



**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 2.2
Effective Date: September 1, 2019**

Aerosol Analysis and Methods Evaluation Section
Chemical Analysis and Emissions Research Branch
Mobile Source Laboratory Division

DISCLAIMER: This procedure has been reviewed by the staff of the California Air Resources Board and approved for publication. Mention of any trade name or commercial product in this Standard Operating Procedure does not constitute endorsement or recommendation of this product by Air Resources Board. Specific brand names and instrument descriptions listed in the Standard Operating Procedure are for equipment used by the Air Resources Board laboratory.

1. Scope and Application

This standard operating procedure (SOP) describes the acid digestion, identification, and quantification of trace elements in particulate matter using Inductively Coupled Plasma Mass Spectrometer (ICP-MS). This method is suitable for the determination of trace elements in particulate matter collected on Teflon filters.

2. Method Summary

- 2.1 Particulate matter collected on Teflon filters is extracted with a mixture of acids in a microwave digestion oven.
- 2.2 The extract is aspirated through a nebulizer into argon plasma, where the sample is ionized. The ions are separated by a series of electronic and magnetic filters, and identified based on the difference in the ion mass to charge ratios. Using helium as a collision gas, kinetic energy discrimination (KED) process effectively reduces polyatomic interferences.
- 2.3 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.
- 2.4 The concentrations of target elements are determined using a daily calibration curve. Internal standards are also used to correct instrumental drifts in sensitivity. Calculations to derive the corrected concentrations of elements are described in Section 12.

3. Interferences and Contaminations

- 3.1 Isobaric elemental interferences: Many 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. If such interference cannot be avoided, mathematical corrections are made to account for the signal from interfering isotopes.
- 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.

It is recommended to monitor non-targeted elements (e.g., Si, S and K) that are potentially found in samples at high concentrations and cause interferences to

targeted elements. If such interferences are observed, affected target elements should be carefully examined to determine validity of the data.

- 3.3 The concentrations of elements in motor vehicle exhaust may vary by orders of magnitude. 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, and may result in instrument instability. High load samples must be run by further diluting the solution to avoid the detector fatigue.
- 3.4 Contaminations must be minimized for trace element analyses. Laboratory work space must always be kept clean. Labware such as pipette tips, vials, and flasks must be soaked in acid for at least 24 hours and rinsed with reagent water (Section 5.5.1) before use.

4. Safety

- 4.1 General safe laboratory practices should be followed. Concentrated acid must only be used in fume hoods. A lab coat, safety glasses, and gloves must be worn.
- 4.2 Hazards associated with this procedure:
 - 4.2.1 Exposure to toxic or carcinogenic metals and acids – samples may contain toxic, mutagenic, carcinogenic, corrosive, and/or irritant chemicals. Always wear personal protective equipment to avoid exposure to potentially harmful materials. Refer to the SDS for specific precautions.
 - 4.2.2 Pressurized gas line and gas cylinders – all gas cylinders must be securely fastened, and must be capped before moving. Check for leak periodically.
 - 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.
 - 4.2.4 Plasma exhaust – hot and possibly harmful gases are generated during the operation. Make sure that the exhaust duct is working properly.

5. Equipment and Supplies

- 5.1 Milestone Ethos UP Microwave Digestion Oven, or equivalent
 - 5.1.1 100 mL volume Teflon vessels equipped with a self-controlled pressure-release and reseal system;
 - 5.1.2 Temperature probe;

5.1.3 Torque wrench, calibrated.

5.2 Thermo Scientific iCAP Qc ICP-MS, or equivalent

5.2.1 Three-channel peristaltic pump and PVC pump tubing;

5.2.2 Y connector for mixing sample and internal standards, PEEK or equivalent;

5.2.3 Nebulizer, perfluoroalkoxy alkanes (PFA);

5.2.4 Spray chamber and Torch, quartz;

5.2.5 Nickel or platinum sampler and skimmer cones;

5.2.6 Instrument control and data acquisition software, Qtegra ISDS 2.7. or higher;

5.2.7 Water chiller.

5.3 Teledyne Cetac ASX-560 Autosampler or equivalent

5.3.1 Test tube rack, 60 position;

5.3.2 0.5 mm ID Carbon sampling probe.

5.4 Labware

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

5.4.2 Calibrated pipettes, 30-300 μ l, 0.5-5ml, 1-10ml;

5.4.3 Metal-free pipette tips;

5.4.4 Teflon or low density polyethylene volumetric flasks;

5.4.5 Powder-free Latex or Nitrile gloves, class 100;

5.4.6 Analytical balance, calibrated, accurate to 0.1mg;

5.4.7 Ceramic blade/scissor;

5.4.8 Teflon cubes;

5.4.9 Tweezers, Teflon or equivalent.

5.5 Reagents

- 5.5.1 Reagent grade water, 18.2 MΩ resistivity at 25 °C;
- 5.5.2 Nitric acid, trace metal grade, 67-70%;
- 5.5.3 Hydrochloric acid, trace metal grade, 33-36%;
- 5.5.4 Digestion acid-mix solution: 17.5% (v/v) nitric acid and 2.6% (v/v) hydrochloric acid;
- 5.5.5 Blank solution: 3.5% (v/v) nitric acid and 0.5% (v/v) hydrochloric acid;
- 5.5.6 Standard stock solution, ICP-MS grade, traceable to NIST Standards;
- 5.5.7 ICP-MS tuning solution, containing 1µg/L of Li, Co, In, Ba, Ce, Bi, and U in 2.5% (v/v) nitric acid and 0.5% (v/v) hydrochloric acid;
- 5.5.8 ICP-MS mass calibration and cross calibration solution in 2.5% (v/v) nitric acid, containing:
 - 35µg/L Be,
 - 20µg/L Zn,
 - 15µg/L Cu and Ni,
 - 10µg/L Al, Ga, and Mg,
 - 8µg/L Co, Li, and Sc,
 - 6µg/L Ag and Mn,
 - 5µg/L Sr,
 - 4µg/L Ba and Tl,
 - 3µg/L Bi, Ce, Cs, Ho, In, Rh, Ta, Tb, U, and Y.

5.6 Gas supplies

- 5.6.1 Argon, 110 psi, 99.999% purity;
- 5.6.2 Helium, 28 psi, greater than 99.999% purity.

5.7 Teflon filters

6. Filter Preparation and Sample Handling

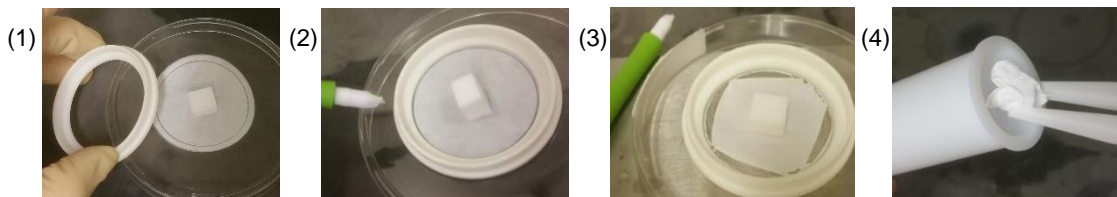
- 6.1 It is recommended that filter preparation is performed in a cleanroom to minimize contaminations during the procedure.
- 6.2 The filter cassette and its filter support (stainless steel screen) must be cleaned before use in accordance with SOP MV-AEROSOL-155, Section 9.1.

6.3 Assemble the filter cassette, the filter support, and the Teflon filter in accordance with SOP MV-AEROSOL-155 Section 6.7.

6.4 When the samples are returned to the laboratory, the samples are stored in a refrigerator until analysis.

7. Sample Digestion

7.1 Place the Teflon filter on a clean petri dish and then put a Teflon cube on the center of the filter. Use a filter cassette or Teflon tweezers to press the support ring of the filter and fix its position while removing the ring from the filter with a ceramic blade. Proceed by making multiple small cuts along all sides of the edge of the filter to keep the filter under tension before completely detaching the filter from the ring. Transfer the filter and the Teflon cube into the microwave digestion vessel.



7.2 Add 10 ml of digestion acid-mix solution (Section 5.5.4) to the digestion vessel.

Note: be sure that the filter is weighed down by the Teflon cube before adding the solution. Otherwise the filter will rise to the surface of the solution due to its hydrophobic nature.

7.3 Assemble the microwave digestion vessel, according to the manufacture's manual.

7.4 Digest the samples: 30 minute ramp to 175 °C, followed by a 30 min hold at 175 °C, proceed by ventilating and cooling to room temperature.

7.5 Disassemble the microwave digestion vessel. Transfer the contents to a 50 ml volumetric flask. Filter the solution if there is any undissolved particulate that can otherwise clog the ICP-MS nebulizer. Dilute the digested solution using reagent grade water to 50 ml.

8. Instrument Setup and Tuning

The analyst must be familiar with the operation of the ICP-MS system.

8.1 Starting ICP-MS

8.1.1 Inspect peristaltic pump tubing. If the tubing is stressed beyond its elastic limit and remains flat, it will need to be replaced. If the tubing is in good condition, continue by locking the tensioners in place.

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

8.1.3 Inspect that the plasma exhaust duct is operating properly. Purge cool, auxiliary, and nebulizer gas lines with argon gas before starting ICP-MS.

8.1.4 Ignite plasma. Make sure to have blank solution in sampling line(s).

Note: open the torch chamber door to immediately abort the ignition process if continuous arcing sounds occur from the torch. The continuous arcing will damage the torch.

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

8.1.6 Allow the instrument to stabilize, typically for 30 minutes.

8.2 Tuning ICP-MS

8.2.1 The instrument performance must be verified daily on both standard (STD) mode and KED mode using the ICP-MS tuning solution (section 5.5.8). Run performance test a minimum five times to validate that the instrument was tuned correctly using the following criteria:

8.2.1.1 Criteria for instrument responses on STD mode:

| <u>Mass</u> | <u>must be</u> | <u>Response</u> | <u>Stability</u> |
|-----------------|----------------|-----------------|------------------|
| 4.5Background | < | 1.0 (cps) | |
| 220.7Background | < | 2.0 (cps) | |
| 7Li | > | 50,000 (cps) | 2.0% |
| 59Co | > | 100,000(cps) | 2.0% |
| 115In | > | 220,000(cps) | 2.0% |
| 238U | > | 300,000(cps) | 2.0% |
| 156CeO/140Ce | < | 0.03 | |
| 137Ba2+/137Ba | < | 0.03 | |

8.2.1.2 Criteria for instrument responses on KED mode:

| <u>Mass</u> | <u>must be</u> | <u>Response</u> | <u>Stability</u> |
|-----------------|----------------|-----------------|------------------|
| 4.5Background | < | 0.5 (cps) | |
| 220.7Background | < | 2.0 (cps) | |
| 59Co | > | 30,000 (cps) | 2.0% |
| 115In | > | 30,000 (cps) | 2.0% |
| 238U | > | 80,000 (cps) | 2.0% |
| 156CeO/140Ce | < | 0.01 | |
| 59Co/35Cl.16O | > | 18.0 | |

8.2.1.3 Criteria for accuracy of instrument mass calibration for STD mode and KED mode:

| <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 |

8.2.2 If the instrument response criteria are not met, perform auto-tune sequences using the ICP-MS tuning solution (section 5.5.8). If the accuracy criteria are not met, perform the Mass Calibration sequence to calibrate the quadrupole using the ICP-MS mass calibration solution (Section 5.5.9). Run the performance test again to make sure the instrument passes all criteria.

8.3 Setting up the Detector.

Perform a Detector Cross Calibration sequence using the ICP-MS cross calibration solution (Section 5.5.9). This sequence runs in the pulse and the analogue mode to calibrate the detector and convert the acquired analogue data into equivalent pulse counting data. Detector should be calibrated monthly or as needed.

9. Method

9.1 Data Acquisition

9.1.1 A data acquisition method designates the isotopes to be monitored at each measurement mode and specifies parameters such as acquisition

settings, scan region, interference corrections and quantification setting. A typical method utilizes the following conditions:

| | |
|--|--|
| <i>Plasma forward power (kW)</i> | 1.55 |
| <i>Cool gas flow rate (L/min)</i> | 14.0 |
| <i>Auxiliary gas flow rate (L/min)</i> | 0.8 |
| <i>Solution uptake rate (mL/min)</i> | 0.4 |
| <i>Number of sweeps</i> | 20 |
| <i>Dwell time (s)</i> | 0.01-0.1 |
| <i>Channels, Spacing (amu)</i> | 1, 0.1 |
| <i>Mass scan region (amu)</i> | 4.6-245.0 |
| <i>Interference corrections</i> | 78Se (KED): -0.0304348 x 83Kr(KED) 82Se(KED): -1.0087 x 83Kr(KED) 115In(KED): -0.0148637 x 118Sn(KED) 208Pb(KED): 206Pb(KED) + 207Pb(KED) |
| <i>Replicates integrations</i> | minimum 3 |
| <i>Measurement mode</i> | KED |

9.1.2 Internal standard addition: an internal standard solution is added to all of the ICP-MS solutions, including blanks, calibration standards, and samples. The internal standard addition is used to correct any instrumental drift in sensitivity. The five elements listed in Table B are used as internal standards, provided that these elements are not part of the target analytes. The concentration of the internal standard solution is suggested to be in the range of 1 µg/L and 20 µg/L.

9.1.3 The sample analysis sequence typically includes an initial blank, a minimum 5-level standard calibration standards, second-source calibration verification standard, sample replicate(s), continuing calibration verification standards, and continuing check-blank.

9.1.4 Make sure that the sample uptake time and the wash time are sufficient for the elements. For example, when elements such as Mo and Au are present at high concentrations, a longer wash time may be required for the instrument response to fall below the instrument detection limit (IDL, see Section 11.3.1).

9.2 Calibration

9.2.1 The instrument must be calibrated in the beginning of day every time sample(s) being analyzed due to the tendency of the instruments drift.

9.2.2 The default matrix for blanks and standards, as well as all other samples, is 3.5% (v/v) HNO₃ and 0.5% (v/v) HCl (section 5.5.5).

- 9.2.3 A valid calibration curve consists of a blank and at least five levels of standards, typically ranging from 0.1 µg/L to 50 µg/L. The minimum coefficient of determination (R^2) must be greater than 0.995. If R^2 is less than 0.995, trouble-shoot the instrument, determine whether there is any spectral or carry-over interference, make the necessary adjustment or repair, then re-tune and re-calibrate the instrument. Calibration standard solutions should be prepared every two weeks or as needed.

10. Quality Assurance and Quality Control

All analysts must demonstrate that the instrument performance/conditions meets or exceeds all of the QA/QC objectives as well as the limits of detection listed in this SOP.

10.1 Accuracy and Precision

- 10.1.1 In order to ensure analytical accuracy, both primary calibration- and secondary second-source- standards must be prepared from certified NIST traceable ICP-MS grade stock solutions. The accuracy of the calibration curve is confirmed by the analysis of a mid-range second-source standard, typically 5 ug/L, immediately after the calibration. All of the results from the mid-range second-source standard analysis must be within $\pm 20\%$ of the expected concentration.
- 10.1.2 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 IDL upper limit.
- 10.1.3 The analytical precision is monitored by duplicate analysis for every 10 sample 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 must be $<20\%$ for the elements above the reporting detection limits. If the RPD is greater than 20%, stop the analysis, check for and correct any instrument malfunction, and reanalyze the batch of 10 samples.

10.2 Internal Standards Response

The response of internal standards must be within 80-120% of the initial response in the first calibration blank. If the response is out of the limit, stop the analysis and determine the cause of the drift. Reanalyze the sample.

10.3 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, as follows:

$$LOD = (t) \times (s)$$

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 7 replicate analyses.

10.3.1 Instrument Detection Limit (IDL)

The IDL verifies the cleanliness and the performance of the instrument by analyzing blank solution (Section 5.5.5) for seven times. Table C shows the typical IDLs and the upper limit. The check-blank samples should be below the IDL upper limit. If the blank is greater than the limit, inspect the instrument. If necessary, clean the nebulizer, the spray chamber and the torch, run blank solution and/or replace the peristaltic pump tubing and cones.

10.3.2 Method Detection Limit (MDL)

The MDL is determined by analyzing seven Teflon filter blanks which were undergone microwave digestion. The MDL is calculated as follows:

$$MDL = (t) \times (s) + (m)$$

where *m = mean of the seven Teflon filters.*

Typical MDLs for each element are listed in Table D.

11. Calculations

11.1 Internal Standard Correction

Using internal standards in the first blank as the reference, all other following runs including calibration standards and samples are corrected as follows:

$$y_{corr}(i) = y_{meas}(i) \times I_{ref}(iS) / I_{meas}(iS)$$

where $y_{corr}(i)$ = the corrected intensity of element i
 $y_{meas}(i)$ = the measured intensity of element i
 I_{ref} = the intensity of internal standard in the reference blank
 I_{meas} = the measured intensity of internal standard in the sample

11.2 Calibration Calculations:

Generate calibration curves for each element. The linear least square fit obtained from each calibration curve can be expressed in the following form:

$$y(i) = a(i) C(i) + b(i)$$

where $y(i)$ = intensity of element i
 $a(i)$ = slope of linear equation for element i
 $C(i)$ = concentration of element i
 $b(i)$ = intercept at the y-axis

11.3 Concentration Calculation:

Calculate the concentration of each element, $C(i)$, in parts per billion (ppb) or ng/ml:

$$C(i) = [y_{corr}(i) - b(i)] / a(i)$$

The unit of the concentration $C(i)$ is converted to ng/filter by multiplying by the final sample volume (i.e., 50 ml).

12. Data Reporting and Handling

12.1 Reporting Detection Limit (RDL)

12.1.1 The RDL for each element is listed in Table E, based on MDL determinations in 2016 and 2017.

12.1.2 RDL should be verified by measuring MDL annually, or reassessed when the method is modified with potential impact on the detection limits.

12.2 The completed sequence and the resulting analytical data are exported in xml format. Data should include sample name, analytical date and time, calculated concentration, and unit.

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

13.3 If needed, the total concentration of an element can be calculated by taking into account of the abundance of the isotope as listed in the Table A.

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 Record

| Revision | Date | Responsible Person | Description of Change | Status |
|----------|----------------|--------------------|---|-------------|
| | December 2010 | Jick Chen | Initial release | Version 1.0 |
| 1 | March 2017 | Noriko Nishino | Updated to new equipment; revised sample digestion process; updated ICP-MS tuning procedures and criteria; updated default matrix and calibration standard range; revised QC criteria; added a section for calculations; changed the target isotope (amu) of Fe from 56 to 57 and Cu from 63 to 65; updated IDL and MDL; removed Tantalum; and added RDL. | Version 2.0 |
| 2 | July 2018 | Noriko Nishino | Updated RDLs for Zr and Sb; Removed rinse solution. | Version 2.1 |
| 3 | September 2019 | Noriko Nishino | Updated division | Version 2.2 |

Table A Target Elements, Characteristic Mass, Relative Abundance, Potential Interferences, and Alternative Masses

| Target Analyte | Characteristic Mass | % Relative Abundance | Polyatomic Interferences | Isobarric Interferences | Alternative Masses (% Relative Abundance) |
|----------------|---------------------|----------------------|--|-------------------------|---|
| Li | 7 | 92.4 | | | |
| Be | 9 | 100 | | | |
| Ti | 47 | 7.44 | $^{31}\text{P}^{16}\text{O}^+$, $^{40}\text{Ar}^7\text{Li}^+$, | | 49 (5.41%) |
| 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 | $^{35}\text{Cl}^{16}\text{OH}^+$, $^{40}\text{Ar}^{12}\text{C}^+$, $^{36}\text{Ar}^{16}\text{O}^+$, $^{37}\text{Cl}^{15}\text{N}^+$, $^{34}\text{S}^{18}\text{O}^+$, $^{36}\text{S}^{16}\text{O}^+$, $^{38}\text{Ar}^{14}\text{N}^+$, $^{36}\text{Ar}^{15}\text{NH}^+$, $^{35}\text{Cl}^{17}\text{O}^+$ | | 53 (9.50%) 54 (2.37%) |
| Mn | 55 | 100 | $^{40}\text{Ar}^{14}\text{NH}^+$, $^{39}\text{K}^{16}\text{O}^+$, $^{37}\text{Cl}^{18}\text{O}^+$, $^{40}\text{Ar}^{15}\text{N}^+$, $^{38}\text{Ar}^{17}\text{O}^+$, $^{36}\text{Ar}^{18}\text{OH}^+$, $^{38}\text{Ar}^{16}\text{OH}^+$, $^{37}\text{Cl}^{17}\text{OH}^+$, $^{23}\text{Na}^{32}\text{S}^+$, $^{36}\text{Ar}^{19}\text{F}^+$ | | |
| Fe | 57 | 2.12 | $^{40}\text{Ar}^{16}\text{OH}^+$, $^{45}\text{Sc}^{12}\text{C}^+$, $^{40}\text{Ca}^{16}\text{OH}^+$, $^{56}\text{Fe}^1\text{H}^+$ | | 56 (91.8%) |
| 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 | $^{31}\text{P}^{16}\text{O}_2^+$, $^{40}\text{Ar}^{23}\text{Na}^+$, $^{47}\text{Ti}^{16}\text{O}^+$, $^{23}\text{Na}^{40}\text{Ca}^+$, $^{46}\text{Ca}^{16}\text{OH}^+$, $^{36}\text{Ar}^{12}\text{C}^{14}\text{NH}^+$, $^{14}\text{N}^{12}\text{C}^{37}\text{Cl}^+$, $^{16}\text{O}^{12}\text{C}^{35}\text{Cl}^+$ | | 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 | $^{40}\text{Ar}^{35}\text{Cl}^+$, $^{59}\text{Co}^{16}\text{O}^+$, $^{36}\text{Ar}^{38}\text{ArH}^+$, $^{38}\text{Ar}^{37}\text{Cl}^+$, $^{36}\text{Ar}^{39}\text{K}^+$, $^{43}\text{Ca}^{16}\text{O}_2^+$, $^{23}\text{Na}^{12}\text{C}^{40}\text{Ar}^+$, $^{12}\text{C}^{31}\text{P}^{16}\text{O}_2^+$ | | |
| Se | 78 | 23.8 | $^{40}\text{Ar}^{38}\text{Ar}^+$ | Kr(0.35%) | 77 (7.64%) 82 (8.73%) |
| Rb | 85 | 72.2 | | | |
| Sr | 88 | 82.6 | | | |

Table A (Continues)

| Target Analyte | Characteristic Mass | % Relative Abundance | Polyatomic Interferences | Isobaric Interferences (% Relative Abundance) | Alternative Masses (% Relative Abundance) |
|----------------|---------------------|----------------------|--|---|---|
| Zr | 90 | 51.5 | | | |
| Nb | 93 | 100 | | | |
| Mo | 95 | 15.9 | $^{40}\text{Ar}^{39}\text{K}^{16}\text{O}^+$, $^{79}\text{Br}^{16}\text{O}^+$ | | 98 (24.2%) |
| 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 | $^{91}\text{Zr}^{16}\text{O}^+$ | | 109 (48.2%) |
| 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 | | | |
| 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 | $^{192}\text{Pt}^{16}\text{O}^+$ | | 206 (24.1%) 207 (22.1%) |
| 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 Typical Instrument Detection Limits (IDL)

| Mass and Element | IDL (ug/L) | Upper Limit | Mass and Element | IDL (ug/L) | Upper Limit |
|------------------|------------|-------------|------------------|------------|-------------|
| 7Li | 0.069 | 0.15 | 103Rh | 0 | 0.004 |
| 9Be | 0.009 | 0.02 | 105Pd | 0.001 | 0.04 |
| 47Ti | 0.054 | 0.2 | 107Ag | 0.001 | 0.006 |
| 51V | 0.031 | 0.05 | 111Cd | 0.001 | 0.04 |
| 52Cr | 0.011 | 0.1 | 118Sn | 0.004 | 0.04 |
| 55Mn | 0.003 | 0.03 | 121Sb | 0.002 | 0.03 |
| 57Fe | 0.226 | 0.5 | 125Te | 0.004 | 0.03 |
| 59Co | 0.001 | 0.03 | 133Cs | 0.001 | 0.006 |
| 60Ni | 0.007 | 0.1 | 137Ba | 0.005 | 0.04 |
| 63Cu | 0.003 | 0.05 | 139La | 0 | 0.006 |
| 66Zn | 0.045 | 0.2 | 140Ce | 0 | 0.008 |
| 75As | 0.006 | 0.02 | 178Hf | 0.001 | 0.004 |
| 78Se | 0.067 | 0.1 | 182W | 0.012 | 0.06 |
| 85Rb | 0.003 | 0.018 | 193Ir | 0 | 0.004 |
| 88Sr | 0.003 | 0.04 | 195Pt | 0 | 0.02 |
| 90Zr | 0.002 | 0.01 | 197Au | 0.04 | 0.08 |
| 93Nb | 0.004 | 0.03 | 205Tl | 0.014 | 0.04 |
| 95Mo | 0.009 | 0.06 | 208Pb | 0.001 | 0.08 |
| 101Ru | 0 | 0.006 | 238U | 0 | 0.004 |

Table D Typical Method Detection Limits (MDL)

| Mass number and Element | MDL (ng/filter) | Mass number and Element | MDL (ng/filter) |
|-------------------------|-----------------|-------------------------|-----------------|
| 7Li | 7.7 | 103Rh | 0.0 |
| 9Be | 0.8 | 105Pd | 1.9 |
| 47Ti | 11 | 107Ag | 0.1 |
| 51V | 3.1 | 111Cd | 0.9 |
| 52Cr | 16 | 118Sn | 1.0 |
| 55Mn | 3.4 | 121Sb | 1.0 |
| 57Fe | 136 | 125Te | 0.6 |
| 59Co | 1.3 | 133Cs | 0.1 |
| 60Ni | 4.9 | 137Ba | 1.6 |
| 63Cu | 2.5 | 139La | 0.1 |
| 66Zn | 49 | 140Ce | 0.1 |
| 75As | 0.7 | 178Hf | 0.0 |
| 78Se | 5.6 | 182W | 2.5 |
| 85Rb | 0.4 | 193Ir | 0.0 |
| 88Sr | 1.0 | 195Pt | 0.3 |
| 90Zr | 0.4 | 197Au | 5.0 |
| 93Nb | 0.8 | 205Tl | 0.6 |
| 95Mo | 3.2 | 208Pb | 1.4 |
| 101Ru | 0.1 | 238U | 0.0 |

Table E Reporting Detection Limits (RDL)

| Mass and Element | RDL (ng/filter) | Mass and Element | RDL (ng/filter) |
|-------------------------|------------------------|-------------------------|------------------------|
| 7Li | 12 | 103Rh | 0.2 |
| 9Be | 1.0 | 105Pd | 3.6 |
| 47Ti | 18 | 107Ag | 0.3 |
| 51V | 6.0 | 111Cd | 3.0 |
| 52Cr | 31 | 118Sn | 2.3 |
| 55Mn | 4.0 | 121Sb | 2.5 |
| 57Fe | 400 | 125Te | 1.7 |
| 59Co | 2.0 | 133Cs | 0.3 |
| 60Ni | 9 | 137Ba | 3.3 |
| 63Cu | 4.9 | 139La | 0.3 |
| 66Zn | 100 | 140Ce | 0.4 |
| 75As | 1.1 | 178Hf | 0.2 |
| 78Se | 7.7 | 182W | 3.7 |
| 85Rb | 0.9 | 193Ir | 0.2 |
| 88Sr | 2.4 | 195Pt | 1.0 |
| 90Zr | 0.9 | 197Au | 5.0 |
| 93Nb | 1.5 | 205Tl | 2.0 |
| 95Mo | 5.6 | 208Pb | 5.4 |
| 101Ru | 0.3 | 238U | 0.2 |