain qualitative analysis on a sample. Instead of having the instrument operating in the peak-hopping mode, which looks at specific mass/charge ratios and is used for quantitative analysis, an analyst could operate it in the scanning mode, looking at ranges of the whole spectrum. The mass spectra and expected abundances for all the isotopes of the six analytes and their internal standards are shown in Figures 4.10.1 - 4.10.4. Significant deviations from the expected abundance ratios indicate interferences. It is in the interpretation process (automatically done by the Elan ICP-MS software) where errors may occur concerning the source of interferences. If significant, these errors will result in non-quantitative approximations.

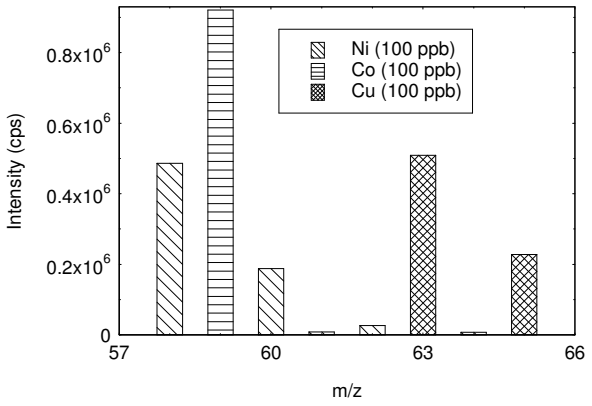

Figure 4.10.1. Mass spectra for nickel, cobalt, and copper.

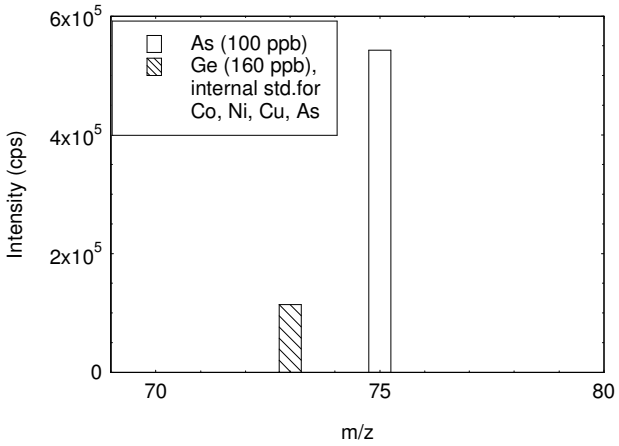

Figure 4.10.2. Mass spectra for arsenic and germanium.

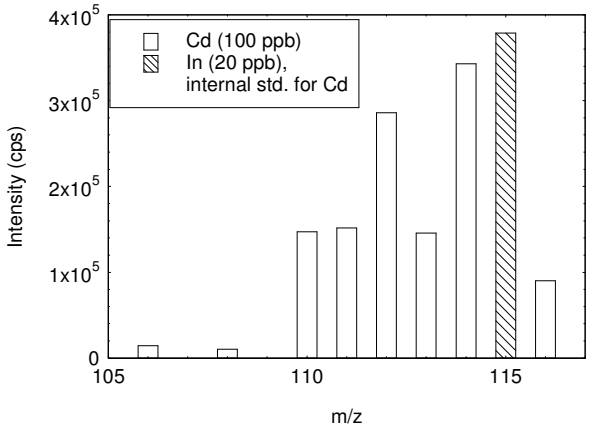

Figure 4.10.3. Mass spectra for cadmium and indium.

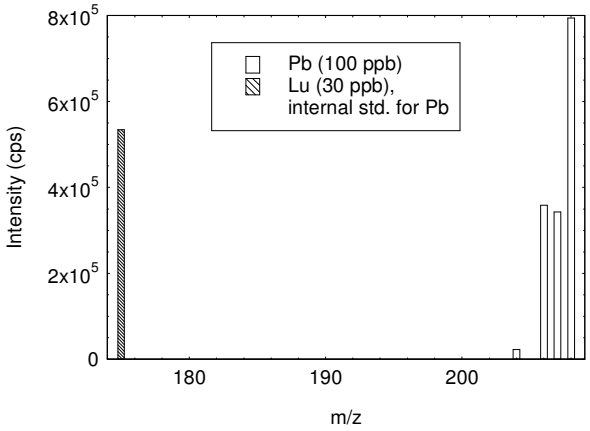

Figure 4.10.4. Mass spectra for lead and lutetium.