# CARLSON ENVIRONMENTAL, INC.

*Sent by Messenger*

April 6, 2000 PN 9566C

Mr. John J. O'Grady
Remedial Project Manager
US EPA Region V
Superfund Division
77 West Jackson
Chicago, Illinois 606064

RE: Supplement to Laboratory Quality Assurance Program
Fansteel, Inc.
North Chicago, Illinois

Dear Mr. O'Grady:

The enclosed material is intended to supplement the *Quality Assurance Program* prepared by Great Lakes Analytical, the laboratory selected by Carlson Environmental, Inc. (CEI) to perform the laboratory analysis required in the proposed site investigation. Specifically, Great Lakes Analytical's *Quality Assurance Program* was submitted as Attachment D to CEI's *Site Investigation Work Plan*, dated April 1998.

The enclosed information supplements the *Quality Assurance Program*, addresses the pertinent comments in your response letter dated July 20, 1998, and includes revised laboratory Standard Operating Procedures (SOPs) for metals. The revisions were made to include tantalum.

Please feel free to contact Margaret Karolyi of CEI at (312) 704-8843 or Kevin Keeley of Great Lakes Analytical if you need any additional information.

Respectfully submitted,

CARLSON ENVIRONMENTAL, INC.

George Varela for

Margaret M. Karolyi, P.E.
Project Manager

enclosure

cc: Kevin Keeley, Great Lakes Analytical
Mark Steger, McBride Baker & Coles
Jon Jackson, Fansteel, Inc.

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Copy #: 6010-001

# GREAT LAKES ANALYTICAL

## STANDARD OPERATING PROCEDURE

## FOR

## ANALYSIS OF METALS USING ICP

## GLA 6010 BG

**Revision 2.2**

Approved By:

Department Manager: _____ Date: 4/5/00

Quality Assurance Manager: _____ Date: 4/5/00

Laboratory Director: _____ Date: 4-5-00

# 1.0 APPLICABILITY

This standard procedure (SOP) provides instructions for analysis of samples for trace metal content by ICP-OES. The procedure for the digestion of liquids is GLA 3015 BG, and for the digestion of solids GLA 3050 BG. This SOP is an interpretation of EPA Methods 200.7, Standard Methods no. 3020, and SW-846 no. 6010B. This SOP is to be used in conjunction with the analysts' in-laboratory training, the Great Lakes Analytical Chemical Hygiene Plan (CHP), and the Great Lakes Analytical Quality Assurance Program.

## 1.1 MATRICES

This method is applicable to digests prepared for ICP analysis from GLA 3015 BG and GLA 3050 BG. Samples are to be analyzed for metals within 6 months. Drinking water samples are analyzed per SM-3113-B.

## 1.2 REGULATORY APPICABILITY

40 CFR 121

# 2.0 SUMMARY

This method describes a technique for the simultaneous (or sequential) multi-element determination of trace elements in solution. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the ICP plasma torch where excitation occurs. The plasma torch consists of a flowing stream of argon which is ionized by an applied radio frequency of about 1.1 KW power (0.95-1.15 KW at 27-41 MHz). The field is inductively coupled to the ionized gas by a water cooled coil. Characteristic atomic-line emission spectra are produced by the high temperatures of the plasma torch (6000-8000 K). The spectra are dispersed by a grating spectrophotometer and the intensities of the lines are monitored by photomultiplier tubes. The currents from the photomultiplier tubes are controlled and processed by a computer system. A background correction technique is required to compensate for variable background contributions to the determination of trace elements.

# 3.0 SAFETY

## 3.1 GENERAL

This SOP does not address all safety issues associated with its use. A reference file of material safety data sheets (MSDS's) is available to all personnel, along with the Great Lakes Analytical Chemical Hygiene Plan. Gloves are worn when handling chemicals and reagents.

## 3.2 CHEMICAL HYGIENE PLAN

The Great Lakes Analytical Chemical Hygiene Plan (CHP) is designed to establish safe work procedures and minimize exposure to hazardous chemicals encountered in the laboratory. The CHP provides information to employees regarding potential hazards and training to minimize these hazards.

## 3.3 HAZARDOUS SAMPLES

All samples that are received by the laboratory have the possibility of containing hazardous pollutants. They should be treated with caution at all times. Gloves are worn when handling samples. Also see the Great Lakes Analytical SOP for Hazardous Sample Management.

### 3.4 PLASMA TORCH

The ICP plasma torch produces temperatures of 6000-8000 K and high levels of ultraviolet radiation. All instrument safety interlocks and shields must be in place and operational at all times.

## 4.0 INTERFERENCES

4.1 All water samples must be preserved by the addition of nitric acid to a pH of 2 or less. A low bias could result due to metals adhering to the sides of the sample container or precipitating out of solution.

4.2 Spectral interferences can be caused by the overlap of a spectral line from another element, unresolved overlap of molecular band spectra, background contribution, or stray light from the line emission of high-concentration elements. Spectral overlap can be corrected after monitoring the interfering element. Each metal must be optimized and the best wavelength chosen. Unresolved overlap requires selection of another wavelength. Background contribution and stray light can be compensated for by performing background correction. An Interference Check Standard and Blank are analyzed at the beginning and end of each day's analyses, and/or every 8 hours, to evaluate the performance of the instrument.

4.3 Changes in viscosity and surface tension can cause significant inaccuracies by interfering with sample flow to the plasma torch, especially in samples containing large amounts of dissolved solids. Physical interferences can be reduced by diluting the sample, by internal standardization with yttrium, or by using standard additions method.

For internal standarization, yttrium is added at a concentration of 1 ppm to all standards, blanks, and samples by the instrument. Sample intensities are adjusted for changes in yttrium response as a function of the instrument program.

4.4 Chemical interferences are characterized by molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not substantial with the ICP technique. They can be minimized by careful selection of operating parameters, buffering of samples, matrix matching, and standard addition procedures. TJA Only: Lithium carbonate (200 ppm) is automatically mixed with all standards and samples before analysis for buffering.

4.5 Daily monitoring test of the deionized water supply must have been performed and pass or meet appropriate criteria for analysis before the water can be used in sample preparation. All glassware to be used in the analysis must be cleaned and rinsed thoroughly with DI water. Periodic cleaning of sample preparation and analysis areas, will be performed.

## 5.0 RECORD KEEPING

5.1 Each analyst is responsible for keeping accurate and up-to-date records of all analyses performed.

5.2 ICP Log Book:

A log book will be maintained for all metals analyses performed on the ICP. All information regarding samples processed in the lab will be entered into this book. This information will include but is not limited to:

- Method reference number
- Sample matrix type
- GLA Sample I.D. (one complete for each set)

- LIMS batch reference number
- LCS and matrix spike information
- Analyst's signature and date analyzed
- Reviewer's signature and date, where applicable
- All dilution factors

This log should also include any unique observations noted in regard to specific samples. Space will be reserved on each page for calculations and notes. All unused portions of logbook pages must be z'ed out.

5.3 An instrument log book is also kept for records of scheduled and unscheduled maintenance. All entries must be initialed and dated.

5.4 Sample Schedule - All samples will be tracked through the lab using GLA sample I.D. numbers generated by the GLA LIMS system.

# 6.0 QUALITY CONTROL

## 6.1 QUALITY CONTROL SAMPLES

Quality control samples are run at a minimum 5% frequency (*i.e.* one set with every batch of twenty or less samples). The results of these samples are used to gauge accuracy and precision of the method. These samples include method blanks (MB), lab control samples (LCS), matrix spikes (MS) and matrix spike duplicates (MSD). The quality control samples contain all reagents and are subjected to all preparation steps. They are processed and analyzed along with test samples.

## 6.2 METHOD BLANK

Matrix-matched method blanks (MB) containing all reagents and subjected to all preparation steps are processed and analyzed along with the samples. Method blanks must produce a concentration below the reporting limit (*e.g.* PQL, EQL, ...) for an analytical batch to be valid. These samples provide a measure of laboratory and/or reagent contamination. Test sample results are not corrected for the method blank concentrations.

## 6.3 LABORATORY CONTROL SAMPLE (LCS)

An external (independently sourced) reference standard is prepared within the working range of the method and analyzed with each matrix per batch of twenty or less samples (*i.e.* minimum 5% frequency). The results of the samples must be within established control limits, or where there is not enough data to calculate control limits, within 15% of the known value. Appendix A contains information on spiking volumes and concentrations.

## 6.4 MATRIX SPIKED SAMPLES

Matrix spiked samples (MS and MSD) will be analyzed with a minimum frequency of 5% (*e.g.* one set per 20 or less samples per matrix) and are used to determine accuracy and precision of a method. The matrix spiked samples will be spiked using the same standards used to spike the LCS samples. The analyzed result of the matrix spikes must be within established control limits, or where there is not enough data to calculate control limits, within 25% of the known value.

## 6.5 INTERFERENCE CHECKS

The ICP instrument is checked initially and following analytical runs for interferences using an Interference Check Standard and an Interference Check Blank. These are samples containing high concentrations of interfering metals (Al, Ca, Mg, Fe). The Interference Check Standard also contains spiked analytes of interest (Ba, Cd, Cr, Pb, Ag).

### 6.6 QUALITY CONTROL TRACKING AND DATA REVIEW

The QC data is considered acceptable and actual samples results can be evaluated and reported by the analyst if all QC samples are within established control limits.

### 6.7 CORRECTIVE ACTION

If a quality control measure fails, corrective action is taken and documented to ensure the accuracy of the data that is reported. Examples of when corrective action sheets are filled out are:

- A sample or QC is re-analyzed. This may be due to the QC parameter failing or mislabeling of samples.
- Samples are reported with a QC result (blank, spike matrix) parameter out of control. In this case, not only should a corrective action be initiated, but the data must be flagged.
- A deviation from the normal SOP for the method is discovered (*e.g.* a digestion goes down to dryness or a different concentration of reagent is used) and the sample is analyzed and reported.
- An error in a previously reported sample is discovered.

## 7.0 SAMPLE MANAGEMENT

**7.1** The procedure for sample management are detailed in the Great Lakes Analytical SOP for sample receipt into the laboratory.

**7.2** Sample Schedule: Analysts keep track of sample throughput by using the Laboratory Information Management System (LIMS). The system is checked daily and a hard copy generated. Samples for this method are queued under "METP". The information includes:

- Client name.
- Sample numbers.
- Project name.
- Matrix.
- Hold time and turnaround time.

## 8.0 METHOD VALIDATION

### 8.1 QUALITY CONTROL BOOK

Method validation must be performed before any actual samples can be analyzed. Method validation studies are required to be stored in the QC logbook. Method exception studies must also be performed to validate any exception taken by proving equivalency with the unaltered method. The contents of the QC book include:

- Copy of the GLA Quality Assurance Program.
- Copies of GLA SOP and source methods.
- Copy of the precision and accuracy study for the method.
- Copies of all method detection limit studies and dates in use.
- Check standard recovery tabulations and control limits.
- Spike and spike duplicate recovery tabulations and control limits.
- Corrective action sheets.

### 8.2 QUALITY ASSURANCE PROGRAM

Internal audits will be performed periodically to assess analytical system performance. Performance evaluation samples will be analyzed periodically to assess laboratory performance. (Refer to the GLA Quality Assurance Program.)

### 8.3 ACCURACY AND PRECISION

Accuracy and precision for this method are tracked by analyzing spike and spike duplicate blanks (sample spikes and duplicates are also analyzed to check for matrix effects). The results are used to establish control limits - average ± 3 standard deviations for each analyte.

In addition, the ICP instrument is calibrated daily, and the calibration checked using a Check Standard Each individual analyte calibration must have a correlation coefficient, $r^2$, of at least 0.9950 to be usable. The concentrations of the Check Standard must be within 10% of the expected values.

### 8.4 METHOD DETECTION LIMIT STUDY

8.4.1 The method detection limit (MDL) is defined as the minimum concentration of analyte that can be determined with 99% confidence. It is determined as follows:

- Prepare a minimum of seven replicate samples at a concentration at or near the expected MDL. Carry these replicates through the entire sample preparation procedure and analysis.
- Calculate the MDL by taking the standard deviation of the results of the seven replicates and multiply by the Student's t value at n-1 degrees of freedom (3.143 for seven replicates).

8.4.2 Other factors such as matrix effects and instrument noise may affect the attainable detection limit. These should be quantified if possible and taken in to account when determining an MDL as the obtainable detection level may be artificially elevated due to these factors.

8.4.3 A new MDL study must be performed to re-evaluate the method if any major instrument maintenance or service is performed, if any new method exceptions or changes are made, or at least annually.

## 9.0 EQUIPMENT

9.1 ICP Emission Spectrophotometer, TJA 61E TRACE, Liberty 100, or equivalent
9.2 Volumetric flasks, 25-100 mL size.
9.3 Volumetric pipets, various sizes.

## 10.0 STANDARDS AND REAGENTS

10.1 Reagent water - ASTM Type II water (DI water). Type I reagent water should be used for the analysis of earth metals and low level lead.
10.2 Nitric acid - concentrated $HNO_3$, ACS/reagent grade, Fisher no. A509. **CAUTION:** Nitric acid is corrosive.
10.3 Hydrochloric acid - concentrated HCl, ACS/analytical reagent grade, Fisher no. A508. **CAUTION:** Hydrochloric acid is corrosive.
10.4 Sulfuric acid - concentrated $H_2SO_4$ - ACS/analytical reagent grade, Fisher no. A300. **CAUTION:** Sulfuric acid is corrosive.
10.5 Calibration standards - Standards are prepared in 10% nitric acid. Aliquot 1000 ppm individual analyte standards (purchased from Spex CertiPrep Assurance, Inorganic Ventures, or Ultra Scientific) for high standard (level 4) per Table 1 into a 100-mL volumetric flask. Add 10 mL of concentrated $HNO_3$, dilute to the mark with reagent water, and mix. Prepare the medium standard (level 3) by dilution of the level 4 standard, 10 mL of level 4, 10 mL of concentrated $HNO_3$, to 100 mL final volume. Prepare the low standard (level 2) by dilution of the level 3 standard, 10 mL of level 3, 10 mL of concentrated $HNO_3$, to 100 mL final volume. The calibration blank (level 1) is prepared by diluting 10 mL of concentrated $HNO_3$ to 100 mL final volume.

10.6 Spiking solutions - GLA-SPK-1A and -4B, purchased from Inorganic Ventures; GLA-SPK-EM (earth metals spike) prepared from individual 10,000 ppm solutions (from Inorganic Ventures) for final concentrations of 2000 ppm of Na, K, Ca, and Mg. As, Se, Ta, and Zr standard - 1000 ppm.

10.7 Calibration check standard - Add 50 mL of concentrated nitric acid to a 500-mL volumetric flask. Accurately aliquot 1.0 mL each of GLA-SPK-1A, -4B, and -EM into the volumetric flask. Aliquot 1.0 mL each of secondary As, Se, Ta, and Zr 1000 ppm standards into the flask. Dilute to the mark with reagent water and mix.

10.8 Interference check solution - 5000 ppm Al, Ca, Mn, and 2000 ppm Fe, Inorganic Ventures no. CLPP-ICS-A.

10.8 Interference check standard ICS-A - Aliquot 50 mL of concentrated sulfuric acid and 50 mL of CLPP-ICS-A into a 500-mL volumetric flask. Dilute to the mark with reagent water and mix.

10.9 Interference check standard ICS-B - Aliquot 50 mL of concentrated sulfuric acid and 50 mL of CLPP-ICS-A into a 500-mL volumetric flask. Then, accurately aliquot 1.0 mL each of GLA-SPK-1A, -4B, and -EM into the volumetric flask. Aliquot 1.0 mL each of secondary As, Se, Ta, and Zr 1000 ppm standards into the flask. Dilute to the mark with reagent water and mix.

10.10 Yttrium standard - 10,000 ppm, purchased from Spex CertiPrep Assurance, Inorganic Ventures, or Ultra Scientific.

10.11 Lithium carbonate - $Li_2CO_3$ powder, Fisher no. 5840 or Mallinckrodt no. L119.

10.12 Buffer/internal standard solution - Weigh approximately 10.7 g of $Li_2CO_3$ and place in a new, clean 2-L fluorinated plastic bottle. Add 1 L of reagent water. Then add 1.0 mL of 10,000 ppm yttrium standard. Carefully add 200 mL of concentrated $HNO_3$. (Solution will effervesce due to release of carbon dioxide.) Dilute to approximately 2 L with reagent water and mix.

10.13 Rinse solution - 10% nitric acid in reagent water.

## 11.0 PROCEDURE

**NOTE:** Method validation (section 8.0) must be performed before samples can be analyzed.

**NOTE:** See Table 1 for the analytes for which this method is applicable. See Appendix B for some recommended wave-lengths, estimated instrumental detection limits (IDL), and potential interferences (at the 100 mg/L level).

**11.1** Assemble all materials and equipment required for the procedure. A daily calibration check of the analytical balance must have been performed prior to its use in weighing samples or standard materials. Record all pertinent sample information in the log book(s) ***before beginning the analysis***.

| Table 1. **Preparation and Concentrations of Calibration Standard Solutions.** | | | | |
|---|---|---|---|---|
| ELEMENT | Volume (mL) of 1000 ppm Standard to Prepare High Standard | High Standard (Level 4) Concentration (ppm) | Medium Standard (Level 3) Concentration (ppm) | Low Standard (Level 2) Concentration (ppm) |
| Ag | 1.0 | 10.0 | 1.00 | 0.100 |
| Al | 2.5 | 25.0 | 2.50 | 0.250 |
| As | 0.5 | 5.0 | 0.50 | 0.050 |
| B | 1.0 | 10.0 | 1.00 | 0.100 |
| Ba | 2.5 | 25.0 | 2.50 | 0.250 |
| Be | 0.5 | 5.0 | 0.50 | 0.050 |
| Ca | 2.5 | 25.0 | 2.50 | 0.250 |
| Cd | 0.5 | 5.0 | 0.50 | 0.050 |
| Co | 1.0 | 10.0 | 1.00 | 0.100 |
| Cr | 1.0 | 10.0 | 1.00 | 0.100 |
| Cu | 1.0 | 10.0 | 1.00 | 0.100 |
| Fe | 2.5 | 25.0 | 2.50 | 0.250 |
| K | 2.5 | 25.0 | 2.50 | 0.250 |
| Mg | 2.5 | 25.0 | 2.50 | 0.250 |
| Mn | 1.0 | 10.0 | 1.00 | 0.100 |
| Mo | 1.0 | 10.0 | 1.00 | 0.100 |
| Na | 2.5 | 25.0 | 2.50 | 0.250 |
| Ni | 1.0 | 10.0 | 1.00 | 0.100 |
| Pb | 0.5 | 5.0 | 0.50 | 0.050 |
| Sb | 1.0 | 10.0 | 1.00 | 0.100 |
| Se | 0.5 | 5.0 | 0.50 | 0.050 |
| Sn | 1.0 | 10.0 | 1.00 | 0.100 |
| Ti | 1.0 | 10.0 | 1.00 | 0.100 |
| Tl | 1.0 | 10.0 | 1.00 | 0.100 |
| V | 1.0 | 10.0 | 1.00 | 0.100 |
| Zn | 2.5 | 25.0 | 2.50 | 0.250 |
| **Note**: See Section 10.5 for complete instructions on calibration standard preparation. | | | | |

| Table 2. Varian Liberty 100 **Preparation and Concentrations of Calibration Standard Solutions.** | | | | | | |
|---|---|---|---|---|---|---|
| ELEMENTS | Volume (ml) of 1000 ppm Standard | Std.1 Conc. ppm | Std.2 Conc. ppm | Std.3 Conc. ppm | Std.4 Conc. ppm | Std.5 Conc. ppm |
| Pb | 1.0 | 10 | 5 | 1 | 0.5 | 0.1 |
| Cd | 1.0 | 10 | 5 | 1 | 0.5 | 0.1 |
| Ta | 1.0 | 10 | 5 | 1 | 0.5 | 0.1 |

### 11.2 INTERFERENCE CHECK STANDARD AND BLANK

An Interference Check Standard, containing high amounts of interfering elements and known concentrations of elements of interest, is analyzed at the beginning and the end of each sequence of samples. The interfering elements are the following concentrations: Al, Ca, Mg - 500 ppm, Fe - 200 ppm. The elements of interest are each spiked at 2.0 ppm (exceptTl, which is 4.0 ppm). Recoveries must be within ± 20% of the expected concentrations.

An Interference Check Blank, containing high amounts of interfering elements, is analyzed at the beginning and end of each sequence of samples. This blank contains the same concentrations of interfering elements as the check standard. The Interference Blank is analyzed for Ba, Cd, Cr, Pb, and Ag. The concentrations detected for these elements must not be above the reporting limits.

Internal Standard (TJA Only) - Yttrium is added at a concentration of approximately 1.0 ppm to all standards, blanks, and samples by the instrument. The intensity is tracked to ensure proper instrument operation.

## 11.3 INSTRUMENT CALIBRATION

The ICP is calibrated daily before samples are analyzed. The standard curve includes one blank and three standards (4 levels). The correlation coefficient, $r^2$, must be at least 0.9950 for each analyte to be run.

The calibration is checked using a Check Standard initially and after every 10 (or fewer) samples. The recovery of the analytes in the Check Standard must be with 10% of expected values. Replicate integrations of the Check Standard must have a %RSD of $\leq$5%. For A2LA required work, the High Level Standard (Level 4)is used as a check of the calibration, and must be within +/-5% of the actual value.

## 11.4 OPERATION OF THE INSTRUMENT

11.4.1 Power up the instrument and ignite plasma according to the manufacturer's instructions.
11.4.2 Allow instrument to warm up at least 30 minutes.
11.4.3 Perform system profile in accordance with the manufacturer's instructions using an approximately 5 ppm As standard.
11.4.4 Go to analysis section and call up method **6010PM1**.
11.4.5 Calibrate instrument using calibration standards. Each analyte to be used must have a correlation coefficient of at least 0.9950.
11.4.6 Run performance and instrument check samples:

| Sample | Criteria |
|---|---|
| A. ICV (check standard) | ±10% |
| B. ICB (calibration blank) | < reporting limit |
| C. High standard | ±10% |
| D. ICS-B | ±20% |
| E. ICS-A | < reporting limit (except Al, Ca, Fe, Mg) |

11.4.7 If all criteria pass, run samples with a CCV and CCB every 10 (or less) samples. The high standard, ICS-B, and ICS-A need to be re-analyzed at the end of the run, or every 8 hours. Each analytical run must end with a calibration blank and a check standard.

11.4.8 Where the sample matrix is so complex that viscosity, surface tension, and components cannot be accurately matched with standards, the method of standard addition (MSA) may be used. This procedure involves adding equal volumes of sample to a reagent water blank and to a standard. The higher the degree of accuracy needed, the greater the number of standard additions. The absorbance for each of the prepared solutions is plotted on the vertical axis, with the corresponding standard concentrations plotted on the horizontal axis. When the resulting line is extrapolated back to zero absorbance, the point at which the line crosses the horizontal axis is the concentration (absolute value) of the sample. The results are considered valid if:

- the plotted curve is linear over the concentration range of concern (slope should be less than 20% different than the slope of the calibration curve).

- the effect of the interference does not vary as the ratio of analyte concentration to sample matrix changes and the standard addition responds in a similar manner as the analyte.
- the determination is free of spectral interferences and corrected for nonspecific background interference.

For a single-addition method, the concentration would be calculated as follows:

$$C_x = \frac{S_B V_S C_S}{(S_A - S_B)\ V_X}$$

where: $C_x$ = Concentration of the sample
$S_B$ = The analytical signal for the sample and water solution (corrected for the blank)
$V_S$ = Volume of the standard solution added
$C_S$ = Concentration of the standard solution added
$S_A$ = The analytical signal for the sample and standard solution (corrected for the blank)
$V_S$ = Volume of the sample added to each solution.

Note: $V_S$ and $C_S$ should be chosen so that $S_A$ is roughly twice $S_B$ on the average. It is best if $V_S$ is made much less than $V_X$ , and thus $C_S$ is much greater than $C_X$, to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure.

## 11.5 CALCULATIONS

11.5.1 Results are corrected for any spectral interferences and backgrounds (by the instrument software).

11.5.2 All analyte concentrations are multiplied by the applicable dilution factor (DF) to obtain concentrations for the original samples.

For waters/liquids:

$$\text{concentration (mg/L)} = \frac{\text{instr. result} \times \text{final digestate volume (mL)} \times \text{DF}}{\text{initial sample volume (mL)}}$$

For soils/solids/sludges:

$$\text{concentration (mg/kg)} = \frac{\text{instr. result} \times \text{final digestate volume (mL)} \times \text{DF}}{\text{initial sample weight (g)}}$$

To report result in dry weight, divide concentration result by decimal percent solids (*e.g.* if %solids is 89%, divide by 0.89).

For paints:

$$\text{concentration (\%)} = \frac{\text{instr. result} \times \text{final digestate volume (mL)} \times \text{DF}}{\text{initial sample weight (g)} \times 10{,}000}$$

10,000 is the factor for converting mg/kg (ppm) to percent.

For wipes:

amount (mg per wipe) = instr. result × final digestate volume (mL) × DF

To report in mg per square foot, divide result by area (supplied by client).
To convert to µg, multiply result by 1000.

11.5.3 Percent Recovery Calculation for spiked samples and LCS:

$$\% \text{ Recovery} = \frac{\text{Calculated Spike Conc.} - \text{Conc. of Sample}}{\text{Spike Conc. Added}} \times 100\%$$

11.5.4 Relative Percent Difference (%RPD) for duplicate analyses:

$$\%\text{RPD} = \frac{|\text{Conc. of 1}^{st}\text{ Analysis - Conc. of Duplicate Analysis}|}{(\text{Conc. of 1}^{st}\text{ Analysis + Conc. of Duplicate Analysis})/2} \times 100\%$$

## 12.0 MAINTENANCE AND TROUBLESHOOTING

### 12.1 GENERAL

Glassware should be cleaned appropriately to avoid sample contamination. Equipment should be kept clean and maintained to avoid sample contamination and assure proper operation. Manuals supplied by the manufacturers with the instrumentation typically have informational and troubleshooting sections.

### 12.2 TECHNICAL SUPPORT

Technical support is available from equipment manufacturers (for example, by telephone, fax, or e-mail). They can be a good resource when troubleshooting options have been exhausted. Technical support departments can readily supply part numbers.

### 12.3 CLEANING THE PLASMA TORCH

The plasma torch must be cleaned weekly. This is accomplished by soaking the torch in a solution of 1 part concentrated HCl and 3 parts concentrated $HNO_3$ overnight. The height of the torch will need adjustment when the torch is replaced.

## 13.0 REFERENCES

13.1 EPA Method 200.7: Inductively Coupled Plasma - Atomic Emission Spectrophotometric Method for Trace Element Analysis of Water and Wastes.
13.2 Method 3120: Metals by Plasma Emission Spectroscopy, Section B (Inductively Coupled Plasma Method); Standard Methods for the Examination of Water and Wastewater, 18th Edition, 1992.
13.3 Method SW-846, 3020B: Inductively Coupled Plasma - Atomic Emission Spectroscopy.
13.4 Great Lakes Analytical Quality Assurance Program.
13.5 Great Lakes Analytical Chemical Hygiene Plan.
13.6 Great Lakes Analytical SOP for Login Department.
13.7 Great Lakes Analytical SOP for Hazardous Sample Management.

## 14.0 DEFINITIONS

Refer to Great Lakes Analytical Quality Assurance Program Plan.

# APPENDIX A.

## STANDARD SPIKING LEVELS AND VOLUMES.

| Standard | Aliquot/Volume | Aliquot/Volume | Aliquot/Volume | Aliquot/Volume | Aliquot/Volume |
|---|---|---|---|---|---|
| GLA-SPK-1A | 0.10/100 | | 0.05/50 | 0.10/50 | 0.10/50 |
| GLA-SPK-3B | | 0.05/50 | | 0.10/50 | 0.10/50 |
| GLA-SPK-4B | 0.10/100 | | | | |
| GLA-SPK-5 | | | 0.05/50 | 0.10/50 | 0.10/50 |
| GLA-SPK-6 | | | | | 0.10/50 |
| As Se Soln. | 0.05/50 | | | | |
| EARTH | 0.10/100 | | 0.05/50 | 0.05/50 | |

## Corresponding Elements and Concentrations (ppm) per matrix

| Set | Element | Solid/Soil | D $H_2O$ FNC | D $H_2O$ ICP | $H_2O$ | TCLP/SPLP Ext. |
|---|---|---|---|---|---|---|
| RCRA | Ag | 1.0 | 0.005 | | 0.01 | 0.51 |
| | As | 0.53 | 0.015 | | 0.03 | 0.03 |
| | Ba | 1.0 | | 0.50 | 1.0 | 1.0 |
| | Cd | 1.0 | 0.001 | | 0.002 | 0.502 |
| | Cr | 1.0 | 0.003 | 0.50 | 1.006 | 1.006 |
| | Hg | | 0.001 | | 0.001 | 0.001 |
| | Pb | 1.0 | 0.015 | | 0.03 | 0.03 |
| | Se | 0.28 | 0.015 | | 0.03 | 0.03 |
| PRIRTY | Be | 1.0 | | 0.50 | 1.0 | 1.0 |
| | Cu | 1.0 | 0.015 | 0.50 | 1.03 | 1.03 |
| | Ni | 1.0 | | 0.50 | 1.0 | 1.0 |
| | Sb | 1.0 | 0.015 | 1.0 | 2.03 | 2.03 |
| | Tl | 2.0 | 0.015 | 1.0 | 2.03 | 2.03 |
| | Zn | 1.0 | | 0.50 | 1.0 | 1.0 |
| TAL | Al | 1.0 | | 0.5 | 1.0 | 1.0 |
| | Co | 1.0 | | 0.5 | 1.0 | 1.0 |
| | Fe | 1.0 | | 0.5 | 1.0 | 1.0 |
| | Mn | 1.0 | | 0.5 | 1.0 | 1.0 |
| | V | 1.0 | | 0.5 | 1.0 | 1.0 |
| EARTH | Ca | 1.0 | | 1.0 | 1.0 | |
| | K | 1.0 | | 1.0 | 1.0 | |
| | Li | 1.0 | | 1.0 | 1.0 | |
| | Na | 1.0 | | 1.0 | 1.0 | |
| | Mg | 1.0 | | 1.0 | 1.0 | |
| EXTRA | B | 1.0 | | 1.0 | 2.0 | 2.0 |
| | Mo | 1.0 | | 1.0 | 2.0 | 2.0 |
| | Si | 1.0 | | 1.0 | 2.0 | 2.0 |
| | Sn | 1.0 | | 1.0 | 2.0 | 2.0 |
| | Ti | 1.0 | | 1.0 | 2.0 | 2.0 |
| | Ta | 1.0 | | 1.0 | 2.0 | 2.0 |

# APPENDIX B.

## EXAMPLE WAVELENGTHS, ESTIMATED INSTRUMENTAL DETECTION LIMITS (IDL), AND POTENTIAL INTERFERENCES AT THE 100 mg/L LEVEL.

| Element | Wavelength (nm) | IDL (µg/L) | Interferent(s) * |
|---|---|---|---|
| Aluminum (Al) | 308.215 | 30 | Mn 0.2, V 1.4 |
| Antimony (Sb) | 206.833 | 21 | Al 0.5, Cr 2.9, Fe 0.1, Ti 0.3, V 0.5 |
| Arsenic (As) | 193.696 | 35 | Al 1.3, Cr 0.4, V 1.1 |
| Barium (Ba) | 455.403 | 0.9 | |
| Beryllium (Be) | 313.042 | 0.2 | Ti 0.04, V 0.05 |
| Boron (B) | 249.678† | 3.8 | |
| Cadmium (Cd) | 226.502 | 2.3 | Fe 0.03, Ni 0.02 |
| Calcium (Ca) | 317.933 | 6.7 | Cr 0.1, Mn 0.04, Ti 0.03, V 0.03 |
| Chromium (Cr) | 267.716 | 4.7 | Mn 0.04, V 0.04 |
| Cobalt (Co) | 228.616 | 4.7 | Cr 0.03, Fe 0.01, Ni 0.03, Ti 0.15 |
| Copper (Cu) | 324.754 | 3.6 | Ti 0.05, V 0.02 |
| Iron (Fe) | 259.940 | 4.1 | Mn 0.1 |
| Lead (Pb) | 220.353 | 28 | Al 0.2 |
| Lithium (Li) | 670.784 | 2.8 | |
| Magnesium (Mg) | 279.079 | 20 | Cr 0.1, Fe 0.1, Mn 0.3, Ti 0.1, V 0.1 |
| Manganese (Mn) | 257.610 | 0.9 | Al 0.01, Cr 0.01 |
| Mercury (Hg) | 194.227† | 17 | |
| Molybdenum (Mo) | 202.030 | 5.3 | Al 0.05, Fe 0.03 |
| Nickel (Ni) | 231.604† | 10 | |
| Phosphorus (P) | 213.618 | 51 | |
| Potassium (K) | 766.491 | ‡ | |
| Selenium (Se) | 196.026 | 50 | Al 0.2, Fe 0.1 |
| Silica ($SiO_2$) | 251.611 | 17 | |
| Silver (Ag) | 328.068 | 4.7 | |
| Sodium (Na) | 588.995 | 19 | Ti 0.08 |
| Strontium (Sr) | 407.771 | 0.3 | |
| Tantalum (Ta) | 226.23 | 31 | |
| Thallium (Tl) | 190.864 | 27 | Al 0.3 |
| Tin (Sn) | 189.9890† | 17 | |
| Titanium (Ti) | 334.941 | 5.0 | |
| Vanadium (V) | 292.402 | 5.0 | Cr 0.05, Fe 0.01, Ti 0.02 |
| Zinc (Zn) | 213.856† | 1.2 | Cu 0.1, Ni 0.3 |

† second order.
‡ highly dependent on operating conditions and plasma position.
* analyte concentration equivalents.

Copy #: 3015-001

# GREAT LAKES ANALYTICAL

## STANDARD OPERATING PROCEDURE

## FOR

## THE DIGESTION OF LIQUIDS FOR THE ANALYSIS OF METALS

## GLA 3015 BG

Revision 3.2

Approved By:

Department Manager: _____ Date: 4/5/00

Quality Assurance Manager: _____ Date: 4/5/00

Laboratory Director: _____ Date: 4-5-00

# 1.0 APPLICABILITY

This standard procedure (SOP) provides instructions for the sample handing and digestion of liquids in preparation for analysis of total metals by ICP-OES and FLAA/GFAAS. This SOP is an interpretation of EPA Methods 300.7 and 300.9; Standard Methods no. 3030, Sections E, F, and K; and SW-846 no. 3015 and 3010M. This SOP is to be used in conjunction with the analysts' in-laboratory training, the Great Lakes Analytical Chemical Hygiene Plan (CHP), and the Great Lakes Analytical Quality Assurance Program.

**NOTE:** The digests produced using this procedure are not suitable for the analysis of mercury (Hg) or hexavalent chromium ($Cr^{6+}$). Arsenic (As) and selenium (Se) cannot be analyzed by FLAA.

## 1.1 MATRICES

This method is applicable to aqueous samples (ground, waste, drinking waters), extracts, and other liquid materials and wastes (such as oil and grease).

## 1.2 REGULATORY APPICABILITY

40 CFR 121

# 2.0 SUMMARY

A representative 5-100 mL portion of sample is digested with nitric acid, or nitric acid and hydrogen peroxide (for As and Se). The digestate is then refluxed with additional nitric acid (GFAAS methods, except for As and Se) or with hydrochoric acid (ICP-OES methods). Aqueous ground waters, extracts, and liquid samples are digested by either standard "hotplate" digestion methods or microwave-assisted digestion methods. Non-aqueous or high dissolved organic containing liquids are digested using the standard hotplate methods, including GLA 3010M, a modified 3010 method. Liquid matrix types include:

- Waters - ground, waste, drinking, other aqueous.
- Extracts - TCLP, SPLP, ASTM D3987-85.
- Miscellaneous - oil, grease, diesel, other.

See Appendix A for method exceptions.

# 3.0 SAFETY

## 3.1 GENERAL

This SOP does not address all safety issues associated with its use. A reference file of material safety data sheets (MSDS's) is available to all personnel, along with the Great Lakes Analytical Chemical Hygiene Plan. Gloves are worn when handling chemicals and reagents.

## 3.2 CHEMICAL HYGIENE PLAN

The Great Lakes Analytical Chemical Hygiene Plan (CHP) is designed to establish safe work procedures and minimize exposure to hazardous chemicals encountered in the laboratory. The CHP provides information to employees regarding potential hazards and training to minimize these hazards.

### 3.3 HAZARDOUS SAMPLES

All samples that are received by the laboratory have the possibility of containing hazardous pollutants. They should be treated with caution at all times. Gloves are worn when handling samples. Also see the Great Lakes Analytical SOP for Hazardous Sample Management.

### 3.4 CHEMICALS SPECIFIC TO DIGESTIONS

30% Hydrogen peroxide is a strong oxidizer in the presence of acids, and can cause burns to eyes and skin. It can react violently when introduced to a sample in concentrated acid. Large volumes of hydrogen gas may be produced. Allow samples to cool thoroughly before adding hydrogen peroxide. Similarly, add concentrated nitric acid to samples carefully.

## 4.0 INTERFERENCES

4.1 Sample matrices can vary greatly, even within specific sample type groups, most notably waste sludges (for example, ground water versus tank removal waste). Any sample types exhibiting significantly different properties, such as high organic content or multi-phase samples, are to be handled as individual matrices, and appropriate matrix spikes should be produced and analyzed.

4.2 In the case of methods for total recoverable and/or dissolved metals, digestion is not always required. It should be noted, however, that the less intensive digestion procedure for total recoverable metals may not be sufficiently vigorous to destroy some metal complexes and may therefore give biased results.

4.3 Daily monitoring test of the deionized water supply must have been performed and pass or meet appropriate criteria for analysis before the water can be used in sample preparation. All glassware to be used in the analysis must be cleaned and rinsed following the procedure outlined in Appendix C. Periodic cleaning of sample preparation and analysis areas, will be performed. At least quarterly, laboratory dust wipes will be prepared and analyzed. Contamination of more than 500 µg of lead (Pb) per square foot is not permitted.

## 5.0 RECORD KEEPING

5.1 Each analyst is responsible for keeping accurate and up-to-date records of all digestions performed.

5.2 Digestion Log Book:

A log book will be maintained for all solid matrix types and associated digestions. All information regarding samples processed in the lab will be entered into this book. This information will include but is not limited to:

- Method reference number
- Client Name for each set of samples
- GLA Sample I.D. (one complete for each set)
- Initial sample volume used
- LIMS batch reference number
- Analyst's signature and date prepared/analyzed
- Reviewer's signature and date
- All readings, dilution factors, and calculated results
- Sample matrix type
- Spiking volumes used
- Spike standard identifier
- Spike standard concentration
- LCS and matrix spike information
- Final digestate volume

This log should also include any unique observations noted in regard to specific samples. Space will be reserved on each page for calculations and notes. All unused portions of logbook pages must be z'ed out.

5.3 Sample Schedule - All samples will be tracked through the lab using GLA sample I.D. numbers generated by the GLA LIMS system.

# 6.0 QUALITY CONTROL

## 6.1 QUALITY CONTROL SAMPLES

Quality control samples are run at a minimum 5% frequency (*i.e.* one set with every batch of twenty or less samples). The results of these samples are used to gauge accuracy and precision of the method. These samples include method blanks (MB), lab control samples (LCS), matrix spikes (MS) and matrix spike duplicates (MSD). The quality control samples contain all reagents and are subjected to all preparation steps. They are processed and analyzed along with test samples.

## 6.2 METHOD BLANK

Matrix-matched method blanks (MB) containing all reagents and subjected to all preparation steps are processed and analyzed along with the samples. Method blanks must produce a concentration below the reporting limit (*e.g.* PQL, EQL, ...) for an analytical batch to be valid. These samples provide a measure of laboratory and/or reagent contamination. Test sample results are not corrected for the method blank concentrations.

## 6.3 LABORATORY CONTROL SAMPLE (LCS)

An external (independently sourced) reference standard is prepared within the working range of the method and analyzed with each matrix per batch of twenty or less samples (*i.e.* minimum 5% frequency). The results of the samples must be within established control limits, or where there is not enough data to calculate control limits, within 15% of the known value.

## 6.4 MATRIX SPIKED SAMPLES

Matrix spiked samples (MS and MSD) will be analyzed with a minimum frequency of 5% (*e.g.* one set per 20 or less samples per matrix) and are used to determine accuracy and precision of a method. The matrix spiked samples will be spiked using the same standards used to spike the LCS samples. The analyzed result of the matrix spikes must be within established control limits, or where there is not enough data to calculate control limits, within 25% of the known value.

## 6.5 SURROGATE MATRIX BLANK AND SPIKED SAMPLES

In cases where no additional sample is available for matrix spiking (*e.g.* wipes samples), a set of surrogate matrix QC samples will be produced by digesting an appropriate substrate "blank" and two spiked samples of the same substrate spiked with the same standards and at the same levels of the LCS.

## 6.6 QUALITY CONTROL TRACKING AND DATA REVIEW

The QC data is considered acceptable and actual samples results can be evaluated and reported by the analyst if all QC samples are within established control limits.

### 6.7 CORRECTIVE ACTION

If a quality control measure fails, corrective action is taken and documented to ensure the accuracy of the data that is reported. Examples of when corrective action sheets are filled out are:

- A sample or QC is re-analyzed. This may be due to the QC parameter failing or mislabeling of samples.
- Samples are reported with a QC result (blank, spike matrix) parameter out of control. In this case, not only should a corrective action be initiated, but the data must be flagged.
- A deviation from the normal SOP for the method is discovered (*e.g.* a digestion goes down to dryness or a different concentration of reagent is used) and the sample is analyzed and reported.
- An error in a previously reported sample is discovered.

## 7.0 SAMPLE MANAGEMENT

**7.1** The procedure for sample management are detailed in the Great Lakes Analytical SOP for sample receipt into the laboratory.

**7.2** Sample Schedule: Analysts keep track of sample throughput by using the Laboratory Information Management System (LIMS). The system is checked daily and a hard copy generated. Samples for this method are queued under "METP". The information includes:

- Client name.
- Sample numbers.
- Project name.
- Matrix.
- Hold time and turnaround time.

## 8.0 METHOD VALIDATION

### 8.1 QUALITY CONTROL BOOK

Method validation must be performed before any actual samples can be analyzed. Method validation studies are required to be stored in the QC logbook. Method exception studies must also be performed to validate any exception taken by proving equivalency with the unaltered method. The contents of the QC book include:

- Copy of the GLA Quality Assurance Program.
- Copies of GLA SOP and source methods.
- Copy of the precision and accuracy study for the method.
- Copies of all method detection limit studies and dates in use.
- Check standard recovery tabulations and control limits.
- Spike and spike duplicate recovery tabulations and control limits.
- Corrective action sheets.

### 8.2 QUALITY ASSURANCE PROGRAM

Internal audits will be performed periodically to assess analytical system performance. Performance evaluation samples will be analyzed periodically to assess laboratory performance. (Refer to the GLA Quality Assurance Program.)

### 8.3 METHOD DETECTION LIMIT STUDY

8.3.1 The method detection limit (MDL) is defined as the minimum concentration of analyte that can be determined with 99% confidence. It is determined as follows:

- Prepare a minimum of seven replicate samples at a concentration at or near the expected MDL. Carry these replicates through the entire sample preparation procedure and analysis.
- Calculate the MDL by taking the standard deviation of the results of the seven replicates and multiply by the Student's t value at n-1 degrees of freedom (3.143 for seven replicates).

8.3.2 Other factors such as matrix effects and instrument noise may affect the attainable detection limit. These should be quantified if possible and taken in to account when determining an MDL as the obtainable detection level may be artificially elevated due to these factors.

8.3.3 A new MDL study must be performed to re-evaluate the method if any major instrument maintenance or service is performed, if any new method exceptions or changes are made or at least annually.

## 9.0 EQUIPMENT

9.1 Beakers, Griffin type, 250-mL size.
9.2 Watch covers, ribbed, 90-mm diameter.
9.3 Volumetric flasks, 25-100 mL.
9.4 Glass funnels.
9.5 Filter paper - 15 cm, Whatman 41, or equivalent.
9.6 Sample containers, 50-100 mL capacity, metal-free.
9.7 Hotplate, adjustable, capable of maintaining a constant temperature for samples of 90-95°C. Monitor temperature of the hotplate by placing an Erlenmeyer flask with approximately 100 mL of cooking oil at the center of the hotplate, and reading the temperature with an ASTM thermometer positioned with the bulb against the bottom of the flask. The temperature must be at least 140°C. Record temperatures in the log book.
9.8 Analytical balance, calibrated - capable of weighing to nearest 0.1 g for soil/sediment/sludge samples, 0.001 g for paints.
9.9 Microwave digestion apparatus:

- Microwave digestion system, capable of monitoring and maintaining 175°C and/or 70 p.s.i. within digestion vessels, CEM model MDS-2100, or equivalent.
- Lined (polyolefin) digestion vessels, 50-mL size.
- Rupture membranes.

## 10.0 STANDARDS AND REAGENTS

10.1 Reagent water - ASTM Type II Water (DI water).
10.2 Nitric acid - concentrated $HNO_3$, ACS/reagent grade, Fisher no. A509. **CAUTION:** Nitric acid is corrosive.
10.3 Hydrochloric acid - concentrated HCl, ACS/analytical reagent grade, Fisher no. A508. **CAUTION:** Hydrochloric acid is corrosive.
10.4 Hydrogen peroxide - 30% $H_2O_2$, ACS/analytical reagent grade, Fisher no. H325.
10.5 Spiking standards - GLA-SPK-1A, -3B, 5, and 6, Inorganic Ventures; GLA-SPK-EM (earth metals spike) prepared from individual 10,000 ppm solutions (from Inorganic Ventures) for final concentrations of 2000 ppm of Na, K, Ca, and Mg. (Refer to Appendix B for concentrations and volumes spiked.)

# 11.0 PROCEDURE

**NOTE:** Method validation (section 8.0) must be performed before samples can be analyzed.

## 11.1 SELECTION OF DIGESTION PROCEDURE

The appropriate method for the required metal analysis must be referenced in order to select the proper digestion procedure. There are several methods for digestions which can be selected based upon the matrix type of the sample and the type of digestion being performed. Use Table 1 to determine which method is most applicable to the samples being analyzed. The proper digestion procedure is selected from Table 2.

**Table 1.**
Digestion Method Reference Chart.

| Analysis | Method Reference | Pre-Digestion Preparation | Microwave Digestions | Standard Digestions | | | Special Matrices |
|---|---|---|---|---|---|---|---|
| | | | | ICP/FLAA | GFAA | Special | |
| Total Metals | SW-846 | Preserve with $HNO_3$ to pH <2 | 3051A | 3010A | 3020A | 7060A (As) 7740A (se) | 3010M for oils, gas, diesel, and waste oil sludges |
| | EPA | | n/a | 4.1.3 200.7 | 4.1.3 200.9 | 206.2 (As) 270.2 (se) | |
| | Std Meth | | SM-3030-K | SM-3030-F | SM-3030-E | | |
| Dissolved Metals | SW-846 | Filter thru 0.45 µ filter, preserve with $HNO_3$ to pH <2 | 3015 | 3010A | 3020A | 7060A (As) 7740A (Se) | 3010M for oils, gas, diesel, and waste oil sludges |
| | EPA | | n/a | 4.4.1/4.1.3 200.7 | 4.1.1/4.1.3 200.9 | 206.2 (As) 270.2 (Se) | |
| | Std Meth | | SM-3030-K | SM-3030-F | SM3030-E | | |
| Total Recoverable Metals | SW-846 | Preserve with $HNO_3$ to pH <2 | n/a | 3005 | n/a | | 3005 |
| | EPA | | n/a | 4.1.4 | 4.4.4 | | 4.1.4 |
| | Std Meth | | n/a | SM-3030-F | SM-3030-F | | SM-3030-F |

**11.2** Assemble all materials and equipment required for the procedure. A daily calibration check of the analytical balance must have been performed prior to its use in weighing samples or standard materials. Record all pertinent sample information in the log book(s) ***before beginning the analysis***.

**CAUTION:** All hotplate digestions must be performed in a fume hood.

**Table 2.**
Procedure Selection Table.

| Digestion Type | Analysis Type (1) | Analysis Method | Applicable Method(s) | Digestion Procedure |
|---|---|---|---|---|
| Microwave | Total Metals<br>Dissolved Metals | Any (2) | SW-846 3015<br>SM-3030-K | 11.4 (MIC) |
| Standard | Total Metals<br>Dissolved Metals | ICP/FLAA | SW-846 3010A<br>EPA 4.1.3<br>EPA 200.7<br>SM-3030-F | 11.5 (ICP) |
| Standard | Total/Dissolved Except As and Se | GFAAS | SW-846 3020A<br>EPA 4.1.3<br>EPA 200.9<br>SM-3030-E | 11.6 (GF) |
| Standard | Total/Dissolved As and Se Only | GFAAS | SW-846 7060A (As)<br>SW-846 7740A (Se)<br>EPA 206.2 (As)<br>EPA 270.2 (Se) | 11.7 (AS) |
| Standard | Total Metals | Any (2) | 3010M (3) | 11.8 (NA) |
| Standard | Total Recoverable Metals | ICP/FLAA | SW-846 3005<br>EPA 4.1.4<br>SM-3030-F | 11.9 (A) |

(1) Dissolved metals require filtration at time of collection (through a 0.45 μ membrane filter) **prior to preservation**. Chain of custody record should be referenced to determine if sample was properly collected, filtered, and preserved.
(2) Any analytical method refers to GLA routine methods : ICP, GFAAS, and FLAA. These digests are not suitable for analysis of mercury or hexavalent chromium.
(3) Method 3010M is a GLA method. It is based upon the SW-846 method 3010A, but the addition of hydrochloric acid has been omitted. It is used exclusively for the analysis of metals in oils, oil waste, gas, diesel fuels, and high organic containing waters.

## 11.3 PREPARATION OF QUALITY CONTROL AND TEST SAMPLES

11.3.1 Method blank - Aliquot 100 mL (45 mL for microwave digestion, section 11.4) of reagent water into a clean digestion vessel.

11.3.2 Laboratory control samples (LCS) - Aliquot 100 mL (45 mL for microwave digestion, section 11.4) of reagent water into a clean digestion vessel. Accurately aliquot 0.2 mL (0.1 for microwave) each of GLA-SPK-1A, -3B, -5, and -EM into the sample. Also add 0.2 mL (0.1 for microwave) of GLA-SPK-6 if spiking Ag and Cd at ICP levels.

11.3.3 Samples - Representative 100 mL (45 mL for microwave digestion, section 11.4) aliquots of samples are aliquoted into clean digestion vessels. For samples with a high solids content (> 1%), a smaller sample size should be used (record the actual volume in the log book).

11.3.4 Matrix spike samples - Measure two additional aliquots 100 mL (45 mL for microwave digestion, section 11.4) of one sample, with volumes similar to the test sample volume, and making sure each aliquot is homogeneous and representative of the entire sample. Accurately aliquot 0.2 mL each of GLA-SPK-1A, 3B, -5, and -EM into the sample. Also add 0.2 mL (0.1 for microwave) of GLA-SPK-6 if spiking Ag and Cd at ICP levels. Mark as MS and MSD.

## 11.4 MICROWAVE-ASSISTED DIGESTION OF AQUEOUS LIQUIDS AND EXTRACTS (MIC)

**NOTE:** Metal analytes for which this digestion is applicable include:
Ag, Al, As, Ba, Be, Cd, Ca, Cr (tot), Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Na, Sb, Se, Tl, V, Zn.

11.4.1 Add 5 mL of concentrated $HNO_3$ to each sample. Stand for 2-10 minutes to allow any vigorous reaction to occur before the vessel is sealed.

11.4.2 The "control vessel" should be selected as the sample appearing to be most reactive. Load the carousel with samples and place in the microwave.

11.4.3 Upon completion of the microwave program, the samples are cooled until the pressure drops below 10 psi (as indicated by the instrument). The pressure sensor is carefully disconnected, temperature probe removed, and the carousel taken out of the instrument.

11.4.4 Each vessel is carefully vented, vent line removed, cap retightened, and shaken to mix.

11.4.5 Each vessel is opened and contents poured into a clean labelled sample cup. If the sample is still warm, or hot, to the touch, it should be cooled further and mixed before analysis. This can be expedited by placing samples in a refrigerator, freezer, or cold water bath for a short time. Observe the volume of each vessel. If loss of sample is apparent (*e.g.* volume less than 50 mL), the sample is discarded and redigested.The container should be labeled with:

- GLA Sample I.D.
- Matrix type
- Date digested
- Dilution factor (where applicable)

11.4.6 Samples are now ready for analysis by ICP, GFAA, or FLAA.

## 11.5 HOTPLATE DIGESTION OF AQUEOUS LIQUIDS AND EXTRACTS FOR ANALYSIS BY ICP-OES (ICP)

**NOTE:** Metal analytes for which this digestion is applicable include:
Al, Ba, Be, Cd, Ca, Cr (tot), Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Na, Tl, V, and Zn.

11.5.1 Add 3 mL of concentrated $HNO_3$, and several boiling chips to each sample, cover with watch glasses, and mix.

11.5.2 Place on a hotplate and maintain at 90-95°C until the volume has been reduced to approximately 5-10 mL. Remove and cool.

11.5.3 Add an additional 3 mL of concentrated $HNO_3$ to each sample, cover, and return to the hotplate for 20 minutes, or until the digestion is complete. Allow the volume to reduce to 5-10 mL. Remove and cool.

11.5.4 Add 5 mL of reagent water and 5 mL of concentrated HCl to each sample, cover, and return to the hotplate for 15 minutes. Remove and cool.

11.5.5 Rinse down the watchglass and sides of the beakers. If necessary, filter the digestate through a Whatman 41 filter paper into a clean 100-mL volumetric flask, dilute to the mark with reagent water, mix, and transfer to a metal-free container. The container should be labeled with:

- GLA Sample I.D.
- Matrix type
- Date digested
- Dilution factor (where applicable)

11.5.6 The samples are ready for analysis by ICP (or FLAA).

## 11.6 DIGESTION OF AQUEOUS LIQUIDS AND EXTRACTS FOR ANALYSIS BY GFAA (GF)

**NOTE:** Metal analytes for which this digestion is applicable include:
Be, Cd, Cr (tot), Pb, Mo, Tl, and V.

11.6.1 Add 3 mL of concentrated $HNO_3$, and several boiling chips to each sample, cover with watch glasses, and mix.

11.6.2 Place on a hotplate and maintain at 90-95°C until the volume has been reduced to approximately 5-10 mL. Remove and cool.

11.6.3 Add an additional 3 mL of concentrated $HNO_3$ to each sample, cover, and return to the hotplate for 20 minutes, or until the digestion is complete. Allow the volume to reduce to 5-10 mL. Remove and cool.

11.6.4 Add 10 mL of reagent water, cover, and return to the hotplate for 15 minutes. Remove and cool.

11.6.5 Rinse down the watchglass and sides of the beakers. If necessary, filter the digestate through a Whatman 41 filter paper into a clean 100-mL volumetric flask, dilute to the mark with reagent water, mix, and transfer to a metal-free container. The container should be labeled with:

- GLA Sample I.D.
- Matrix type
- Date digested
- Dilution factor (where applicable)

11.6.6 The samples are ready for analysis by GFAAS.

## 11.7 DIGESTION OF AQUEOUS LIQUIDS AND EXTRACTS FOR ANALYSIS OF As AND Se ONLY BY GFAA (AS)

**NOTE:** This digestion is applicable only for analysis of arsenic (As) and selenium (Se) by GFAAS.

11.7.1 Add 1 mL of concentrated $HNO_3$, 2 mL of 30% hydrogen peroxide, and several boiling chips to each sample, cover with watch glasses, and mix.

11.7.2 Place on a hotplate and maintain at 90-95°C until the volume has been reduced to approximately 50 mL. Remove and cool.

11.7.3 Rinse down the watchglass and sides of the beakers. If necessary, filter the digestate through a Whatman 41 filter paper into a clean 100-mL volumetric flask, dilute to the mark with reagent water, mix, and transfer to a metal-free container. The container should be labeled with:

- GLA Sample I.D.
- Matrix type
- Date digested
- Dilution factor (where applicable)

11.7.4 The samples are ready for analysis by GFAAS (for As and Se).

## 11.8 HOTPLATE DIGESTION OF NON-AQUEOUS AND MULTI-PHASE LIQUIDS FOR ANALYSIS BY ICP, GFAA, OR FLAA (NA) - METHOD 3010M

**NOTE:** Metal analytes for which this digestion is applicable include:
Ag, Al, As, Ba, Be, Cd, Ca, Cr (tot), Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Sb, Se, Na, Tl, V, and Zn.

11.8.1 Add 5 mL of concentrated $HNO_3$, and several boiling chips to each sample, cover with watch glasses, and mix.

11.8.2 Place on a hotplate and maintain at 90-95°C for 15 minutes, or until the volume has been reduced to approximately 10 mL. Remove and cool.

11.8.3 Add an additional 5 mL of concentrated $HNO_3$ to each sample, cover, and return to the hotplate for 30 minutes, or until the digestion is complete. Allow the volume to reduce to 5-10 mL. Remove and cool. Add an additional 5 mL of concentrated $HNO_3$, cover, and heat for an another 30 minutes. Allow the volume to reduce to 5-10 mL. Remove and cool.

11.8.4 Add 2 mL of reagent water and 3 mL of 30% hydrogen peroxide to each sample, cover, and return to the hotplate for 15 minutes. Remove and cool.

11.8.5 Rinse down the watchglass and sides of the beakers. Filter the digestate through a Whatman 41 filter paper into a clean 100-mL volumetric flask, dilute to the mark with reagent water, mix, and transfer to a metal-free container. The container should be labeled with:
- GLA Sample I.D.
- Matrix type
- Date digested
- Dilution factor (where applicable)

11.8.6 The samples are ready for analysis by ICP/GFAA/FLAA.

## 11.9 HOTPLATE DIGESTION OF AQUEOUS AND NON-AQUEOUS LIQUIDS FOR ANALYSIS OF TOTAL RECOVERABLE METALS BY ICP, GFAA, OR FLAA (A)

**NOTE:** Metal analytes for which this digestion is applicable include:
Ag, Al, As, Ba, Be, Cd, Ca, Cr (tot), Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Sb, Se, Na, Tl, V, and Zn.

11.9.1 Add 2 mL of concentrated $HNO_3$, 5 mL of concentrated HCl, and several boiling chips to each sample, cover with watch glasses, and mix.

11.9.2 Place on a hotplate and maintain at 90-95°C until the volume has been reduced to approximately 5-10 mL. **Do not boil samples!** Remove and cool.

11.9.3 Rinse down the watchglass and sides of the beakers. Filter the digestate through a Whatman 41 filter paper into a clean 100-mL volumetric flask, dilute to the mark with reagent water, mix, and transfer to a metal-free container. The container should be labeled with:
- GLA Sample I.D.
- Matrix type
- Date digested
- Dilution factor (where applicable)

11.9.4 The samples are ready for analysis by ICP/GFAA/FLAA.

# 12.0 MAINTENANCE AND TROUBLESHOOTING

## 12.1 GENERAL

Glassware should be cleaned appropriately to avoid sample contamination. Equipment should be kept clean and maintained to avoid sample contamination and assure proper operation. Manuals supplied by the manufacturers with the instrumentation typically have informational and troubleshooting sections.

## 12.2 TECHNICAL SUPPORT

Technical support is available from equipment manufacturers (for example, by telephone, fax, or e-mail). They can be a good resource when troubleshooting options have been exhausted. Technical support departments can readily supply part numbers.

# 13.0 REFERENCES

13.1 EPA Method 200.7: Inductively Coupled Plasma - Atomic Emission Spectrophotometric Method for Trace Element Analysis of Water and Wastes.
13.2 EPA Method 200.9: Determination of Trace Elements by Stabilized Temperature Graphite Furnace Atomic Absorption Spectrometry.
13.3 Method 3030: Preliminary Treatment of Samples, Sections E (Nitric Acid Digestion), F (Nitric Acid-Hydrochloric Acid Digestion), and K (Microwave-Assisted Digestion); Standard Methods for the Examination of Water and Wastewater, 18th Edition, 1992.
13.4 Method SW-846, 3050B: Acid Digestion of Sediments, Sludges, and Soils.
13.5 Great Lakes Analytical Quality Assurance Program.
13.6 Great Lakes Analytical Chemical Hygiene Plan.
13.7 Great Lakes Analytical SOP for Login Department.
13.8 Great Lakes Analytical SOP for Hazardous Sample Management.

# 14.0 DEFINITIONS

See References.

# APPENDIX A.

# METHOD EXCEPTIONS.

## A.1 Section 1.0 - Sample Preservation

EPA 200 Series, section 4.1.4:

- Amounts of nitric and hydrochloric acids added to the preserved sample are in accordance with SW-846 Method 3005.

SM-3030-F:

- Amounts of nitric and hydrochloric acids added to the preserved sample are in accordance with SW-846 Method 3005.

## A.2 Section 11.5 (ICP)

EPA Method 200.7:

- Section 11.2.3 - Acid concentrations are made in accordance with SW-846 3010A. The higher concentrations of acid will not compromise the digestion process.
- Sections 11.2.2-11.2.6 - Pre-concentration of samples is not performed unless detection levels are required that are below those attainable by current analytical procedures.

SM-3030-F:

- Additions of acid are made in accordance with SW-846 3010B. The higher concentrations of acid will not compromise the digestion process.

## A.3 Section 11.6 (GF)

EPA Method 200.9:

- Section 11.3.3 -The addition of hydrochloric acid in step 11.3.3 has been omitted, and an additional additions of nitric acid are made in its place. The interferences associated with chloride in graphite furnace analysis are well documented (for example, in EPA 200 Series, section 4.1.3).
- Sections 11.2.2-11.2.6 - Pre-concentration of samples is not performed unless detection levels are required that are below those attainable by current analytical procedures.

SM-3030-E:

- Additions of acid are made in accordance with SW-846 3010B. The higher concentrations of acid will not compromise the digestion process.

## A.4 Section 11.7 (AS)

SW-846 Methods 7060A and 7740A:

- The digestates are not pre-mixed with nickel nitrate modifier. The modifier is added to the sampler by the instrument autosampler at the time of analysis.

EPA 200 Series, Methods 206.2 and 270.2:

- The digestates are not pre-mixed with nickel nitrate modifier. The modifier is added to the sampler by the instrument autosampler at the time of analysis.

### A.5 Section 11.8 (NA)

Modified SW-846 Method 3010A (GLA Method 3010M):

- This method parallels SW-846 Method 3010A. The addition of hydrochloric acid has been replaced by addition of 3 mL of nitric acid. This method is used exclusively for the digestion of gasoline, diesel, oil, and oil sludge waste samples, and aqueous samples with a high organic content. These materials show a wide variance of analyte levels and these digestates are analyzed by ICP, GFAAS, or FLAA.
- For non-aqueous or multi-phase samples, a 5-25 g sample is taken, depending upon organic content and allowable regulatory detection levels required. This dilution factor is included in the final calculations of analyte concentrations.

# APPENDIX B.

## STANDARD SPIKING LEVELS AND VOLUMES.

| Standard | Aliquot/Volume | Aliquot/Volume | Aliquot/Volume | Aliquot/Volume |
|---|---|---|---|---|
| GLA-SPK-1A | | 0.05/50 | 0.10/50 | 0.10/50 |
| GLA-SPK-3B | 0.05/50 | | 0.10/50 | 0.10/50 |
| GLA-SPK-4B | | | | |
| GLA-SPK-5 | | 0.05/50 | 0.10/50 | 0.10/50 |
| GLA-SPK-6 | | | | 0.10/50 |
| EARTH | | 0.10/50 | 0.10/50 | |
| Tantalum Soln. | | 0.10/50 | 0.10/50 | 0.10/50 |

## Corresponding Elements and Concentrations (mg/L) per Matrix

| Set | Element | D $H_2O$ FNC | D $H_2O$ ICP | $H_2O$ | TCLP/SPLP Ext. |
|---|---|---|---|---|---|
| | Ag | 0.005 | | 0.01 | 0.51 |
| | As | 0.015 | | 0.03 | 0.03 |
| R | Ba | | 0.50 | 1.0 | 1.0 |
| C | Cd | 0.001 | | 0.002 | 0.502 |
| R | Cr | 0.003 | 0.50 | 1.006 | 1.006 |
| A | Hg | 0.001 | | 0.002 | 0.002 |
| | Pb | 0.015 | | 0.03 | 0.03 |
| | Se | 0.015 | | 0.03 | 0.03 |
| P | Be | | 0.50 | 1.0 | 1.0 |
| R | Cu | 0.015 | 0.50 | 1.03 | 1.03 |
| I | Ni | | 0.50 | 1.0 | 1.0 |
| R | Sb | 0.015 | 1.0 | 2.03 | 2.03 |
| T | Tl | 0.015 | 1.0 | 2.03 | 2.03 |
| Y | Zn | | 0.50 | 1.0 | 1.0 |
| | Al | | 0.5 | 1.0 | 1.0 |
| T | Co | | 0.5 | 1.0 | 1.0 |
| A | Fe | | 0.5 | 1.0 | 1.0 |
| L | Mn | | 0.5 | 1.0 | 1.0 |
| | V | | 0.5 | 1.0 | 1.0 |
| E | Ca | | 1.0 | 1.0 | |
| A | K | | 1.0 | 1.0 | |
| R | Li | | 1.0 | 1.0 | |
| T | Na | | 1.0 | 1.0 | |
| H | Mg | | 1.0 | 1.0 | |
| E | B | | 1.0 | 2.0 | 2.0 |
| X | Mo | | 1.0 | 2.0 | 2.0 |
| T | Si | | 1.0 | 2.0 | 2.0 |
| R | Sn | | 1.0 | 2.0 | 2.0 |
| A | Ta | | 1.0 | 2.0 | 2.0 |
| | Ti | | 1.0 | 2.0 | 2.0 |

## APPENDIX B (cont.)

Spiking standard stock solutions :

**GLA-SPK-1A**

| | |
|---|---|
| Sb, B, Mo, Si, Sn, Ti | 1000 mg/L |

**GLA-SPK-3B**

| | |
|---|---|
| Sb, As, Cu, Pb, Se, Tl | 15 mg/L |
| Ag | 5 mg/L |
| Cr | 3 mg/L |
| Cd. Hg | 1 mg/L |

**GLA-SPK-4B**

| | |
|---|---|
| Tl | 2000 mg/L |
| Al, Ba, Be, Cd, Cr, Co, Cu, | 1000 mg/L |
| Fe, Pb, Mn, Ni, Ag, V, Zn | 1000 mg/L |
| As, Se | 30 mg/L |

**GLA-SPK-5**

| | |
|---|---|
| Tl | 1000 mg/L |
| Al, Ba, Be, Cr, Co, Cu, | 500 mg/L |
| Fe, Mn, Ni, v, Zn | 500 mg/L |

**GLA-SPK-6**

| | |
|---|---|
| Cd, Ag | 250 mg/L |

**CLPP-ICS-A**

| | |
|---|---|
| Al, Ca, Mg | 5000 mg/L |
| Fe | 2000 mg/L |

**EARTH METALS**

| | |
|---|---|
| Ca. Mg, K, Na | 10000 mg/L |

**Tantalum Solution**

| | |
|---|---|
| Ta | 1000 mg/L |

## APPENDIX C.

# METALS GLASSWARE PREPARATION

**All glassware to be used in the preparation of solutions for metals analysis will be prepared according to the following procedure:**

**1. All beakers, funnels, flasks, stoppers and watch covers will be examined for gross contamination and soil removal.**

**2. Any analyst processing glassware through the laboratory dishwasher will use the appropriate detergent supplied.**

**3. All glassware shall subsequently be *hand-washed* using Neutrad soap (anionic detergent) and triple rinsed with tap water, then triple rinsed with de-ionized water, paying special attention to any glassware unduely etched, cracked or otherwise likely break and/or cause contamination of samples.**

**4. All glassware which will come into contact with samples to be analyzed for metals will be rinsed with a 50% Nitric Acid solution and triple rinsed with de-ionized water immediately prior to use. Glassware to be used for other inorganic analyses should be rinsed with an acid appropriate to the test. (e.g. - dilute sulfuric for nitrate/nitrite) and triple rinsed with de-ionized water.**

Copy #: 3050-001

# GREAT LAKES ANALYTICAL

## STANDARD OPERATING PROCEDURE

## FOR

## THE DIGESTION OF SOLIDS FOR THE ANALYSIS OF METALS

## GLA 3050 BG

Revision 3.2

Approved By:

Department Manager: _____ Date: 4/5/00

Quality Assurance Manager: _____ Date: 4/5/00

Laboratory Director: _____ Date: 4-5-00

# 1.0 APPLICABILITY

This standard procedure (SOP) provides instructions for the sample handing and digestion of solids in preparation for analysis of total metals by ICP-OES and FLAA/GFAAS. This SOP is an interpretation of EPA Methods 300.7 and 300.9; Standard Methods no. 3030, Sections E, F, and K; and SW-846 no. 3050B. This SOP is to be used in conjunction with the analysts' in-laboratory training, the Great Lakes Analytical Chemical Hygiene Plan (CHP), and the Great Lakes Analytical Quality Assurance Program.

**NOTE:** The digests produced using this procedure are not suitable for the analysis of mercury (Hg) or hexavalent chromium ($Cr^{6+}$).

## 1.1 MATRICES

This method is applicable to soils, solids (such as wipes and paints), sediments, and sludges. This method is a very strong acid digestion that will dissolve almost all elements; however, silicate structures are not normally dissolved.

## 1.2 REGULATORY APPICABILITY

40 CFR 121

# 2.0 SUMMARY

A representative portion of sample is digested with nitric acid and hydrogen peroxide, and then refluxed with additional nitric (for SW-846 method 3050B) or nitric/hydrochoric acids (EPA method 200.7). The digestate is then filtered and diluted for analysis by ICP, GFAAS, and/or FLAA. A separate sample is dried if necessary for dry weight calculations. Solid matrix types and amounts used include:

- Soils and sediments - 1-2 g portion.
- Paint chips - up to 2 g.
- Paint or dust wipes and filters - entire wipe or filter (including washings).
- Waste sludges - a larger portion may be taken based upon the dry weight, up to 2 g of solid.
- Miscellaneous - mixed solids, waste oil sludges (may require particle size reduction and sub-sampling).

The approximate linear upper ranges for a 2-g sample size are:

- As, Be, Cd, Co, Cr, Cu, Mo, Ni, Se, Ta, Tl, V, Zn - 1,000,000 mg/kg.
- Pb, Sb - 200,000 mg/kg.
- Ag, Ba - 2500 mg/kg.

Smaller sample sizes should be taken if limits are exceeded.

See Appendix A for method exceptions.

# 3.0 SAFETY

## 3.1 GENERAL

This SOP does not address all safety issues associated with its use. A reference file of material safety data sheets (MSDS's) is available to all personnel, along with the Great Lakes Analytical Chemical Hygiene Plan. Gloves are worn when handling chemicals and reagents.

### 3.2 CHEMICAL HYGIENE PLAN

The Great Lakes Analytical Chemical Hygiene Plan (CHP) is designed to establish safe work procedures and minimize exposure to hazardous chemicals encountered in the laboratory. The CHP provides information to employees regarding potential hazards and training to minimize these hazards.

### 3.3 HAZARDOUS SAMPLES

All samples that are received by the laboratory have the possibility of containing hazardous pollutants. They should be treated with caution at all times. Gloves are worn when handling samples. Also see the Great Lakes Analytical SOP for Hazardous Sample Management.

### 3.4 CHEMICALS SPECIFIC TO DIGESTIONS

30% Hydrogen peroxide is a strong oxidizer in the presence of acids, and can cause burns to eyes and skin. It can react violently when introduced to a sample in concentrated acid. Large volumes of hydrogen gas may be produced. Allow samples to cool thoroughly before adding hydrogen peroxide. Similarly, add concentrated nitric acid to samples carefully.

## 4.0 INTERFERENCES

4.1 Sample matrices can vary greatly, even within specific sample type groups, most notably waste sludges (for example, soil versus water treatment waste sludge). Any sample types exhibiting significantly different properties, such as high organic content or multi-phase samples, are to be handled as individual matrices, and appropriate matrix spikes should be produced and analyzed.

4.2 Daily monitoring test of the deionized water supply must have been performed and pass or meet appropriate criteria for analysis before the water can be used in sample preparation. All glassware to be used in the analysis must be cleaned and rinsed following the procedure outlined in Appendix C. Periodic cleaning of sample preparation and analysis areas, will be performed.

## 5.0 RECORD KEEPING

5.1 Each analyst is responsible for keeping accurate and up-to-date records of all digestions performed.

5.2 Digestion Log Book:

A log book will be maintained for all solid matrix types and associated digestions. All information regarding samples processed in the lab will be entered into this book. This information will include but is not limited to:

- Method reference number
- Client Name for each set of samples
- GLA Sample I.D. (one complete for each set)
- Initial sample weight used
- LIMS batch reference number
- Analyst's signature and date prepared/analyzed
- Reviewer's signature and date
- All readings, dilution factors, and calculated results
- Sample matrix type
- Spiking volumes used
- Spike standard identifier
- Spike standard concentration
- LCS and matrix spike information
- Final digestate volume

This log should also include any unique observations noted in regard to specific samples. Space will be reserved on each page for calculations and notes. All unused portions of logbook pages must be z'ed out.

5.3 Sample Schedule - All samples will be tracked through the lab using GLA sample I.D. numbers generated by the GLA LIMS system.

# 6.0 QUALITY CONTROL

## 6.1 QUALITY CONTROL SAMPLES

Quality control samples are run at a minimum 5% frequency (*i.e.* one set with every batch of twenty or less samples). The results of these samples are used to gauge accuracy and precision of the method. These samples include method blanks (MB), lab control samples (LCS), matrix spikes (MS) and matrix spike duplicates (MSD). The quality control samples contain all reagents and are subjected to all preparation steps. They are processed and analyzed along with test samples.

## 6.2 METHOD BLANK

Matrix-matched method blanks (MB) containing all reagents and subjected to all preparation steps are processed and analyzed along with the samples. Method blanks must produce a concentration below the reporting limit (*e.g.* PQL, EQL, ...) for an analytical batch to be valid. These samples provide a measure of laboratory and/or reagent contamination. Test sample results are not corrected for the method blank concentrations.

## 6.3 LABORATORY CONTROL SAMPLE (LCS)

An external (independently sourced) reference standard is prepared within the working range of the method and analyzed with each matrix per batch of twenty or less samples (*i.e.* minimum 5% frequency). The results of the samples must be within established control limits, or where there is not enough data to calculate control limits, within 15% of the known value.

## 6.4 MATRIX SPIKED SAMPLES

Matrix spiked samples (MS and MSD) will be analyzed with a minimum frequency of 5% (*e.g.* one set per 20 or less samples per matrix) and are used to determine accuracy and precision of a method. The matrix spiked samples will be spiked using the same standards used to spike the LCS samples. The analyzed result of the matrix spikes must be within established control limits, or where there is not enough data to calculate control limits, within 25% of the known value.

## 6.5 SURROGATE MATRIX BLANK AND SPIKED SAMPLES

In cases where no additional sample is available for matrix spiking (*e.g.* wipes samples), a set of surrogate matrix QC samples will be produced by digesting an appropriate substrate "blank" and two spiked samples of the same substrate spiked with the same standards and at the same levels of the LCS.

## 6.6 QUALITY CONTROL TRACKING AND DATA REVIEW

The QC data is considered acceptable and actual samples results can be evaluated and reported by the analyst if all QC samples are within established control limits.

### 6.7 CORRECTIVE ACTION

If a quality control measure fails, corrective action is taken and documented to ensure the accuracy of the data that is reported. Examples of when corrective action sheets are filled out are:

- A sample or QC is re-analyzed. This may be due to the QC parameter failing or mislabeling of samples.
- Samples are reported with a QC result (blank, spike matrix) parameter out of control. In this case, not only should a corrective action be initiated, but the data must be flagged.
- A deviation from the normal SOP for the method is discovered (*e.g.* a digestion goes down to dryness or a different concentration of reagent is used) and the sample is analyzed and reported.
- An error in a previously reported sample is discovered.

## 7.0 SAMPLE MANAGEMENT

7.1 The procedures for sample management are detailed in the Great Lakes Analytical SOP for sample receipt into the laboratory.

7.2 Sample Schedule: Analysts keep track of sample throughput by using the Laboratory Information Management System (LIMS). The system is checked daily and a hard copy generated. Samples for this method are queued under "METP". The information includes:

- Client name.
- Sample numbers.
- Project name.
- Matrix.
- Hold time and turnaround time.

## 8.0 METHOD VALIDATION

### 8.1 QUALITY CONTROL BOOK

Method validation must be performed before any actual samples can be analyzed. Method validation studies are required to be stored in the QC logbook. Method exception studies must also be performed to validate any exception taken by proving equivalency with the unaltered method. The contents of the QC book include:

- Copy of the GLA Quality Assurance Program.
- Copies of GLA SOP and source methods.
- Copy of the precision and accuracy study for the method.
- Copies of all method detection limit studies and dates in use.
- Check standard recovery tabulations and control limits.
- Spike and spike duplicate recovery tabulations and control limits.
- Corrective action sheets.

### 8.2 QUALITY ASSURANCE PROGRAM

Internal audits will be performed periodically to assess analytical system performance. Performance evaluation samples will be analyzed periodically to assess laboratory performance. (Refer to the GLA Quality Assurance Program.)

### 8.3 METHOD DETECTION LIMIT STUDY

8.3.1 The method detection limit (MDL) is defined as the minimum concentration of analyte that can be determined with 99% confidence. It is determined as follows:

- Prepare a minimum of seven replicate samples at a concentration at or near the expected MDL. Carry these replicates through the entire sample preparation procedure and analysis.
- Calculate the MDL by taking the standard deviation of the results of the seven replicates and multiply by the Student's t value at n-1 degrees of freedom (3.143 for seven replicates).

8.3.2 Other factors such as matrix effects and instrument noise may affect the attainable detection limit. These should be quantified if possible and taken in to account when determining an MDL as the obtainable detection level may be artificially elevated due to these factors.

8.3.3 A new MDL study must be performed to re-evaluate the method if any major instrument maintenance or service is performed, if any new method exceptions or changes are made or at least annually.

## 9.0 EQUIPMENT

9.1 Beakers, Griffin type, 250-mL size.
9.2 Watch covers, ribbed, 90-mm diameter.
9.3 Volumetric flasks, 25-100 mL (wide mouth).
9.4 Glass funnels.
9.5 Filter paper - 9 and 15 cm, Whatman 41, or equivalent.
9.6 Sample containers, 50 or 100-mL capacity, metal-free.
9.7 Hotplate, adjustable, capable of maintaining a constant temperature for samples of 90-95°C. Monitor temperature of the hotplate by placing an Erlenmeyer flask with approximately 100 mL of cooking oil at the center of the hotplate, and reading the temperature with an ASTM thermometer positioned with the bulb against the bottom of the flask. The temperature must be at least 140°C. Record temperatures in the log book.
9.8 Analytical balance, calibrated - capable of weighing to nearest 0.1 g for soil/sediment/sludge samples, 0.001 g for paints.
9.9 Hot block digestion apparatus:
- HotBlock, Environmental Systems, set to maintain a sample temperature of 90-95°C.
- Polyolefin digestion vessels, 50-mL size, with watch covers and snap-on caps.

## 10.0 STANDARDS AND REAGENTS

10.1 Reagent water - ASTM Type II Water (DI water).
10.2 Nitric acid - concentrated $HNO_3$, ACS/reagent grade, Fisher no. A509. **CAUTION:** Nitric acid is corrosive.
10.3 Hydrochloric acid - concentrated HCl, ACS/analytical reagent grade, Fisher no. A508. **CAUTION:** Hydrochloric acid is corrosive.
10.4 Hydrogen peroxide - 30% $H_2O_2$, ACS/analytical reagent grade, Fisher no. H325. **CAUTION:** Hydrogen peroxide is an oxidizer.
10.5 Spiking standards - GLA-SPK-1A and -4B, Inorganic Ventures; GLA-SPK-EM (earth metals spike) prepared from individual 10,000 ppm solutions (from Inorganic Ventures) for final concentrations of 2000 ppm of Na, K, Ca, and Mg. (Refer to Appendix B for concentrations and volumes spiked.)

## 11.0 PROCEDURE

**NOTE**: Method validation (section 8.0) must be performed before samples can be analyzed.

### 11.1 SELECTION OF DIGESTION PROCEDURE

The appropriate method for the required metal analysis must be referenced in order to select the proper digestion procedure. There are several methods for digestions which can be selected based upon the matrix type of the sample and the type of digestion being performed. Use Table 1 to determine which method is most applicable to the samples being analyzed. The proper digestion procedure is selected from Table 2.

**Table 1.**
Digestion Method Reference Chart.

| Analysis | Method Reference | Microwave Digestions | Standard Digestions | | |
|---|---|---|---|---|---|
| | | | ICP/FLAA | GFAA | Special |
| Total Metals | SW-846 | 3051A | 3050B + HCl | 3050B + $HNO_3$ | 7060A (As) 7740A (Se) |
| | EPA | n/a | 200.7 | 200.9 | 206.2 (As) 270.2 (Se) |
| Air Filters | NIOSH | n/a | 7082 | 7082 | n/a |

**Table 2.**
Procedure Selection Table.

| Digestion Type | Analysis Type | Analysis Method | Applicable Method(s) | Digestion Procedure |
|---|---|---|---|---|
| Standard | Total Metals | Any (1) | SW-846 3050B EPA 200.9 (3) | 11.4 (GEN) |
| Standard | Air Filter - Lead Only | Any (1) | NIOSH 7082 | 11.4 (GEN) |
| Standard | Total Metals (2) | ICP/FLAA | SW-846 3050B EPA 200.7 (4) | 11.5 (ICP) |
| HotBlock | Total Metals | Any (1) | SW-846 3050B | 11.6 (HB) |

(1) Any analytical method refers to GLA routine methods : ICP, GFAAS, and FLAA. These digests are not suitable for analysis of mercury or hexavalent chromium.
(2) For samples requiring addition of hydrochloric acid. This procedure produces digestates which can only be analyzed by ICP-OES.
(3) Samples are refluxed with nitric acid for metals determination by all analytical methods.
(4) Samples are refluxed with hydrochloric acid for metals determination by ICP-OES only.

**11.2** Assemble all materials and equipment required for the procedure. A daily calibration check of the analytical balance must have been performed prior to its use in weighing samples or standard materials. Record all pertinent sample information in the log book(s) ***before beginning the analysis***.

**CAUTION:** All hotplate digestions must be performed in a fume hood.

## 11.3 PREPARATION OF QUALITY CONTROL AND TEST SAMPLES

11.3.1 Soil, sediment, and other solid samples:

- Samples - A representative 2.0g +/- 0.01g (1.0 g for hotblock digestion, section 11.6) aliquot is weighed into a clean beaker (or digestion tube for hotblock digestion).
- Matrix spikes - Measure two additional aliquots of one sample, with weights similar to the test sample weight, and making sure each aliquot is homogeneous and representative of the entire sample. Accurately aliquot 0.1 mL each of GLA-SPK-1A, -4B, As/Se Soln., Tantalum Soln., and -EM into the sample replicates, and mark them as MS and MSD.
- LCS – Combine 7.5ml of reagent water and 7.5ml of nitric acid. Accurately aliquot 0.05ml each of GLA-SPK-1A, -4B, As/Se Soln., Tantalum Soln., and -EM into the solution, and mark the sample as LCS.

  Note: If requested, the sample weight can be based on dry-weight –corrected soil.. Refer to SOP GLA160BG for instructions on determining dry weight.

11.3.2 Sludge/high water content samples:

- Samples - Each sample should be well mixed before taking a representative portion for digestion. If the sample contains significant water, upon client request, a dry weight determination may be performed prior to digestion (See SOP GLA160BG for dry weight determination), and the sample size adjusted and/or calculated as follows:

$$\textit{sample weight (g)} = \frac{\textit{2.0 (1.0 for hotblock) g}}{\textit{dry weight (as decimal percent)}}$$

- Matrix spikes - Measure two additional aliquots of one sample, with weights similar to the test sample weight, and making sure each aliquot is homogeneous and representative of the entire sample. Accurately aliquot 0.1 mL each of GLA-SPK-1A, -4B, As/Se Soln., Tantalum Soln., and -EM into the sample replicates. Add 5 mL of reagent water to each, washing the spike solutions into the beakers or vessels. Mark as MS and MSD.
- LCS – Combine 7.5ml of reagent water and 7.5ml of nitric acid. Accurately aliquot 0.05ml each of GLA-SPK-1A, -4B, As/Se Soln., Tantalum Soln., and -EM into the solution, and mark the sample as LCS.

11.3.3 Wipes samples (surrogate matrix QC):

- Samples - Transfer the entire wipe into a clean beaker along with any liquid and/or loose material which has fallen off the wipe. Rinse the sample container with three successive portions of reagent water, adding each rinsate to the beaker.
- Surrogate matrix blank - Place a 9- or 15-cm Whatman 41 filter paper into a clean beaker. Add 15 mL of reagent water.
- LCS - Place 9- or 15-cm Whatman 41 filter paper into two clean and dry beakers. Weigh 0.02-0.04 g of NIST SRM1579a onto the filter paper. Allow any paint dust from the SRM addition to settle, and record an accurate weight in the log book to the nearest 0.0001 g. Carefully add 15 mL of reagent water.

11.3.4 Paint/paint dust samples:

- Samples - Weigh as large a portion as possible, up to 2 g (accurately to the nearest 0.0001 g), into a clean beaker. Record the weight(s) in the log book.
- Surrogate matrix spike samples - Place 9 (or 15) cm Whatman 41 filter paper into two clean and dry beakers. Weigh 0.02-0.04 g of NIST SRM1579a onto the filter paper. Allow any paint dust from the SRM addition to settle, and record an accurate weight in the log book to the nearest 0.0001 g. Carefully add 15 mL of reagent water.

## 11.4 HOTPLATE DIGESTION OF SOLIDS FOR ANALYSIS BY ICP-OES, GFAAS, OR FLAA (GEN)

**NOTE** Metal analytes for which this digestion is applicable include:
Ag Al, As, Ba, Be, Cd, Ca, Cr (tot), Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Na, Sb, Se, Ta, Tl, V, Zn.

11.4.1 Add 5 mL of reagent water (except for wipes samples), 5 mL of concentrated $HNO_3$, and several boiling chips to each sample, cover with watchglasses, and mix.

11.4.2 Place on a hotplate and maintain at 90-95°C for 15 minutes. Remove and cool.

11.4.3 Add an additional 5 mL of concentrated $HNO_3$ to each sample, cover, and return to the hotplate for 30 minutes. Remove and cool.

11.4.4 Add a third 5 mL portion of concentrated $HNO_3$ to each sample, cover, and return to the hotplate for 30 minutes. Allow solutions to evaporate to approximately 5 mL. Remove and cool.

11.4.5 After the samples have cooled, add 2 mL of reagent water and 3 mL of 30% hydrogen peroxide to each. Warm gently if necessary to start the peroxide reaction. Heat until the effervescence subsides. Make further 1 mL additions of hydrogen peroxide until the effervescence is minimal, or the general sample appearance remains unchanged. Return to the hot plate for 15 minutes to destroy excess peroxide.

11.4.6 Transfer the digestate to a 100-mL volumetric flask. Dilute to the mark with reagent water and mix. If samples are to be analyzed immediately, filter the digestate through a Whatman 41 filter paper into a metal-free container. Otherwise, samples may be allowed to settle 1 hour, or overnight, prior to analysis. The container should be labeled with:

- GLA Sample I.D.
- Matrix type
- Date digested
- Dilution factor, if other than standard weight or volume (where applicable)

11.4.7 The samples are ready for analysis by ICP, GFAAS, or FLAA.

## 11.5 HOTPLATE DIGESTION OF SOLIDS FOR ANALYSIS BY ICP-OES OR FLAA ONLY (ICP)

**NOTE:** Metal analytes for which this digestion is applicable include:
Al, Ba, Be, Cd, Ca, Cr (tot), Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Na, Tl, V, and Zn.

11.5.1 Add 5 mL of reagent water (except for wipes samples), 5 mL of concentrated $HNO_3$, and several boiling chips to each sample, cover with watch glasses, and mix.

11.5.2 Place on a hotplate and maintain at 90-95°C for 15 minutes. Remove and cool.

11.5.3 Add an additional 5 mL of concentrated $HNO_3$ to each sample, cover, and return to the hotplate for 30 minutes. Remove and cool.

11.5.4 Add a third 5 mL portion of concentrated $HNO_3$ to each sample, cover, and return to the hotplate for 30 minutes. Allow solutions to evaporate to approximately 5 mL. Remove and cool.

11.5.5 After the samples have cooled, add 2 mL of reagent water and 3 mL of 30% hydrogen peroxide to each. Warm gently if necessary to start the peroxide reaction. Heat until the effervescence subsides. Make further 1 mL additions of hydrogen peroxide until the effervescence is minimal, or the general sample appearance remains unchanged. Return to the hot plate for 15 minutes to destroy excess peroxide.

11.5.6 Add 5 mL of concentrated HCl and 10 mL of reagent water to each sample. Cover and return to hotplate for 15 minutes. Remove and cool.

11.5.7 Transfer the digestate to a 100-mL volumetric flask. Dilute to the mark with reagent water and mix. Filter the digestate through a Whatman 41 filter paper into a metal-free container. The container should be labeled with:
- GLA Sample I.D.
- Matrix type
- Date digested
- Dilution factor, if other than standard weight or volume (where applicable)

11.5.8 The samples are ready for analysis by ICP or FLAA.

### 11.6 HOTBLOCK DIGESTION OF SOLIDS FOR ANALYSIS BY ICP-OES, GFAAS, OR FLAA (HB)

**NOTE:** Metal analytes for which this digestion is applicable include:
Al, As, Ba, Be, Cd, Ca, Cr (tot), Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Na, Sb, Se, Ta, Tl, V, Zn.

**NOTE:** This procedure is not applicable for wipes samples.

11.6.1 Add 5 mL of reagent water (except for wipes samples) and 7.5 mL of concentrated $HNO_3$, to each sample. Cover and mix.

11.6.2 Place in digestor and heat for 75 minutes, maintaining sample temperatures of 95-100°C. Remove and cool.

11.6.3 After the samples have cooled, slowly and carefully add 1 mL of 30% hydrogen peroxide to each. Allow vigorous reaction to subside. Place in digestor and heat for 15 minutes, maintaining sample temperatures of 95-100°C. Remove and cool.

11.6.4 Bring total sample volumes to 50 mL each with reagent water, cover and mix. Allow samples to settle at least 1 hour (or overnight). If immediate analysis is required, samples may be filtered through Whatman 41 filter paper. The container should be labeled with:
- GLA Sample I.D.
- Matrix type
- Date digested
- Dilution factor (where applicable)

11.6.5 The samples are ready for analysis by ICP, GFAAS, or FLAA.

## 12.0 MAINTENANCE AND TROUBLESHOOTING

### 12.1 GENERAL

Glassware should be cleaned appropriately to avoid sample contamination. Equipment should be kept clean and maintained to avoid sample contamination and assure proper operation. Manuals supplied by the manufacturers with the instrumentation typically have informational and troubleshooting sections.

### 12.2 TECHNICAL SUPPORT

Technical support is available from equipment manufacturers (for example, by telephone, fax, or e-mail). They can be a good resource when troubleshooting options have been exhausted. Technical support departments can readily supply part numbers.

## 13.0 REFERENCES

13.1 EPA Method 200.7: Inductively Coupled Plasma - Atomic Emission Spectrophotometric Method for Trace Element Analysis of Water and Wastes.
13.2 EPA Method 200.9: Determination of Trace Elements by Stabilized Temperature Graphite Furnace Atomic Absorption Spectrometry.
13.3 Method 3030: Preliminary Treatment of Samples, Sections E (Nitric Acid Digestion), F (Nitric Acid-Hydrochloric Acid Digestion), and K (Microwave-Assisted Digestion); Standard Methods for the Examination of Water and Wastewater, 18th Edition, 1992.
13.4 Method SW-846, 3050B: Acid Digestion of Sediments, Sludges, and Soils.
13.5 NIOSH Method 7082: Analysis of Lead in Air Filters.
13.6 Great Lakes Analytical Quality Assurance Program.
13.7 Great Lakes Analytical Chemical Hygiene Plan.
13.8 Great Lakes Analytical SOP for Login Department.
13.9 Great Lakes Analytical SOP for Hazardous Sample Management.

## 14.0 DEFINITIONS

Refer to the Great Lakes Analytical Quality Assurance Program Manual.

# APPENDIX A.

# METHOD EXCEPTIONS.

## A.1 Section 1.0 - Sample Preservation

EPA 200 Series, section 4.1.4:

- Amounts of nitric and hydrochloric acids added to the preserved sample are in accordance with SW-846 Method 3005.

SM-3030-F:

- Amounts of nitric and hydrochloric acids added to the preserved sample are in accordance with SW-846 Method 3005.

## A.2 Section 11.4 - Sample Digestion (GEN)

EPA Method 200.7:

- Section 11.2.3 - Acid concentrations are made in accordance with SW-846, 3010B. The higher concentrations of acid will not compromise the digestion process.
- Sections 11.2.2-11.2.6 - Pre-concentration of samples is not performed unless detection levels are required that are below those attainable by current analytical procedures.

SM-3030-F:

- Additions of acid are made in accordance with SW-846, 3010B. The higher concentrations of acid will not compromise the digestion process.

## A.3 Section 11.5 - Sample Digestion (ICP)

EPA Method 200.9:

- Section 11.3.3 - The addition of hydrochloric acid has been omitted an additional addition of nitric acid made its place. The interferences associated with chloride in the graphite furnace analysis are well documented in many reference documents (for example, EPA 200 Series, section 4.1.3).
- Sections 11.2.2-11.2.6 - Pre-concentration of samples is not performed unless detection levels are required that are below those attainable by current analytical procedures.

SM-3030-E:

- Additions of acid are made in accordance with SW-846, 3010B. The higher concentrations of acid will not compromise the digestion process.

# APPENDIX B.

## STANDARD SPIKING LEVELS AND VOLUMES.

| | Standard | Aliquot/Volume |
|---|---|---|
| | GLA-SPK-1A | 0.10/100 |
| | GLA-SPK-4B | 0.10/100 |
| | As/Se | 0.05/50 |
| | EARTH | 0.05/100 |
| | Tantalum Soln | 0.05/100 |

## Corresponding Elements and Concentrations (mg/Kg)

| Set | Element | Soil/Solid |
|---|---|---|
| RCRA | Ag | 1.0 |
| | As | 0.53 |
| | Ba | 1.0 |
| | Cd | 1.0 |
| | Cr | 1.0 |
| | Hg | |
| | Pb | 1.0 |
| | Se | 0.28 |
| PRIRTY | Be | 1.0 |
| | Cu | 1.0 |
| | Ni | 1.0 |
| | Sb | 1.0 |
| | Tl | 2.0 |
| | Zn | 1.0 |
| TAL | Al | 1.0 |
| | Co | 1.0 |
| | Fe | 1.0 |
| | Mn | 1.0 |
| | V | 1.0 |
| EARTH | Ca | 1.0 |
| | K | 1.0 |
| | Li | 1.0 |
| | Na | 1.0 |
| | Mg | 1.0 |
| EXTRA | B | 1.0 |
| | Mo | 1.0 |
| | Si | 1.0 |
| | Sn | 1.0 |
| | Ta | 1.0 |
| | Ti | 1.0 |

## APPENDIX B (cont.)

Spiking standard stock solutions :

**GLA-SPK-1A**

| | |
|---|---|
| Sb, B, Mo, Si, Sn, Ti | 1000 mg/L |

**GLA-SPK-4B**

| | |
|---|---|
| Tl | 2000 mg/L |
| Al, Ba, Be, Cd, Cr, Co, Cu, | 1000 mg/L |
| Fe, Pb, Mn, Ni, Ag, V, Zn | 1000 mg/L |
| As, Se | 30 mg/L |

**EARTH METALS**

| | |
|---|---|
| Ca, Mg, K, Na | 10000 mg/L |

**As/Se Solution**

| | |
|---|---|
| As, Se | 1000 mg/L |

**Tantalum Solution**

| | |
|---|---|
| Ta | 1000 mg/L |

# APPENDIX C.

# METALS GLASSWARE PREPARATION

**All glassware to be used in the preparation of solutions for metals analysis will be prepared according to the following procedure:**

**1. All beakers, funnels, flasks, stoppers and watch covers will be examined for gross contamination and soil removal.**

**2. Any analyst processing glassware through the laboratory dishwasher will use the appropriate detergent supplied.**

**3. All glassware shall subsequently be *hand-washed* using Neutrad soap (anionic detergent) and triple rinsed with tap water, then triple rinsed with de-ionized water, paying special attention to any glassware unduely etched, cracked or otherwise likely break and/or cause contamination of samples.**

**4. All glassware which will come into contact with samples to be analyzed for metals will be rinsed with a 50% Nitric Acid solution and triple rinsed with de-ionized water immediately prior to use. Glassware to be used for other inorganic analyses should be rinsed with an acid appropriate to the test. (e.g. - dilute sulfuric for nitrate/nitrite) and triple rinsed with de-ionized water.**