ESS Laboratory
Division of Thielsch Engineering
Cranston, RI

SOP NO. 30_6010
INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROSCOPY
(SW 846 METHOD 6010B,C/ EPA METHOD 200.7)

APPROVED BY:

Operations Manager	Date 4/22/08
QA Manager	Date 4/22/08
Laboratory Director	Date 4/18/08

INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROSCOPY (SW 846 METHOD 6010B,C/ EPA METHOD 200.7)

1.0 SCOPE AND APPLICATION

1.1 Inductively coupled argon plasma analysis (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 extracts, industrial and organic wastes, soils, sludge, sediments, and other solid wastes, require digestion prior to analysis.

1.2 Elements for which Method 6010/ 200.7 is applicable are listed in Table 3. Detection limits, sensitivity, and optimum ranges of the metals will vary with the matrices. The data shown in Table 3 provide typical reporting limits for clean aqueous samples.

2.0 METHOD SUMMARY

2.1 Prior to analysis, samples must be solubilized or digested using sample preparation method 3005A (SOP 30_3005A) for aqueous and method 3050B (SOP 30_3050B) for solids.

2.2 When analyzing for dissolved constituents, acid digestion is not necessary if the samples are filtered and acid preserved prior to analysis.

2.3 Method 6010B describes the simultaneous 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 a photosensitive device monitors the intensities of the lines. 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 correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences named in Section 5.0 should also be recognized and appropriate corrections made. Tests for their presence are described in Step 7.2.2.5.

3.0 HEALTH AND SAFETY

3.1 Each employee has been trained and has acknowledged being trained in the safe use and handling of chemicals being used in the laboratory. This training has been

performed according to the ESS Training SOP 80_0016 and by the Chemical Hygiene Plan, SOP No. 90_0001, in conjunction with the Safety orientation.

3.2 All sample and material handling should be done in a hood while using proper protective equipment to minimize exposure to liquid or vapor. Minimum personnel protective equipment includes the use of laboratory safety glasses, a lab coat or apron, and protective gloves.

3.3 The MSDSs for the concentrated chemicals used in the laboratory are kept on file in a central location that is available for all employees to review.

3.4 The laboratory employee should review proper emergency response to spills or injury prior to attempting this procedure. Employees must know the location of spill kits, eyewashes, showers, and fire fighting equipment. Employees must also have knowledge of disaster evacuation routes.

4.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING AND STORAGE

4.1 Prior to analysis, all aqueous samples are to be preserved with nitric acid (HNO_3) to a pH of less than two. If upon receipt the pH requires adjusting, nitric acid is added to the sample container until the pH has stabilized at pH<2, the sample is then held for 16 hours prior to digestion.

4.2 After digestion, samples are stored in specimen containers or Hot Block Tubes.

4.3 Hold time for aqueous preserved samples is 180 days from day of sampling for all metals except mercury. The hold time for samples to be analyzed for mercury is 28 days. Samples prepared and/or analyzed after this date are to be flagged as estimated values.

4.4 Prior to use, all glassware will be soaked in a 10% HNO_3 bath for at least 15 minutes and rinsed a minimum of three times with ICP solution (refer to SOP 30_0001). The HNO_3 bath is checked for contamination on a weekly basis and recorded in the batch log. When aqueous samples are digested by the Hot Block procedure plastic ware is used, so this step may be omitted.

4.5 All results for solid samples are to be corrected for a dry weight determination at 105°C.

4.6 For dissolved metals analysis, a non-preserved sample must be filtered through a 0.45 µm filter within 24 hours of collection and preserved to a pH of less than 2.

5.0 INTERFERENCES AND POTENTIAL PROBLEMS

5.1 Spectral interferences are caused by: (1) overlap of a spectral line from another element at the analytical or background measurement wavelengths; (2) unresolved overlap of molecular band spectra; (3) background contribution from continuum or

recombination phenomena; and (4) stray light from the line emission of high-concentration elements. Computer correcting the raw data after monitoring and measuring the interfering element can compensate for spectral overlap. Unresolved overlap requires selection of an alternative wavelength. Background contribution and stray light can usually be compensated for by a background correction adjacent to the analyte line.

5.1.1 Analysts must verify the absence of spectral interferences from an element in a sample for which there is no instrument detection channel. Laboratory standard wavelengths are listed in Table 3.

5.1.2 Element specific interference is expressed as analyte concentration equivalents (i.e., false analyte concentrations) arising from 100 mg/L of the interference element. For example, assume that Cd is to be determined (at 226.502 nm) in a sample containing approximately 10 mg/L of Fe. 100 mg/L of Fe would yield a false signal for Cd equivalent to approximately 0.007 mg/L. Therefore, the presence of 10 mg/L of Fe would result in a false signal for Cd equivalent to approximately 1 ppb. The interference correction factors should be determined annually. The possibility of interferences other than those determined does exist. The analyst should be aware of these interferences when conducting analyses.

5.1.3 Generally, interferences are discernable if they produced peaks, or background shifts, corresponding to 2% to 5% of the peaks generated by analyte concentrations.

5.2 Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. This SOP uses yttrium as an internal standard to minimize this effect. Differences in solution volatility can also cause inaccuracies when organic solvents are involved. If physical interferences are present, they must be reduced by diluting the sample. A problem that can occur with high dissolved solids is salt build-up at the top of the nebulizer, which affects aerosol flow rate and causes instrumental drift. Changing the nebulizer and removing salt build-up at the tip of the torch sample injector can be used as a measure to control salt build-up. Control of the argon flow rate does improve instrument performance.

5.3 Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant with the ICP technique. If observed, they can be minimized by careful selection of operating conditions (incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.

6.0 EQUIPMENT/APPARATUS

6.1 **Inductively coupled argon plasma emission spectrometer with background correction**.

6.1.1 Perkin Elmer 4300DV Serial #077N1032302, using an AS-91 Autosampler and a Polyscience Chiller, Serial # G54802.

6.1.2 Perkin Elmer 3100XL Serial #069N8031701, using an AS-91 Autosampler and a Neslab Chiller, Serial # CFT-33.

6.2 **Gases**:

6.2.1 Liquid **Argon** gas supply.

6.2.2 Liquid **Nitrogen** gas supply.

6.3 **Auto-sampler**, AS-90.

6.4 **Class A volumetric flasks**, 50 ml, 100 ml and 250 ml

6.5 **Variable transfer pipettes**, 1.0 to 5.0 ml and 0.1 to 1.0 ml calibrated according to SOP 110.0005. Also, 0.01 ml to 0.1 ml micropipettes

6.6 **DELETED**

6.7 A **temperature adjustable hot plate** capable of maintaining a temperature of 95^{o}C.

6.8 **Data system**:

6.8.1 **Computers:** The Metals laboratory has two ICP-AES systems analyzing per Method 200.7/6010B. One system is a DELL OptiPlex 170L computer with a Windows XP Pro/SP2 operating sytem and the other is a HP 5100 computer, again with XP Pro/SP2. All computer systems are networked to a Windows 2000 server, which is the destination of all files. A differential back-up is performed nightly and a full back is performed each weekend using Veritas Backup Exec to tapes. As the systems acquires and stores data onto the server, the server becomes full. The data is downloaded and archived onto CDs.

6.8.2 **Software:** ICP WINLAB32 with revision (3.1.0).

7.0 REAGENTS AND STANDARDS

7.1 **Reagents**: reagent grade or better chemicals are used in all tests. If the purity of a reagent is in question, it is analyzed for contamination.

7.1.1 **Hydrochloric acid (conc.)**, HCl: Trace Grade.

7.1.2 **Hydrochloric acid (1:1)**, HCl: Add 500 ml concentrated HCl to 400 ml water and dilute to 1 liter in an appropriate beaker. Never add water to acid.

7.1.3 **Nitric acid (conc.)**, HNO_3: Trace Grade.

7.1.4 **Nitric acid (1:1)**, HNO3: Add 500 ml concentrated HNO_3 to 400 ml water and dilute to 1 liter in an appropriate beaker. Never add water to acid.

7.1.5 **De-Ionized Water** (DI): The deionized water is checked daily by reading the conductivity meter, which is connected to the water system. The conductivity is recorded daily in a log. The conductivity should not be allowed to drop below 10 megaohms. At this point, the cartridges should be replaced. The conductivity must also be checked and recorded according to SOP 110_0003. The lab supervisor needs to be notified if the conductivity is > 1 µmhos/cm.

7.1.6 **ICP solution**: Any type of diluting (primary standards or samples) is done using ICP solution. It is prepared by adding 20 ml of nitric acid and 30ml of hydrochloric acid to every liter of reagent water.

7.1.7 **Ghost Wipe**: Environmental Express Part No. 4210.

7.2 **Standards**:

7.2.1 **Primary Stock Solutions:** They are stored at room temperature and not used beyond the manufacturer's expiration date. See manufactures certificate of analysis for concentrations.

Standard	Vendor	Elements
Mixed Standard 1	VHG	Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sn, Ti, Tl, V, Zn
ICCV	CPI	Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sn, Ti, Tl, V, Zn

7.2.2 **Working standard solutions** are used to calibrate the instruments. They are prepared daily. Initial analyte concentrations are obtained from the bottle label or the vendor's certificate of analysis. Calibration concentrations may be

viewed and/or adjusted in the calibration page of the method editor window (refer to ICP Winlab Software Guide).

7.2.2.1 **Standard 1**: Add 0.2 ml of Mixed Standard 1 (see 7.2.1) to a 200 ml volumetric flask and dilute to the mark with ICP solution.

7.2.2.2 **Standard 2**: Add 1.0 ml of Mixed Standard 1 (see 7.2.1) to a 200 ml volumetric flask and dilute to the mark with ICP solution. This standard is also used as the **CCV** (continuing calibration verification).

7.2.2.3 **Standard 3**: Add 1.0 ml of Mixed Standard 1 (see 7.2.1) to a 100 ml volumetric flask and dilute to the mark with ICP solution.

7.2.2.4 **Standard 4**: Add 0.2 ml of Mixed Standard 1 (see 7.2.1) to 10 ml volumetric flask and dilute to the mark with ICP solution.

7.2.2.5 **Standard 5**: Add 0.5 ml of Mixed Standard 1 (see 7.2.1) to 10 ml volumetric flask and dilute to the mark with ICP solution.

ICP Standard concentration (mg/L)

Elements	Std 1	Std 2	Std 3	Std 4	Std 5
Be	0.01	0.05	0.10	0.20	0.50
Ag, Cd	0.05	0.25	0.50	1.00	2.50
As, B, Ba, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Sn, Ti, Tl, V, Zn	0.10	0.50	1.00	2.00	5.00
Se	0.20	1.00	2.00	4.00	10.00
Al, Fe	0.50	2.50	5.00	10.00	25.00
Ca, Mg	1.0	5.0	10.0	20.0	50.0
K, Na	5.0	25.0	50.0	100.0	250.0

NOTE: Standards 4 and 5 are used primarily for Ba, Pb, Zn but may also be used for other metals as long as all quality control criteria are met for the element.)

7.2.2.6 The **instrument check standard** (ICV: initial calibration verification) is used to verify the instrument calibration. It is prepared by adding 0.5 ml of ICCV)see 7.2.1) to a 100 ml volumetric flask and diluting to the mark with ICP solution.

7.2.2.7 The **interference check solutions** contain known concentrations of interfering elements, and are run at the beginning of each analytical run in order to test correction factors.

7.2.2.7.1 **ICSA** is prepared by adding 12.5 ml of Inorganic Venture's CLP-ICS-A to a 250 ml volumetric flask and diluting to the mark with ICP solution.

7.2.2.7.2 **ICSAB** is prepared by adding 12.5 ml of Inorganic Venture's CLPP-ICS-A and 1.25 ml of CLPP-ICS-B in a 250 ml volumetric flask and diluting to the mark with ICP solution.

7.2.2.8 Three **CRI Standards** are used to determine the detection limits below the lowest point of the calibration curve. Three solutions are prepared to cover the range of reporting limits.

7.2.2.8.1 **CRI1** is prepared by adding 25 ml of Standard 1 (see 7.2.2.1) to a 50 ml centrifuge tube and diluting to the 50 ml mark with ICP solution.

7.2.2.8.2 **CRI2** is prepared by adding 1 ml of Standard 3 (see 7.2.2.3 to a 50 ml centrifuge tube and diluting to the 50 ml mark with ICP solution.

7.2.2.8.3 **CRI3** is prepared by adding 0.5 ml of Standard 3 (see 7.2.2.3 to a 50 ml centrifuge tube and diluting to the 50 ml mark with ICP solution.

7.2.2.9 Low Level ICV and Low Level CCV (SW846-6010C only)

7.2.2.9.1 These are identical to CRI Standards (see § 7.2.2.8)

7.3 **Two types of blanks** are required for the analysis. The calibration blank is used in establishing the analytical curve, and as an initial and periodic check for contamination throughout the analytical run. The method blank ID is created through the Element LIMS and is linked to the Batch ID. For example, BG52701-BLK1 where B = Batch, G = Month, 5 = Year, 27 = Date, 01 = Batch Number.

7.3.1 The **calibration blank** (ICB, CCB) is prepared in the same manner as ICP solution. (See 7.1.6).

7.3.2 The **method blank** must contain all the reagents and in the same volumes as used in the processing of the samples. The method blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

7.4 **Internal standard** is added to all standards and samples in a known amount and used to measure relative responses of other analytes in the same solution. A 5 ppm yttrium standard is used for the 3100XL and 4300DV . It is prepared by adding 5 ml of a 1000 ppm standard (purchased from Perkin Elmer – Cat# PE#N9300167) to a 1000 ml volumetric flask and diluting to the mark with ICP solution. Expiration of 5 ppm Yttrium standard is determined by the manufacturer and is recorded on the container label.

7.5 The **Manganese X, Y optimization standard** (1.0 ppm) is used to fine tune the X, Y adjustment of the torch. Prepared by adding 0.25 ml of 1000 ppm Manganese Standard (SCP Science Cat# 140-051-251) to a 250 ml volumetric flask and diluting to the mark with ICP solution. Expiration of 1 ppm Manganese standard is determined by the manufacturer and is recorded on the container label.

8.0 PROCEDURE

8.1 Preliminary treatment of most matrices is necessary because of the complexity and variability of sample matrices. Water samples that have been pre-filtered and acidified do not need acid digestion as long as the samples and standards are matrix matched and the dissolved solids are < 0.2% w/v. Solubilization and digestion procedures are presented in Sample Preparation Method SOP 30_3005A and 30_3050B. ***NOTE: It is ESS Laboratory's policy to digest all dissolved samples.***

8.2 Set up the instrument with proper operating parameters. The instrument must be allowed to become thermally stable before beginning (usually requiring at least 15 minutes of operation prior to calibration).

8.2.1 Operating Conditions: The analyst should follow the instructions provided by the instrument manufacturer. For operation with organic solvents, use of the auxiliary argon inlet is recommended, as is solvent-resistant tubing, increased plasma (coolant) argon flow, decreased nebulizer flow, and increased RF power to obtain stable operation and precise measurements. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be established for each analyte line on that particular instrument. All measurements must be within the instrument linear range where spectral interference correction factors are valid. The analyst must (1) verify that the instrument configuration and operating conditions satisfy the analytical requirements and (2) maintain quality control data confirming instrument performance and analytical results.

8.3 Optimize and calibrate the instrument according to the instrument manufacturer's recommended procedures, using the typical mixed calibration standard solutions described in Step 7.2.2 and the manganese optimization standard described in Step 7.5.

8.3.1 Double click **Winlab 32** Icon. Wait for the status check to be completed for the instruments and accessories.

8.3.2 Select Method.

8.3.3 Click on **Plasma** Icon on tool bar. Turn the virtual switch to the **on** position or press **F9** to automatically ignite the plasma.

8.3.4 After the plasma has ignited, allow the instrument to stabilize for 30 minutes before calibration.

8.3.5 Place centrifuge tube containing 1.0 ppm Mn solution on the auto-sampler tray. Press F10 and select appropriate location or click on **Analysis** column above the tool bar. Choose **auto-sampler Go To location** and enter the appropriate auto-sampler location to move the arm to the Mn solution. Click on **tools** and choose **spectrometer control**. Click on **AlignView**. The optimization should be reported in the Mn Profile Logbook (See Attachment A).

8.3.6 Flush the system with the calibration blank (Step 7.3.1) between each standard or as the manufacturer recommends. Press F10 and select **Wash**. (Use the average intensity of multiple exposures for both standardization and sample analysis to reduce random error.) The calibration curve should consist of a blank and a minimum of three standards.

8.3.6.1 Click on **File**. Choose **New**, **Sample Info File**. Enter batch ID number, which is the date, followed by x for the 3100 instrument only, and then a through z depending on the file number for the day. (i.e. 092798xa – date, 3100 instrument, first file.)

8.3.6.2 Click on **Default setup for 3100XL or ESS setup of 4300DV** Icon. The starting location is always 9 (1-8 reserved for standard and QC). For **sample number range**, adjust the end indicator to equal the number of samples being analyzed. Enter the sample IDs in the **Sample ID** column.

8.3.6.3 For duplicates and spikes, click on the **Matrix Check Samples** box to the right of the duplicate or matrix spike ID.

8.3.6.3.1 For duplicates, select option **Duplicate** and make sure that the reference sample number corresponds to the original sample. Click **OK**.

8.3.6.3.2 For matrix spikes, select option **Recovery set #**, which is always equal to 1. Make sure that the reference sample number corresponds to the original sample. Click **OK**.

8.3.6.3.3 For Serial Dilutions, select option **Matrix Check Samples**. Select option **Diluted**. Enter **5**. Make sure that the reference sample number corresponds to the original sample. Click **OK**.

8.3.6.3.4 For post digestion spikes, select option **Recovery set #**, which is always equal to 1. Make sure that the reference sample number corresponds to the original sample. Click **OK**.

8.3.6.4 There are currently two methods being used on the ICP, **EVERYTHINGX** and **EVERYTHING-DV**. For both methods, click on **Analyze QC's before**. In the cell at the top of the column, enter 1, 4,6-9,2,3,5,6 or select 00Daily Cal from open Sample Info File to calibrate before running samples.

8.3.6.5 For both methods, arrow down 10 cells and enter **after 5,6**. Repeat this for every ten cells. This will ensure that the CCV and CCB will run every 10 samples.

8.3.6.6 At the end of the run, enter **5,6,2,3**. This will finish off all QC that is required to run at the end of an analysis. These QC numbers are all defined in the method. QC will run before the wash step.

8.3.6.7 Click on **File**, **Save As**, **and Sample Info File**; enter same file # as batch ID.

8.3.6.8 Click on **AUTO** Icon. On the setup screen, click on **Method** Cell to choose the appropriate method.

8.3.6.8.1 Make certain that the **SIF ID** is correct in the SIF cell.

8.3.6.8.2 Open **Results Data Set Name** under Q:\Metals\Results ICP#\Results and assign the appropriate ID to the data set. The ID is the Batch ID with 'ad' added to the end (xad for 3100XL)

8.3.6.8.3 Make sure that the **Save Data** and **Print Log** option boxes are selected.

8.3.6.8.4 Click on **Analyze tab**. Click on **Print List** at bottom of analyze window and print this out. Click **Analyze All** to start the run.

8.4 Before beginning the sample run, check that the %RSD for each element in each standard is <5%, and then reanalyze the mixed calibration standard 2 as if it were a sample. Concentration values obtained should not deviate from the actual values by more than 10% for 6010B or 5% for 200.7. If they do, follow the recommendations of the instrument manufacturer to correct for this condition and then recalibrate.

8.5 Analyze the instrument check standard (see 7.2.2.6) and the calibration blank (see 7.3.1). Analyze CRI – 1, 2, 3 (low level calibration standard), then the ICSAB and ICSA solutions (see 7.2.2.7.1 and 7.2.2.5.2) immediately before the first before sample analysis. Analyze the continuing calibration standard (CCV, see 7.2.2.2) after every ten samples and at the end of the run. Thus, the low level calibration standard(s) is run whenever an analytical batch is run, which will be more often than once per day.

8.6 Below is a typical analytical sequence for a batch of twenty samples:

- Standard Blank (S0)
- Calibration Standard(s)
- Re-analyzed Calibration Standard; 2 ± 10%, RPD ≤5% (± 5% for 200.7)
- Instrument Check Standard (ICV); ± 10%, RPD ≤5%
- Low Level Instrument Check Standard (LLICV; 6010C only); ± 30% limit.
- Calibration Blank (ICB) <MDL
- CRI1 ±30% (DoD QSM 4.1 ±20%)
- CRI2 ±30% (DoD QSM 4.1 ±20%)
- CRI3 ±30% (DoD QSM 4.1 ±20%)
- Interference Check Sample (ICSA) ± MRL
- Interference Check Sample (ICSAB) ± 20%
- Method blank- BLK
- Blank spike- BS
- Blank spike duplicate- BSD
- Sample 1
- Matrix duplicate
- Matrix spike
- Serial dilution
- Post digestion spike
- Samples 2-3
- CCV
- CRI1 ±30% (DoD QSM 4.1 ±20%)
- CRI2 ±30% (DoD QSM 4.1 ±20%)
- CRI3 ±30% (DoD QSM 4.1 ±20%)
- CCB
- Samples 4-11
- Matrix duplicate
- Matrix spike
- CCV
- CRI1 ±30%(DoD QSM 4.1 ±20%)
- CRI2 ±30% (DoD QSM 4.1 ±20%)
- CRI3 ±30% (DoD QSM 4.1 ±20%)
- CCB
- Serial dilution
- Post digestion spike
- Samples 12-19
- CCV
- CRI1 ±30% (DoD QSM 4.1 ±20%)
- CRI2 ±30% (DoD QSM 4.1 ±20%)
- CRI3 ±30% (DoD QSM 4.1 ±20%)
- CCB
- Sample 20
- CCV
- CRI1 ±30% (DoD QSM 4.1 ±20%)

- CRI2 ±30% (DoD QSM 4.1 ±20%)
- CRI3 ±30% (DoD QSM 4.1 ±20%)
- CCB
- Interference Check Sample (ICSA) ± MRL
- Interference Check Sample (ICSAB) ± 20%

8.7 All sample information is recorded in the run logbook (see Attachment B) and typed into the sample info file (SIF) on the ICP. The run log is used to load the auto-sampler tray. The sample information printout is compared to the run log for accuracy.

9.0 CALCULATIONS - Note: The instrument printout is in mg/L.

9.1 All results should be reported with up to three significant figures.

9.2 The following calculation for **aqueous samples** will provide results in mg/L:

$$\text{Final conc.} = \frac{\text{mg/l (raw)} \times \text{dilution factor} \times \text{final volume}}{\text{Initial volume}}$$

9.3 The following calculation for **solid/soil samples** will provide results in mg/kg dry weight:

$$\text{Final conc.} = \frac{\text{mg/l (raw)} \times \text{dilution factor} \times \text{final volume (ml)}}{\text{Initial weight (g)/ (\%solids/100)}}$$

9.4 When reporting results, include date analyzed and initials of analyst on summary sheets and actual runs.

9.5 Hardness. The preferred method for determining hardness is to compute it from the results of separate determinations of calcium and magnesium (SM 2340B):

Hardness, mg equivalent $CaCO_3$ /L = 2.497 [Ca, mg/L] + 4.118 [Mg, mg/L]

9.6 The following calculation for **wipe samples** will provide results in µg/square foot dry weight:

Final conc. = mg/l (raw) x dilution factor x final volume (ml)

10.0 QUALITY ASSURANCE/QUALITY CONTROL

10.1 All quality control data should be maintained and available for easy reference or inspection. A summary of Method Quality Objectives may be found in Table 4.

10.2 The upper limit of the Linear Dynamic Range (LDR) must be established for each wavelength utilized. It must be determined from a linear calibration prepared in the

normal manner using the established analytical operating procedure for the instrument. The Linear Dynamic Range should be determined by analyzing a minimum of three consecutively higher standard concentrations of the analyte until the observed analyte concentration is no more than ± 10% outside the stated concentration of the standard. Determined LDRs must be documented and kept on file. The analysis from the resulting data establishes the LDR, which may be used for the analysis of samples. Determined sample analyte concentrations that are greater than 90% of the determined upper LDR limit must be diluted and reanalyzed. The LDRs should be verified semi-annually or whenever, in the judgment of the analyst, a change in analytical performance caused by either a change in instrument hardware or operating conditions would dictate they be re-determined. Record is filed in Directory Q:\Quality\QA\LDR .***NOTES: 1) When analyzing samples for MA MCP projects, samples above the initial calibration range must be diluted within the calibration range. 2) On a quarterly basis a Linear range calibration check standard must be run to verify the linear dynamic range is still valid (AFCEE). Results must be within ±10% of true value.***

10.3 Instrument detection limits (IDL) are calculated by running the calibration blank seven consecutive times. Calculate the standard deviation and multiply by three to determine the IDL. IDL shall be ≤LOD. The IDL must be determined after initial set-up and after any significant change. Record is filed in Directory Q:\Quality\QA\IDL.

10.4 Calibration for the ICP consists of a blank and a minimum of three standards. The correlation coefficient (R) for each element calibration curve must be ≥ 0.995 (≥ 0.998 for 6010C).

10.5 Initial and Periodic Method QC Demonstrations: The procedures specified in Section 10.3.1 through 10.3.2 must be conducted as an initial demonstration of laboratory capability, prior to the analysis of any samples. Subsequent to this initial demonstration, additional evaluations of this nature should be conducted on a periodic basis, in response to changes in instrumentation or operations, and/or in response to confirmed or suspected systems, method, or operational problems.

10.5.1 Accuracy and Precision: To demonstrate initial laboratory capability, analyze a minimum of four initial calibration verification standards. The mean concentration must be within ± 10 % of the stated values. (± 5% for 200.7)

10.5.2 Method Detection Limits (MDL) for Individual Analytes: MDLs must be determined for each analyte/matrix/instrument combination at initial set-up and thereafter annually. See SOP 110_0013 for specific instruction on MDL determination.

10.6 Dilute and reanalyze samples that are more concentrated than the linear range study or use an alternate, less sensitive line for which quality control data is already established.

10.7 It is recommended that whenever a new or unusual sample matrix is encountered, or per preparatory batch at a minimum, a series of tests is performed prior to reporting

concentration data for analyte elements. These tests, as outlined in Steps 10.6.1 and 10.6.2 will ensure the analyst that neither positive nor negative interferences are operating on any of the analyte elements to distort the accuracy of the reported values.

10.7.1 Serial dilution: If the analyte concentration is sufficiently high (50x the instrumental detection limit after dilution), an analysis of a 1+4 (5x) dilution should agree within ± 10% of the original determination. If not, a chemical or physical interference effect should be suspected.

10.7.1.1 Prepare the serial dilution by diluting the sample with ICP solution. If the sample was diluted to bring the result within the linear dynamic range, then the serial dilution must be performed on that dilution (Ex. Sample result based on 5x dilution, then serial dilution must be 25x for the applicable metals.)

10.7.2 Post digestion spike addition: An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 85% to 115% (75-125% for method 6010B) of the known value. The spike addition should produce a minimum level of 20 times and a maximum of 100 times the instrumental detection limit. If the spike is not recovered within the specified limits, a matrix effect should be suspected.

10.7.2.1 Measure out 5 ml of prepared sample into a centrifuge tube. Add 0.05 ml of mixed standard 1 (see 7.2.1), then bring to 10 ml with sample. Mix and set up to run after the serial dilution. The post digestion spike is performed on that dilution that the sample result was obtained.

10.8 Check the instrument standardization by analyzing appropriate check standards as follows:

10.8.1 Verify calibration every 10 samples and at the end of the analytical run, using a calibration blank (Step 7.3.1) and a continuing calibration check standard (Step 7.2.2.2).

10.8.1.1 The results of the check standard (ICV and CCV) should agree within 10% of the expected value and %RPD ≤5%. See section 11.0 for corrective action for out of criteria results.

10.8.1.2 Method 6010C requires that a low level ICV and low level CCV be run, meeting an accuracy criteria of 30% (20% per DoD QSM 4.1) .

10.8.1.3 The results of the calibration blank should be no greater than the MDL. See section 11.0 for corrective action for out of criteria results.

10.8.2 Verify the interelement and background correction factors at the beginning and end of each analytical run (***the end interelement check is only required for***

MA MCP samples by method 6010B). Do this by analyzing the interference check solution (Step 7.2.2.5). Results should be within ±20% for analytes found in the ICSAB and ± MRL, or **< the LOD if DoD QSM criteria need to be met**, for analytes not found in the ICSA (verified trace impurity from one of the spiked analytes). If outside of limits, stop analysis and recheck background corrector points and/or interelement correction factors. Re-analysis interelement check solutions. Samples may not be analyzed without a valid interference check.

10.8.3 Replicate samples are to be analyzed at a frequency of 10% or per analytical batch, whichever is more frequent.

10.8.3.1 The relative percent difference between replicate determinations is to be calculated as follows:

$$RPD = \frac{D_1 - D_2 \times 100}{(D_1 + D_2)/2}$$

Where:

RPD = relative percent difference
D_1 = first sample value
D_2 = second sample value (replicate)

10.8.3.2 A control limit of ±20% RPD shall be used for aqueous samples that are ≥5x the MRL and ±MRL for when <5x MRL. A control limit of ±35% RPD shall be used for soil/sediment samples that are ≥5x the MRL and ±2xMRL for when <5x MRL. ***When analyzing USACE samples the %RPD must be ≤25%, DoD/Navy ≤20% (if MS/MSD is analyzed instead of matrix duplicate these RPD would apply for USACE/DoD/Navy).*** See section 11.0 for corrective action for out of criteria results.

10.8.4 Spiked samples are to be analyzed at a frequency of 10% or per analytical batch, whichever is more frequent.

10.8.4.1 The spiked sample recovery is calculated as follows:

$$\% \text{ Recovery} = \frac{SSR - SR}{SA} \times 100$$

Where:

SSR = Spiked Sample Result
SR = Sample Result
SA = Spike Added to Sample

10.8.4.2 A control limit of 25% shall be used for all sample matrices. See Table 2 for DoD/Navy and AFCEE control limits, sporadic marginal exceedance limits are same as for blank spike (section 10.10.2) See section 11.0 for corrective action for out of criteria results.

10.8.4.3 AFCEE requires that an matrix spike duplicate be analyzed instead of matrix duplicate. Control limits are ≤20% for aqueous samples and ≤30% for soil samples.

10.9 Employ a minimum of one method blank per sample batch to determine if contamination is occurring during sample preparation. The method blank must contain all the reagents and in the same volumes as used in the processing of the samples. It must be carried through the complete procedure as the sample solution used for analysis.

10.9.1.1 The value for the method blank should be less than ½ the MRL. See section 11.0 for corrective action for out of criteria results.

10.10 At least one BS/BSD must be analyzed for each batch of samples. These should be prepared and analyzed in the same manner as the samples (see SOP 30_3005 and 30_3050B.

10.10.1 The BS/BSD recovery range must be within the range of 80-120% (85-115% for 200.7), ***see Table 2 for DoD and AFCEE blank spike recovery acceptance criteria.*** The RPD must be ≤20% for aqueous and ≤ 30% for soils, ***USACE %RPD <25% and for DoD/Navy %RPD <20% for all matrices***. *USACE/DoD/Navy/AFCEE allow for sporadic marginal exceedance (USACE has expanded criterion of 60-140%, DoD/Navy/AFCEE see Table 2 for expanded criteria).*

10.10.2 If the BS or BSD falls outside of this range, see section 11.0 for corrective action for out of criteria results. Sporadic Marginal Exceedance number is as follows:

Number of Analytes in BS	Allowable number of Marginal Exceedances
>90	5
71-90	4
51-70	3
31-50	2
11-30	1
<11	0

Exceedances should be within marginal exceedance limits (Table 2) or expanded criterion listed above.

10.11 Method Reporting Limit Standards (CRIs) are run at the beginning of every analytical run. Results should agree to ± 30% (**± 20% if DoD QSM Criteria are to be met**). If not, review blank data for contamination.

10.12 BS/BSDs are plotted in Element to determine if in-house limits are within default limits.

11.0 DATA VALIDATION

11.1 Data validation will be accomplished by reviewing all of the quality control parameters and assuring that they are within recommended ranges and recording any deviations in the ICP Tray Sequence Logbooks (Attachments B-1 and B-2). The only exceptions made to ranges would be the following:

11.1.1 For duplicates, ±20% RPD shall be used for aqueous samples that are ≥5x the MRL and ±MRL for when <5x MRL. A control limit of ±35% RPD shall be used for soil/sediment samples that are ≥5x the MRL and ±2xMRL for when <5x MRL. ***When analyzing USACE samples %RPD ≤25%, DoD/Navy samples %RPD ≤ 20%, AFCEE samples aqueous %RPD ≤20% and soil %RPD ≤30%.*** However, there are cases where duplicates may not work. If this is the case, inform client in narrative concerning sample non-homogeneity.

11.1.2 For matrix spikes, the % Recovery should be ±25%. If the matrix spike is >30%, check the LCS. If the LCS is within limits, matrix interferences are present and must be noted in the narrative. ***See Table 2 for DoD/Navy/AFCEE MS control limits.*** If the matrix spike is <30% and non-detected results were found re-digest sample and MS to confirm matrix interference(for Navy/DoD work perform Method of Standard additions, see addendum 1).

11.1.3 PDS and Serial dilution (section 10.7) are used to test the presence of matrix affect when the matrix spike or duplicate is outside criteria. When the PDS or SD is used, their failure is to be reported in the projective narrative as a confirmation of matrix affect.

11.1.4 For the BS/BSD, the % Recovery must be within 80-120% (85-115% for 200.7). ***See Table 2 for DoD/Navy/AFCEE MS control limits.*** If the BS or BSD is outside criterion, then re-prep and re-analyze samples with the following exception: ***For high BS/BSDs, those samples that are non-detects may be reported.***

11.1.5 Analytical batches with Method blanks above the MRL (will be re-prepped and re-analyzed with the following exceptions:

11.1.5.1 Samples that are that are at least twenty times higher than the method blank may be reported.

11.1.5.2 When the method blank is less than 5% of the regulatory limit associated with the analyte the method blank would be acceptable.

11.1.5.3 If the analyte is found in the method blank above the MRL but is not in any of the associated samples, no corrective action is needed.

11.1.5.4 Any results that are reported with method blank contamination must be B-flagged.

11.1.6 All unusual observations and method deviations will be noted in the narrative accompanying the data report presented to the client.

11.2 All unusual observations and method deviations will be noted on the data review checklist and will be included in the project narrative accompanying the data report presented to the client. (See Attachment C)

12.0 REFERENCES

12.1 SW846 Methods 6010B and C, Inductively Coupled Plasma – Atomic Emission Spectrometry; third edition, Update III and SW846 On-line, respectively.

12.2 ICP Winlab Software Guide, Perkin Elmer. Part No. 0993-8966.

12.3 Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma- Atomic Emission Spectrometry, Method 200.7, EPA/600/R-04/111 May 1994.

12.4 Environmental Express procedure for Lead Analysis with the Ghost Wipe, per HUD Guidelines for Lead in Dust Wipes, Appendix A-5.0 and NIOSH Standard 7082.

12.5 NELAC/NELAP, Chapter 5, June 2003

12.6 DoD Quality Systems Manual, Final Revision 4.1, April 2009

13.0 POLLUTION PREVENTION and WASTE MANAGEMENT

13.1 ESS Laboratory's policies on pollution prevention and waste management are covered in SOP 90_0002, Hazardous Waste Contingency and Emergency Response Plan. All employees are trained in the requirements of the SOP.

14.0 METHOD PERFORMANCE

14.1 Precision and Accuracy data must be generated by all employees before performing this analysis on client samples. The data is generated by analyzing a method blank and four blank spike samples. Acceptance criteria are 85-115% Recovery and %RSD of $\leq$ 20%.

14.2 The precision and accuracy data in Table 1 are typical for aqueous metals analysis.

15.0 TABLES, DIAGRAMS, ATTACHMENTS, AND VALIDATION DATA

Table 1. Typical Precision and Accuracy data generated 2/14/2005

Compound Name	Spk	Avg	%Rec	%RSD	Compound Name	Spk	Avg	%Rec	%RSD
Silver	0.25	0.2409	96.4	3	Manganese	0.5	0.4863	97.3	4
Aluminum	2.5	2.5089	100.4	4	Molybdenum	0.5	0.4919	98.4	4
Arsenic	0.5	0.4615	92.3	5	Sodium	25	24.0496	96.2	4
Boron	0.5	0.4843	96.9	4	Nickel	0.5	0.4991	99.8	4
Barium	0.5	0.4803	96.1	4	Lead	0.5	0.4856	97.1	4
Beryllium	0.05	0.0489	97.8	4	Antimony	0.5	0.4652	93.0	3
Calcium	5	4.8144	96.3	4	Selenium	1	0.9435	94.3	4
Cadmium	0.25	0.2258	90.3	4	Tin	0.5	0.4809	96.2	4
Cobalt	0.5	0.4838	96.8	4	Strontinum	0.05	0.0490	98.0	4
Chromium	0.5	0.4878	97.6	4	Titanium	0.5	0.4845	96.9	4
Copper	0.5	0.5010	100.2	4	Thallium	0.5	0.4727	94.5	5
Iron	2.5	2.4523	98.1	4	Vanadium	0.5	0.5030	100.6	4
Potassium	25	22.0020	88.0	4	Zinc	0.5	0.4614	92.3	4
Mangnesium	5	4.7553	95.1	4					

Attachments:

Table 2 DoD QSM & AFCEE QAPP BS/MS QC Limits

Table 3 Instrument Wavelengths and Limits

Table 4 DoD QSM Summary of Method Quality Objectives

Attachment 1 Method of Standard Additions

Attachment A-1 Mn Profile Logbook, ICP II

Attachment A-2 Mn Profile Logbook, ICP III

Attachment B-1 ICP II Tray Sequence Logbook

Attachment B-2 ICP III Tray Sequence Logbook

16.0 DEFINITIONS

16.1 **Calibration Blank (CB)** -- A volume of reagent water fortified with the same matrix as the calibration standards, but without the analytes.

16.2 **Calibration Standard (CAL)** -- A solution prepared from the primary dilution standard solution or stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

16.3 **Blank spike (BS, LCS)** -- An aliquot of reagent water or other blank matrices to which known quantities of the method analytes are added in the laboratory. The BS 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. When it is necessary to test for lead, per HUD specifications, the LCS is prepared by spiking a Ghost Wipe (ASTM E 1792, current lot) with an appropriate amount of ICV solution.

16.4 **Matrix spike (MS)** -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The MS 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 MS corrected for background concentrations.

16.5 **Matrix spike duplicate (MSD)** -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The MSD is analyzed exactly like a sample, and its purpose is to determine the precision of 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 MSD corrected for background concentrations.

16.6 **Method Blank (MB)** -- An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, and reagents that are used with other samples. The MB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

16.7 **Method Detection Limit (MDL)** -- The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero.

16.8 **Quality Control Sample (QCS)** -- A solution of method analytes of known concentrations that is used to fortify an aliquot of BS or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

16.9 **Stock Standard Solution (SSS)** -- A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

17.0 PERSONNEL QUALIFICATIONS

17.1 Analysts who perform this analysis must have a working knowledge or quantitative and qualitative analysis, instrumental methods of analysis, chemical laboratory methods, and equipment.

17.2 All analysts, before performing any analysis, participate in the ESS Laboratory training program (SOP 80_0016). The training process consists of reading the Standard Operating Procedure, gaining instruction on the procedure from an experienced analyst, and performing the initial demonstration of capability.

18.0 TROUBLESHOOTING/MAINTENANCE

18.1 **Instrument Maintenance**:

18.1.1 **Daily:**

- Inspect water level in re-circulating water chiller and inspect for leaks.
- Inspect peristaltic pump tubing, replace if worn.
- Inspect RF coil for excess condensation, wipe down to avoid arcing. Also, the coil should be cool to the touch, which indicates that cooling water is circulating through system.
- Inspect purge window and clean as needed.

18.1.2 **Monthly**

- Check ventilation filters clean as needed.

18.1.3 **Bi-annually**

- Replace chiller water.
- Vacuum ICP air vents

18.2 Record all maintenance in the instrument's maintenance logbook.

18.3 Extraordinary problems may require assistance from Perkin-Elmer Corporation. ESS Laboratory maintains a service contract with this vendor.

19.0 Data Management And Records

19.1 **Data Management** - ESS Laboratory's utilizes the Promium Element LIMS system as part of its Data Management system. Client sample information is entered into ELEMENT LIMS and analyses are assigned to each sample. The LIMS allows EPA

hold times, minimum batch QC requirements, and QC criteria to be assigned to each analysis. Standards can be entered and assigned to QC samples through the LIMS. Once analysis has been performed, data is imported using DataTool avoiding manual errors. In conjunction with Crystal Reports, the ELEMENT system allows for a wide variety of reporting formats.

19.2 **Records** – The specific retention periods required in the NELAC Standards, EPA-CFR and state and local statutes are followed or exceeded. At a minimum, data records are retained for five years from last use (10 years for drinking water). If there is a question about whether a record should be retained or disposed because no specific requirement could be found, the record is retained until such time as a retention period is specified. Records are stored in specified-labeled locations and are easily retrievable. All raw data associated with testing is also retained including; computer printouts, chromatograms, review forms, and logbooks.

Table 2 DoD Quality Systems Manual and AFCEE QAAP Blank Spike / Matrix Spike QC Limits

	DoD				AFCEE			
Aqueous								
Analyte	LCL	UCL	LMEL	UMEL	LCL	UCL	LMEL	UMEL
Silver	80	120	75	120	80	120	80	120
Aluminum	80	120	80	120	80	120	75	120
Arsenic	80	120	80	120	80	120	80	120
Barium	80	120	80	120	80	120	80	120
Beryllium	80	120	80	120	80	120	80	120
Calcium	80	120	80	120	80	120	80	120
Cadmium	80	120	80	120	80	120	80	120
Cobalt	80	120	80	120	80	120	80	120
Chromium	80	120	80	120	80	120	80	120
Copper	80	120	80	120	80	120	80	120
Iron	80	120	80	120	80	120	80	120
Potassium	80	120	80	120	80	120	80	120
Mangnesium	80	120	80	120	80	120	80	120
Manganese	80	120	80	120	80	120	80	120
Molybdenum	80	120	75	120	79	120	75	120
Sodium	80	120	80	120	80	120	80	120
Nickel	80	120	80	120	80	120	80	120
Lead	80	120	80	120	80	120	80	120
Antimony	80	120	80	120	80	120	80	120
Selenium	80	120	75	120	80	120	75	120
Thallium	80	120	80	120	80	120	80	120
Vanadium	80	120	80	120	80	120	80	120
Zinc	80	120	80	120	80	120	80	120
Solid								
Silver	75	120	70	125	75	120	70	120
Aluminum	80	120	75	120	79	120	75	120
Arsenic	80	120	80	120	80	120	80	120
Barium	80	120	80	120	80	120	80	120
Beryllium	80	120	80	120	80	120	80	120
Calcium	80	120	80	120	80	120	80	120
Cadmium	80	120	80	120	80	120	80	120
Cobalt	80	120	80	120	80	120	80	120
Chromium	80	120	80	120	80	120	80	120
Copper	80	120	80	120	80	120	80	120
Iron	80	120	80	120	80	120	80	120
Potassium	80	120	80	120	80	120	80	120
Mangnesium	80	120	80	120	80	120	80	120
Manganese	80	120	80	120	80	120	80	120
Molybdenum	80	120	75	120	80	120	75	120
Sodium	80	120	80	120	80	120	80	120
Nickel	80	120	80	120	80	120	80	120
Lead	60	130	60	130	60	130	60	130
Antimony	80	120	75	120	80	120	75	120
Selenium	80	120	75	120	80	120	75	120
Thallium	80	120	80	120	80	120	80	120
Vanadium	80	120	80	120	80	120	80	120
Zinc	80	120	80	75	80	120	75	120

TABLE 3

INSTRUMENT WAVELENGTHS AND LIMITS

Detection Element	Wavelength(nm)
Aluminum	237.313
Antimony	206.836
Arsenic	188.979
Barium	233.527
Beryllium	313.107
Boron	182.528
Cadmium	228.802
Calcium	315.886
Chromium	267.716
Cobalt	228.616
Copper	324.752
Iron	238.204
Iron	302.107
Lead	220.353
Magnesium	279.077
Manganese	257.610
Molybdenum	202.031
Nickel	231.604
Potassium	766.491
Selenium	196.026
Silver	328.068
Sodium	330.237
Thallium	190.801
Tin	189.927
Titanium	337.279
Vanadium	292.402
Zinc	213.857

The wavelengths listed are utilized because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference (see step 5.1).

Table 4
Summary of Method Quality Objectives for Method 200.7/6010B
Metals by Inductively Coupled Plasma

QC Element	Frequency	Criteria	Corrective Action
Initial Calibration	Daily following optimization of ICP and prior sample analysis.	• Minimum of blank and three standards. • Low standard at MRL • R ≥0.995 (Do not force through zero for LR)	• No allowance. Perform maintenance and recalibrate.
ICV	Immediately following daily initial calibration.	• %Rec = 90-110%, %RPD < 5%. • Use separate source from initial calibration standards.	• If criteria exceeded, remake and re-analyze ICV. If second consecutive ICV is within criteria then calibration is accepted, otherwise recalibrate.
Low Level Calibration Standard (CRI)	Daily after initial calibration to support MRL.	• Only used if low standard is not at the MRL. • %Recovery 70-130%.**(80-120% if DoD criteria are to be met)** • MRL is at level of last successfully passed CRI.	• If no CRI passes, MRL at concentration in lowest calibration standard.
CCV	After calibration, every 10 samples and at end of analytical run.	• Concentration level near midpoint of curve • Same source as calibration standard. • %Rec = 90-110%, %RPD ≤5% (200.9 first CCV 95-105%)	• If criteria are exceeded, then remake and re-analyze CCV. If second consecutive CCV is within criteria, then calibration is verified, otherwise re-calibrate system and re-analyze any sample since the last valid CCV.
Continuing Calibration Blank	After calibration, every 10 samples and at end of analytical run.	• Must be matrix-matched (same acid concentration as standards and QC samples.) • Analytes < MRL (< 2x MDL for DoD QSM Criteria)	• Re-calibrate and re-analyze all samples since last valid CCB.
Method Blank	One per analytical batch of 20 or fewer samples.	• Matrix specific • Analytes < MRL (< ½ MRL for USACE/DoD/Navy/USACE)	• Report exceedance in the project narrative. • Samples that are non-detect may be reported. • Samples with concentrations that are 20x higher than the method blank may be reported. • Samples reported with a contaminated blank must be "B" flagged.
Blank spike (BS)	One per analytical batch of 20 or fewer samples.	• Use standard source different than used for initial calibration and Matrix specific • Concentration level should be between low and mid-level standard	• Report exceedance in the project narrative. • If LCS is biased high and sample is non-detect, then may report sample result.

		• Percent recoveries 80-120%. (85-115% for 200.7)	• Re-digest and re-analyze if the above exceptions do not apply.
Blank spike duplicate (BSD)	One per analytical batch of 20 or fewer samples.	• Prepared as above • Percent recoveries same as above • %RPD ≤ 20% aqueous and ≤ 30% soil. USACE %RPD ≤ 25% and DoD/Navy %RPD ≤ 20%	• Report exceedance in the project narrative. • If LCS is biased high and sample is non-detect, then may report sample result. • Re-digest and re-analyze if the above exceptions do not apply.
Matrix Spike	One per analytical batch of 10 or fewer samples	• Prepared using the same source as the blank spike • Concentration level should be between low and mid-level standard • Percent recoveries between 75-125%. See Table 2 for DoD/Navy/AFCEE	• Report exceedance in the project narrative. • Laboratories are expected to develop in-house control limits per each media. Control limits should fall within default limits.
Matrix duplicate	One per analytical batch of 10 or fewer samples	• **Aqueous**: Relative percent difference is ±20% for samples > 5x MRL and ±MRL for samples <5x the MRL. • **Soil**: Relative percent difference is ±35% for samples > 5x MRL and ±2xMRL for samples <5x the MRL. • ***USACE ≤25% and DoD/Navy ≤20%.***	• Note exceedance in project narrative. • If MS %Recovery is >30% and LCS is in control, no corrective action is required. If %Recovery is <30% and non-detect results found perform PDS.
Serial Dilution	One per analytical batch of 10 or fewer samples, performed on Dup/Spk sample.	• Result of 5x dilution must be ±10% of undiluted sample when result is ≥25x MRL.	• Narrate serial dilution QC out of control. May be indication of matrix affect.
Post Digestion Spike (PDS)	One per analytical batch of 10 or fewer samples, performed on Dup/Spk sample.	• Perform PDS if Serial dilution is not in control or if sample is < 25x the MRL. • Percent recovery must be 85-115% (75-125% for 6010B).	• Narrate PDS out of control if MS is also out of control. May be indication of matrix affect.
Linear Dynamic Range	Semi-annually	• Use successively higher concentrated standards against calibration curve until a standard is reached that is >10% difference from true value. Upper LDR is 90% of the highest standard within criteria.	• N/A
Instrument Detection Limit	Quarterly	• Analyze ten replicates of the calibration blank.	• N/A

ATTACHMENT I

SOP Modification

Method of Standard Additions

SOP(s) Modified: Inductively Coupled Plasma-Atomic Emission Spectroscopy (SW 846 Method 6010B/ EPA Method 200.7

Modification Objective: This addendum defines when the method of standard additions must be performed and how to perform the procedure.

Method Summary: The standard addition technique involves adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift.

For DoD/Navy projects, the method of standard additions (MSA) shall be used when the matrix spike or matrix spike duplicate is outside control limits and the failure is confirmed by the serial dilution/post digestion spike test. MSA calculation will only be applied to the metal(s) that failed.

MSA Procedure: The simplest version of this technique is the single-addition method, in which two identical aliquots of the sample solution, each of volume V_x, are taken. To the first (labeled A) is added a known volume V_S of a standard analyte solution of concentration C_S. To the second aliquot (labeled B) is added the same volume Vx of the solvent. The analytical signals of A and B are measured and corrected for non-analyte signals (performed by the ICP). The unknown sample concentration C_X is calculated:

$$C_X = \frac{S_B \times V_S \times C_S}{(S_A - S_B) \times V_x}$$

Where S_A and S_B are the analytical signals of solutions A and B, respectively. V_S and C_S should be chosen so that S_A is roughly twice S_B on the average, avoiding excess dilution of the sample.

Since ESS Laboratory performs a post digestion spike (PDS) on each sample it has chosen for the matrix spike the results from the spiked and unspiked aliquots will be used in the MSA calculation.

Example: MS result for Titanum was 56.8% and the PDS was at 69%. MSA calculated as follows:

$V_x = 10$ ml $V_S = 0.05$ ml $C_S = 100$ mg/L

Signal S_A (spiked aliquot) = 109644
Signal S_B (unspiked aliquot) = 19801

$$C_X = \frac{(19801 \times 0.05 \text{ ml} \times 100 \text{ mg/L})}{(109644 - 19801) \times 10 \text{ ml}} = 0.11 \text{ mg/L}$$

ATTACHMENT A – 1

ESS LABORATORY
Mn Profile Logbook

Date	Min Intensity	Max Intensity	X Offset	Y Offset	Analyst	Date	Min Intensity	Max Intensity	X Offset	Y Offset	Analyst

Reviewed by________________________________ **CONTROL# 30.0016-0502A**

Page__________

Values obtained from a 1ppm Mn Std (viewed at 257.610 nm wavelength), during the OptXY procedure of the Optima 3000XL and 3100XL instruments.

ATTACHMENT A-2

ESS LABORATORY
Mn Profile Logbook
ICP III

			Axial		Radial					Axial		Radial	
Date	Min Intensity	Max Intensity	X Offset	Y Offset	X Offset	Analyst	Date	Min Intensity	Max Intensity	X Offset	Y Offset	X Offset	Analyst

Reviewed by_______________________________ CONTROL# 30.0040-0602A

Page___________

Values obtained from a 1ppm Mn Std (viewed at 257.610 nm wavelength), during the OptXY procedure of the Optima 4300DV and 3100XL instruments.

ATTACHMENT B-1

ESS LABORATORY
ICP II TRAY SEQUENCE LOGBOOK

#	SAMPLE	#	SAMPLE	#	SAMPLE	#	SAMPLE
1	STD 1:	31		61		91	
2	STD 2:	32		62		92	
3	STD 3:	33		63		93	
4	STD 4:	34		64		94	
5	ICV:	35		65		95	
6	CRI 1:	36		66		96	
7	CRI 2:	37		67		97	
8	CRI 3:	38		68		98	
9		39		69		99	
10		40		70		100	
11		41		71		101	
12		42		72		102	
13		43		73		103	
14		44		74		104	
15		45		75		105	ICSAB:
16		46		76		106	ICSA:
17		47		77			
18		48		78			
19		49		79			
20		50		80			
21		51		81			
22		52		82			
23		53		83			
24		54		84			
25		55		85			
26		56		86			
27		57		87			
28		58		88			
29		59		89			
30		60		90			

Internal Standard

ID:_____

Counts:_____

SIF:_____

RDS:_____

METHOD:_____

METHOD:_____

ANALYST:_____

DATE:_____

Comments:_____

2nd Review:_____ Date:_____

CONTROL# 30.0006-0802A PAGE____

ATTACHMENT B-2

ESS LABORATORY
ICP III TRAY SEQUENCE LOGBOOK

#	SAMPLE	#	SAMPLE	#	SAMPLE	#	SAMPLE
1	STD 1:	31		61		91	
2	STD 2:	32		62		92	
3	STD 3:	33		63		93	
4	STD 4:	34		64		94	
5	ICV:	35		65		95	
6	CRI 1:	36		66		96	
7	CRI 2:	37		67		97	
8	CRI 3:	38		68		98	
9		39		69		99	
10		40		70		100	
11		41		71		101	
12		42		72		102	
13		43		73		103	
14		44		74		104	
15		45		75		105	ICSAB:
16		46		76		106	ICSA:
17		47		77			
18		48		78			
19		49		79			
20		50		80			
21		51		81			
22		52		82			
23		53		83			
24		54		84			
25		55		85			
26		56		86			
27		57		87			
28		58		88			
29		59		89			
30		60		90			

Internal Standard

ID:_____

Counts:_____

SIF:_____

RDS:_____

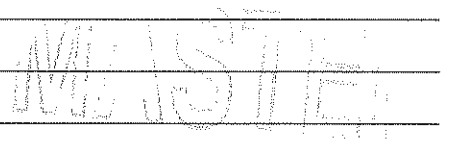
METHOD:_____

METHOD:_____

ANALYST:_____

DATE:_____

Comments:_____



2nd Review:_____ Date:_____

CONTROL# 30.0038-0803A PAGE____