

**California Environmental Protection Agency**



**Air Resources Board**

**PROCEDURE FOR THE DETERMINATION OF TRACE ELEMENTS IN  
PARTICULATE MATTER EMITTED FROM MOTOR VEHICLE  
EXHAUST USING INDUCTIVELY COUPLED PLASMA MASS  
SPECTROMETRY (ICP-MS)**

SOP MV-AEROSOL-152  
Version 1.0

Effective Date: December 15, 2010

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This procedure has been reviewed by the staff of the Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board, nor does the mention of trade names or commercial products constitute endorsement or recommendation for use.

## **1. Scope and Application**

1.1 This standard operating procedure (SOP) describes the acid digestion, followed by the identification and quantification of trace elements in particulate matters, using the Thermo Electron X series inductively coupled plasma mass spectrometer (ICP-MS) with collision cell technology (CCT).

1.2 This method is suitable for the determination of trace elements in particulate matter collected on a Teflon filter, emitted from motor vehicle exhaust.

## **2. Method Summary**

2.1 The particulate matter collected on a Teflon filter is digested with a mixture of acids in a microwave digestion oven.

2.2 The resulting aqueous solution is aspirated through a nebulizer into argon plasma, where the sample is ionized in the plasma, separated by a series of electronic and magnetic filters, and identified based on the difference in the ion mass to charge ratio. The CCT technology of Thermo X Series ICP-MS effectively reduces polyatomic interferences to a negligible level.

2.3 The Thermo Electron X Series ICP-MS is capable of simultaneous analysis of multiple elements with a concentration range spanning at least six orders of magnitude.

2.4 The target elements are identified by their characteristic mass. The elements of interest and their characteristic masses of this method are listed in Table A.

2.5 The concentration of target elements is quantified using internal standard method. The elements used as the internal standard in this method are listed in Table B.

## **3. Interferences and Contaminations**

3.1 Isobaric elemental interferences: Most elements have multiple isotopes and some elements have isotopes with a nominal mass shared by another element (e.g.  $^{82}\text{Kr} = 81.9134$  and  $^{82}\text{Se} = 81.9167$ ). In some cases, the instrument may not have the resolution required to separate these isotopes. Isotopes free from this type of interference should be chosen when a list of targeted elements is created.

3.2 Polyatomic interferences: Plasma-sourced interferences are generated when sample matrix ions combine to form a mass/charge ( $m/z$ ) similar to that of the analyte. Common examples include oxides, hydrides, and chlorides of argon, rare-earth element oxides, and double-charged ions of barium. Refer to Table A for a specific list of common interferences.

3.3 The concentrations of targeted elements in motor vehicle exhaust may vary by orders of magnitude. Pay close attention to the nature of the digest solution introduced into the ICP-MS. Precautions must be taken to protect the electron multiplier from detector fatigue caused by exposure to high chemical concentrations (high ion currents). This fatigue can last from several seconds to many hours depending on the extent of exposure. During this period, response factors are constantly changing, which causes instrument instability that invalidates the calibration curves and therefore invalidates all associated sample results.

3.4 The concentration of the acid mixture affects the detected results of the final aliquot. The acid content of the digested sample solution, or its final dilution, must match the acid content of the calibration standards. Use the reagent blank to make dilutions.

#### **4. Safety**

4.1 General safe laboratory practices should be followed. Concentrated acid must only be used in the exhausting fume hoods. A labcoat, safety glasses, and gloves must be worn.

4.2 Hazards associate with this procedure:

4.2.1 Exposure to toxic or carcinogenic metals and acids – prepared sample solutions contain 0.5% hydrofluoric acid. Refer to the MSDS for specific precautions.

4.2.2 Pressurized gas line and gas cylinders – the argon line feeds the instrument has high positive pressure at 110psi. All gas cylinders must be securely fastened, and must be capped before moving.

4.2.3 Ultra-violet light – the light escaping from the torch assembly chamber is only partially filtered. Avoid prolong eye exposure to the plasma.

#### **5. Apparatus and Equipment**

5.1 CEM Mars Microwave Digestion Oven, or equivalent

5.1.1 HP-500 Plus digestion vessel;

5.1.2 RTP-300 Plus temperature probe;

5.1.3 ESP-1500 Plus pressure sensor.

5.2 Thermo Electron X series inductively coupled plasma mass spectrometer (ICP-MS) with collision cell technology (CCT) , or equivalent

5.2.1 Peristaltic pump.

5.2.2 Nebulizer or Spray chamber, quartz;

5.2.3 Torch, quartz;

5.2.4 Nickel or platinum sampler and skinner cones;

5.3 Labware

5.3.1 Polypropylene auto-sampler tubes (17x100mm), or 15ml centrifuge tubes;

- 5.3.2 Calibrated pipettes, 2-100 $\mu$ l, 100-1000 $\mu$ l, 0.5-10.0ml;
- 5.3.3 Metal-free pipette tips;
- 5.3.4 Teflon or low density polyethylene volumetric flasks;
- 5.3.5 Powder-free polyethylene or nitrile gloves;
- 5.3.6 Analytical balance, calibrated, accurate to 0.1mg;
- 5.3.7 Ceramic knife/scissor;
- 5.3.8 Teflon tweezers

## 6. Reagents and Consumable Materials

- 6.1 Reagent grade water, 18.2 M $\Omega$  resistivity;
- 6.2 Ethanol, ACS grade, 99.5%;
- 6.3 Nitric acid, trace metal grade, 67-70%;
- 6.4 Hydrochloric acid, trace metal grade, 33-36%;
- 6.5 Hydrofluoric acid, trace metal grade, 45-50%;
- 6.6 Digestion acid-mix solution: To prepare 500 ml of acid mix solution, add 150 ml reagent water, 250 ml nitric acid, 75 ml of hydrochloric acid, and 25 ml of hydrofluoric acid.
- 6.7 5% (v/v) nitric acid: Mix 50 ml of nitric acid (6.3) in 1 L of reagent water (6.1).
- 6.8 Standard stock solution, ICP-MS grade, traceable to NIST Standards;
- 6.9 Argon gas supply, 110psi, 99.999% purity;
- 6.10 ICP-MS tuning solution A, 10.0 $\mu$ g/L, containing <sup>7</sup>Li, <sup>9</sup>Be, <sup>59</sup>Co, <sup>115</sup>In, <sup>137</sup>Ba, <sup>140</sup>Ce, and <sup>238</sup>U;
- 6.11 Peristaltic pump tubing:
  - 6.11.1 0 – 2 ml/min flow rate, yellow/orange
  - 6.11.2 0 – 5 ml/min flow rate, white/white
- 6.12 Teflon Filter, 47mm, 2.0 $\mu$ m.

## 7. Filter Preparation and Sample Handling

- 7.1 Teflon filters must be used to collect particulate matter for ICP-MS analysis.
- 7.2 The Teflon filters purchased from commercial suppliers contain random amounts of elements of interest. Therefore all Teflon filters must be soaked in 1:1 (v/v) HNO<sub>3</sub>

solution for at least 24 hours, rinsed with reagent grade water, and dried in an oven at 40 °C for at least one hour before they can be used.

7.3 The filter cassette and its filter support (stainless steel screen) must be disassembled, soap washed, rinsed thoroughly with tap water, followed by at least three times rinse with reagent water, and dried in an oven at 80 °C for a minimum of 30 minutes.

7.4 Assemble the filter cassette, the filter support, and the Teflon filter together. Place the assembled filter cassette assembly in a Petri dish, sealed with Teflon tape prior to PM sample collection.

7.5 When the samples are returned to the laboratory, the samples are stored in the sealed, labeled Petri dishes until analysis.

## **8. Sample Digestion**

8.1 Carefully remove the polyethylene ring of the Teflon sample filter with a ceramic scissor. Place the filter in the CEM Microwave HP-500 Plus digestion vessel.

8.2 Wet the Teflon filter with 0.2 ml of ethanol in the digestion vessel. Ethanol improves the contact of aqueous solution and Teflon. Then add 10 ml of digestion acid-mix solution from section 6.6 to the sample vessel.

8.3 Assemble the HP-500 Plus digestion vessel; see the CEM manual.

8.4 Digest the samples using the following microwave digestion protocol: 15 minute ramp to 200 C, followed by 1 hour hold at 200 C, and 1 hour of ventilating and cooling.

8.5 Filter the solution and discard any residue. Dilute the digested solution using reagent grade water to 100 ml.

## **9. Instrument Setup and Tuning**

9.1 Inspect the ICP-MS. Initial conditions must be met before igniting the plasma.

9.1.1 Inspect the torch chamber. The cones must be clean and free of any deposits. The torch must be clean and free of residue. Verify that there is a tight seal between the torch glassware and the spray chamber.

9.1.2 Inspect the peristaltic pump tubing. If the tubing is stressed beyond its elastic limit and remains flat, it needs to be replaced. If the tubing is in good condition, lock the tensioners in place.

9.1.3 Inspect the water chiller and make sure there is enough water to circulate through the system.

9.1.4 Supply the autosampler rinse container with 5% trace elemental grade HNO<sub>3</sub> (v/v) solution. Verify the waste reservoir has enough capacity.

## 9.2 Booting-up the Thermo X-Series ICP-MS

9.2.1 Turn on the chiller.

9.2.2 Use the Instrument page of the Thermo PlasmaLab software to turn on and boot up the ICP-MS instrument. Open the torch chamber door to immediately abort the boot up process if continuous arcing sounds occur from the torch. The continuous arcing will damage the torch.

9.2.3 Verify that the peristaltic pump is rotating and the spray chamber is draining properly. Inspect the tubing connections for leaks.

9.2.4 Allow the instrument to warm up for at least 30 minutes before tuning.

## 9.3 Tuning the Thermo X-Series ICP-MS

9.3.1 Move the autosampler probe to a vial containing 1 µg/L of the ICP-MS tuning solution A.

9.3.2 Perform the “Stages” autotune sequences follow by the “HPI Cones Standard Mode” in the Instrument page.

9.3.3 Run a performance check sequence to validate that the instrument was tuned correctly using the following criteria:

### 9.3.3.1 Criteria for instrument responses:

<u>Mass</u>	<u>must be</u>	<u>Response</u>	<u>Stability</u>
7Li	>	20,000 (cps)	2.0%
9Be	>	5,000 (cps)	
59Co	>	30,000 (cps)	2.0%
115In	>	60,000 (cps)	2.0%
220Bkg	<	1 (cps)	
238U	>	45,000 (cps)	2.0%
156CeO/140Ce	<	0.0230	
137Ba <sup>2+</sup> /137Ba	<	0.0350	

### 9.3.3.2 Criteria for accuracy of instrument mass calibration:

<u>Mass</u>	<u>Max Error (amu)</u>	<u>Peak Width (amu)</u>	
		<u>Minimum</u>	<u>Maximum</u>
7Li	0.10	0.65	0.85
59Co	0.10	0.65	0.85
115In	0.10	0.65	0.85
238U	0.10	0.65	0.85

9.3.4 If the instrument response criteria in 9.3.3.1 are not met, trouble-shoot the instrument, adjust the parameters if necessary, and retune the instrument until it meets the response criteria.

9.3.5 If the accuracy criteria in 9.3.3.2 are not met, the Mass Calibration Procedure must be performed. Place the autosampler probe in a vial containing 1 µg/L of the ICP-MS tuning solution A. Select and perform the Mass Calibration sequence to calibrate the Quadrupole. Run the Performance check sequence again to make sure the Mass Calibration passes the accuracy criteria

9.3.6 Move the autosampler probe to a vial containing 10 µg/L of the ICP-MS tuning solution A. Manually adjust the following parameter settings in the instrument tuning page:

<u>Parameter</u>	<u>Settings</u>
Focus	0 V
Hex Bias	-10 V
Pole Bias	-7 V
D.A.	-20 V
Lens 3	-200 V
Aux. Gas (7% H <sub>2</sub> /He)	3.5 – 4.5 ml/min

9.3.7 Perform the “HPI Cones CCT-KED Mode” autotune sequence in the Instrument page.

9.3.8 If the resulting auxiliary gas setting is less than 3.5 ml/min after the CCT-KED autotune, manually adjust it to 4 ml/min again. Save this CCT-KED tune file.

9.3.9 Run a “HPI Cones CCT-KED Mode” performance check sequence to validate that the instrument was tuned correctly using the following criteria:

<u>Mass</u>	<u>must be</u>	<u>Response</u>	<u>Stability</u>
59Co	>	20,000 (cps)	2.0%
78Se	<	100 (cps)	
115In	>	50,000 (cps)	2.0%

## 9.4 Setting up the Detector

9.4.1 Perform a Detector Cross Calibration sequence. This sequence generates the detector cross calibration that is used to convert acquired analogue data into equivalent pulse counting data.

## 9.5 Sequence Pre-qualification parameters

9.5.1 Monitor the sample take-up time and verify that the sample time in the sequence is sufficient.

9.5.2 Monitor the rinse-out time for analytes, such as Zn or Rh, and verify that the sample wash time in the sequence is sufficient for the elements in the method, which means the time needed for instrument response of these analytes to fall below the IDL.

9.5.3 Move the autosampler probe to the rinse position of a vial containing blank solution to aspirate while setting up the sample vials for the sequence.

# 10. Method Calibration and Analytical Sequence Setup

## 10.1 Experiment (Method) Set-up

10.1.1 The experiment file (the instrument software analytical commend file) designates the isotopes to be monitored at each scanning mode and parameters, such as mass window, scan type, integration time and detector mode. It also defines the number of acquisition scans at each scanning mode.

10.1.2 The experiment used for an analytical sequence is determined by the type of samples to be analyzed and the elements required. Specific experiments have been constructed for each project.

10.1.3 Internal standard addition: An internal standard solution is added to all of the ICP-MS analysis, including blanks, calibration standards and samples. The purpose of the internal standard addition is to correct any post acquisition drift in sensitivity. A mixing coil and peristaltic pump are utilized for on-line addition of the internal standard addition.

## 10.2 Experiment (Method) Calibration

10.2.1 It is recommended that the instrument be calibrated in the beginning of day every time sample(s) being analyzed due to the tendency of the instruments drift.

10.2.2 The default matrix for blanks and standards, as well as all other samples, is 5% HNO<sub>3</sub> (v/v). This matrix may be changed as required by a specific project. However, the samples, blanks and the standards should be analyzed in the same matrix.

10.2.3 The internal standard calibration technique is preferred over external standard calibration technique. A mixture of some or all of the elements listed in Table B may be used as internal standards, provided that these elements are not part of the target analytes of the project. The concentration of the internal standard solution is suggested to be in the range of 2 and 50 µg/L.

10.2.4 A valid calibration curve consists of a blank and at least five levels of standards ranging from 1 µg/L to 100 µg/L or higher. The minimum correlation coefficient of the linear regression should be greater than 0.995. If the correlation coefficient is less than 0.995, the analyst must trouble-shoot the instrument to determine whether there is any spectral or carry-over interference, make the necessary adjustment or repair, then retune and recalibrate the instrument.

## 10.3 Analytical Sequence Set-up

10.3.1 Data acquisition consists of a sequence file with a list of calibration standards, check standards, blanks, and samples to be analyzed. The sample information includes the sample name; acquisition method used, calibration, autosampler uptake time, and wash time.

10.3.2 The standard analytical sequence includes an initial blank, a minimum 5-level standard calibration, second-source calibration verification, continuing calibration verification samples, and continuing check-blank samples.

# 11. Quality Assurance and Quality Control

All analysts must demonstrate that he or she is capable of meeting or exceeding all of the QA/QC objectives as well as the limits of detection listed in this SOP before any analytical results can be reported.

## 11.1 Accuracy and Precision

11.1.1 In order to ensure analytical accuracy, both primary calibration standards and secondary second-source standard must be prepared from certified NIST

traceable ICP-MS grade stock solutions. Any other grades of standards, such as AA or ICP-AES grades, may contain trace amount of impurity of other elements. ICP-MS is capable of extremely low detection limits and these trace amount of the impurity will severely affect the accuracy of the results particularly at low levels. All standards and their preparations must be documented in a Trace Element Standard logbook.

11.1.2 The accuracy of the calibration curve is confirmed by the analysis of a midrange second-source standard immediately after the calibration. All of the results from this analysis must be within  $\pm 15\%$  of the expected concentration.

11.1.3 The analytical accuracy is monitored by the analysis of a mid-range continuing calibration verification sample followed by a continuing check-blank sample every 10 samples or less in the sequence. The continuing calibration verification must be within  $\pm 20\%$  of the expected concentration. The continuing check-blank sample must be less than or equal to the MDL.

~~11.1.3~~ 11.1.4 The analytical precision is monitored by duplicate analysis for 10%, or less, of the samples in the sequence. These duplicate samples are used to estimate method precision, expressed as relative percent difference (RPD). The RPD between the duplicate and duplicate final concentrations should be  $<20\%$  for Li, Cr, Ni, Se, Rh, Cd, Ba, W, and Pd. If the RPD is greater than 20%, the analyst should stop the analysis, check for and correct any instrument malfunction, and reanalyze the whole batch of samples.

## 11.2 Limit of Detection (LOD)

LOD is a calculated value that represents the minimum reportable concentration of an analyte with 99% confidence. Calculate the LOD for each analyte isotope according to the reference method, EPA Compendium Method IO-3.5, as follows:

$$\text{LOD} = (t) \times (s)$$

where:

- t --- Student's t value for a 99% confidence level and a standard deviation estimated with n-1 degrees of freedom.  $t = 3.14$  for seven replicates.
- s --- Standard deviation of the replicate analyses.

### 11.2.1 Instrument Detection Limit (IDL)

11.2.1.1 The instrument detection limits (IDL) must be established for all of the elements of interest. The IDLs must be verified at least once a year, or whenever a significant change in background or the instrument response is expected.

11.2.1.2 The IDL is determined by analyzing the reagent blank for seven times. The IDLs are tabulated in Table C.

### 11.2.2 Method Detection Limit (MDL)

11.2.2.1 The MDL is determined by analyzing seven Teflon filter blanks which were undergone microwave digestion. The MDL can be established by the analysis of Teflon filter blanks from various Teflon filter batch. The MDL is calculated as follows:

$$\text{MDL} = (t) \times (s) + (m)$$

where:

- m --- Mean of the seven Teflon filters.

11.2.2.2 Since all Teflon filters contain some impurity, at least one Teflon filter blank must be analyzed for every Teflon filter batch. The initial batch of Teflon filter blank data are tabulated in Table D.

#### 11.2.3 Reporting Detection Limit (RDL)

The reporting detection limit (RDL) is established by repeatedly analyzing the MDL for a minimum of five times, each time on a different day. The RDL is the average values for each analyte from these MDLs. The RDL must be re-evaluated when the MDL is determined for a new batch of Teflon filters.

## 12. Data Handling

12.1 The completed sequence and the resulting analytical data can be exported in xml format. Data should include sample name, analytical date and time, dilution factor, isotope number, calculated concentration, unit, standard deviation, and percent relative standard deviation.

12.2 The Microsoft Excel or any other spreadsheet program can be used to process and calculate the final value for data reporting.

## 13. References

13.1 EPA Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air, Method IO-3.1, Selection, Preparation and Extraction of Filter Material.

13.2 EPA Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air, Method IO-3.5, Determination of Metals in Ambient Particulate Matter Using Inductively Coupled Plasma / Mass Spectrometer (ICP/MS).

13.3 EPA Method 200.8, Determination of Trace Elements in Waters by Inductively Coupled Plasma – Mass Spectrometry.

13.4 EPA SW-846 Method 3051, Microwave Assisted Acid Digestion of Sediments, Sludges, Soil, and Oils.

13.5 EPA SW-846 Method 6020, Inductively Coupled Plasma – Mass Spectrometer.

## 14. Revision History

14.1 The name of this SOP changed from SOP No. MLD 152 to SOP MV-AEROSOL-152 to reflect the division name change.

**Table A**

**Target Elements, Characteristic Mass, Relative Abundance, and Potential Interferences**

Target Analyte	Characteristic Mass	% Relative Abundance	Polyatomic Interferences	Isobarric Interferences
Li	7	92.4		
Be	9	100		
Ti	47	7.44		
V	51	99.8	$^{35}\text{Cl}^{16}\text{O}^+$ , $^{34}\text{S}^{16}\text{OH}^+$ , $^{38}\text{Ar}^{13}\text{C}^+$ , $^{36}\text{Ar}^{15}\text{N}^+$ , $^{36}\text{Ar}^{14}\text{NH}^+$ , $^{37}\text{Cl}^{14}\text{N}^+$ , $^{36}\text{S}^{15}\text{N}^+$ , $^{33}\text{S}^{18}\text{O}^+$ , $^{34}\text{S}^{17}\text{O}^+$	
Cr	52	83.8	$^{35}\text{Cl}^{16}\text{OH}^+$ , $^{40}\text{Ar}^{12}\text{C}^+$ , $^{36}\text{Ar}^{16}\text{O}^+$ , $^{37}\text{Cl}^{15}\text{N}^+$ , $^{34}\text{S}^{18}\text{O}^+$ , $^{36}\text{S}^{16}\text{O}^+$ , $^{38}\text{Ar}^{14}\text{N}^+$ , $^{36}\text{Ar}^{15}\text{NH}^+$ , $^{35}\text{Cl}^{17}\text{O}^+$	
Mn	55	100	$^{40}\text{Ar}^{14}\text{NH}^+$ , $^{39}\text{K}^{16}\text{O}^+$ , $^{37}\text{Cl}^{18}\text{O}^+$ , $^{40}\text{Ar}^{15}\text{N}^+$ , $^{38}\text{Ar}^{17}\text{O}^+$ , $^{36}\text{Ar}^{18}\text{OH}^+$ , $^{38}\text{Ar}^{16}\text{OH}^+$ , $^{37}\text{Cl}^{17}\text{OH}^+$ , $^{23}\text{Na}^{32}\text{S}^+$ , $^{36}\text{Ar}^{19}\text{F}^+$	
Co	59	100	$^{43}\text{Ca}^{16}\text{O}^+$ , $^{42}\text{Ca}^{16}\text{OH}^+$ , $^{24}\text{Mg}^{35}\text{Cl}^+$ , $^{36}\text{Ar}^{23}\text{Na}^+$ , $^{40}\text{Ar}^{18}\text{OH}^+$ , $^{40}\text{Ar}^{19}\text{F}^+$	
Ni	60	26.2	$^{44}\text{Ca}^{16}\text{O}^+$ , $^{23}\text{Na}^{37}\text{Cl}^+$ , $^{43}\text{Ca}^{16}\text{OH}^+$	
Cu	63	69.2	$^{31}\text{P}^{16}\text{O}_2^+$ , $^{40}\text{Ar}^{23}\text{Na}^+$ , $^{47}\text{Ti}^{16}\text{O}^+$ , $^{23}\text{Na}^{40}\text{Ca}^+$ , $^{46}\text{Ca}^{16}\text{OH}^+$ , $^{36}\text{Ar}^{12}\text{C}^{14}\text{NH}^+$ , $^{14}\text{N}^{12}\text{C}^{37}\text{Cl}^+$ , $^{16}\text{O}^{12}\text{C}^{35}\text{Cl}^+$	
Cu	65	30.8		
Zn	66	27.9	$^{50}\text{Ti}^{16}\text{O}^+$ , $^{34}\text{S}^{16}\text{O}_2^+$ , $^{33}\text{S}^{16}\text{O}_2\text{H}^+$ , $^{32}\text{S}^{16}\text{O}^{18}\text{O}^+$ , $^{32}\text{S}^{17}\text{O}_2^+$ , $^{33}\text{S}^{16}\text{O}^{17}\text{O}^+$ , $^{32}\text{S}^{34}\text{S}^+$ , $^{33}\text{S}_2^+$	
As	75	100	$^{40}\text{Ar}^{35}\text{Cl}^+$ , $^{59}\text{Co}^{16}\text{O}^+$ , $^{36}\text{Ar}^{38}\text{ArH}^+$ , $^{38}\text{Ar}^{37}\text{Cl}^+$ , $^{36}\text{Ar}^{39}\text{K}^+$ , $^{43}\text{Ca}^{16}\text{O}_2^+$ , $^{23}\text{Na}^{12}\text{C}^{40}\text{Ar}^+$ , $^{12}\text{C}^{31}\text{P}^{16}\text{O}_2^+$	

**Table A (Continues)**

Target Analyte	Characteristic Mass	% Relative Abundance	Polyatomic Interferences	Isobarric Interferences
Se	77	7.64	$^{40}\text{Ar}^{37}\text{Cl}^+$ , $^{36}\text{Ar}^{40}\text{ArH}^+$ , $^{38}\text{Ar}_2\text{H}^+$ , $^{12}\text{C}^{19}\text{F}^{14}\text{N}^{16}\text{O}_2^+$	
Se	82	8.73	$^{12}\text{C}^{35}\text{Cl}_2^+$ , $^{34}\text{S}^{16}\text{O}_3^+$ , $^{40}\text{Ar}_2\text{H}_2^+$	Kr(11.6)
Rb	85	72.2		
Sr	88	82.6		
Zr	90	51.5		
Nb	93	100		
Mo	95	15.9	$^{40}\text{Ar}^{39}\text{K}^{16}\text{O}^+$ , $^{79}\text{Br}^{16}\text{O}^+$	
Ru	101	17.1	$^{40}\text{Ar}^{61}\text{Ni}^+$ , $^{64}\text{Ni}^{37}\text{Cl}^+$	
Rh	103	100		
Pd	105	22.3		
Ag	107	51.8	$^{91}\text{Zr}^{16}\text{O}^+$	
Cd	111	12.8	$^{95}\text{Mo}^{16}\text{O}^+$ , $^{94}\text{Zr}^{16}\text{OH}^+$ , $^{39}\text{K}_2^{16}\text{O}_2\text{H}^+$	
Sn	118	24.2	$^{102}\text{Ru}^{16}\text{O}^+$ , $^{102}\text{Pd}^{16}\text{O}^+$	
Sb	121	57.2	$^{105}\text{Pd}^{16}\text{O}^+$	
Te	125	7.14		
Cs	133	100	$^{101}\text{Ru}^{16}\text{O}_2^+$	
Ba	137	11.2		
La	139	99.9		
Ce	140	88.4		
Hf	178	27.3		
Ta	181	100	$^{165}\text{Ho}^{16}\text{O}^+$	
W	182	26.5	$^{166}\text{Er}^{16}\text{O}^+$	
Ir	193	62.7		
Pt	195	33.8		
Au	197	100	$^{181}\text{Ta}^{16}\text{O}^+$	
Tl	205	70.5		
Pb	208	52.3	$^{192}\text{Pt}^{16}\text{O}^+$	
U	238	99.3		

**Table B****Internal Standard Elements, and their Characteristic Mass, Relative Abundance, Potential Interferences**

Internal Standard	Characteristic Mass	% Relative Abundance	Polyatomic Interferences
Sc	45	100	$^{12}\text{C}^{16}\text{O}_2\text{H}^+$ , $^{13}\text{C}^{16}\text{O}_2^+$ , $^{28}\text{Si}^{16}\text{OH}^+$ , $^{29}\text{Si}^{16}\text{O}^+$ , $^{14}\text{N}_2^{16}\text{OH}^+$
Y	89	100	
In	115	95.7	
Tb	159	100	$^{143}\text{Nd}^{16}\text{O}^+$
Bi	209	100	

**Table C**

**Thermo ICP-MS X-Series I  
Instrument Limits of Detection**

Element	IDL (ug/L)	Element	IDL (ug/L)
7Li	0.700	105Pd	0.007
9Be	0.000	107Ag	0.000
47Ti	0.320	111Cd	0.256
51V	0.070	118Sn	0.000
52Cr	0.000	121Sb	0.014
55Mn	0.150	125Te	0.013
56Fe	8.780	133Cs	0.125
59Co	0.005	137Ba	0.950
60Ni	0.000	139La	0.005
65Cu	0.238	140Ce	0.003
66Zn	3.437	178Hf	0.000
75As	0.000	181Ta	0.000
78Se	0.146	182W	0.000
85Rb	0.434	193Ir	0.001
88Sr	0.052	195Pt	0.000
90Zr	0.002	197Au	0.000
93Nb	0.000	205Tl	0.011
95Mo	0.005	208Pb	2.648
101Ru	0.001	238U	0.000
103Rh	0.000		

**Table D**

**Method Limits of Detection  
(Initial Teflon Filter Batch Blank Data)**

Element	MDL (ng/filter)	Element	MDL (ng/filter)
7Li	87.4	105Pd	5.8
9Be	0.9	107Ag	1.4
47Ti	491.0	111Cd	25.6
51V	72.0	118Sn	88.7
52Cr	165.0	121Sb	42.7
55Mn	78.4	125Te	1.3
56Fe	10408.2	133Cs	12.5
59Co	7.1	137Ba	1495.8
60Ni	1982.4	139La	5.5
65Cu	1534.5	140Ce	10.9
66Zn	1512.5	178Hf	32.8
75As	24.8	181Ta	102.0
78Se	14.6	182W	0.8
85Rb	43.4	193Ir	21.7
88Sr	237.4	195Pt	56.7
90Zr	84.8	197Au	17.3
93Nb	24.0	205Tl	1.1
95Mo	8.5	208Pb	264.8
101Ru	0.1	238U	0.5
103Rh	0.1		