# Analysis of Surface Waters for Trace Elements by Inductively-Coupled Plasma Mass Spectrometry

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## 1.0 Introduction

This document outlines a complete method for the determination of a suite of trace metals in surface waters. All phases of the process are discussed, from equipment preparation and sampling techniques, to instrumental analysis, and field and laboratory QA/QC. Each phase is of equal importance in producing quality data, and failure to strictly adhere to the protocols at each step of the process can severely compromise data integrity. The method describes the use of inductively-coupled plasma mass spectrometry (ICP-MS) for the determination of Aluminum (Al), Arsenic (As), Cadmium (Cd), Chromium (Cr), Copper (Cu), Lead (Pb), Silver (Ag), and Zinc (Zn). ICP-MS protocols generally follow methods 200.8 and 6020 CLP-M, with modifications to allow quantification at low ng $L^{-1}$ levels and to prevent contamination of the instrument. Detailed descriptions of field methods are not presented in this manuscript. The primary focus of this document is on analytical methods and quality assurance. Separate documents are available which describe in great detail field methods employed in studies of a variety of surface water systems.

## 2.0 Equipment Preparation

### 2.1 General

Most stages of field apparatus cleaning and preparation are performed within a clean lab. The most critical steps of preparation are carried out within laminar flow benches, located in the clean lab. The sampling equipment (sampler, sample bottles, filtration system, acidification vials, tubing) are fabricated from Teflon PFA or Teflon FEP. These materials were selected as most suitable for sample contact because of their generally low trace metal content, resistance to degradation during rigorous cleaning procedures, and hydrophobic character. Trace metal grade acids are used in all final cleaning and storage stages. Field manipulations and potential for contamination are minimized by prepackaging apparatus in the clean lab. Polyethylene gloves are used at all times when handling sample bottles and filtration apparatus in the lab and field. Samplers, bottles, and acidification acid are "blanked" before use in the field. Dedicated blank studies have demonstrated that contamination from the samplers and filtration apparatus are minor components of the method blank. For a detailed description of field methods refer to the field methods document specific to a given study.

### 2.2 Cleaning and Packaging

#### 2.2.1 Teflon Bottle Preparation Procedure
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Never place a Teflon bottle directly onto a counter top. Always place a new piece of plastic down on counter before placing bottles on counter.

(a) Bottle ID

Verify that the Teflon bottle has an ID number etched into its side. If the bottle has not been etched, set aside and verify with a supervisor the appropriate number to etch at a later date.

(b) Acetone Wash

Fill bottles with acetone (ACS Reagent), leach for two hours, remove acetone, rinse twice with milli-Q water. Record date on cleaning log. The used acetone is placed into glass containers labeled *Use Acetone For Bottle Cleaning*, and may be reused five times before disposing. Note on acetone bottle number of uses.

(c) 50% HCl Leach

Fill bottle to top of neck with 50% HCl (ACS Reagent), leach for three to four days at room temperature, remove HCl, rinse three times with milli-Q water. The 50% acid is prepared and stored in 2.5 L acid bottles - Clearly Labeled 50% HCl For Teflon Bottle Cleaning. The acid may be reused five times before disposing. Note on acid bottle number of uses. The acid may be added to the Teflon bottle directly from the acid bottle, with or without the aid of a funnel; or may first be placed into a plastic beaker. Do not touch lip of acid bottle to lip of Teflon bottle. After filling a batch of bottles, place into a large plastic bag. Seal bag, label bag with date, type of acid, and your name.

(d) 50% $HNO_3$ Leach

Fill bottle to top of neck with 50% $HNO_3$ (ACS Reagent), place in 20% $HNO_3$ acid bath, leach inside and out for three to four days at room temperature. Remove bottle from bath and thoroughly rinse outside of bottle with milli-Q water. Remove 50% $HNO_3$ acid, and rinse three times with milli-Q water. The 50% acid is prepared and stored in 2.5 L acid bottles - Clearly Labeled 50% $HNO_3$ For Teflon Bottle Cleaning. The acid may be reused five times before disposing. Note on acid bottle number of uses. The acid may be added to the Teflon bottle directly from the acid bottle, with or without the aid of a funnel; or may first be placed into a plastic beaker. Do not touch lip of acid bottle to lip of Teflon bottle. Record on the 20% acid bath the date the bottles went in.

(e) 1% High Purity $HNO_3$ Leach

Fill bottle with 1.0% $HNO_3$ (Baker Trace Metal Grade; TMA), and store in this manner until bottle is required, but at least three days. The diluted acid is best prepared in original, clean 2.5 L acid bottles. Fill to just below neck with milli-Q water, add 25 mL concentrated TMA (use Teflon Beaker), cap, mix, and dispense. A 2.5 L bottle should be Clearly Labeled 1% TMA For Teflon Bottle Cleaning and used exclusively for preparation of dilute acid. Discard any unused dilute acid. An alternate filling method is to fill bottles ½ full with MQ from 20 L

carboy; dispense concentrated acid via a Teflon beaker and a Teflon measuring vial; top off bottle with MQ.

(f) Drying

Remove and discard dilute acid, rinse four times with milli-Q water, dry bottle and cap under laminar flow hood. Sign out hood for this step, and make sure it is relatively free of other apparatus. *Be extremely careful not to Contaminate the Cap and Bottle*. Do not leave bottle/cap in hood for longer than it takes to dry them and never longer than six hours.

(g) Taring

Assemble bottle and cap under hood and obtain bottle tare weight (±0.02 g) using top-loading balance next to clean bench. Bottle weights are recorded in the Teflon Bottle Weigh Log. Cap all bottles first; use your clean gloved hand to handle bottles; use dirty gloved hand to record data on cleaning log sheet. Make sure a clean piece of plastic is covering balance tray. After weighing, return bottles to laminar flow hood for bagging.

(h) Double Bagging

(i) Notes

Under laminar flow hood, place bottle in appropriately sized polyethylene (PE) zip-lock bag. Double bag with another PE zip-lock bag labeled with sample bottle ID. Use a new clean pair of PE gloves for these steps. A black Sharpie is used to label outer bag with bottle ID. Double check that bottle ID corresponds to bag ID.

1. All preparation steps must be performed in the clean room.

2. Acetone and 50% acid use must be under a fume hood.

3. Do not place Teflon bottles onto an uncoated lab bench. Make sure the bench has a clean plastic surface (place new plastic even over Teflon overlay).

4. You must wear clean polyethylene gloves when handling Teflon ware.

5. Follow all clean room protocols when cleaning Teflon ware (clean lab coat, shoe covers, etc.).

6. All acid dilutions are performed with milli-Q water.

7. Tighten bottle caps thoroughly to prevent acid leakage.

8. Use only designated Teflon beaker for TMA.

Experiments have shown that Teflon bottles prepared in this manner introduce undetectable levels of Al, Cd, Cr, Cu, Fe, Pb, and Zn to samples stored at 4°C for periods of at least nine months. In parallel experiments, no loss of trace metal was observed in spiked sample pairs.

2.2.2 Sampler, Filtration Apparatus, Acid Vial, Preparation
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All components of samplers (except polyethylene extension pole), filtration apparatus, and acid vials are cleaned as follows:

(a) Leach, in acid bath, three to four days in 50% HCl (ACS Reagent) at room temperature, rinse three times with milli-Q.

(b) Leach, in acid bath, three to four days in 50% $HNO_3$ (ACS Reagent) at room temperature, rinse three times with milli-Q.

(c) Leach, in acid bath, four to five days in 1% $HNO_3$ (Baker Trace Metal Grade), rinse four times with milli-Q water.

(d) Dry under laminar-flow hood, assemble (if required) components under clean bench, double bag in clean polyethylene bags. Do not leave vials under clean bench for longer than two hours.

Acidification vials are cleaned in 1 L wide-mouth Teflon bottles.

Polyethylene extension poles are cleaned by scrubbing pole with clean room wipers soaked in 10% $HNO_3$, and thoroughly rinsing with milli-Q water. After cleaning the poles are sealed in ultra high molecular weight polyethylene (UHMWPE) bags.

2.2.3 ICP-MS Sub-Sample Tube Preparation

Polypropylene tubes with polypropylene snap caps (17 x 100 mm) are used to contain sample during ICP-MS analysis.

(a) Leach, cap and body, two to three days in 10% $HNO_3$ (ACS Reagent) at room temperature, rinse three times with milli-Q.

(b) Leach, cap and body, two to three days in 2% $HNO_3$ (Baker Trace Metal Grade), rinse four times with milli-Q water.

(c) Dry under laminar-flow hood, assemble, and store in clean polyethylene bag.

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Procedures For Recycling Field Supplies

(a) Acidification Vials

1. Rinse vials/caps inside and outside with MQ three to four times.
2. Place in 50% reagent nitric acid bath in Teflon bottle for two days.
3. Rinse vials/caps with MQ three to four times.
4. Place vials/caps in 1-2% Trace Metal Nitric Acid (TMA) in Teflon bottle for three days.
5. Rinse vials/caps four times with MQ, shake off excess water.
6. Dry under laminar flow hood for no longer than two hours.
7. Fill with acidification acid, or cap vials and place in labeled zip-lock to be filled later.

**Note**: All steps to be performed in clean lab, with gloved hands, and clean lab coat. If vials are placed onto a lab bench, it must be covered with new plastic.

(b) SPM/DOC Bottles

1. Rinse 1 L bottle/cap inside and outside with MQ three to four times.
2. Fill bottle with new 10% reagent nitric acid.
3. Leach for a minimum of two days.
4. Dump acid and rinse bottle/cap four times with MQ.
5. Shake out excess water and dry under laminar flow hood for no longer than four to five hours.
6. Cap bottles and place in labeled bag.

**Note**: All steps to be performed in clean lab, with gloved hands, and clean lab coat. If bottles are placed onto a lab bench, it must be covered with new plastic.

(c) Teflon Sample Bottles

1. Refer to complete cleaning protocol.

2. Start procedure from 50% ACS reagent nitric step.

3. Follow protocol to end.

**Note:** All steps to be performed in clean lab, with gloved hands, and clean lab coat. If bottles are placed onto a lab bench, it must be covered with new plastic.

(d) TTAF and PCR (TCR)

1. Rinse with MQ.

2. Place in 50% reagent nitric acid bath for two days.

3. Rinse with MQ.

4. Place in 1-2% Trace Metal Acid bath for three days.

5. Rinse with MQ four times.

6. Dry under Laminar Flow Hood for no more than two hours.

7. Double-bag in labeled zip-lock bags

8. Record cleaning date on outer zip-lock.

9. Steps 2 through 4 may be replaced with a 24-hour near-boiling concentrated nitric acid bath leach following Hg bottle cleaning protocols.

**Note:** All steps to be performed in clean lab, with gloved hands, and clean lab coat. If adapters are placed onto a lab bench, it must be covered with new plastic.

(e) Tubing Rinse Acid Carboy

1. Dump out any remaining acid.

2. Rinse carboy with MQ three times.

3. Fill carboy to 2" below neck with MQ.

4. Add 400 mL concentrated Trace Metal Nitric Acid (TMA). Use a Teflon beaker dedicated for TMA to deliver acid.

5. Cap carboy and bag with large poly bag.

**Note**: All steps to be performed in clean lab, with gloved hands, and clean lab coat.

(f) ICP-MS Sub-Sample Tubes

Tubes are not reused.

2.2.5 Filling of Field Acidification Vials

(a) Field Acidification Solution Preparation

1. Prepare a 25 mg $L^{-1}$ solution of Rare Earth Elements (Y, Yb, Ho, Th) REE (1 mL each/40 mL (final volume) of 2% Ultrex $HNO_3$) using the 1000 ppm stock solutions from High Purity Standards.

2. Prepare a 50% Ultrex $HNO_3$ Acid solution (v/v). Allow the solution to cool to room temperature. Calculate the density (g/mL) of the 50% acid by weighing three replicates of 1.000 mL. Use the average of the three values. Record the values on the Field Acidification Preparation data sheet.

3. To make the final solution, add 2.000 mL of the 25 mg $L^{-1}$ REE stock to the mass equivalent of 298.00 mL of the 50% Ultrex Acid Solution. This yields a solution containing Y, Ho, Yb, Th = 166.7 µg L-1 (scale the recipe as necessary).

4. Label the new acidification solution with the date and batch ID. The batch ID is assigned sequentially beginning with FS9501 for the 1995 sampling year. Check the Trace Metal Preservative Log Book for the most recent batch. Place the data sheet into the QC log.

5. A dilution of the acidification solution must be analyzed by ICP-MS to verify the REE concentrations and the absence of elements of interest. A 5.0 mL (approx.) volume of the solution also needs to be archived.

6. Use 3.000 mL of acidification solution for preserving both 250 mL Total and 250 mL Filtrable metal samples (Final concentration of 0.6%).

(b) Dispensing Acidification Solution

Wear poly gloves and clean-room suit at all steps.

1. Arrange Teflon vials under the laminar flow bench on a new plastic sheet.

2. Set up digital pipet with a leached tip and set to deliver 1.500 mL. Do not let clean tip touch any surface during filling procedure.

3. Pour an aliquot of acid solution into the designated clean Teflon beaker.

4. Rinse tip twice by dispensing acid into a waste container, and then begin filling Teflon vials with 3.000 mL of acid solution (2 x 1.500).

5. Replace vial caps and wrench tight with green plastic wrenches.

6. Place vials into zip lock bag and then insert bag into a labeled zip-lock bag.

2.2.6 Preparation of Polycarbonate Filters for Trace Metal Filtration Revision 3 November 1994.

**Note**: This procedure was not used for the LMMB Tributary Study.

Polycarbonate track-etched filters (47mm or 90mm diameter, 0.4 µm pore size) are used to obtain particulate samples and suspended mass levels. They are prepared as follows:

(a) Petri-Dish Preparation

Filters are placed individually into polystyrene petri dishes. The dishes are pre-cleaned by soaking tops and bottoms separately in 10% $HNO_3$ (ACS Reagent) for 24 hours, followed by rinsing with milli-Q water. Dishes are then dried under a laminar flow clean bench. Dishes are then assembled under the clean bench and bagged for later use.

(b) Filter Weighing

Clean petri dishes are labeled top and bottom with a sequence number and pore size using a black Sharpie. Filters are placed into the dishes and allowed to equilibrate in the balance room for at least two hours before taring. Filters are handled only with all plastic forceps. While equilibrating the partially opened dishes are loosely covered with a clean plastic bag. Every seventh filter is designated as a temperature and humidity control, and is so designated in the filter log book and on the petri dish. Filters are tared on a Perkin Elmer microbalance (AD-4) to a significance level of 1 µg after equilibration for 60 seconds. Balance calibration is recorded in the filter log book, and is performed with a CLASS M weight before weighing each batch of filters, and is checked after ever tenth filter. 10% of the filters are re-weighed. Polonium ionization sources are used to eliminate static charges. Refer to *Filter Weighing SOP* for details.

(c) Filter Leaching

Tared filters are leached individually in their previously cleaned polystyrene petri dishes. A 1 molar (63 mL or 89.5 g concentrated reagent per liter of milli-Q water) solution of $HNO_3$ (Baker Ultrex II Grade) is prepared in a dedicated polyethylene bottle. The 1M solution is transferred to a clean polyethylene wash bottle and then added to the bottom portion of the petri dish to nearly fill the

contained volume (approx. 10 mL per dish). The top half of the petri dish is then replaced and the filter leached for 48 hours at room temperature. All filter leaching and rinsing is performed in the clean lab.

(d) Filter Rinsing

After leaching for the required time the acid solution is poured off into a plastic waste beaker. The filters are then rinsed 10 times with milli-Q water by squirting in approx. Ten mL with a polyethylene wash bottle, discarding rinse, and repeating this process 10 times. The rinsing process is performed under the laminar flow clean bench. The leached and rinsed filters are stored in a few mL's of milli-Q water until used.

2.2.7 Loading of Teflon Filter Columns

**Note**: This procedure was not used for the LMMB Tributary Study.

Pre-cleaned and rinsed filters (see [4]) are loaded into all-Teflon filter columns for use in the field. The columns consist of a Teflon filter support base and a threaded Teflon column segment with Teflon cap. The segment will contain approx. 150 mL of sample. Filters are loaded into the Teflon columns under the laminar clean bench. After loading, the filter columns are individually doubled bagged with polyethylene zip-lock bags.

## 3.0 Clean Room Protocols

**Note**: Refer to the Clean Room Operations SOP for more detailed descriptions of procedures. A few specific points are outlined below.

3.1 All personnel entering clean rooms must wear full clean-room garb (coveralls, eyes-only hoods, and foot covers.

3.2 Particle counts (>0.3 µm) in the room are to be monitored with a portable laser-based counter and logged on a daily basis (ICP-MS clean-room only) [Two locations, 10 min integrations, sampled every hour for four hours].

3.3 Floors are to be wiped with a clean room tacky mat mop on a weekly basis; more often if judged necessary.

3.4 Paper towels and wipers must not be used in clean room; only clean room wipers are allowed.

3.5 Shipping containers (cardboard, paper, etc.) are not allowed in the room.

3.6 Tacky mats are to be positioned at entrance to clean room.

3.7 Food and drinks are not permitted in the clean room.

3.8 Positive pressure is to be maintained in the clean room at all times. Daily readings of the magnehellic gauge are to be taken and recorded in the particle count log book.

# 4.0 Trace Metal Sampling

**Note:** The procedures outlined in Sections 4.1 through 4.3 are not those used in the LMMB Tributary loading study. Refer to the separate document outlining Field Trace Metal Protocols for LMMB Tributary Monitoring.

## 4.1 General

Trace metal samples will be obtained by personnel trained in trace level sample collection. The procedures that they will be following will be fully documented, and available for review in the field. The two-person trace metal team must wear trace metal - compatible garments and clean polyethylene gloves during the sample collection period or whenever handling trace metal samples.

Two "blanked" trace metal clean samplers will be used. Our grab sampler will be used in flowing river systems where depth profiling is not practical or necessary. Where depth and longitudinal integration is required, a modified, all Teflon USGS DH-81 sampler is applied. Ease of use under less than optimum field conditions was an important design criterium. The grab sampler consists of a heavy Teflon collar affixed to the end of a 2 meter long polyethylene pole, which serves to remove operator from immediate vicinity of sampling point. The collar was designed to securely hold a 500 mL FEP Teflon bottle.

A Teflon closing mechanism, threaded onto the bottle, enables the operator to open and close the bottle under water, thereby avoiding surface microlayer contamination. A Teflon pull cord, attached to the seal device, allows operator to remotely select to bring seal plate position. Rigorous "clean-hands" - "dirty-hands" procedures are an integral part of sampling protocol. The bottle and clean end of sampler is handled only by personal with clean shoulder-length PE gloves and full clean suit. The sample bottle, immediately upon recovery, is placed in the inner trace metal clean zip-lock bag by the "clean-hands" person, and then double bagged. Loading and un-loading of samplers with bottles is performed within large polyethylene bags.

## 4.2 Filtration

The field filtration apparatus consists of a 1 L Teflon PFA vacuum jar, a Teflon lid with three ¼" fittings, and pre-loaded 47 mm Teflon PFA filter holders mated with 150 mL Teflon PFA columns. To use, a filter unit/column is attached to vacuum jar and a representative aliquot of total metal sample is added directly to the column. Suction from a peristaltic pump is applied to the jar, and filtrate collected directly in 125 mL Teflon bottle after a rinse step. The complete filtration procedure is performed within an argon-flushed plexiglass glove box. This type of filtration system has significant advantages over other designs in that contact surfaces are minimized, all critical components can be pre-packaged in a clean lab, and exposure to ambient air is eliminated by use of sealed columns and glove box.

The apparatus can be operated in a pressure mode if required. Filtration is initiated as soon as possible after sample collection, typically within 15 minutes. After filtration is complete the 125 mL bottle is double bagged.

4.3 Acidification

Total (500 mL bottle) and filtrate (125 mL bottle) samples are acidified within the glove box using 50% Ultrex nitric acid contained in pre-packaged, individually dosed, Teflon PFA vials. Vials are opened with plastic hex wrenches. Acidification is at a rate of 5 mL concentrated nitric acid per liter. Alternatively, if filtration is carried out on a boat, acidification can be performed in the open air immediately after sample collection using strict clean-hands-dirty hands protocols. In this case, both field personnel must be garmented in clean suit coveralls. Sub-samples (20 mL) of acidification acid are saved at the time of preparation in Teflon vials, and trace element levels determined by ICP-MS. If the level of any element of concern in a 2% MQ solution of this acid is greater than five times the average acid MQ calibration blank metal concentration, then that acid batch is rejected.

# 5.0 Field Quality Assurance Protocols

5.1 Recovery Spikes

5.1.1 Rare Element Spike

All samples are acidified with 50% Ultrex $HNO_3$ containing four rare elements, Yttrium (Y), Holmium (Ho), Ytterbium (Yb), and Thorium (Th). Teflon PFA vials containing pre-measured quantities of acid-spike solution is used to deliver the spike with acidification acid. Indigenous levels of these elements in each river system are quantified before monitoring begins. Spiking levels of approx. 3 µg $L^{-1}$ are employed, a level easily measured and of similar concentration to many of the trace elements of concern, yet well above extremely low indigenous levels. The recovery control range for all rare elements (except Thorium) is 70-125%. If all three elements (Y, Ho, Yb) fail, the sample results are flagged as estimated, and the sample should be diluted and reanalyzed. If any two elements fail, the sample results are also flagged as estimated and dependent upon the degree of failure, these samples should also be reanalyzed. Sample data will not be flagged if just one surrogate element falls outside the control range.

5.1.2 Trace Metal Spike

Replicate Total and Filtrate samples both taken at a frequency of 10%, will be spiked with an acid-mix of the metals of concern. The spike will be delivered as described in [1] above. The spike is designed to approx. double ambient concentrations of each metal of concern, or elevate ambient levels by 15 ng $L^{-1}$, whichever is larger. All trace element spikes must recover in the range of 70-125 %. If any element fails, the sample will be reanalyzed after dilution or other matrix modification technique, only after ruling out field conditions (field technician error, high ambient metals levels, etc.) as a reason for potential bias.

5.1.3 Blank Spike

A field MQ-blank will be spiked with trace metals whenever a sample spike is performed. Frequency of 5%. Procedure is identical to [2] above.

5.2 Blanks

5.2.1 Bottle Blanks

Every batch of 20 field bottles will include one field bottle blank (5% Frequency). These bottles are prepared in an identical manner to sample bottles except that prior to final packaging, they are filled with MQ-blank water. An additional lab bottle blank (5% Frequency) is prepared at the same time. Field blanks are brought to sampling sites and acidified in the field using trace metal clean protocols as described in Section 4.3.

5.2.2 Filtration Blanks

Filter and tubing blanks will be performed at a frequency of about one in every 40 samples (2.5%). Eight liters of MQ water are sent to the field in two large Teflon Bottles as part of a dedicated Field Blank Kit. This water is used to blank, separately, Calyx filters, and the Teflon Tubing Sampling Line. A sub-sample of the feed MQ is also obtained to serve as a reference level.

5.2.3 Spike Blanks

Every batch of 20 field bottles will include one blank for field spiking (5% Frequency). See Section 5.1.3.

5.3 Replication

Our goal for the Lake Michigan Tributary Monitoring Project / Lake Michigan Mass Balance Project is 15% to 20% replication of field samples, excluding QC samples. This will be accomplished by completely duplicating individual sites on a frequency of one in five revisitations. Our goal should be to limit field "replicate" error to ±15% for analytes greater than five times the analytical reporting limit.

5.4 Interlaboratory Comparison

At least once during the duration of the study, field samples will be collected and split for shipment to a cooperating laboratory.

5.5 Field Quality Assurance Summary

| Type | Frequency |
|---|---|
| Recovery Spikes | |
| ---- rare element | all samples |
| ---- analyte in sample | 10% |
| ---- analyte in blank | 5% |

| Type | Frequency |
|---|---|
| Blanks | |
| ---- bottle (field) | 5% |
| ---- bottle (lab) | 5% |
| ---- filter | 2.5% |
| ---- tubing | 2.5% |
| Replication | |
| ---- samples (ex. QC) | 15-20% |
| Interlab Comparison | |
| ---- split samples/method comparison | once |
| Audit | |
| ---- internal field | twice |
| ---- external field | once |

# 6.0 Laboratory Sample Handling

6.1 Sample Logging

Upon arrival at laboratory, the field data sheet will be recovered, copied and filed, and samples logged into the appropriate databases. The following data are logged into the Trace Metal sample database upon arrival of samples at laboratory:

1. Site coding
2. Sample bottle coding
3. Sample type
   - (a) Blank
     - i. Bottle
     - ii. Filter
     - iii. Tubing
     - iv. Feed
   - (b) Replicate
   - (c) Spike
     - i. Sample
     - ii. Blank
   - (d) Sample
     - i. Unfiltered
     - ii. Filtered
4. Sampling date and time

5. Shipping date
6. Arrival date
7. Acidification acid batch
8. Spike acid batch
9. Calyx filter batch
10. Pump-head tubing batch

After log-in the double-bagged Trace Metal samples are placed in plastic egg-crates in a cold room (2-6°C).

6.2 Sample Taring

The double bagged bottles are taken into the clean lab after placing them into large, clean HDPE bags. In the clean lab, garmented (gloves, frock, booties) personnel will remove and discard the outer sample bags after verifying that the etched bottle ID corresponds with bag designation. After re-gloving the sample handler weighs the bottles after temporarily removing them from the inner bag. Bottle weights are recorded in the sample bottle database, and sample volume calculated. Batches of sample bottles (in inner zip-lock bags) are then doubled bagged into two new large UHMWPE bags and refrigerated (2-6°C).

6.3 Spiking

Batch runs of approximately 20 samples are developed, and on the day prior to ICP-MS analysis, the designated samples are retrieved from storage. Clean-room personnel working under a laminar flow clean bench remove sample bottles from inner bag, and spike a previously calculated volume of mixed internal standard solution into the sample bottle. Sample volumes are determined after bottle and sample weights have been recorded. The sample is mixed and allowed to equilibrate for at least one hour. An approx. 12 mL subsample for ICP-MS analysis is then removed by pouring into a trace metal clean polypropylene capable tube (17 x 100 mm). Tubes are capped, mixed by gently shaking, and placed into polypropylene racks. Racks of tubes are sealed in UHMWPE bags and kept refrigerated in the clean lab until actual analysis begins.

6.4 Holding Times

ICP-MS analysis of any given sample will be completed within a maximum holding period of six months. If holding times are exceeded, the sample(s) in question will be flagged as estimated.

6.5 Pre-treatment

6.5.1 Filtrates

Field filtered samples acidified to a level of 0.6% with Ultrex $HNO_3$ are analyzed without further pre-treatment.

6.5.2 Totals

Acid-recoverable metals are determined on "total" samples as follows. Un-filtered samples are acidified in the field to a level of 0.6% Ultrex $HNO_3$. In the clean-laboratory, after

taring, the samples are spiked with an additional 2.5 mL of concentrated Ultrex $HNO_3$, bringing the acid concentration to 1.6%. Sample bottles are placed in a laboratory oven maintained at 60°C, after replacement of field outer bags with designated oven outer bags. Samples are heated for a period of 12 hours, after which they are allowed to cool at room temperature. Bottle seal integrity is checked before placing samples in temporary refrigerated storage. The samples are not filtered after heating.

# 7.0 Instrumental Analysis

7.1 Mass Selection

7.1.1 Analyses

| | |
|---|---|
| Aluminum (Al): | monoisotopic, mass 27 |
| Chromium (Cr): | masses 50, 52 and 53 monitored. |
| Copper (Cu): | masses 63 and 65 monitored. |
| Zinc (Zn): | masses 64, 66, and 68 monitored. |
| Arsenic (As): | monoisotopic, mass 75 |
| Silver (Ag): | masses 107 and 109 monitored. |
| Cadmium (Cd): | masses 114, 111, and 110 monitored. |
| Lead (Pb): | masses 206, 207, and 208 monitored. |

**Note**: Elements Aluminum and Silver are not included in the Lake Michigan Tributary Loading Study, but are monitored for research studies.

7.1.2 Internal Standards

| (a) Field Spiked | | (b) Lab Spiked | |
|---|---|---|---|
| Yttrium (Y): | mass 89 | Gallium (Ga): | mass 71 |
| Holmium (Ho): | mass 165 | Indium (In): | mass 115 |
| Ytterbium (Yb): | mass 174 | Bismuth (Bi): | mass 209 |
| Thorium (Th): | mass 232 | | |

7.1.3 Isobaric and Spectral Interference

For those analyses with multiple isotopes, several isotopes are monitored to facilitate spectral corrections. In addition, a suite of masses of potential elemental and molecular interferences are monitored to allow for spectral corrections at the extremely low ambient analyte levels. The spectral correction equations used will be reported with each run

A summary of molecular and elemental interferant masses to be evaluated for each analyte element are as follows:

| | |
|---|---|
| Aluminum: | none |
| Arsenic: | masses 77, 82 |
| Cadmium: | masses 98, 106, 108, 118, 120 |

| | |
|---|---|
| Chromium: | masses 13 |
| Copper: | 60, 61, 62 |
| Indium: | mass 118 |
| Lead: | none |
| Silver: | 90, 98 |
| Zinc: | none |

Interference equations for the analyses of interest are summarized below:

?%BKGD = ( I101 + I125 ) / 2
?AL27 = I27 - ?%BKGD
?CR52 = I52 - ?%BKGD
?%CLO51 = I51 - (415 * I50)
?%CLO53 = I53 - (0.1133652 * ?CR52)
?%ARCL77 = I77 - (0.84842 * I82) - ?%BKGD
?%ARCL75 = ?%ARCL77 * 3.06
?%CAOO76 = I76 - 5.368 * (I78-2.669*(I82-I83))
?%CAOO75 = 0.0671 * (?%CAOO76 - ?%BKGD)
?CR53 = I53 - (0.328 * ?%CLO51) - ?%BKGD - (0.0031 * I13)
?CU63 = I63 - ?%BKGD
?CU65 = I65 - ?%BKGD
?ZN66 = I66 - ?%BKGD
?AS75 = I75 - ?%BKGD
?CD110 = I110 - (0.00079 * I98) - ?%BKGD
?CD111 = I111 - (0.0014 * I98) - ?%BKGD
?CD114 = I114 - (0.0268 * (I118 - ?%BKGD)) - ?%BKGD
?AG107 = I107 - (0.0006 * I98) - (0.001 * I90) - ?%BKGD
?AG109 = I109 - (0.0004 * I98) - ?%BKGD
?IN115 = I115 - (0.0149 * I118)
?PB206 = I206 - I211
?PB207 = I207 - I211
?PB208 = (I208 - I211) + ?PB206 + ?PB207
?%CAOH59 = 0.312 * (I61 - (0.0478 * I60)) - ?%BKGD
?%AROH59 = 0.604 * (I53 - 0.113 * (I52 - ?%BKGD))
?CO59 = I59 - ?%CAOH59 - ?%BKGD

I = Intensity at a given mass.
BKGD = Background intensity.

7.1.4 Oxide Formation

At least one of the following three sets of parent/oxide/hydroxide masses will be monitored to assess the extent of oxide formation:

Yttrium (Y,89)
Yttrium Oxide (YO, 105)
Yttrium Hydroxide (YOH, 106)

Cerium (Ce, 140)
Cerium Oxide (CeO, 156)
Cerium Hydroxide (CeOH, 157)

Thorium (Th, 232)
Thorium Oxide (Th, 248)
Thorium Hydroxide (Th, 249)

7.1.5 Instrument Background

The following masses will be monitored to assess background instrumental noise: 99, 101, 125, and 211.

7.1.6 Element Menu

An example element menu is outlined in Appendix 5.

7.2 Contamination Reduction

7.2.1 Glassware

Sample introduction components (front-end) of the ICP-MS are regularly decontaminated to ensure optimum performance at ultra-trace levels. All glassware (torch, spray chamber, elbow, nebulizer, tube adaptor) is soaked in 25% reagent grade nitric acid overnight, rinsed with MQ water, installed, and flushed (by nebulization) with 3% trace metal grade nitric acid before use. The glassware is re-cleaned after every run sequence/batch. Change of glassware is noted on the ICP-MS operational log.

7.2.2 Tubing

All tubing from peri-pump to pneumatic nebulizer, from peri-pump to ultrasonic nebulizer, and from ultrasonic nebulizer to torch is Teflon. The Teflon tubing is initially cleaned in the same manner as all other Teflon ware [acetone, 50% HCl, 50% $HNO_3$, 1% $HNO_3$ (see Equipment Preparation)]. Flexible peri-pump tubing is changed at least once per week and is initially prepared by pumping 1 L of 3% trace metal grade $HNO_3$ through tubing. Tubing changes are noted on the ICP-MS operational log.

7.2.3 Cones

Instrument cones (sampler and skimmer) are changed after every run sequence. They are cleaned by polishing with POLARIS powder, followed by sonication for two 15 minute periods in MQ water (water is changed between periods) and a final 15 minute sonication in acetone. Clean cones are placed in polyethylene gloves and stored in small plastic jars.

7.2.4 Handling

Cleaning of components is performed in the clean room, and clean cones, glassware, and tubing is handled only with PE gloved hands.

Extreme care must be taken to minimize the possibility that the ICP-MS could become contaminated by samples with high metal concentrations. Samples with transition metal levels greater than 25 µg $L^{-1}$ should either be diluted or run on a different instrument. To achieve optimum performance it may be required to group samples of similar matrix.

7.3 ICP-MS Setup and Pre-qualification

A QA notebook containing dedicated forms for each of the control procedures is maintained, and where practical a parallel electronic database is also kept (See Summary Table I).

7.3.1 Warm up

Instrument shall warm up in analyze mode (multiplier on-line) while nebulizing an acidified (2-3% $HNO_3$, Trace Metal Grade ) MQ rinse solution for an minimum of 30 minutes before calibration and blank checks are performed.

7.3.2 Mass Calibration

A 5 µg $L^{-1}$ (pneumatic) or 1 µg $L^{-1}$ (ultrasonic) tuning solution [Be(9); Co(59); In(115); La(139) or Ce(140); Bi(209); U(238)] is used for instrument mass calibration. The tuning solution is run prior to analyte calibration, and whenever response/resolution is altered. Masses must agree within 0.1 amu of actual before proceeding with analyses. A record of tuning solution preparation is kept in the standard solution log. Tuning data will be logged on a dedicated form in the QA document.

7.3.3 Response Calibration-Mass Linearity

Linearity of response as a function of mass is examined by performing a response calibration with a tuning solution. The guidance criteria for response of Be, Co, La, and Bi with respect to In are: $^{9}Be/^{115}In$ = 0.25-1.0; $^{59}Co/^{115}In$ = 0.75-1.50; $^{139}La/^{115}In$ = 0.75-1.25; $^{209}Bi/^{115}In$ = 0.5-1.1. These criteria are used as predictors of possible sensitivity problems with analyte elements. As long as analyte sensitivity criteria are met, failure of response calibration criteria is considered as a warning to check instrument, but does not invalidate run sequence. Response calibration data are logged in QA document.

7.3.4 Detector Cross-Calibration

Pulse-counting and analog modes of detector are cross-calibrated by running a higher level tuning solution. The procedure is performed at least twice a week and when ever multiplier settings are altered.

7.3.5 Resolution Check

Appropriate resolution is confirmed from a scan of a 5 µg $L^{-1}$ multi element tuning solution. The baseline between isotope peaks of a high mass element (Pb: 206, 207, 208) and low mass element (Mg: 25, 26) are examined. Baseline must be resolved within at

least 10 raw counts. Resolution data, and confirmation (hard copy of scan) is logged in QA document. If mass calibration or resolution are out of control then the instrument must be tuned or otherwise adjusted to meet criteria before analyses can proceed.

7.3.6 Memory Check

A memory check solution containing all the analyte elements at 25 µg $L^{-1}$, followed by two MQ blanks, is run to check rinse out performance. Currently our protocols call for an eight minute rinse between samples. Rinse out performance will be checked once a day on a tuned and calibrated instrument before actual samples are run. Rinse levels in second MQ blank (mean of seven replicate acquisitions) may not exceed reporting limits. If rinse levels are out of control, then the Memory Check test is repeated. If second test fails then the source of contamination must be isolated and corrected before samples are run.

7.3.7 Blank Acceptance

After mass, resolution, and response calibrations, and memory check have been executed, a calibration blank is run for 10 replicate acquisitions. Interference corrected analyte blank levels in either (a) calibration blank, or (b) second MQ rinse of Memory Check must be below previously established limits. If blank criteria are not met, the source of contamination must be isolated before proceeding with analyses. Blank criteria are shown in the table below:

**Blank Criteria (µg $L^{-1}$)**

| Element | Pneumatic | Ultrasonic |
|---|---|---|
| Aluminum | 0.4 | 0.4 |
| Arsenic | 0.060 | 0.040 |
| Cadmium | 0.007 | 0.004 |
| Chromium | 0.2 | 0.1 |
| Copper | 0.060 | 0.040 |
| Lead | 0.007 | 0.005 |
| Silver | 0.007 | 0.004 |
| Zinc | 0.060 | 0.040 |

**Note**: Elements Aluminum and Silver are not included in the Lake Michigan Tributary Loading Study, but are monitored for research studies.

7.3.8 Calibration - Sensitivity

High purity, individual metal, NIST traceable, metal standards (prepared with $HNO_3$) are obtained from High Purity Standards Corporation. Diluted, multi-element calibration solutions are prepared with MQ water, stabilized with 1-2% Ultrex $HNO_3$, and are stored in FEP bottles. These standards are coded and recorded in standard solution log. Working solutions are prepared approximately bi-weekly. Linear ranges are established in dedicated studies run prior to sample analysis, and results logged in QA document. Analyte calibration is established using one standard and a calibration blank during routine sample analysis. The following calibration concentrations are used:

**Calibration Standard Concentrations**
**µg $L^{-1}$**

| Element | Pneumatic | | Ultrasonic | |
|---|---|---|---|---|
| | Check | High | Check | High |
| Ag | 2.0 | 1.0 | 1.0 | 2.0 |
| As | 2.0 | 5.0 | 1.0 | 2.0 |
| Al | 2.0 | 20. | 1.0 | 10. |
| Cd | 2.0 | 1.0 | 1.0 | 2.0 |
| Cr | 2.0 | 5.0 | 1.0 | 2.0 |
| Cu | 2.0 | 5.0 | 1.0 | 2.0 |
| Pb | 2.0 | 5.0 | 1.0 | 2.0 |
| Zn | 2.0 | 5.0 | 1.0 | 2.0 |

The calibration slope is determined by fitting a line from 0,0 to the blank subtracted standard. Calibration information for each run is summarized in a dedicated form which becomes part of the QA document.

Sensitivity criteria have been established and must be met before sample analysis can proceed. Sensitivity is verified during the analyte calibration procedure. If the initial sensitivity test fails, then both cones should be replaced. If cone replacement does not restore necessary sensitivity, and other front-end factors have been checked, then multiplier voltage level should be adjusted to correct sensitivity. Sensitivity factors and multiplier settings are recorded on a dedicated form in the QA document.

Sensitivity threshold criteria are given below:

**Sensitivity Criteria**
**CPS/ppb**

| Element | Pneumatic | Ultrasonic |
|---|---|---|
| Aluminum (27) | 60,000 | 400,000 |
| Arsenic (75) | 8,000 | 30,000 |
| Cadmium (114) | 15,000 | 60,000 |
| Chromium (52) | 50,000 | 400,000 |
| Copper (63) | 30,000 | 150,000 |
| Lead (208) | 60,000 | 350,000 |
| Silver (107) | 25,000 | 150,000 |
| Zinc (66) | 7,000 | 30,000 |

**Note**: Elements Aluminum and Silver are not included in the Lake Michigan Tributary Loading Study, but are monitored for research studies.

7.3.9 Stability

Stability is verified with the analyte calibration solution. RSD's (minimum of four replicates) for each element must be better than control specification (currently 5%) before continuing with analyses. Stability data is logged on dedicated form in QA document.

7.3.10 ICP-MS Operation Log

Significant ICP-MS operating parameters, gas flows, vacuum levels, lens settings, power levels, operators, etc are recorded for each run sequence in the instrument log book.

7.4 Data Acquisition

7.4.1 General

Elemental quantification will be in the peak-jumping mode. A minimum of four replicate integrations are obtained during each sample analysis. Samples are aspirated for at least 30 seconds after appearance of peak before collecting data. Metal concentrations in units of $\mu g\ L^{-1}$ are recorded in the instrument data report for each integration. The mean value will be entered into an electronic spreadsheet/database. The RSD of replicate integrations for any given sample analysis must be <15% for analyses less than five times reporting limit. If RSD criteria fails then the sample must be re-run. If upon re-run, the RSD criteria is still not met, then the data will be judged estimated. Failed samples are recorded in the QA document. Data from calibration blanks, background noise evaluation,

sensitivity, and high-purity water analysis will be used in determining appropriate blank to subtract for any given run.

7.4.2 Internal Standards (IS)

A minimum of three internal standards are used to correct for matrix suppression and sensitivity variations. The internal standards used are: Ga (71), In (115), and Bi (209), added at a concentration of 5 μg $L^{-1}$ for ultrasonic and pneumatic nebulization. Internal standards are added to the sample with electronic digital pipets, not with the peri-pump. For samples, our internal standard response criteria is >30% and <140% of the internal standard response in the calibration blank. Samples are re-run with new cones and/or a 1+1 dilution if IS response criteria are not met. Failed samples are recorded in the QA document. The criteria for standards in 1-2% $HNO_3$ is an internal standard response between 50% and 125% of calibration blank. If standards fail then the previous sample results are marked as estimated, and are later re-run with new cones. Selected samples from each of the tributaries are screened for the presence of indigenous internal standard elements. The internal standard spiking solution is scanned for the presence of contaminants and stability.

# 8.0 ICP-MS QA/QC

8.1 ICV

The initial calibration verification solution (ICV) is run immediately after the first calibration and must agree within ±10/15% (PNU/USN) before proceeding with analyses. If the ICV fails, the run is stopped, the instrument recalibrated, and the ICV re-run with a new solution. The ICV is prepared separately from the calibration solution and at a different concentration so that response linearity can be verified. ICV results are recorded on a dedicated form in the QA document.

8.2 Check Standard

The continuing calibration verification solution (CCV) and continuing calibration blank (CCB) are run after a maximum of 10 samples and at the end of a run. Calibration slopes (blank corrected) must agree within 10/15%, (PNU/USN) for all metals except Al, and Cr, which must agree within ±15% (PNU). If calibration is out of control, then either the instrument must be recalibrated and the set of out of control samples re-run, or sample results resloped after consultation with QA manager. If a sample re-run as a result of a CCV failure, again falls under a CCV failure then the sample data will be judged acceptable if the CCV falls within the range of ±15% (±20% Al, Cr); and judged estimated if CCV falls within the range of ±25% (±30% Al,Cr). CCV results are recorded on a dedicated form in the QA document.

8.3 IDL

An IDL subset determination is performed on a daily basis by running a spiked blank. [three times the average of the standard deviations of seven consecutive measurements of a spiked blank (5x-15x IDL) obtained on three nonconsecutive days]. Typical spike concentrations are 200 ng $L^{-1}$. Run sequence results are logged on a dedicated form in the QA document. Metal concentrations in this standard are well below levels in the high calibration solution so that

intensity linearity may be confirmed at near reporting limit levels. An additional IDL estimate can be obtained from the 10 replicates of the calibration blank. Blank spikes must recover within ±15% (As, Cd, Pb, Zn); ±20% (Cu); and ±25% (Cr) of accepted values.

8.4 Check Blanks

Check blanks are run before the ICV (ICB) and paired with each of the three CCV's (CCB's). Analyte levels in check blanks and calibration blank are considered acceptable if they do not exceed Blank Acceptance Criteria (see Table) or do not represent more than 5% of actual sample signal. Sample and QC data may be blank corrected if a definite trend in CCB data above background levels is observed.

8.5 SRM's and LCS

One certified standard reference solution (SRM) and one laboratory control sample (LCS) are run with each batch sequence. The SRM is run three times during the run sequence. Our current SRM is the Canadian trace element standard, SLRS-3. The LCS is a pooled Lake Michigan tributary sample, amended with certain metals. LCS "certified" concentrations will be established by seven replicate ICP-MS analyses. SRM and LCS data from each run are logged on a dedicated form and kept in the QA document. Control limits for the SRM and LCS standards are given in the table below. If at least one of the three SRM controls run during the batch sequence falls within the control limits, then the sample data will be considered in control. Samples must be re-run if all three SRM's are out of control. Sample data will be judged estimated if upon re-run, all three SRM samples are again out of control.

**SRM - Criteria**
**µg $L^{-1}$**

| Element | SLRS-3[#] | |
|---|---|---|
| | **Certified Levels** | **Control Range** |
| Aluminum | 31 ± 3 | 25 - 37 |
| Arsenic | 0.72 ± 0.05 | 0.58 - 0.86 |
| Cadmium | 0.013 ± 0.002 | 0.009 - 0.017 |
| Chromium | 0.30 ± 0.04 | 0.21 - 0.39 |
| Copper | 1.35 ± 0.07 | 1.15 - 1.55 |
| Lead | 0.068 ± 0.007 | 0.054 - 0.082 |
| Silver | not certified | not certified |
| Zinc | 1.04 ± 0.09 | 0.94 - 1.36 |

[#]Canadian Riverine Water Reference Material for Trace Metals.
National Research Council Canada - Institute for Environmental Chemistry

**Note**: Elements Aluminum and Silver are not included in the Lake Michigan Tributary Loading Study, but are monitored for research studies.

**LCS - Criteria**
**µg $L^{-1}$**

| Element | LCS (0524) | |
|---|---|---|
| | **Certified Levels** | **Control Range** |
| Aluminum | 24 ± 2.5 | 19 - 29 |
| Arsenic | 0.35 ± 0.03 | 0.28 - 0.42 |
| Cadmium | 0.003 ± 0.001 | 0.002 - 0.004 |
| Chromium | 0.41 ± 0.05 | 0.29 - 0.53 |
| Copper | 0.14 ± 0.02 | 0.11 - 0.17 |
| Lead | 0.088 ± 0.007 | 0.070 - 0.106 |
| Silver | not certified | not certified |
| Zinc | 0.40 ± 0.04 | 0.32 - 0.48 |

8.6 Replication

At a minimum, 20% of actual samples are replicated. The acceptance criteria (RPD) for within run sample duplicates for sample values >5x reporting limit are ±10% for As, Cu, Pb, and Zn; ±15% for Al, Cd and Cr. If a given replicate does not fall within control limits then it must be re-run. If after re-run, the relative standard deviation of the three determinations is >10% (As, Cu, Pb, Zn), >15% (Al, Cd, Cr) then the data is judged as estimated. Steps are taken at this point to determine the reason for the variance: Variation of individual integrations within a given analysis are examined and sample matrix is scrutinized. At least two sample - replicate pair are run within every 20 sample batch run. The acceptance criteria (RPD) for sample replicates run in different batches for sample values >5x reporting limit are ±15% for As, Cu, Pb, and Zn; ±20% for Al, Cd and Cr. If a given replicate does not fall within control limits then it must be re-run. If after re-run, the relative standard deviation of the three determinations is >15% (As, Cu, Pb, Zn), >20% (Al, Cd, Cr) then the data is judged as estimated.

8.7 Matrix Spike

Matrix spikes must recover within 70% to 125% of accepted value. At least two spike sample pairs are run with each batch of 20 actual samples (typically two lab spike pairs and one field spike pair). Representative spiking levels are: 0.050 µg $L^{-1}$ Cd; 1.00 µg $L^{-1}$ As, Cr, Cu, Pb, and 2.00 µg $L^{-1}$ Zn. If any element fails, the sample must be reanalyzed after dilution or other matrix modification technique. Spiked blanks are also run. If recovery of analyte is outside of control limits on re-analysis then results are qualified as estimated.

8.8 Interference Check

An interference check solution along with a mixed trace element standard is run at least once per week at the end of a run sequence to verify interference correction equations. Levels of interferents in the test solution are listed in the table below. The analyses of concern are run at a level of 5.0 µg $L^{-1}$. Acceptance criterium is ±20% of established value.

**Interference Check Solution**
**Levels in mg $L^{-1}$**

| Element | Concentration |
|---|---|
| Aluminum | 100 |
| Calcium | 100 |
| Carbon | 50 |
| Chloride | 500 |
| Iron | 100 |
| Magnesium | 100 |
| Molydenum | 0.005 |
| Phosphorus | 5 |
| Potassium | 20 |
| Sodium | 50 |
| Sulfur | 50 |

8.9 ICP/MS Sequence, Sample Order Summary

1 CALIB BLANK
2 "HIGH STD - 5 ppb Cr, Cu, As, Pb; 10 ppb Zn; 1 ppb Cd"
3 ICB
4 ICV - 2 ppb ALL
5 SLRS-3 #1
6 LCS
7 SAMPLE 1
8 SAMPLE 1 DUP
9 "SAMPLE 1 LAB SPIKE ( 1.000 µg/L Cr, Cu, As, Pb; 2µg/L Zn; 0.050 µg/L Cd)"
10 SAMPLE 2
11 SAMPLE 2 LAB SPIKE
12 SAMPLE 3
13 SAMPLE 4
14 SAMPLE 4 DUP
15 CCB#1
16 CCV#1 - 2PPB SOLN
17 BLANK SPIKE 0.200 µg/L

18 SAMPLE 5 (METHOD BLANK)
19 SAMPLE 6 (METHOD BLANK)
20 SAMPLE 7
21 SAMPLE 8 (FIELD SPIKE OF SAMPLE 7)
22 SAMPLE 9
23 SAMPLE 10
24 SAMPLE 11
25 SAMPLE 12
26 SAMPLE 13
27 CCB#2
28 CCV#2
29 SLRS-3 #2
30 SAMPLE 14
31 SAMPLE 15
32 SAMPLE 16
33 SAMPLE 17
34 SAMPLE 18
35 SAMPLE 19
36 SAMPLE 20
37 CCV#3
38 CCB#3
39 SLRS-3 #3
40 RINSE
41 HIGH STD
42 INTERFERENCE CHK
43 RINSE

8.10 Quality Assurance Documentation Summary

ICP-MS Prequalification Logs

10. Instrument log of operating settings and conditions.
11. Mass calibration data.
12. Mass resolution data.
13. Response calibration - linearity.
14. Short term stability.
15. Blank data [acceptance test].
16. Sensitivity summary.
17. IDL summary.
18. Memory check results.
19. Internal standard purity scan.

ICP-MS Calibration Logs

20. Calibration solutions - dates of preparation and scans of purity.
21. Calibration linear ranges.
22. Calibration data - slopes.
23. Interference equations applied.

ICP-MS Run QC

24. Batch design.
25. CCV, CCB run summary.
26. LCS, SRM run summary.
27. Run replicate summary.
28. Run spike summary (lab).
29. Internal standard recovery summary.

Field QC

30. Field spike summary - rare element recovery.
31. Field spike summary - metals of concern.
32. Field blank summary - bottle blanks.
33. Field blank summary - filtration blanks.
34. Field blank summary - tubing - sampler blanks.
35. Field replicate summary.

## 9.0 Detection Levels

ICP-MS detection limits for ultrasonic and pneumatic nebulization for the elements of concern are shown in the table below.

**Detection Limits[#]**
**ng $L^{-1}$**

| Element | Pneumatic | Ultrasonic |
|---|---|---|
| Aluminum | 25 | 15 |
| Arsenic | 15 | 10 |
| Cadmium | 2.5 | 0.5 |
| Chromium | 20 | 8 |
| Copper | 8 | 4 |
| Lead | 3 | 0.5 |
| Silver | 1.5 | 0.3 |
| Zinc | 10 | 2.5 |

[#]Three times the standard deviation of seven consecutive measurements of a spiked blank (5x-15x IDL).

# Appendix 1.

## ICP-MS Batch Analysis QA Outline

**15-18 Samples per Batch**

| Sample Type | Frequency |
|---|---|
| ICP-MS Qualification | |
| -Blank Levels | Before each sample batch |
| -Stability | Before each sample batch |
| -Sensitivity | Before each sample batch |
| -Resolution | Before each sample batch |
| -Interference Check | Once per week |
| Blanks Levels During Run | |
| Calibration Blank | One per batch |
| Check Blanks | Four per batch |
| Memory Check | One per batch |
| Recovery | |
| Lab Analyte Spike, Blank Matrix | One per batch |
| Lab Analyte Spike, Sample Matrix | Two per batch |
| Internal Standards, 3-metals | All Samples |
| Precision | |
| Replicate Sample Acquisitions | Four per sample |
| Lab Sample Replicates (within batch) | Two per batch |
| Lab Sample Replicates (different batch) | 20% |
| Accuracy | |
| Standard Reference Material (SLRS-3) | Three per batch |
| Laboratory Control Sample (Trib Matrix) | One per batch |

# Appendix 2.

## Summary of ICP-MS QA/QC Protocols

**Summary of ICP-MS QC Protocol**
**Pre-Qualification A**

| Type | Frequency | Concentration | Acceptance Criteria |
|---|---|---|---|
| Warm - Up | Daily | 2-3% HNO | > 30 minutes in Analyze Mode |
| Mass Calibration | Before Each Batch Tuning Solution | 5 µg $L^{-1}$ Pneumatic<br>1 µg $L^{-1}$ Ultrasonic | ≤ 0.1 amu from actual value.<br>$^{9}Be$, $^{59}Co$, $^{115}In$, $^{139}La$, $^{209}Bi$, $^{238}U$ |
| Response Calibration# | Before Each Batch Tuning Solution | 5 µg $L^{-1}$ Pneumatic<br>1 µg $L^{-1}$ Ultrasonic | $^{9}Be/^{115}In$ = .25-1.0; $^{59}Co/^{115}In$ = .75-1.5<br>$^{139}La/^{115}In$ = .75-1.25; $^{209}Bi/^{115}In$ = .5-1.1 |
| Detector Cross Calibration | Twice Per Week | 50 µg $L^{-1}$ Pneumatic<br>5 µg $L^{-1}$ Ultrasonic | For $^{115}In$: Pulse/Analog >200 |
| Resolution Check | Before Each Batch Tuning + Mg, Pb | 5 µg $L^{-1}$ | Baseline resolved to ≤ 10 raw counts for Mg(25,26) and Pb(206,207,208) |
| Internal Standards IS | Every Acquisition $^{71}Ga$, $^{115}In$, $^{209}Bi$ | 5 µg $L^{-1}$ | 50-125% of Cal. Blk. For Standards<br>30-140% of Cal. Blk. For Samples |

# Informational Test - other checks of performance take precedence (see text).

# Appendix 2.

## Summary of ICP-MS QA/QC Protocols - Continued

**Summary of ICP-MS QC Protocol**
**Pre-Qualification B**

| Type | Frequency | Units | Acceptance Criteria (Pneumatic /Ultrasonic) | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | $^{75}$As | $^{114}$Cd | $^{52}$Cr | $^{63}$Cu | $^{208}$Pb | $^{66}$Zn |
| Memory Check 25 µg $L^{-1}$ | Before Each Batch | ng $L^{-1}$ | 60 | 7 | 200 | 60 | 7 | 60 |
| Stability Check | Before Each Batch | RSD | 4% @ 5 ppb | 4% @ 1 ppb | 4% @ 5 ppb | 4% @ 5 ppb | 4% @ 5 ppb | 4% @ 5 ppb |
| Blank Qualification | Before Each Batch | ng $L^{-1}$ | 60 / 40 or <5% | 7 / 4 or <5% | 200 / 100 or <5% | 60 / 40 or <5% | 7 / 5 or <5% | 60 / 40 or <5% |
| Sensitivity Qualification | Before Each Batch | CPS/ ppb | 8,000 / 30,000 | 15,000 / 60,000 | 50,000 / 400,000 | 30,000 / 150,000 | 60,000 / 350,000 | 7,000 / 30,000 |
| Interference Check | End of Run 2 per week | % of true | ± 20% | ± 20% | ± 20% | ± 20% | ± 20% | ± 20% |

# Appendix 2.

## Summary of ICP-MS QA/QC Protocols - Continued

**Summary of ICP-MS QC Protocol**
**Run Sequence Part A**

| Type | Frequency | Units | Acceptance Criteria | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | $^{75}$As | $^{114}$Cd | $^{52}$Cr | $^{63}$Cu | $^{208}$Pb | $^{66}$Zn |
| Initial Check Blank, ICB | 1 per Batch Before ICV | ng $L^{-1}$ | 60 / 30 or < 5% | 7 / 4 or < 5% | 200/100 or < 5% | 60 / 20 or < 5% | 7 / 5 or < 5% | 60 / 25 or < 5% |
| Initial, ICV Calib. Verif. 2 or 1 µg $L^{-1}$ | 1 per Batch Before Samples | % | ±10/15% | ±10/15% | ±10/15% | ±10/15% | ±10/15% | ±10/15% |
| Check, CCV Standard 2 or 1 µg $L^{-1}$ | Every 10 Samples 3 per Batch | % | ±10/15% | ±10/15% | ±15% | ±10/15% | ±10/15% | ±10/15% |
| Check Blank CCB | Every 10 Samples 3 per Batch | ng $L^{-1}$ | 60 / 40 or < 5% | 7 / 4 or < 5% | 200/100 or < 5% | 60 / 40 or < 5% | 7 / 5 or < 5% | 60 / 40 or < 5% |
| Method Blanks | 2 per Batch | ng $L^{-1}$ | 100 | 16 | 160 | 80 | 16 | 120 |

# Appendix 2.

## Summary of ICP-MS QA/QC Protocols - Continued

**Summary of ICP-MS QC Protocol**
**Run Sequence Part B**

| Type | Frequency | Units | Acceptance Criteria (Pneumatic/Ultrasonic) | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | $^{75}$As | $^{114}$Cd | $^{52}$Cr | $^{63}$Cu | $^{208}$Pb | $^{66}$Zn |
| Analyte Spike Blank - Lab | 1 per Batch MDL | % of true | ± 15 % @ 0.2 ppb | ± 15 % @ 0.2 ppb | ± 25 % @ 0.2 ppb | ± 20 % @ 0.2 ppb | ± 15 % @ 0.2 ppb | ± 15 % @ 0.2 ppb |
| Analyte Spike Matrix - Lab | 2 per Batch | % of true | 70 - 125% @ 1 ppb | 70 - 125% @ 0.5 ppb | 70 - 125% @ 1 ppb | 70 - 125% @ 1 ppb | 70 - 120 % @ 1 ppb | 70 - 120 % @ 2 ppb |
| Analyte Spike Matrix - Field | 1 per Batch** | % of true | 70 - 125% | 70 - 125% | 70 - 125% | 70 - 125% | 70 - 125% | 70 - 125% |
| Analyte Spike Blank - Field | 1 per Batch** | % of true | ± 15 % | ± 15 % | ± 25 % | ± 20 % | ± 15 % | ± 15 % |
| SRM SLRS-3 | 3 per Batch | µgL$^{-1}$ | .58-.86 | .009-.017 | .21-.39 | 1.15-1.55 | .054 - .082 | .94 - 1.36 |
| LCS# Trib. Mix | 1 per Batch | µgL$^{-1}$ | 1.02-1.83 (1.46) | 0.033-0.059 (.047) | 0.90-1.61 (1.29) | 1.20-2.15 (1.72) | .53 - .94 (.75) | 3.00 - 5.30 (4.24) |

** One field spiked sample is run with each batch, either a blank or river sample.
# LCS samples will vary over duration of study: values shown are for LCS-2-(a new LCS undergoing certification)
Values in parentheses are mean level of analyte in new LCS.

# Appendix 2.

## Summary of ICP-MS QA/QC Protocols - Continued

**Summary of ICP-MS QC Protocol**
**Run Sequence Part C**

| Type | Frequency | Units | Acceptance Criteria | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | $^{75}$As | $^{114}$Cd | $^{52}$Cr | $^{63}$Cu | $^{208}$Pb | $^{66}$Zn |
| Replicate Acquisitions | 4 per Sample | RPD | ±10% >5x RL | ±15% >5x RL | ±15% >5x RL | ±10% >5x RL | ±10% >5x RL | ±10% >5x RL |
| Duplicate Samples Within Run | 2 per Batch | RPD | ±10% >5x RL | ±15% >5x RL | ±15% >5x RL | ±10% >5x RL | ±10% >5x RL | ±10% >5x RL |
| Duplicate Samples Overall | 20% | RPD | ±15% >5x RL | ±20% >5x RL | ±20% >5x RL | ±15% >5x RL | ±15% >5x RL | ±15% >5x RL |

# LCS samples will vary over duration of study
(values shown are outdated - a new LCS is under certification)

RL = Reporting Limit

# Appendix 3.

## Summary of Calculation Procedure
## Outline of calculation methods used by UW-Water Chemistry Program to generate concentration data from ICP-MS instrumentation for LMMB study

1. Count rates are obtained by peak-jumping to specific isotopes as the quadrapole "sweeps" the mass range. We look at three points (0.05 AMU apart) on the peak for each selected mass, which are subsequently averaged. Dwell times on each peak vary (see attached isotope list), but range from 10-200 msec. For an acquisition time of 90 seconds, approximately five "sweeps" are made.

2. The initial calibration, run just prior to the start of a batch, and after the instrument has passed a series of pre-qualification tests (see our SOP) involves running:

   a. An acidified mixed-metal calibration standard (see SOP for levels)
   b. An acidified high-purity water calibration blank

   The isotope count rates obtained from these analyses are processed through the correction equations (see below) and a line is fit through the *blank-subtracted* count rate and *0,0* to generate an initial response slope for each isotope.

   Linearity of response is determined in dedicated studies and is verified occasionally.

3. Three internal standards are spiked into each sample just before analysis, and used to evaluate changes in the response characteristics of the instrument over the course of a run. For each individual acquisition four response regions are defined over the mass spectrum by the internal standards. Linear interpolation between regions is used to generate a isotope specific response factor, which is ratioed with the response from the internal standards in the calibration blank. This ratio is applied to the raw count data before processing by correction equations.

4. We apply a series of equations to the internal standard processed count rate data to correct for electron multiplier noise, and isobaric and spectral interferences (see attached list). Multiplier noise (BKGD in interference equations) is obtained by collecting count rates at masses where no known isotopes/species exist. The equation corrected, response normalized data from one 90 second aspiration is stored and printed as one acquisition.

5. Three additional acquisitions are performed, stored and printed, and the mean of these four analyses is what we are reporting as the sample concentration.

6. In general no "blank" is subtracted from the sample results reported in Step 5. If the four to five check blanks run over the course of an analysis sequence indicate that a specific analyte was being picked up from the front-end of the instrument (e.g. cones or nebulizer), then a blank correction may be applied to the sample results after review in light of other QC checks and consultation with QA manager. If a sample is "instrument blank" corrected it is flagged and the magnitude of the correction reported. Specific instrument blank limits have been established and are given in our ICP-MS analysis SOP.

7. The contribution of analytes from the sample acidification solution that we use (50% Ultrex $HNO_3$, refer to SOP for amounts added to samples) is negligible, and therefore we do not report a blank subtraction for this contribution.

8. Other potential blank components, such as Teflon bottles, field handling, filter, sampling line, etc. were routinely quantified as part of the field QA program. In general the quantity of added analyte from these sources is extremely small and therefore no blank corrections have been applied to actual samples.

# Appendix 4.
## Example of Element Menu

ELEMENT MENU

File Name : TRACE ELEMENT USN 021795

Date Created : Wed 1 Dec 1993 Time Created : 15:32:30
Date Last Used : Wed 1 Dec 1993 Time Last Used : 15:32:30

Scan Parameters ...

Channels per AMU : 20
PC Dwell time (ms) : 320
Analog Dwell Time (ms) : 320
Collector Type : DUAL
Mass Range for Scan : 5.60 -> 249.54 amu

Skipped Mass Regions ...

| PC ... | Analog ... From | To |
|---|---|---|
| Automatic | 11.40 | 12.60 |
| | 19.40 | 22.60 |
| | 37.40 | 41.60 |
| | 79.40 | 80.60 |

Isotopes Selected/Peak Jump Parameters ...

| Element Name | Symbol | Mass | Abundance | Dwell Time | Points/peak | Collector |
|---|---|---|---|---|---|---|
| Aluminium | Al | 27 | 100.0 | 2000 | 3 | DUAL |
| SO | M+ | 48 | 99.8 | 10000 | 3 | DUAL |
| Chromium | Cr | 50 | 4.3 | 20000 | 3 | DUAL |
| Vanadium | V | 51 | 99.8 | 50000 | 3 | DUAL |
| Chromium | Cr | 52 | 83.8 | 50000 | 3 | DUAL |
| Chromium | Cr | 53 | 9.5 | 20000 | 3 | DUAL |
| Cobalt | Co | 59 | 100.0 | 10000 | 3 | DUAL |
| Nickel | Ni | 60 | 26.2 | 20000 | 3 | DUAL |
| MgCl | M+ | 61 | 27.8 | 20000 | 3 | DUAL |
| Nickel | Ni | 62 | 3.7 | 20000 | 3 | DUAL |
| Copper | Cu | 63 | 69.1 | 40000 | 3 | DUAL |
| Zinc | Zn | 64 | 48.9 | 20000 | 3 | DUAL |
| Copper | Cu | 65 | 30.9 | 40000 | 3 | DUAL |
| Zinc | Zn | 66 | 27.8 | 50000 | 3 | DUAL |
| Ba++ | M+ | 68 | 11.3 | 20000 | 3 | DUAL |
| Gallium | Ga | 71 | 39.8 | 25000 | 3 | DUAL |
| Germanium | Ge | 72 | 27.4 | 50000 | 3 | DUAL |
| Arsenic | As | 75 | 100.0 | 50000 | 3 | DUAL |
| CaO2 | M+ | 76 | 0.0 | 20000 | 3 | DUAL |
| CaO2 | M+ | 77 | 0.0 | 20000 | 3 | DUAL |
| CaO2 | M+ | 78 | 0.0 | 20000 | 3 | DUAL |
| Selenium | Se | 82 | 8.8 | 50000 | 3 | DUAL |
| Krypton | Kr | 83 | 11.5 | 50000 | 3 | DUAL |
| Yttrium | Y | 89 | 100.0 | 10000 | 3 | DUAL |
| Zirconium | Zr | 90 | 51.5 | 50000 | 3 | DUAL |
| Niobium | Nb | 93 | 100.0 | 50000 | 3 | DUAL |
| Molybdenum | Mo | 95 | 16.8 | 20000 | 3 | DUAL |
| Molybdenum | Mo | 98 | 24.0 | 20000 | 3 | DUAL |
| Ruthenium | Ru | 99 | 12.8 | 50000 | 3 | DUAL |
| Ruthenium | Ru | 101 | 17.0 | 50000 | 3 | DUAL |
| RuHe | M+ | 104 | 14.9 | 50000 | 3 | DUAL |

# Appendix 4. (cont'd)
## Example of Element Menu

| | | | | | | |
|---|---|---|---|---|---|---|
| YO | M+ | 105 | 99.8 | 20000 | 3 | DUAL |
| YOH | M+ | 106 | 99.7 | 20000 | 3 | DUAL |
| Silver | Ag | 107 | 51.3 | 200000 | 3 | DUAL |
| Palladium | Pd | 108 | 26.7 | 50000 | 3 | DUAL |
| Silver | Ag | 109 | 48.6 | 200000 | 3 | DUAL |
| Cadmium | Cd | 110 | 12.4 | 100000 | 3 | DUAL |
| Cadmium | Cd | 111 | 12.9 | 100000 | 3 | DUAL |
| Cadmium | Cd | 114 | 28.8 | 50000 | 3 | DUAL |
| Indium | In | 115 | 95.8 | 20000 | 3 | DUAL |
| Tin | Sn | 118 | 24.0 | 50000 | 3 | DUAL |
| Tin | Sn | 120 | 33.0 | 50000 | 3 | DUAL |
| Antimony | Sb | 121 | 57.2 | 10000 | 3 | DUAL |
| Tellurium | Te | 125 | 7.0 | 50000 | 3 | DUAL |
| Barium | Ba | 138 | 71.7 | 2000 | 3 | DUAL |
| Cerium | Ce | 140 | 88.5 | 10000 | 3 | DUAL |
| CeO | M+ | 156 | 88.3 | 20000 | 3 | DUAL |
| CeOH | M+ | 157 | 88.5 | 20000 | 3 | DUAL |
| Holmium | Ho | 165 | 100.0 | 10000 | 3 | DUAL |
| Ytterbium | Yb | 174 | 31.8 | 10000 | 3 | DUAL |
| Mercury | Hg | 202 | 29.8 | 50000 | 3 | DUAL |
| Mercury | Hg | 204 | 6.8 | 100000 | 3 | DUAL |
| Lead | Pb | 206 | 25.1 | 50000 | 3 | DUAL |
| Lead | Pb | 207 | 21.1 | 50000 | 3 | DUAL |
| Lead | Pb | 208 | 52.4 | 50000 | 3 | DUAL |
| Bismuth | Bi | 209 | 100.0 | 20000 | 3 | DUAL |
| PbOH | M+ | 211 | 21.1 | 50000 | 3 | DUAL |
| Thorium | Th | 232 | 100.0 | 50000 | 3 | DUAL |
| Uranium | U | 238 | 99.3 | 50000 | 3 | DUAL |
| ThO | M+ | 248 | 99.8 | 20000 | 3 | DUAL |
| ThOH | M+ | 249 | 99.7 | 20000 | 3 | DUAL |