



Title: Quality Assurance and Quality Control Requirements and Performance Standards for SVW-846 Method 6010B, Trace Metals by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES)

Table III A-3 Routine QA/QC Reporting Requirements for SW-846 Method 6010B

| Parameter | Required Analytical Deliverable |
|---|---|
| Initial Calibration | NO |
| Initial Calibration Verification (ICV) | NO |
| Initial Calibration Blank (ICB) | NO |
| Low Level Calibration Check standard | NO |
| Continuing Calibration Verification (CCV) | NO |
| Continuing Calibration Blank (CCB) | NO |
| Interference Check Standards (ICS A and B) | NO |
| Method (Preparation) Blank | YES |
| Laboratory Control Samples (LCS) | YES |
| LCS Duplicate (or project-specific MD or MSD) | YES |
| Project-specific Matrix Spike Sample (MS) | YES, <u>only</u> if requested by the LSP |
| Project-specific Matrix Duplicate (MD) | YES, <u>only</u> if requested by the LSP |
| Project-specific Matrix Spike Duplicate (MSD) | YES, <u>only</u> if requested by the LSP |
| Linear Range Analysis | NO |
| Inter-element Spectral Interference Correction Analysis | NO |
| General Reporting – sample specific reporting limits | YES |



Title: Quality Assurance and Quality Control Requirements and Performance Standards for SW-846 Method 6010B, Trace Metals by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES)

4.0 Regulatory Limits for Metals under 310 CMR 40.000

The most stringent (lowest) MCP Reportable Concentrations (RCs) and Method 1 Standards for metals analyzable by SW-846 Method 6010B are as follows:

| Metal | RQ Pounds | RC GW-1 mg/L - (ppm) | RC S-1 mg/kg - (ppm) | Method 1 Groundwater ug/L - ppb | Method 1 Soils ug/g - ppm |
|----------------------|--------------|-------------------------|----------------------------|---------------------------------------|---------------------------------|
| Antimony | 50 | 0.006 | 10 | 6 | 10 |
| Arsenic | 1 | 0.05 | 30 | 50 | 30 |
| Barium | 100 | 2 | 1000 | 2000 | 1000 |
| Beryllium | 5 | 0.004 | 0.7 | 4 | 0.7 |
| Cadmium | 5 | 0.005 | 30 | 5 | 30 |
| Chromium (III) | 100 | 0.1 | 1000 | 100 | 1000 |
| Chromium (VI) | 100 | 0.1 | 1000 | 50 | 200 |
| Cobalt | 50 | 5 | 500 | NS | NS |
| Copper | 100 | 10 | 1000 | NS | NS |
| Lead | 5 | 0.02 | 300 | 15 | 300 |
| Lithium | 10 | 1 | 100 | NS | NS |
| Mercury ¹ | 1 | 0.001 | 20 | 2 | 20 |
| Nickel | 10 | 0.08 | 300 | 80 (GW-3) | 300 |
| Phosphorous | 1 | NA | NA | NS | NS |
| Potassium | 10 | NA | NA | NS | NS |
| Selenium | 10 | 0.05 | 400 | 50 | 400 |
| Silver | 50 | 0.007 | 100 | 7 (GW-3) | 100 |
| Sodium | 5 | NA | NA | NS | NS |
| Thallium | 50 | 0.002 | 8 | 2 | 8 |
| Vanadium | 50 | 0.05 | 400 | 50 | 400 |
| Zinc | 50 | 0.9 | 2500 | 900 (GW-3) | 2500 |

NA – Not Applicable

RQ – Reportable Quantity

RC – Reportable Concentration for Groundwater (GW-1) and Soils (S-1)

Method 1 Groundwater – GW-1 Category unless otherwise noted

Method 1 Soils – Category S-1/GW-1 in all cases

NS – No MCP Method 1 Standard has been promulgated by the Department.

¹ Mercury values presented for completeness only. Analyze mercury by SW-846 Methods 7470A and 7471



Title: Sample Collection, Preservation, And Handling Procedures for SW-846 Method 6010B, Trace Metals by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES)

Sample preservation, container and analytical holding time specifications for surface water, groundwater, soil, sediment and wastes matrices for metal analyses conducted in support of MCP decision-making are summarized below and presented in Appendix VII-A of WSC-CAM-VIIA, Quality Assurance and Quality Control Guidelines for Sampling, Data Evaluation, and Reporting Activities for the Massachusetts Contingency Plan (MCP). Additional guidance may be found in SW-846, Chapter Three

| Matrix | Sample Container(s) ¹ | Preservative | Holding Time ² |
|--|---|--|---|
| Total Metals Groundwater and Surface Water | (1) 1-L Polyethylene Bottle for Total Metals | HNO ₃ to pH < 2, | 180 days: all metals except mercury 28 days: mercury |
| Dissolved Metals Groundwater and Surface Water | (1) 1-L Polyethylene Bottle for field-filtered sample for Dissolved Metals | Filter (0.45 µm) unpreserved sample on site; or at the laboratory (prior to acid preservation) within 24 hours of collection, then HNO ₃ to pH <2, | 180 days: all metals except mercury 28 days: mercury |
| Suspended Metals Groundwater and Surface Water | Submit Suspended Solids on Filter to Laboratory | Filter on site Filter 100 – 500 ml of unpreserved sample | 180 days: all metals except mercury 28 days: mercury |
| Soils and Sediments | (1) 4-ounce glass jar | Cool, 4°C | 180 days: all metals except mercury 28 days: mercury |
| Concentrated Waste Samples | 125 mL wide mouth glass or plastic | Cool to 4°C | 180 days: all metals except mercury 28 days: mercury |

1 The number of sampling containers specified is not a requirement. For specific analyses, the collection of multiple sample containers is encouraged to avoid resampling if sample is consumed or compromised.

2 From date of sample collection.



Title: Methods for Sample Digestion or Preparation by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES)

| SW-846 Method | Method Description |
|--------------------------|---|
| 3005 | Method prepares ground water and surface water samples for total recoverable and dissolved metal determinations by FLAA, ICP-AES, or ICP-MS. The unfiltered or filtered sample is heated with dilute HCl and HNO prior to metal determination. |
| 3010 | Method prepares waste samples for total recoverable metal determinations by FLAA, ICP-AES, or ICP-MS. The samples are vigorously digested with nitric acid followed by dilution with hydrochloric acid. The method is applicable to aqueous samples, EP and mobility-procedure extracts. |
| 3015 | Method prepares aqueous samples, mobility-procedure extracts, and wastes that contain suspended solids for total recoverable metal determinations by FLAA, GFAA, ICP-AES, or ICP-MS. Nitric acid is added to the sample in a Teflon digestion vessel and heated in a microwave unit prior to metals determination. |
| 3031 | Method prepares waste oils, oil sludges, tars, waxes, paints, paint sludges and other viscous petroleum products for analysis by FLAA, GFAA, and ICP-AES. The samples are vigorously digested with nitric acid, sulfuric acid, hydrochloric acid, and potassium permanganate prior to analysis. |
| 3040 | Method prepares oily waste samples for determination of soluble metals by FLAA, GFAA, and ICP-AES methods. The samples are dissolved and diluted in organic solvent prior to analysis. The method is applicable to the organic extract in the oily waste EP procedure and other samples high in oil, grease, or wax content |
| 3050 | Method prepares waste samples for total recoverable metals determinations by FLAA and ICP-AES, or GFAA and ICP-MS depending on the options chosen. The samples are vigorously digested in nitric acid and hydrogen peroxide followed by dilution with either nitric or hydrochloric acid. The method is applicable to soils, sludges, and solid waste samples. |
| 3051 | Method prepares sludges, sediments, soils and oils for total recoverable metal determinations by FLAA, GFAA, ICP-AES or ICP-MS. Nitric acid is added to the representative sample in a fluorocarbon digestion vessel and heated in a microwave unit prior to metals determination. |
| 3052 | Method prepares siliceous and organically based matrices including ash, biological tissue, oil, oil contaminated soil, sediment, sludge, and soil for total analysis by FLAA, CVAA, GFAA, ICP-AES, and ICP-MS. Nitric acid and hydrofluoric acid are added to a representative sample in a fluorocarbon digestion vessel and heated in a microwave unit prior to analysis |

Analytical Method Information

| Analyte | MDL | Reporting Limit | Surrogate %R | Duplicate RPD | Matrix Spike %R | RPD | Blank Spike / LCS %R | RPD |
|---|-------|------------------------|--------------|---------------|--------------------|-----|----------------------|-----|
| CAM 17 GFAA or ICP/MS in Soil (EPA 7000) | | | | | | | | |
| Preservation:Store cool at 4°C | | | | | | | | |
| Container:8 oz. jar | | Amount Required:10 g | | | Hold Time:180 days | | | |
| Arsenic | 0.036 | 0.25 mg/kg | | | 75 - 125 | 30 | 75 - 125 | 25 |
| Lead | | 0.25 mg/kg | | | 75 - 125 | 30 | 75 - 125 | 25 |
| Selenium | 0.097 | 0.25 mg/kg | | | 75 - 125 | 30 | 75 - 125 | 25 |
| Thallium | 0.059 | 0.25 mg/kg | | | 75 - 125 | 30 | 75 - 125 | 25 |
| CAM 17 ICP in Soil (EPA 6010B) | | | | | | | | |
| Preservation:Store cool at 4°C | | | | | | | | |
| Container:8 oz. jar | | Amount Required:500 mL | | | Hold Time:180 days | | | |
| Antimony | 2.0 | 2.5 mg/kg | | | 75 - 125 | 30 | 75 - 125 | 25 |
| Barium | 0.57 | 1.0 mg/kg | | | 75 - 125 | 30 | 75 - 125 | 25 |
| Beryllium | 0.050 | 0.50 mg/kg | | | 75 - 125 | 30 | 75 - 125 | 25 |
| Cadmium | 0.15 | 0.50 mg/kg | | | 75 - 125 | 30 | 75 - 125 | 25 |
| Cobalt | 0.080 | 1.0 mg/kg | | | 75 - 125 | 30 | 75 - 125 | 25 |
| Chromium | 0.31 | 1.0 mg/kg | | | 75 - 125 | 30 | 75 - 125 | 25 |
| Copper | 0.30 | 1.0 mg/kg | | | 75 - 125 | 30 | 75 - 125 | 25 |
| Lead | 0.87 | 2.5 mg/kg | | | 75 - 125 | 30 | 75 - 125 | 25 |
| Molybdenum | 0.24 | 1.0 mg/kg | | | 75 - 125 | 30 | 75 - 125 | 25 |
| Nickel | 0.21 | 1.0 mg/kg | | | 75 - 125 | 30 | 75 - 125 | 25 |
| Silver | 0.18 | 0.50 mg/kg | | | 75 - 125 | 30 | 75 - 125 | 25 |
| Vanadium | 0.090 | 1.0 mg/kg | | | 75 - 125 | 30 | 75 - 125 | 25 |
| Zinc | 0.27 | 1.0 mg/kg | | | 75 - 125 | 30 | 75 - 125 | 25 |
| Arsenic | 0.85 | 10 mg/kg | | | 75 - 125 | 30 | 75 - 125 | 25 |
| Mercury, CAM17 in Soil (EPA 7471A) | | | | | | | | |
| Preservation:Store cool at 4°C | | | | | | | | |
| Container:8 oz. jar | | Amount Required:10 g | | | Hold Time:28 days | | | |
| Mercury | | 0.10 mg/kg | | | 75 - 125 | 25 | 75 - 125 | 25 |

CLS Labs

STANDARD OPERATING PROCEDURES APPROVAL FORM

| | | | |
|-----------------|---|----------------|-------------------|
| EPA Method: | 6010B | Revision No.: | 6010B-4 |
| Title of SOP: | Inductively Coupled Plasma-Atomic Emission Spectrometry | Revision Date: | November 19, 2002 |
| Author: | Charles Semuas, Richard Kelso | Replaces No.: | 6010B-2 |
| Author's Title: | QA/QC Mgr. | Dated: | July 17, 2000 |

The following people have reviewed this Standard Operating Procedure (SOP) and have recommended its approval.

Signature and Title:

| | |
|------------------------------|-------|
| _____ | _____ |
| SOP Author | Date |
| _____ | _____ |
| Department Manager Review | Date |
| _____ | _____ |
| QA/QC Manager Approval | Date |
| _____ | _____ |
| Laboratory Director Approval | Date |

Periodic Review:

| Signature | Title | Date |
|-----------|-------|-------|
| _____ | _____ | _____ |
| _____ | _____ | _____ |
| _____ | _____ | _____ |

TABLE OF CONTENTS

| | PAGE NO. |
|--|-----------|
| 1.0 SCOPE AND APPLICATION | 1 |
| 2.0 METHOD SUMMARY | 1 |
| 3.0 DEFINITIONS | 1 |
| 4.0 HEALTH AND SAFETY | 2 |
| 5.0 SAMPLE HANDLING AND PRESERVATION | 3 |
| 6.0 INTERFERENCES | 4 |
| 7.0 APPARATUS AND MATERIALS | 4 |
| 8.0 QUALITY CONTROL | 5 |
| 9.0 ANALYTICAL PROCEDURES | 6 |
| 10.0 DOCUMENTATION | 8 |
| 11.0 REFERENCES | 8 |
| | |
| APPENDIX A Table 1, Reagents & Solvents | 9 |
| B Table 2A, Standard 1M | 10 |
| C Table 2B, Standard 2M | 11 |
| D Table 2C, Standard 3M | 12 |
| E Table 3, ICV/CCV | 13 |
| F Table 4, ICSAB | 14 |
| G Table 5, Spiking Standards | 15 |

1.0 SCOPE AND APPLICATION

- 1.1 Inductively coupled plasma-atomic emission spectroscopy (ICP) determines trace elements, including metals, in solution. The method is applicable to all of the elements listed in Table 3. All matrices, including ground water, aqueous samples, TCLP and EP extracts, industrial and organic wastes, soils, sludges, sediments, and other solid wastes, require digestion prior to analysis.
- 1.2 Elements for which Method 6010A is applicable are listed in Table 3. Detection limits, sensitivity, and optimum ranges of the metals will vary with the matrices and model of spectrometer. Use of this method is restricted to spectroscopists who are knowledgeable in the correction of spectral, chemical, and physical interferences.

2.0 METHOD SUMMARY

- 2.1 Prior to analysis, samples must be solubilized or digested using appropriate sample preparation methods (e.g. Methods 3005A-3050A). When analyzing for dissolved constituents, acid digestion is not necessary if the samples are filtered and acid preserved prior to analysis.
- 2.2 Method 6010B describes the simultaneous, or sequential, multi-elemental determination of elements by ICP. The method measures element-emitted light by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the lines are monitored by photomultiplier tubes. Background correction is required for trace element determination. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured.

Background photo-multiplier-correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result.

3.0 DEFINITIONS

- 3.1 Laboratory Duplicates (LD1 and LD2) -- Two sample aliquots taken in the analytical laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 give a measure of the precision associated with laboratory procedures, but not with sample collection, preservation storage procedures.

- 3.2 Field Duplicates (FD1 and FD2) -- Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.
- 3.3 Laboratory Reagent Blank (LRB) *aka* (Method Blank) -- An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.
- 3.4 Field Reagent Blank (FRB) *aka* (Trip Blank) -- Reagent water placed in a sample container in the laboratory and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.
- 3.5 Laboratory Performance Check Solution (LPC) -- A solution of method analytes, surrogate compounds, and internal standards used to evaluate the performance of the instrument system with respect to a defined set of method criteria.
- 3.6 Laboratory Fortified Blank (LFB) *aka* (LCS) -- An aliquot of reagent water to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements at the required method detection limit.
- 3.7 Laboratory Fortified Sample Matrix (LFM) *aka* (Matrix Spike) -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

4.0 HEALTH AND SAFETY

- 4.1 The toxicity or carcinogenicity of any chemicals present in the sample are not precisely defined by this method. Therefore, to insure your safety and the safety of other co-workers, each sample should be treated as a potential health hazard. Potential exposure must be reduced to the lowest possible level by following these simple rules:
 - 4.1.1 YOU are responsible for your own safety, not your supervisor.

- 4.1.2 When handling samples, wear glasses, gloves, and lab coat and work with the sample under a hooded area, when applicable.
 - 4.1.3 If you do not know the hazards of the chemical you are working with, then assume that the chemical is highly toxic, and take all precautions to prevent exposure to the chemical. Special attention must be taken to read the MSDS sheet on the chemical prior to using the chemical.
 - 4.1.4 If a chemical is spilled, take all precautions to limit your exposure to the substance and to contain and clean up the spill. If necessary, quarantine the spill area, and warn co-workers of the situation. Notify the Safety Officer immediately of the accident. Refer to The Chemical Hygiene Plan (Section 10).
- 4.2 Specific Safety Precautions:
- 4.2.1 Nitric and hydrochloric acids are very corrosive. Wear gloves when handling digestates.
 - 4.2.2 Most standards have high concentrations of many different metal ions in acidic solutions. Wear gloves when handling standards.
 - 4.2.3 The following are suspected carcinogens: Arsenic, Beryllium, Barium, Cadmium, Manganese, and Sodium.
- 4.3 Material Safety Data Sheets (MSDS): Each analyst is responsible for reading and understanding the MSDS for each chemical reagent he or she works with. If there is any doubt concerning the content of the MSDS or if the MSDS sheet is missing for a particular chemical, contact the Safety Officer promptly.
- 4.4 Instrumentation Safety Precautions:
- 4.4.1 Be sure that all exhaust systems are operative before starting the instrument.
 - 4.4.2 Check the waste container frequently to be sure overflow of waste does not occur.
 - 4.4.3 Refer to ICAP instrument operator's manual for specific operating procedures.

5.0 SAMPLE HANDLING AND PRESERVATION

- 5.1 The recommended container for water samples is polyethylene or glass and for soil samples the recommended container is glass or brass tube. The minimum collection volume for water is 250 mL and minimum collection weight for solids is 10 g.

- 5.2 Water samples require preservation by nitric acid to a pH of <2. Soil samples are not preserved.
- 5.3 The holding time for metals (other than mercury) is 180 days. All samples should be stored at 4°C until analyzed.

6.0 INTERFERENCES

- 6.1 There are three main types of interference effects that can produce inaccuracies in the determination of trace elements, unless they are compensated or removed.

- 6.1.1 Spectra Types

- 6.1.1.1 Spectral interferences are caused by the overlap of adjacent spectra lines.

- 6.1.1.2 Background from continuous or recombination phenomena or stray light from the emission of high concentration elements. This is sometimes called background shifts.

- 6.1.2 Physical Types

- 6.1.2.1 Interferences due to surface tension and changes in viscosity can cause inaccurate results.

- 6.1.3 Chemical Types

- 6.1.3.1 Interferences due to ionization effects, molecular compound formation and vaporization effects can be present.

- 6.2 Methods For Compensating or Removing Interferences.

- 6.2.1 Spectral interferences can be compensated by computer correction of the raw data. Background shifts can be compensated by using the spectrum shifter available with the instrument.

- 6.2.2 Physical interferences can be compensated for by using a peristaltic pump to deliver the aqueous solution to the nebulizer or by using method of standard additions. The physical interference can sometimes be removed by dilution.

- 6.2.3 Chemical interferences can be compensated for by matrix matching or method of standard additions.

7.0 APPARATUS AND MATERIALS

7.1 Instrument Configuration

7.1.1 Thermo Jarrell Ash model Enviro 36 Inductively Coupled Plasma Spectrometer with twenty eight element channels.

7.1.2 NEC-286 computer

7.1.3 Computer controlled autosampler

7.1.4 Peristaltic pump, two channel

7.2 Liquid argon is used regularly; however, high pressure argon cylinders are on hand for backup.

7.3 All standards for calibration, quality control checks, and spiking are purchased from commercial vendors. Tables 1, 2, 3, 4, and 5 list the preparation methods.

7.4 An appropriate volume of stock spiking solution is added to a sample prior to digestion. The laboratory check sample is prepared by adding the same amount of spiking solution to a reagent blank. See Table 5.

7.5 All commercial standards when received are given a code and logged into the standard receiving log. The prepared intermediate and working solutions also receive a code and are logged into the standards preparation log. See SOP # QA001, Standards.

8.0 QUALITY CONTROL

8.1 QC types, Frequency, Limits and Corrective Actions:

8.1.1 Initial Calibration Verification (ICV) is performed after calibration but prior to sample analysis and should not deviate by more than 5% of actual true values or corrective action is required. See Table 3 for true values.

8.1.2 Initial Calibration Blank (ICB) is performed after calibration but prior to sample analysis and should not be greater than the reporting limit.

8.1.3 Continuing Calibration Verification (CCV) is performed at a 10% frequency with control limits of $\pm 10\%$ of true value. When results are beyond control limits, reanalyze the CCV once; if it is still beyond control limits, take corrective action. Reanalyze the previous ten samples. See Table 3 for true values.

8.1.4 Continuing Calibration Blank (CCB) is performed at a 10% frequency with control limits of $<$ the reporting limit. When results are beyond control limits, reanalyze the CCB once; if it is still beyond control limits, take corrective action. Reanalyze the previous ten samples.

- 8.1.5 Interelemental Check Standard (ICSAB) is performed at least twice per eight-hour shift with control limits of $\pm 20\%$ of true value. When results are beyond the control limits, take corrective action. Reanalyze ICSAB. See Table 4.
 - 8.1.6 For CLP run: ICSA, ICSAB, and CRI. Samples should be performed at the beginning and end of the run. There are no control limits determined for CRI.
 - 8.1.7 Preparation Blank (PB) contains all the reagents and goes through the entire sample preparation procedure. The frequency for the PB is one per digestion batch or one per 20 samples with control limits $<$ the reporting limit. When results are beyond the control limits, redigestion may be required.
 - 8.1.8 Laboratory Control Sample (LCS) contains analytes and reagents that go through the entire sample preparation procedure. The frequency for the LCS is one per digestion batch of 20 samples with recovery control limits of $\pm 20\%$ for waters and $\pm 25\%$ for soils. If the analysis of an LCSD is required, then the RPDs must be less than or equal to the control limits. Sample redigestion may be required. See Table 5.
 - 8.1.9 Matrix Spike and Matrix Spike duplicate (MS and MSD) samples are performed at a frequency of one per digestion batch or every twenty samples, whichever is more frequent with advisory recovery control limits of $\pm 25\%$ for both waters and soils. The RPD should be $\pm 25\%$ for sample values greater than ten times the instrument detection limit.
 - 8.1.10 For CLP only, if both sample and duplicate values are greater than or equal to 5 times CRDL, then the RPD must be less than or equal to 20% to be in control. If either sample or duplicate values are less than 5 times CRDL, then the absolute difference between the two values must be less than the CRDL to be in control. If both values are below the CRDL, then no control limit is applicable.
 - 8.1.11 Post spike and linear dilution will be done according to CLP protocol.
- 8.2 IDL studies are performed quarterly. MDL studies are performed annually.
- 8.2.1 MDL's are accomplished by preparing a working solution with element concentrations approximately three to five times the estimated MDL. Seven to ten aliquots of this working solution are handled as if they were samples and taken through the complete digestion and ICP analysis process.

9.0 ANALYTICAL PROCEDURES

9.1 The current instrument settings for TJA ENVIRO 36 are as follows:

| | |
|----------------------|------------|
| Argon Flow to Torch | 15 L/min |
| Auxiliary Argon Flow | 0 |
| Argon Sample Flow | 0.65 L/min |
| Peristaltic Pump | 800 |
| Forward Power | 1.1 KW |

The settings above may be changed to improve ICAP performance if necessary.

- 9.2 See the digestion/extraction SOP's (Methods 3010A and 3050B) for detailed explanations of the various digestion/extraction procedures.
- 9.3 All standards, QC check samples and samples are loaded onto the autosampler which is controlled by the computer. A peristaltic pump introduces the aqueous digestate into the nebulizer which produces an aerosol inside the spray chamber. This aerosol is brought into the torch by the argon sample flow.
- 9.4 The analytes are automatically identified by the program software and stored in the data base.
- 9.5 The analytes are automatically quantitated by the program software based on the values of the standards and stored in the data base.
- 9.6 See the TJA operator's manual for a detailed explanation of computer program software quantitation.
- 9.7 Calibration
- 9.7.1 Set up the instrument with the operating parameters established in 9.1 and allow the instrument to become thermally stable.
- 9.7.2 Perform a vertical and horizontal profile and save the results in a file and record the results in the Logbook.
- 9.7.2.1 Use a 5 mg/L manganese standard to test the peak intensity and position of the spectra.
- 9.7.2.2 The acceptable range of peak position must be less than the absolute value of 0.0200.
- 9.7.2.3 The acceptable range of peak intensity must be in between 500 and 700.

9.7.3 Calibration: Three-point standardization using three standards.

9.7.3.1 Standard Blank/Calibration blank that is 1% HNO₃/5% HCL.
All three calibration standards are prepared from three bottles of customer standards in the same matrix.

9.7.3.2 Standard 1M - See Table 2A

9.7.3.3 Standard 2M - See Table 2B

9.7.3.4 Standard 3M - See Table 2C

9.7.4 The instrument calibration is checked by analyzing the highest mixed calibration standards. The concentration values obtained must be within $\pm 5\%$ of the actual values. After the high standards are analyzed, an initial calibration verification solution (ICV) and an initial calibration blank (ICB) are analyzed. The concentration values obtained for the ICV should not deviate from the actual values by more than $\pm 10\%$ and the ICB should be $<$ the Report Limit. See Table 3 for true values of ICV.

9.7.5 When calibration criteria are not achieved, corrective actions are taken and samples are not analyzed until calibration criteria are achieved.

9.7.6 Dilute and reanalyze samples that are more concentrated than the linear calibration limit.

10.0 DOCUMENTATION

10.1 A copy of the raw data will be placed in the job folder along with any calculations needed to report the data in the LIMS format.

10.2 A copy of the LIMS report will be included in the job folder.

11.0 REFERENCES

11.1 USEPA, Test Methods for Evaluating Solid Waste (SW-846), Update III, May, 1997.

TABLE 2A - STANDARD 1M

| Element (Name) | Standard Conc. (mg/L) | Standard Volume Used | Final Volume | Standard Conc. (mg/L) |
|----------------|-----------------------|----------------------|--------------|-----------------------|
| Aluminum | 5000 | 0.1 mL | " | 5 |
| Antimony | 1000 | 0.1 mL | " | 1 |
| Arsenic | 1000 | 0.1 mL | " | 1 |
| Barium | 100 | 0.1 mL | " | 0.1 |
| Beryllium | 100 | 0.1 mL | " | 0.1 |
| Boron | 500 | 0.1 mL | " | 0.5 |
| Cadmium | 200 | 0.1 mL | " | 0.2 |
| Calcium | 5000 | 0.1 mL | " | 5 |
| Chromium | 100 | 0.1 mL | " | 0.1 |
| Cobalt | 100 | 0.1 mL | " | 0.1 |
| Copper | 100 | 0.1 mL | " | 0.1 |
| Iron | 2000 | 0.1 mL | " | 2 |
| Lead | 200 | 0.1 mL | " | 0.2 |
| Magnesium | 5000 | 0.1 mL | " | 5 |
| Manganese | 100 | 0.1 mL | " | 0.1 |
| Molybdenum | 300 | 0.1 mL | " | 0.3 |
| Nickel | 200 | 0.1 mL | " | 0.2 |
| Potassium | 10000 | 0.1 mL | " | 10 |
| Selenium | 1000 | 0.1 mL | " | 1 |
| Silver | 200 | 0.1 mL | " | 0.2 |
| Sodium | 10000 | 0.1 mL | " | 10 |
| Strontium | 100 | 0.1 mL | " | 0.1 |
| Thallium | 1000 | 0.1 mL | " | 1 |
| Titanium | 1000 | 0.1 mL | " | 1 |
| Tin | 1000 | 0.1 mL | " | 1 |
| Vanadium | 100 | 0.1 mL | " | 0.1 |
| Zinc | 200 | 0.1 mL | " | 0.2 |

Working standards expire one month from the date of preparation except when one or more of the source standards expire on an earlier date. In such a case, the earliest expiration date becomes the expiration date of the working standard.

TABLE 2B - STANDARD 2M

| Element (Name) | Standard Conc. (mg/L) | Standard Volume Used | Final Volume | Standard Conc. (mg/L) |
|----------------|-----------------------|----------------------|--------------|-----------------------|
| Aluminum | 5000 | 0.5 mL | " | 25 |
| Antimony | 1000 | 0.5 mL | " | 5 |
| Arsenic | 1000 | 0.5 mL | " | 5 |
| Barium | 100 | 0.5 mL | " | 0.5 |
| Beryllium | 100 | 0.5 mL | " | 0.5 |
| Boron | 500 | 0.5 mL | " | 2.5 |
| Cadmium | 200 | 0.5 mL | " | 1 |
| Calcium | 5000 | 0.5 mL | " | 2.5 |
| Chromium | 100 | 0.5 mL | " | 0.5 |
| Cobalt | 100 | 0.5 mL | " | 0.5 |
| Copper | 100 | 0.5 mL | " | 0.5 |
| Iron | 2000 | 0.5 mL | " | 10 |
| Lead | 200 | 0.5 mL | " | 1 |
| Magnesium | 5000 | 0.5 mL | " | 25 |
| Manganese | 100 | 0.5 mL | " | 0.5 |
| Molybdenum | 300 | 0.5 mL | " | 1.5 |
| Nickel | 200 | 0.5 mL | " | 1 |
| Potassium | 10000 | 0.5 mL | " | 50 |
| Selenium | 1000 | 0.5 mL | " | 5 |
| Silver | 200 | 0.5 mL | " | 1 |
| Sodium | 10000 | 0.5 mL | " | 50 |
| Strontium | 100 | 0.5 mL | " | 0.5 |
| Thallium | 1000 | 0.5 mL | " | 5 |
| Titanium | 1000 | 0.5 mL | " | 5 |
| Tin | 1000 | 0.5 mL | " | 5 |
| Vanadium | 100 | 0.5 mL | " | 0.5 |
| Zinc | 200 | 0.5 mL | " | 1 |

Working standards expire one month from the date of preparation except when one or more of the source standards expire on an earlier date. In such a case, the earliest expiration date becomes the expiration date of the working standard.

TABLE 2C - STANDARD 3M

| Element (Name) | Standard Conc. (mg/L) | Standard Volume Used | Final Volume | Standard Conc. (mg/L) |
|-------------------|-----------------------------|----------------------------|-----------------|--------------------------|
| Aluminum | 5000 | 1.0 mL | " | 50 |
| Antimony | 1000 | 1.0 mL | " | 10 |
| Arsenic | 1000 | 1.0 mL | " | 10 |
| Barium | 100 | 1.0 mL | " | 1 |
| Beryllium | 100 | 1.0 mL | " | 1 |
| Boron | 500 | 1.0 mL | " | 5 |
| Cadmium | 200 | 1.0 mL | " | 2 |
| Calcium | 5000 | 1.0 mL | " | 50 |
| Chromium | 100 | 1.0 mL | " | 1 |
| Cobalt | 100 | 1.0 mL | " | 1 |
| Copper | 100 | 1.0 mL | " | 1 |
| Iron | 2000 | 1.0 mL | " | 20 |
| Lead | 200 | 1.0 mL | " | 2 |
| Magnesium | 5000 | 1.0 mL | " | 50 |
| Manganese | 100 | 1.0 mL | " | 1 |
| Molybdenum | 300 | 1.0 mL | " | 3 |
| Nickel | 200 | 1.0 mL | " | 2 |
| Potassium | 10000 | 1.0 mL | " | 100 |
| Selenium | 1000 | 1.0 mL | " | 10 |
| Silver | 200 | 1.0 mL | " | 2 |
| Sodium | 10000 | 1.0 mL | " | 100 |
| Strontium | 100 | 1.0 mL | " | 1 |
| Thallium | 1000 | 1.0 mL | " | 10 |
| Titanium | 1000 | 1.0 mL | " | 10 |
| Tin | 1000 | 1.0 mL | " | 10 |
| Vanadium | 100 | 1.0 mL | " | 1 |
| Zinc | 200 | 1.0 mL | " | 2 |

Working standards expire one month from the date of preparation except when one or more of the source standards expire on an earlier date. In such a case, the earliest expiration date becomes the expiration date of the working standard.

TABLE 3
ICV/CCV

| Element (Name) | Standard Conc. (ppm) | Standard Vol./Wt. Used | Solvent/ Diluent (name) | Final Volume | Desired Working Standard Conc. (ppm) |
|----------------|----------------------|------------------------|-------------------------------|--------------|--------------------------------------|
| Aluminum | 2500 | 1 mL (a) | 1% HNO ₃ 5% HCL | 100 mL | 25 |
| Antimony | 1000 | 1 mL (b) | " | " | 10 |
| Arsenic | 500 | 1 mL (a) | " | " | 5 |
| Barium | 50 | 1 mL (a) | " | " | 0.5 |
| Beryllium | 50 | 1 mL(a) | " | " | 0.5 |
| Boron | 500 | 1 mL (a) | " | " | 5 |
| Cadmium | 100 | 1 mL (a) | " | " | 1 |
| Calcium | 2500 | 1 mL (a) | " | " | 25 |
| Chromium | 50 | 1 mL(a) | " | " | 0.5 |
| Cobalt | 50 | 1 mL (a) | " | " | 0.5 |
| Copper | 50 | 1 mL (a) | " | " | 0.5 |
| Iron | 1000 | 1 mL (a) | " | " | 10 |
| Lead | 100 | 1 mL(a) | " | " | 1 |
| Magnesium | 2500 | 1 mL (a) | " | " | 25 |
| Manganese | 50 | 1 mL (a) | " | " | 0.5 |
| Molybdenum | 100 | 1 mL (b) | " | " | 1 |
| Nickel | 100 | 1 mL (a) | " | " | 1 |
| Potassium | 2500 | 1 mL (a) | " | " | 25 |
| Selenium | 1000 | 1 mL (a) | " | " | 10 |
| Silver | 100 | 1 mL (a) | " | " | 1 |
| Sodium | 2500 | 1 mL (a) | " | " | 25 |
| Strontium | 100 | 1 mL (a) | " | " | 1 |
| Thallium | 1000 | 1 mL (a) | " | " | 10 |
| Tin | 500 | 1 ml (b) | " | " | 5 |
| Titanium | 1000 | 1 mL (b) | " | " | 10 |
| Vanadium | 50 | 1 mL (a) | " | " | 0.5 |
| Zinc | 100 | 1 mL (a) | " | " | 1 |

- (a) Al,Ca,Mg,K,Na,Fe,Se,Tl,As,B,Cd,Pb,Ni,Ag,Sr,Zn,Ba,Be,Cr,Co,Cu,Mn,V are in a mixed standard.
 (b) Sb,Ti,Sn,Mo are in a mixed standard.

Working standards expire one month from the date of preparation except when one or more of the source standards expire on an earlier date. In such a case, the earliest expiration date becomes the expiration date of the working standard.