

# **Laboratory Methods for ICP-MS Analysis of Trace Metals in Precipitation**

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# Laboratory Methods for ICP-MS

## Analysis of Trace Metals in Precipitation

### 1.0 Preparation of 20% Nitric Acid for Cleaning Purposes

#### 1.1 Preparation of Nitric Acid Bath

This bath, located in the Air Toxic Metals (ATM) Preparation Lab (see Section 20.2), is used for cleaning those items which must be soaked, i.e. centrifuge tubes, Teflon bottles, beakers and graduated cylinders. (See Sections 2.0 and 3.0)

##### 1.1.1 Supplies

Deionized water  
Reagent grade HNO<sub>3</sub>  
Polyethylene gloves

##### 1.1.2 Equipment

Polyethylene tank (Nalgene 12 x 12 x 12)

##### 1.1.3 Acid Bath Preparation Procedure

- a) Rinse polyethylene tank twice with deionized water.
- b) Fill tank with 21 L of deionized water.
- c) Measure 6 L of reagent grade HNO<sub>3</sub> and add to tank.  
(Formula is 1 L deionized water: 286 ml HNO<sub>3</sub>)

##### 1.1.4 Comments

The acid bath should be remade every two months. Discard old acid bath appropriately.

#### 1.2 Preparation of Nitric Acid to Fill 10 L Polyethylene Carboy

The carboy is kept in the ATM Prep Lab, and the acid is used to fill volumetric glassware when cleaning. (See Section 4.0)

##### 1.2.1 Supplies

Deionized water  
Reagent grade HNO<sub>3</sub>  
Polyethylene gloves

##### 1.2.2 Equipment

10 L Polyethylene Carboy with spigot

##### 1.2.3 Acid Preparation Procedure

- a) Rinse polyethylene carboy twice with deionized water.

- b) Initially, fill carboy with 7 L of deionized water.
- c) Add 2 L of reagent grade HNO<sub>3</sub>.
- d) As the level of 20% nitric acid in the carboy decreases, replenish it according to the formula 1 liter deionized water: 286 mL HNO<sub>3</sub>.

## 2.0 Cleaning Sample Tubes

Due to problems of zinc contamination, new tubes should be acid-cleaned before use. Although new tubes are preferable, used tubes can also be cleaned using this method. New tubes *should not* be acid-cleaned but rather be used directly from the package if they are to contain samples to be analyzed for either sodium or aluminum.

### 2.1 Supplies

ASTM Type I water  
Deionized water  
20% HNO<sub>3</sub> (see Section 1.1)  
Polyethylene gloves

### 2.2 Equipment

Nitric Acid bath (see Section 1.1)  
Tube racks

### 2.3 Cleaning Procedure

- 2.3.1 Rinse tubes and caps with deionized water, filling each fully and discarding water.
- 2.3.2 Place tubes and caps in 20% acid bath, making sure that each is fully submerged in the bath. Soak for no less than 24 hours.
- 2.3.3 Rinse tubes and caps with ASTM Type I water three times.
- 2.3.4 Shake off excess water and allow tubes and caps to dry fully using tube racks.
- 2.3.5 Store tubes and caps in the styrofoam racks in which they are shipped; they can be stored indefinitely.

## 3.0 Cleaning Teflon Bottles, Graduated Cylinders and Beakers

### 3.1 Supplies

ASTM Type I water  
Deionized water  
20% HNO<sub>3</sub> (see Section 1.1)  
Polyethylene gloves

### 3.2 Equipment

Nitric Acid bath (see Section 1.1)



### 3.3 Cleaning Procedure

- 3.3.1 Rinse all items with deionized water, filling each fully and discarding water. Repeat once.
- 3.3.2 Place all items in the 20% nitric acid bath, making sure each is fully submerged. Soak for no less than 24 hours.
- 3.3.3 Rinse each item with deionized water 2-3 times.
- 3.3.4 Final rinse each item with ASTM Type I water three times.
- 3.3.5 Completely fill each bottle with ASTM Type I water, cap and store for use in the designated cabinet in the Air Toxic Metals (ATM) preparation laboratory.
- 3.3.6 Let all other items dry completely, cover with parafilm, and store for use in the designated cabinet in the ATM preparation laboratory.

## 4.0 Cleaning Volumetric Glassware

### 4.1 Supplies

ASTM Type I water  
Deionized water  
20% HNO<sub>3</sub> from carboy (see Section 1.2)  
Polyethylene gloves

### 4.2 Cleaning Procedure

- 4.2.1 Rinse all volumetric glassware with deionized water, filling each item fully and discarding water. Repeat once.
- 4.2.2 Fill each item with 20% nitric acid and let soak in the hood in the ATM preparation laboratory for at least two to three hours.
- 4.2.3 Rinse each item with deionized water two to three times.
- 4.2.4 Final rinse each item with ASTM Type I water three times.
- 4.2.5 Completely fill each item with ASTM Type I water, stopper and store for use in the designated cabinet in the Air Toxic Metals (ATM) preparation laboratory.

## 5.0 Preparation of 2% Ultrapure Nitric Acid

### 5.1 Supplies

ASTM Type I water  
Ultrapure concentrated HNO<sub>3</sub>

Polyethylene gloves

5.2 Equipment

500 mL Teflon bottle  
25 mL graduated cylinder

5.3 2% HNO<sub>3</sub> Preparation Procedure

5.3.1 Rinse 500 mL Teflon bottle twice with ASTM Type I water.

5.3.2 Fill with 500 mL ASTM Type I water.

5.3.3 Measure 14 mL ultrapure concentrated HNO<sub>3</sub> and add to bottle.

5.3.4 Invert bottle and mix well. Store in prep area and replenish as needed.

## **6.0 Multi-element Calibration Standards Preparation**

6.1 Supplies

Certified elemental standards (Spex 1000 µg/mL Plasma Standards)  
2% Ultrapure HNO<sub>3</sub> (see Section 5.0)  
Pipet tips  
Internal standard solution (see Section 16.0)  
Acid cleaned polypropylene 15 mL centrifuge tubes (see Section 2.0)

6.2 Equipment

Pipettes  
Eppendorf repeater pipet  
Two Acid cleaned 125 mL Teflon bottles (see Section 3.0)  
Two Acid cleaned 100 mL volumetric flasks (see Section 4.0)

6.3 Calibration Standards Preparation Procedure

6.3.1 Prepare a 10 µg/mL mixed stock standard containing the following elements: Arsenic (As), Cadmium (Cd), Chromium (Cr), Copper (Cu), Lead (Pb), Manganese (Mn), Nickel (Ni), Selenium (Se), Titanium (Ti), Vanadium (V), and Zinc (Zn). Pipet 1 mL of each of the 1000 µg/mL certified standards into a clean 100 mL volumetric flask. Dilute to 100 mL with ASTM Type I water containing 2% (w/w) ultrapure nitric acid (see Section 5.0). Invert flask and mix well. Transfer to a clean 125 mL Teflon bottle.

6.3.2 Prepare a 100 ng/mL mixed stock standard. Pipet 1 mL of the prepared 10 µg/mL stock standard into a clean 100 mL volumetric flask. Dilute to 100 mL with ASTM Type I water containing 2% (w/w) ultrapure nitric acid. Invert flask and mix well. Transfer to a clean 125 mL Teflon bottle.

- 6.3.3 Prepare Blank, 0.1, 0.3, 0.5, 0.7, 1.0, 3.0, 5.0, 7.0 and 10.0 ng/mL calibration standards daily.



- 6.3.4 Into ten cleaned and labelled polypropylene 15 mL centrifuge tubes, pipet 0, 10, 30, 50, 70, 100, 300, 500, 700 and 1000  $\mu\text{L}$  of the 100 ng/mL multi-element standard respectively.
- 6.3.5 Add 10.00, 9.99, 9.97, 9.95, 9.93, 9.90, 9.70, 9.50, 9.30 and 9.00 mL ASTM Type I water containing 2% (w/w) ultrapure nitric acid (see Section 5.0) to each tube respectively.
- 6.3.6 Pipet 100  $\mu\text{L}$  internal standard into each tube using an Eppendorf repeater pipet (see Section 16.0). Cap tubes and shake well.

**Note:** Alternative to pipette addition, internal standards can be added on-line directly to sample and standards using the appropriate tubing, a mixing tee, and the peristaltic pump.

## **7.0 Calibration Standards Preparation for Sodium and Aluminum**

### 7.1 Supplies

Certified elemental standards (Spex 1000  $\mu\text{g}/\text{mL}$  Plasma Standards  
2% Ultrapure  $\text{HNO}_3$  (see Section 5.0)  
Pipet tips  
Internal standard solution (see Section 16.0)  
New, unwashed polypropylene 15 mL centrifuge tubes

### 7.2 Equipment

Pipettes  
Eppendorf repeater pipet  
One Acid cleaned 125 mL Teflon bottle (see Section 3.0)  
One Acid cleaned 100 mL volumetric flask (see Section 4.0)

### 7.3 Calibration Standards Preparation Procedure

- 7.3.1 Prepare a 1000 ng/mL mixed stock standard containing Aluminum (Al) and Sodium (Na). Pipet 100  $\mu\text{L}$  of both the Al and Na 1000  $\mu\text{g}/\text{mL}$  certified standards into a clean 100 mL volumetric flask. Dilute to 100 mL with ASTM Type I water containing 2% (w/w) ultrapure nitric acid (see Section 5.0). Invert flask and mix well. Transfer to a clean 125 mL Teflon flask.
- 7.3.2 Prepare Blank, 1.0, 3.0, 5.0, 7.0, 10.0, 30.0, 50.0, 70.0 and 100.0 ng/mL calibration standards daily.
- 7.3.3 Into 10 new, unwashed, labelled polypropylene 15 mL centrifuge tubes, pipet 0, 10, 30, 50, 70, 100, 300, 500, 700 and 1000  $\mu\text{L}$  of the 1000 ng/mL Na and Al standard respectively.
- 7.3.4 Add 10.00, 9.99, 9.97, 9.95, 9.93, 9.90, 9.70, 9.50, 9.30 and 9.00 mL ASTM Type I water containing 2% (w/w) ultrapure nitric acid (see Section 5.0) to each tube respectively.



- 7.3.5 Pipet 100  $\mu\text{L}$  internal standard into each tube using and Eppendorf repeater pipet (see Section 16.0). Cap tubes and shake well.

**Note:** Alternative to pipette addition, internal standards can be added on-line directly to sample and standards using the appropriate tubing, a mixing tee, and the peristaltic pump.

## **8.0 Independent Check Standard Preparation**

### 8.1 Supplies

Certified elemental standards (Spex 1000  $\mu\text{g}/\text{mL}$  Plasma Standards)  
2% Ultrapure  $\text{HNO}_3$  (see Section 5.0)  
Pipet tips  
Internal Standard solution (see Section 16.0)  
Acid cleaned polypropylene 15 mL centrifuge tubes (see Section 2.0)

### 8.2 Equipment

Pipettes  
Eppendorf repeater pipet  
One Acid cleaned 125 mL Teflon bottle (see Section 3.0)  
Three Acid cleaned 1000 mL Teflon bottles (see Section 3.0.)  
One Acid cleaned 100 mL volumetric flask (see Section 4.0)  
Three Acid cleaned 1000 mL volumetric flasks (see Section 4.0)

### 8.3 Independent Check Standard Preparation Procedure

- 8.3.1 Prepare a 1  $\mu\text{g}/\text{mL}$  mixed stock standard containing the following elements: Arsenic (As), Cadmium (Cd), Chromium (Cr), Copper (Cu), Lead (Pb), Manganese (Mn), Nickel (Ni), Selenium (Se), Titanium (Ti), Vanadium (V), and Zinc (Zn). Pipet 100  $\mu\text{L}$  of each of the 1000  $\mu\text{g}/\text{mL}$  elemental standards into a clean 100 mL volumetric flask. Be sure that these standards are from different lots than those used to prepare the calibration standards. Dilute to 100 mL with ASTM Type I water containing 2% (w/w) ultrapure nitric acid (see Section 5.0). Transfer to a clean 125 mL Teflon bottle.
- 8.3.2 Prepare nominal 0.45, 2.5 and 7.5 ng/mL check standards by pipetting 450, 2500 and 7500  $\mu\text{L}$  mixed stock standard into acid cleaned 1000 mL volumetric flasks respectively. Dilute to 1000 mL with ASTM Type I water containing 2% (w/w) ultrapure nitric acid (see Section 5.0). Invert flasks and mix well. Transfer to acid washed, labelled 1000 mL Teflon bottles. Store bottles a maximum of 6 months in cold room when not in use.
- 8.3.3 Alternatively prepare nominal 0.3, 0.8, and 5.0 ng/mL check standards by pipetting 300, 800, and 5000  $\mu\text{L}$  of mixed stock standards into a acid cleaned 1000 mL volumetric flasks. Dilute to 1000 mL with ASTM Type 1 water containing 2% (w/w) ultrapure nitric acid (see Section 5.0). Invert flasks and mix well. Transfer to acid washed, labeled 1000 mL Teflon bottles. Store bottles a maximum of 6 months in cold room when not in use.

**Note:** Concentrations for selenium should be 3.0, 8.0, and 50 ng/mL in this check standard rather than 0.3, 0.8, and 5.0 ng/mL respectively. For selenium appropriate aliquots should be taken to prepare these levels.

8.3.4 Into three cleaned and labelled 15 mL polypropylene centrifuge tubes, pipet 10 mL of one of the sets of check standard solutions respectively. Repeat for as many sets of check standards as are needed (see Section 18.4).

8.3.5 Add 100  $\mu$ L internal standard to each tube using an Eppendorf repeater pipette (see Section 16.0). Cap tubes and shake well.

**Note:** Alternative to pipette addition, internal standards can be added on-line directly to sample and standards using the appropriate tubing, a mixing tee, and the peristaltic pump.

## **9.0 Independent Check Standard Preparation for Aluminum and Sodium**

### **9.1 Supplies**

Certified elemental standards (Spex 1000  $\mu$ g/mL Plasma Standards)  
2% Ultrapure HNO<sub>3</sub> (see Section 5.0)  
Pipet tips  
Internal Standard solution (see Section 16.0)  
New, unwashed polypropylene 15 mL centrifuge tubes

### **9.2 Equipment**

Pipettes  
Eppendorf repeater pipet  
One Acid cleaned 125 mL Teflon bottle (see Section 3.0)  
Three Acid cleaned 1000 mL Teflon bottles (see Section 3.0)  
One Acid cleaned 100 mL volumetric flask (see Section 4.0)  
Three Acid cleaned 1000 mL volumetric flasks (see Section 4.0)

### **9.3 Independent Check Standard Preparation Procedure**

9.3.1 Prepare a 10  $\mu$ g/mL mixed stock standard containing Aluminum (Al) and Sodium (Na). Pipet 1 mL of both the Na and Al 1000  $\mu$ g/mL elemental standards into a clean 100 mL volumetric flask. Be sure that these standards are from different lots than those used to prepare the calibration standards. Dilute to 100 mL with ASTM Type I water containing 2% (w/w) ultrapure nitric acid (see Section 5.0). Transfer to a clean 125 mL Teflon bottle.

9.3.2 Prepare nominal 7.5, 25.0 and 75.0 ng/mL check standards by pipetting 750, 2500 and 7500  $\mu$ L of the Na and Al standard into acid cleaned 1000 mL volumetric flasks respectively. Dilute to 1000 mL with ASTM Type I water containing 2% (w/w) ultrapure nitric acid (see Section 5.0). Invert flasks and mix well. Transfer to acid washed, labelled

1000 mL Teflon bottles. Store indefinitely in cold room when not in use.

9.3.3 Into three new, labelled, unwashed 15 mL polypropylene centrifuge tubes, pipet 10 mL 7.5, 25.0, and 75.0 ng/mL check standard solutions respectively. Repeat for as many sets of check standards as are needed (see Section 18.4).

9.3.4 Add 100  $\mu$ L internal standard to each tube using an Eppendorf repeater pipet (see Section 16.0). Cap tubes and shake well.

## **10.0 Sample Preparation**

### 10.1 Supplies

Pipet tips

Internal standard solution (see Section 16.0)

Acid cleaned polypropylene 15 mL centrifuge tubes (see Section 2.0)

**Note:** The best results are obtained if these tubes are acid-washed before they are used to rid them of zinc contamination. DO NOT, however, use acid-washed tubes to analyze for sodium! (see Sections 2.0 and 11.0)

### 10.2 Equipment

Pipettes

Eppendorf repeater pipet

### 10.3 Sample Preparation Procedure

10.3.1 Pipet 10 mL of sample into a labelled, acid cleaned 15 mL centrifuge tube. Repeat for each sample.

10.3.2 Add 100  $\mu$ L internal standard to each centrifuge tube using an Eppendorf repeater pipet (see Section 16.0). Cap tubes and shake well.

**Note:** Alternative to pipette addition, internal standards can be added on-line directly to sample and standards using the appropriate tubing, a mixing tee, and the peristaltic pump.

**Note:** The concentration of most metals in precipitation is expected to be at sub-ng/mL levels. The ICP-MS will be calibrated to 10 ng/mL for all elements except Sodium and Aluminum (see Sections 6.0 and 7.0.). This should be a sufficient calibration range in which to analyze the metals of interest. If any result should fall above 10% of the upper calibration limit, the sample will be diluted appropriately and reanalyzed.

## **11.0 Sample Preparation for Analysis of Sodium and Aluminum**

### 11.1 Supplies

Pipet tips

Internal standard solution (see Section 16.0)  
New, unwashed polypropylene 15 mL centrifuge tubes

**Note:** The centrifuge tubes must be new and unwashed when analyzing samples for Sodium and Aluminum. Acid-washing actually contaminates the centrifuge tubes with these elements, thus making it difficult to get consistent results.

## 11.2 Equipment

Pipettes  
Eppendorf repeater pipet

## 11.3 Sample Preparation Procedure

11.3.1 Pipet 10 mL of sample into a new, labelled, unwashed 15 mL centrifuge tube. Repeat for each sample.

11.3.2 Add 100  $\mu\text{L}$  internal standard to each centrifuge tube using an Eppendorf repeater pipet (see Section 16.0). Cap tubes and shake well.

**Note:** Alternative to pipette addition, internal standards can be added on-line directly to sample and standards using the appropriate tubing, a mixing tee, and the peristaltic pump.

**Note:** The concentration of sodium and aluminum in precipitation is expected to be at the ng/mL level. The ICP-MS will be calibrated to 100 ng/mL for these two elements (see Section 7.0.) This should be an appropriate calibration range in which to analyze the metals of interest. If any result falls outside 10% of the upper calibration limit, the sample will be diluted appropriately and reanalyzed in another run.

## 12.0 Reagent Blank Preparation

### 12.1 Supplies

Pipet tips  
2% Ultrapure  $\text{HNO}_3$  (see Section 5.0)  
Internal standard solution (see Section 16.0)  
Acid cleaned 15 mL polypropylene centrifuge tubes (see Section 2.0)

### 12.2 Equipment

Pipettes  
Eppendorf repeater pipet

### 12.3 Reagent Blank Preparation

12.3.1 Pipet 10 mL ASTM Type I water containing 2% (w/w) ultrapure nitric acid (see Section 5.0) into as many clean 15 mL polypropylene centrifuge tubes as needed (see Section 18.4).

12.3.2 Add 100  $\mu\text{L}$  internal standard to each tube using an Eppendorf repeater pipet (see Section 16.0). Cap tubes and shake well.

**Note:** Alternative to pipette addition, internal standards can be added on-line directly to sample and standards using the appropriate tubing, a mixing tee, and the peristaltic pump.

## 13.0 Reagent Blank Preparation When Analyzing for Sodium and Aluminum

### 13.1 Supplies

Pipet tips  
2% Ultrapure HNO<sub>3</sub> (see Section 5.0)  
Internal standard solution (see Section 16.0)  
New, unwashed 15 mL polypropylene centrifuge tubes

### 13.2 Equipment

Pipettes  
Eppendorf repeater pipet

### 13.3 Reagent Blank Preparation

13.3.1 Pipet 10 mL ASTM Type I water containing 2% (w/w) ultrapure nitric acid (see Section 5.0) into as many new, labelled 15 mL polypropylene centrifuge tubes as needed (see Section 18.4).

13.3.2 Add 100 µL internal standard to each tube using an Eppendorf repeater pipet (see Section 16.0). Cap tubes and shake well.

## 14.0 Sample Spike Preparation

### 14.1 Supplies

Pipet tips  
Internal standard solution (see Section 16.0)  
100 ng/mL Mixed stock standard calibration solution (see Section 6.0)  
Acid cleaned 15 mL polypropylene centrifuge tubes (see Section 2.0)

### 14.2 Equipment

Pipettes  
Eppendorf repeater pipet

### 14.3 Sample Spike Preparation

Spikes should be prepared such that the spike concentration is close to the sample concentration, i.e. a 1 ng/mL sample should be spiked with 1 ng/mL. However, the spike should be prepared at sufficiently high concentrations (usually 5 times MDL) such that instrument sensitivity does not affect recoveries of the matrix spike. Below is the procedure for preparing a 1 ng/mL spike; adjust



it as necessary to achieve the proper spike level.

- 14.4 Pipet 10 mL selected sample into a labelled, acid cleaned 15 mL centrifuge tube.

**Note:** Diluted samples should be spiked after the dilution is made.

- 14.5 Pipet 100  $\mu\text{L}$  of the 100 ng/mL mixed stock standard calibration solution into the centrifuge tube. This adds 10 ng of each of the spike elements, creating a final concentration for each element of 1 ng/mL. The spike elements include Aluminum (Al), Arsenic (As), Cadmium (Cd), Chromium (Cr), Copper (Cu), Lead (Pb), Manganese (Mn), Nickel (Ni), Selenium (Se), Sodium (Na), Titanium (Ti), Vanadium (V), and Zinc (Zn).

- 14.6 Pipet 100  $\mu\text{L}$  internal standard into the centrifuge tube using an Eppendorf repeater pipet (see Section 16.0). Cap the tube and shake well.

**Note:** Alternative to pipette addition, internal standards can be added on-line directly to sample and standards using the appropriate tubing, a mixing tee, and the peristaltic pump.

## 15.0 Sample Spike Preparation for Sodium and Aluminum

- 15.1 Supplies

Pipet tips

Internal standard solution (see Section 16.0)

1000 ng/mL Na and Al stock standard calibration solution (see Section 7.0)

New, unwashed 15 mL polypropylene centrifuge tubes

- 15.2 Equipment

Pipettes

Eppendorf repeater pipet

- 15.3 Sample Spike Preparation

Spikes should be prepared such that the spike concentration is close to the sample concentration, i.e. a 10 ng/mL sample should be spiked with 10 ng/mL. Below is the procedure for preparing a 10 ng/mL spike; adjust it as necessary to achieve the proper spike level.

- 15.3.1 Pipet 10 mL selected sample into a new, labelled 15 mL centrifuge tube.

**Note:** Diluted samples should be spiked after the dilution is made.

- 15.3.2 Pipet 100  $\mu\text{L}$  of the 1000 ng/mL Na and Al stock standard calibration solution into the centrifuge tube. This adds 100 ng of each of the spike elements creating a final concentration for each element of 10 ng/mL. The spike elements are Sodium (Na) and Aluminum (Al).

- 15.3.3 Pipet 100  $\mu\text{L}$  internal standard into the centrifuge tube using an Eppendorf repeater pipet

(see Section 16.0). Cap the tube and shake well.

## 16.0 Internal Standard Preparation

### 16.1 Supplies

Certified elemental standards (Spex 1000  $\mu\text{g}/\text{mL}$  Plasma Standards) for Lithium (Li), Yttrium (Y) and Thallium (Tl) 2% Ultrapure  $\text{HNO}_3$  (see Section 5.0)  
Pipet tips

### 16.2 Equipment

Pipettes  
One Acid cleaned 100 mL Teflon bottle (see Section 3.0)  
One Acid cleaned 100 mL volumetric flask (see Section 4.0)

### 16.3 Internal Standard Preparation, 1 mL = 10 $\mu\text{g}$

16.3.1 Pipet 1 mL of 1000  $\mu\text{g}/\text{mL}$  certified standard for each internal standard element (Li, Y and Tl) into a cleaned 100 mL volumetric flask.

16.3.2 Dilute to 100 mL with ASTM Type I water containing 2% (w/w) ultrapure nitric acid (see Section 5.0). Invert flask and mix well. Transfer to a cleaned and labelled 100 mL Teflon bottle. Store indefinitely in cold room for use throughout the project.

### 16.4 Comments

Internal standards must be present in all samples, standards and blanks at identical levels. This is achieved by directly adding an equal aliquot of the above internal standard solution to all solutions to be analyzed. The concentration of the internal standard should be sufficiently high in order to obtain good precision in the measurement of the isotope used for data correction and to minimize the possibility of correction errors if the internal standard is naturally present in the sample. The normal intensity range for an internal standard is between 100,000 and 500,000 ions/second. A concentration of 100 ng/mL is used for each standard in this protocol (100  $\mu\text{L}$  of a 10  $\mu\text{g}/\text{mL}$  stock solution). Internal standards should be added to all solutions in a like manner, in this case by using an Eppendorf repeater pipet, so that dilution effects resulting from the addition may be disregarded.

An alternative approach to adding internal standards to all samples standards, and blanks at a constant level is by using on-line addition. The internal standards maybe added directly on-line to all samples, standards, and blanks using the appropriate tubing, a mixing tee, and the peristaltic pump.

## 17.0 Sensitivity Check Solution Preparation

This solution is used for checking instrument sensitivity prior to analysis. Internal standards are *not* added to this solution.



17.1 Supplies

Certified elemental standards (Spex 1000 µg/mL Plasma Standards) for Magnesium (Mg), Rhodium (Rh) and Lead (Pb)  
Ultrapure concentrated HNO<sub>3</sub>  
Pipet tips

17.2 Equipment

Pipettes  
One Acid cleaned 1000 mL Polypropylene bottle (see Section 3.0)  
One Acid cleaned 1000 mL volumetric flask (see Section 4.0)

17.3 Sensitivity Check Solution Preparation, 1 mL = 10 ng

17.3.1 Pipet 10 µL of each 1000 µg/mL certified standard (Mg, Rh and Pb) into a cleaned 1000 mL volumetric flask.

17.3.2 Dilute to 1000 mL with ASTM Type I water containing 2% (w/w) ultrapure nitric acid (see Section 5.0).

17.3.3 Invert flask and mix well. Transfer to a cleaned and labelled 1000 mL polypropylene bottle. This solution can be stored near the ICP-MS for easy access; it need not be kept in a cold room.

## **18.0 ICP-MS Instrument Operation**

18.1 Supplies

ICP-MS sensitivity check solution (see Section 16.0)  
Manifold tubing for peristaltic pump

18.2 Equipment

Perkin-Elmer Elan 5000 ICP-MS  
Argon gas supply, high-purity grade, 99.99%  
Perkin-Elmer AS 90 Autosampler  
IBM PS2 Model 70 microcomputer  
Xenix operating system  
Microsoft Windows 286  
Perkin-Elmer Elan 5000 software version 2.0  
Gilson Peristaltic Pump

18.3 ICP-MS Instrument Operation Procedure

18.3.1 Connect waste and sample manifold tubing to peristaltic pump. This tubing should be changed daily.

- 18.3.2 Light plasma by pressing ignition button on front panel.
- 18.3.3 When plasma is ignited, start peristaltic pump.
- 18.3.4 Turn on autosampler.
- 18.3.5 Turn on computer monitor and then computer. Wait for ":" prompt and press return. When password prompt appears, press "Control D". Correct date if necessary; otherwise press "Return". At login prompt, type "Elan".
- 18.3.6 Initialize autosampler to include 90 second read delay and a 30 second wash time. Fill the wash reservoir with ASTM Type I water. This wash serves as a rinse blank to flush the system between samples and minimize carry-over.
- 18.3.7 Consult ICP-MS manual for normal operation.
- 18.3.8 In graphics mode, perform a sensitivity check. Aspirate sensitivity solution (see Section 17.0) and press "read" button on computer keyboard. Record ion counts, power, nebulizer gas flow and base pressure in instrument log. Compare the present ion counts versus those previously recorded. If sensitivities are 10-15% below previous counts, stop and troubleshoot as specified in instrument manual. Otherwise, continue with analysis.
- 18.3.9 Place calibration standards and samples in autosampler tube rack. See below for sequence of standards and samples.
- 18.3.10 Set up the analysis routine in quantitative analysis mode on the computer as described in ELAN 5000 software manual using the following settings in the parameter file:
- |                      |           |
|----------------------|-----------|
| For Time Factor      | 1         |
| Replicate Time (ms)  | 1000      |
| Dwell Time (ms)      | 10        |
| Scanning Mode        | Peak Hop  |
| Sweeps/Reading       | 100       |
| Readings/Replicate   | 1         |
| Number of Replicates | 3         |
| Points/Spectral Peak | 3         |
| Resolution           | Normal    |
| Transfer Frequency   | Replicate |
| Baseline Time (ms)   | 0         |
| Polarity             | +         |
- 18.3.11 Analyze calibration standards and print calibration report. If  $r \geq 0.999$ , continue with analysis of samples. Otherwise, stop analysis, determine source of error, correct problem and repeat analysis of calibration standards.

18.4 Analysis sequence:

Blank  
 Calibration standards  
 Reagent blank  
 Check standards  
 SLRS-2 or SLRS-3 standard (certified performance standard)  
 EPA-1 or EPA-2 (diluted certified performance standard)  
 Samples 1-10  
 Duplicate sample  
 Spiked sample  
 Reagent Blank  
 Check standards  
 SLRS-2 or SLRS-3 standard (certified performance standard)  
 EPA-1 or EPA-2 (diluted certified performance standard)  
 Samples 11-20  
 Duplicate sample  
 Spiked sample  
 Reagent blank  
 Check standards  
 SLRS-2 or SLRS-3 standard (certified performance standard)  
 EPA-1 or EPA-2 (diluted certified performance standard)

### 18.5 Isotopes Analyzed

Element	Symbol	Isotope	Corrections Programmed <sup>+</sup>
Sodium	Na	23	
Aluminum	Al	27	
Titanium	Ti	48	Ca
Vanadium	V	51	
Chromium	Cr	52	
Manganese	Mn	55	
Nickel	Ni	58	Fe
Nickel	Ni	60 (used later)	
Copper	Cu	63	TiO*
Zinc	Zn	66	
Arsenic	As	75	
Selenium	Se	82	Kr
Cadmium	Cd	114	Sn
Lead	Pb	208	

+ The Perkin-Elmer Elan 5000 software has pre-programmed elemental equations which are applied to the indicated elements to correct for the isobaric interferences. (See Section 19.1)

\* See Section 19.3 for the elemental equation entered manually for the TiO correction.

### 18.6 Certified Standard Concentrations

#### 18.6.1 SLRS-2 standard (certified performance standard) concentrations:

Sodium (Na)	1860	+/- 110	ng/mL
Aluminum (Al)	84	+/- 3.4	ng/mL

Arsenic (As)	0.77	+/-	0.09	ng/mL
Cadmium (Cd)	0.028	+/-	0.04	ng/mL (below lowest standard)
Chromium (Cr)	0.45	+/-	0.07	ng/mL
Copper (Cu)	2.76	+/-	0.17	ng/mL
Lead (Pb)	0.129	+/-	0.011	ng/mL
Manganese (Mn)	10.1	+/-	0.3	ng/mL
Nickel (Ni)	1.03	+/-	0.10	ng/mL
Vanadium (V)	0.25	+/-	0.06	ng/mL
Zinc (Zn)	3.33	+/-	0.15	ng/mL

18.6.2 SLRS-3 standard (certified performance standard) concentrations:

Arsenic (As)	0.72	+/-	0.08	ng/mL
Chromium (Cr)	0.30	+/-	0.06	ng/mL
Copper (Cu)	1.35	+/-	0.11	ng/mL
Manganese (Mn)	3.9	+/-	0.45	ng/mL
Nickel (Ni)	0.83	+/-	0.12	ng/mL
Vanadium (V)	0.30	+/-	0.03	ng/mL
Zinc (Zn)	1.04	+/-	0.14	ng/mL

18.6.3 EPA-1 standard (diluted certified performance standard) concentrations:

Arsenic (As)	5.0 ng/mL	Nickel (Ni)	5.0 ng/mL
Cadmium (Cd)	5.0 ng/mL	Selenium (Se)	5.0 ng/mL
Chromium (Cr)	5.0 ng/mL	Titanium (Ti)	5.0 ng/mL
Copper (Cu)	5.0 ng/mL	Vanadium (V)	5.0 ng/mL
Lead (Pb)	5.0 ng/mL	Zinc (Zn)	5.0 ng/mL
Manganese (Mn)	5.0 ng/mL		

**Note:** Also contains the following elements at 5.0 ng/mL each which are not being analyzed for this project: Antimony, Beryllium, Calcium, Cobalt, Iron, Lithium, Magnesium, Molybdenum, and Strontium. Although Lead is also present in EPA-1, the quantitative results for it are inaccurate because Thallium is also present in the solution, and Thallium is the internal standard used to quantitate Lead.

18.6.4 EPA-2 standard (diluted certified performance standard) concentrations:

Aluminum (Al)	5.0 ng/mL
Sodium (Na)	5.0 ng/mL

**Note:** Also contains the following elements at 5.0 ng/mL each which are not being analyzed for this project: Barium, Boron, Potassium, Silicon and Silver.

18.6.5 Independent Check Standard at 0.8 ng/mL maybe used as the certified performance standard for these elements not certified or below the method detection limit in the SLRS-2 and SLRS-3 standards. The acceptance range is +/- 10% so that the acceptable ranges are:

Titanium (Ti)	0.8 +/-	0.8	ng/mL
Selenium (Se)	8.0 +/-	0.8	ng/mL

Cadmium (Cd)	0.8 +/-	0.08	ng/mL
Lead (Pb)	0.8 +/-	0.08	ng/mL



## 19.0 Interferences

Several interference sources may cause inaccuracies in the determination of trace metals by ICP-MS. The following descriptions are taken in large part from the Environmental Monitoring Systems Laboratory Office of Research and Development, U.S. Environmental Protection Agency Method 200.8 for the "Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma - Mass Spectrometry", Revision 4.3, August 1990.

- 19.1 Isobaric elemental interferences are caused by isotopes of different elements which form singly or doubly charged ions of the same nominal mass-to-charge ratio and which cannot be resolved by the mass spectrometer in use. All data obtained under such conditions must be corrected by measuring the signal from another isotope of the interfering element and subtracting the appropriate signal ratio from the isotope of interest. This is done automatically by pre-programmed correction factors in the Perkin-Elmer Elan 5000 software.
- 19.2 Abundance sensitivity is a property defining the degree to which the wings of a mass peak contribute to adjacent masses. The abundance sensitivity is affected by ion energy and quadrupole operating pressure. Wing overlap interferences may result when a small ion peak is being measured adjacent to a large one. Such interferences can be minimized by adjusting the spectrometer resolution appropriately.
- 19.3 Isobaric polyatomic ion interferences are caused by polyatomic species which have the same nominal mass-to-charge ratio as the isotope of interest, and which cannot be resolved by the mass spectrometer in use. These ions are commonly formed in the plasma or interface system from support gases or sample components, and are therefore highly dependent on the sample matrix and chosen instrument conditions. Such interferences must be recognized, and when they cannot be avoided by the selection of alternative analytical isotopes, appropriate corrections must be made by programming in a correction factor for the elements which are affected. In this study, elemental correction equations will be applied to copper whose mass is overlapped by titanium oxide ( $Ti^{47}O^{16}$ ):

$$\text{corrected } Cu^{63} = Cu^{63} - (0.06 * Ti^{47})$$

- 19.4 Physical interferences are associated with the physical processes which govern the transport of sample into the plasma, sample conversion processes in the plasma, and the transmission of ions through the plasma-mass spectrometer interface. These interferences may result in differences between instrument responses for the sample and the calibration standards. Physical interferences may occur in the transfer of solution to the nebulizer (e.g. viscosity effects), at the point of aerosol formation and transport to the plasma (e.g. surface tension), or during excitation and ionization processes within the plasma itself. High levels of dissolved solids in the sample may contribute deposits of material on the extraction and/or skimmer cones reducing the effective diameter of the orifices and therefore ion transmission. Precipitation samples are expected to be well within the recommended limit of 0.2% (w/v) dissolved solids which will help to minimize such effects. Internal standardization may be effectively used to compensate for many physical interference effects. Internal standards ideally should have similar analytical behavior to the elements being determined. In this study, the internal standards include Lithium (mass 7) for Sodium (23) and Aluminum (27), Thallium (205) for Lead (208), and Yttrium (89) for the remaining elements in the center of the mass range.

- 19.5 Memory interferences result when isotopes of elements in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the sampler and skimmer cones and from the buildup of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the element. Memory interferences can be minimized by keeping the cones, torch and spray chamber clean and by flushing the system with a rinse blank between samples (see Section 18.3.6).

## 20.0 Quality Control Information

### 20.1 QA/QC Objectives:

- 20.1.1 Calibration standards are to be prepared each day of analysis (See Section 6.0).
- 20.1.2 Appropriate check standards should be prepared for the duration of the project (See Section 3.6.). Check standards will be control-charted for monitoring purposes.
- 20.1.3 QC standards shall include: reagent blank, check standards, duplicate, spike, and certified standards.
- 20.1.4 No more than 10 samples shall be run between sets of QC standards.
- 20.1.5 Calibration coefficients shall have at least three 9's before proceeding with samples ( $r = 0.999$ ).
- 20.1.6 For every 10 samples or fraction thereof, one sample is randomly selected to be duplicated and one sample is randomly selected to be spiked for QC purposes. The sample spike should be prepared such that the spike concentration is close to the sample concentration but still be within the calibration range.
- 20.1.7 The following limits shall be met before data is deemed acceptable and passed on to the QA/QC officer.
- 20.1.7.1 Duplicates: <10% difference or percent difference less than the method detection limit, whichever is greater percent difference as calculated using the following equation:

$$(C_{measured}^o - C_{measured}^d) / [(C_{measured}^o + C_{measured}^d)/2] * 100 = \% \text{ Difference}$$

Where  $C_{measured}$  = measured concentration  
 $o$  = the original sample  
 $d$  = the duplicate sample

20.1.7.2 Spikes: 85-115% recovery as calculated using the following equation:

$$[(C_{measured} * V^*) - (C_{measured} * V)] / \text{mass of spike} * 100 = \% \text{ Spike Recovery}$$

Where  $C_{measured}$  = measured concentration

$V$  = volume and an asterisk

(\*) = the spiked sample

20.1.7.3 Check standards: <10% relative standard deviation (RSD) within run (or relative percent difference for only two data points) <15% RSD of all data points in the project.

20.1.7.4 Certified standards: Must be within certified range (See Section 3.14.3 for current certified standard values).

If any one of the above criteria is not met and an explanation can be given for deviation from the above limits, the data can be deemed acceptable. Otherwise, all samples must be reanalyzed.

## 20.2 Laboratory Preparation Area

A laboratory in the high hazard section of the Hazardous Waste Research and Information Center (HWRIC) has been designated exclusively for all preparation and glassware cleaning associated with this project. Although not a clean room in the strict sense, it is kept as clean as possible and no other preparation work is done in that room. Gloves and lab coats are required at all times. Individual work spaces are lined with absorbent protective paper which is changed periodically. All glassware and teflon is washed in a special tank in the hood in this same room (see Sections 2.0, 3.0, 4.0). Additionally, all equipment (glassware, pipets, consumable supplies, etc.) for this project are also stored in this room.

## 20.3 Table of Detection Limits and Analytical Ranges

<u>Element</u>	<u>Monitored Analytical Mass</u>	<u>Method Detection Limit (<math>\mu\text{g/L}</math>)</u>	<u>Analytical Range (<math>\mu\text{g/L}</math>)</u>
Aluminum	27	0.1	0.1 - 1000
Arsenic	75	0.1	0.1 - 1000
Cadmium	114	0.1	0.1 - 1000
Chromium	52	0.1	0.1 - 1000
Copper	63	0.1	0.1 - 1000
Lead	208	0.1	0.1 - 1000
Manganese	55	0.1	0.1 - 1000
Nickel	58	0.1	0.1 - 1000
Nickel	60 (used later)	0.1	0.1 - 1000
Selenium	82	1.0	1.0 - 1000
Sodium	23		
Titanium	48	0.1	0.1 - 1000

Vanadium	51	0.1	0.1 - 1000
Zinc	66	0.1	0.1 - 1000