ANALYSIS OF SELECTED METALS BY DUAL VIEW INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROSCOPY (ICP-AES)

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1. SCOPE AND APPLICATION

1.1. This standard operating procedure (SOP) details the analysis of metals in waters, soils, wastes, and other environmental samples utilizing an Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES). It covers analyses by EPA Method 200.7 (test ID's W-ICP, W-ICP-F, and W-SI-ICP-F), EPA Method

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6010D (test ID's W-ICP-R, W-ICP-R-F, S-ICP, and WASTE-ICP), EPA Method 6010C (test ID S-ICP-TO), and Standard Method 2340B (test IDs W-HARD and W-HARD-F, see DEP SOP **MT-058**).

1.2. The Perkin Elmer ICP-OES (model AVIO 500) is an optical emission spectrometer possessing the capability of both axially and radially oriented viewing positions. This instrument uses inductively coupled argon plasma as the excitation source. The AVIO 500 model uses a **S**egmented-array, **C**harge-coupled **D**evice (SCD) as the detector, capable of analyzing up to 76 elements simultaneously and offers a wide linear dynamic range with a resolution of approximately 6 pm at 200 nm. The procedure performed in this laboratory analyzes 29 elements simultaneously.

2. SUMMARY OF METHOD

2.1. Digested water, sediment, waste, and tissue samples are analyzed and reported as 'total recoverable metals.' With the exception of silver, where EPA method 200.7 is approved for the determination of metals and metalloids in drinking water, samples may be analyzed directly by pneumatic nebulization without acid digestion if the sample has been properly preserved with acid and has a turbidity of < 1 NTU at the time of analysis. Sediment samples digested using hydrofluoric acid and microwave radiation are reported as 'total metals.' Filtered water samples are analyzed without digestion and reported as 'dissolved metals.' Soils and sediments are reported on a dry weight basis; wastes and tissues are reported on a wet weight basis.

2.2. The following is a list of the 29 elements currently analyzed along with the approximate spectral line in nanometers (nm) used:

Element	Spectral Line	Element	Spectral Line	Element	Spectral Line
Al	396.164	Cu	327.391	Na	589.611
Sb	206.834	Fe	273.935	Sr	421.549
As	188.980	Pb	220.350	Tl	190.791
Ba	233.528	Mg	279.080	Sn	189.926
Be	313.099	Mn	257.606	Ti	334.938
B	208.890	Mo	202.028	V	292.399
Cd	228.800	Ni	231.602	Zn	206.195
Ca	317.930	K	766.500	SiO_2	251.609
Cr	267.709	Se	196.023	Li	670.759
Co	228.613	Ag	328.067	Sc *	361.384
				Sc *	357.251

* Internal standard

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2.3. The instrument is calibrated with 1 standard (see Section 4.10.) and a blank. The calibration equation is linear. Since only two points are used, the calibration curve is forced through the blank. **Data are not reported outside of this established range of linearity unless they are properly diluted within this established range of linearity.**

The calibration curve linearity is verified on every run by analyzing a second source standard, a continuing calibration verification (CCV) sample, and a limit of quantitation (LOQ) sample. The calibration is verified by analyzing the second source standard purchased from a vendor that is different from the primary used for the calibration standards (ICPMINC, ICPMETC, and AG-SIO2C; Sections 4.10.2 - 4.10.4.). The analytes present in these second source standards are at the same concentration as the appropriate calibration standard. If the determined concentration for any analyte in these standards is less than or equal to 95 % or greater than or equal to 105 % of the stated value, then the data for that analyte cannot be reported unless it is properly qualified and commented.

Initial calibration verification standards (CCVC i.e. ICPMINCCVC, ICPMETCCVC, and AG-SIO2CCVC; Sections 4.11.1. - 4.11.3.) are analyzed for each analyte and these standards must be determined to be no less than or equal to 95 % or no greater than or equal to 105 % of the stated value for each analyte in the standard and the Relative Standard Deviation (RSD) from the four replicate integrations must be less than 3 % for each analyte. If the determined concentration or RSD for any analyte is outside of this range, then no data can be reported for that analyte unless properly qualified and commented. In addition, the instrument practical quantitation limit (PQL) solution (see Sections 4.12.5. – 4.12.7.), which corresponds to the LOQ, is run after the instrument calibration on every analytical batch with established control limits of 70 – 130 %. If an analyte is outside of the control limits, samples requiring results for the affected analyte must be either rerun or qualified using the criteria for positive and negative bias according to DEP SOP **LB-027.**

3. APPARATUS AND EQUIPMENT

3.1. Perkin Elmer AVIO model 500 Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES), S/N: 081S2004242.

3.1.1. Perkin Elmer AS-93 Plus or S10 autosampler.

3.1.2. ESI Pergo argon humidifier.

3.1.3. PolyScience WhisperCool chiller.

3.2. 17 x 100 mm polypropylene round bottom culture test tubes - FS - Cat. No. 14-956-7E.

3.3. 1.14 mm ID, PVC manifold (pump) tubing - Red/Red - FS - Cat. No. 14-190-507.

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3.4. 0.38 mm ID, PVC manifold (pump) tubing - Orange/Green - FS - Cat. No 14-190-501.

3.5. 0.76 mm ID, PVC manifold (pump) tubing - Black/Black - FS - Cat. No 14-190-504.

3.6. Gas supply

3.6.1 Argon gas supplied from the laboratory's MicroBulk argon delivery system.

3.6.2 Plasma Shear and Purge gases

3.6.2.1 Shear gas - compressed air.

3.6.2.2 Purge gas - nitrogen gas, supplied from the laboratory's MicroBulk N_2 delivery system.

3.7. HF Scientific Inc. MicroTPW Portable Turbidimeter, S/N: 2026070140.

3.8. Class A glass volumetric flasks, assorted volumes.

3.9. Eppendorf pipettes, assorted volumes.

3.10. Teflon bottles, assorted volumes.

4. REAGENTS AND STANDARDS

Note: Be careful not to contaminate solutions with trace metals or minerals during preparation and use. Be sure to mix all solutions thoroughly immediately after they are prepared. Standard solutions must be stored in Teflon bottles. Use Eppendorf pipettes in the preparation of standards, standard reference materials (SRMs), and spike solutions. Check the calibration of pipettes every month as described in DEP SOP **CM-032** with the Mettler Toledo XPE105DR balance and the Check and Track software. Save the acceptable pipette calibration report to network folder: \\floridadep\data\DEAR\Labs\Lab5\Chemistry\Pipette\Inorganic_Metals.

All calibration standards, calibration verification standards, calibration check solutions, and PQL solutions should contain 2 % HNO_3 and 1 % HCl unless otherwise noted.

Note: There are two options for preparing stable acidic aqueous silver solutions. The first option is a nitric only matrix. These solutions are stable to photo-reduction. The second option is a hydrochloric acid matrix that forms a soluble chloride complex which will undergo photo-reduction.

The expiration dates for standards prepared from purchased metal standards will be no later than the soonest expiration date provided by the manufacturer of the purchased single element stock standards from which the standard was made. All purchased and prepared standards must be logged into the LIMS standard prep tracker. A label with a serial number and expiration date must be placed on the bottle of standard. All certificates of analysis for standards and reagents must be scanned or downloaded and

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saved to the network folder: \\floridadep\data\DEAR\Labs\Lab5\Chemistry\InorganicPrep\Certificates of Analysis for Reagents and Standards.

Note: See DEP SOP **MT-069** for instructions on reagent preparation documentation and expiration dates. All bottles of reagents in the laboratory are required to have unique identifiers. This is accomplished by logging purchased and prepared reagents into the LIMS standard prep tracker. A label, which includes a serial number, must be printed and placed on the bottle of reagent.

4.1. De-ionized (DI) water - From the laboratory DI water supply system.

4.2. Trace metal grade nitric acid (HNO_3) - Stored in acid cabinet under the hood. Expiration date provided by the manufacturer.

4.3. Trace metal grade hydrochloric acid (HCl) - Stored in the acid cabinet under the hood. Expiration date provided by the manufacturer.

4.4. Rinse Water - 200 mL HNO_3 and 100 mL HCl in 10 L of DI water. Expires 1 year after the preparation date.

4.5. Acid Rinse Solution - Dilute 50 mL HNO_3 and 10 mL of HCl to 1 L with DI water; this solution contains 5 % HNO_3 and 1 % HCl. Expires 1 year after the preparation date.

4.6. Mn Profile Solutions – Used to automatically align the torch viewing position for the highest signal intensity.

Expires according to the manufacturer's expiration date of the stock manganese standard; however, this standard's expiration may be extended as long as the manganese concentration is stable, and a stable signal is produced when aspirating the solution.

4.6.1. Radial View - 10 mg/L Mn solution: Pipette 1.0 mL of a stock supply of 10,000 mg/L Mn solution into a 1 L volumetric flask containing 900 mL of DI water, 20 mL of HNO_3, and 10 mL of HCl. Dilute to the mark with DI water.

4.6.2. Axial View - 1 mg/L Mn solution: Pipette 0.10 mL of 10,000 mg/L Mn solution into a 1 L volumetric flask containing 900 mL of DI water, 20 mL of HNO_3, and 10 mL of HCl. Dilute to the mark with DI water.

4.7. Internal Standard - 10 mg/L Sc: Pipette 2 mL of scandium standard (10,000 mg/L) into a 2 L flask containing 1 L DI water and 40 mL of HNO_3 and 20 mL of HCl. Dilute to the mark with DI water. Expires according to the manufacturer's expiration date of the stock scandium standard, however, this standard's expiration may be extended as long as the scandium concentration is stable, and a stable signal is produced when aspirating the solution.

4.8. Primary Single Element Standards - 10,000 mg/L or 1,000 mg/L NIST-traceable single element standards are purchased from vendors such as SPEX, High Purity,

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Exaxol, etc. Used for calibration standard preparation (see Section 4.10). Expiration dates assigned by the manufacturer.

4.9. Secondary Single Element Standards - 10,000 mg/L or 1,000 mg/L NIST-traceable single element standards are purchased from vendors such as SPEX, High Purity, Exaxol, etc. Used for second source calibration verification standard preparation (see Section 4.12.). The commercial source of the secondary single-element standards must be different than the commercial source of the single-element standards used to prepare the calibration standards. Expiration dates assigned by the manufacturer.

4.10. Calibration Standards

The expiration dates of the prepared calibration standards will be no later than the soonest expiration date provided by the manufacturer of the purchased primary single element standards from which they were made. Prepare the calibration standards from the primary purchased single element standards and store in a Teflon bottle at room temperature.

4.10.1. Calibration Blank (INITIAL BLANK, CCB, I-BLK) - In a 1 L Teflon bottle, add 700 mL DI water, then 20 mL HNO_3 and 10 mL HCl and dilute to the mark with DI water. This solution contains 2 % HNO_3 and 1 % HCl.

4.10.2. ICPMIN

- 200 mg/L Ca, Na
- 100 mg/L Fe, Mg
- 50 mg/L Al
- 20 mg/L K

4.10.3. ICPMET

- 10 mg/L Cr, Cu, Pb, Mn, Sr, V and Zn
- 5 mg/L Ba
- 1 mg/L Sb, As, B, Cd, Co, Mo, Ni, Se, Tl, Sn, Li and Ti
- 0.5 mg/L Be

4.10.4. AG-SIO2

- 0.25 mg/L Ag
- 50 mg/L SiO_2

4.11. Continuing Calibration Verification (CCV and CCVC) Standards

The expiration date of the prepared CCV standards will be no later than the soonest expiration date provided by the manufacturer of the purchased single element standards from which they were made. Prepare the continuing calibration verification standards from the primary purchased single element standards and store in a Teflon bottle at room temperature.

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4.11.1. ICPMINCCV/ICPMINCCVC

ICPMINCCV is the continuing calibration verification solution for these six elements, and ICPMINCCVC is the initial calibration verification solution for these six elements:

- 100 mg/L Ca, Na
- 50 mg/L Fe, Mg
- 25 mg/L Al
- 10 mg/L K

4.11.2. ICPMETCCV/ICPMETCCVC

ICPMETCCV is the continuing calibration verification solution for these 20 elements, and ICPMETCCVC is the initial calibration verification solution for these 21 elements:

- 5 mg/L for Cr, Cu, Pb, Mn, Sr, V, and Zn
- 2.5 mg/L for Ba
- 250 µg/L for Be
- 500 µg/L for Sb, As, B, Cd, Co, Mo, Ni, Se, Tl, Sn, Ti, and Li.

4.11.3. AG-SIO2CCV/AG-SIO2CCVC

AG-SIO2CCV is the continuing calibration verification solution for silver and silica, and AG-SIO2CCVC is the initial calibration verification solution for silver and silica:

- 0.125 mg/L Ag
- 25 mg/L SiO_2.

4.12. Calibration Check Solutions

The expiration dates of the prepared calibration check standards will be no later than the soonest expiration date provided by the manufacturer of the purchased single element standards from which they were made. Prepare the calibration check standards from the secondary purchased single element standards and store in a Teflon bottle at room temperature.

4.12.1. ICPMINC

Second source check standard. This is the minerals calibration verification solution. Must be prepared from the secondary single element standards (see Section 4.9.).

- 200 mg/L Ca, Na
- 100 mg/L Fe, Mg
- 50 mg/L Al
- 20 mg/L K.

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4.12.2. ICPMETC

Second source check standard. This is the trace metal calibration verification solution. Must be prepared from the secondary single element standards (see Section 4.9.).

- 10 mg/L Cr, Cu, Pb, Mn, Sr, V and Zn
- 5 mg/L Ba
- 0.5 mg/L Be
- 1 mg/L Sb, As, B, Cd, Co, Mo, Ni, Se, Tl, Sn, Ti, and Li.

4.12.3. AG-SIO2C

Second source check standard. This is the Ag and SiO_2 calibration verification solution. Must be prepared from the secondary single element standards (see Section 4.9.).

- 0.25 mg/L Ag
- 50 mg/L SiO_2

4.12.4. SPECTRAL INTERFERENCE CHECKS:

4.12.4.1 ICS2007A: Pipette 1 mL of Sb Stock Standard (1000 mg/L), 0.3 mL of Sn, and Li Stock Standard (1000 mg/L), 0.03 mL of Sr Stock Standard (10,000 mg/L), 1 mL of 2007ICS # 3 Standard, 1 mL of 2007ICS # 1 Standard, and 20 mL of 2007ICS # 4 Standard into a 1 L volumetric flask containing 600 mL of DI water, 20 mL of HNO_3 and 10 mL HCl. Dilute to the mark with DI water. Refer to **APPENDIX A** for concentrations.

4.12.4.1.1 2007ICS # 1 – Custom NIST-traceable standard prepared by SPEX, Inorganic Ventures, or another suitable vendor. Contains B at 500 mg/L, Mo at 300 mg/L, SiO_2 at 230 mg/L, and Ti at 1000 mg/L.

4.12.4.1.2 2007ICS # 3 – Custom NIST-traceable standard prepared by SPEX, Inorganic Ventures, or another suitable vendor. Contains As, Pb, and Tl at 1000 mg/L; Ba, Cd, Cr, Co, Cu, Ni, Ag, V, and Zn at 300 mg/L; Be at 100 mg/L, Mn at 200 mg/L, K at 20,000 mg/L, and Se at 500 mg/L.

4.12.4.1.3 2007ICS # 4 – Custom NIST-traceable standard prepared by SPEX, Inorganic Ventures, or another suitable vendor. Contains Al at 3000 mg/L, Ca at 15000 mg/L, Fe at 12500 mg/L, Mg at 7500 mg/L, and Na at 2500 mg/L.

4.12.4.2. Single element SIC checks: Prepare the following single element standards from the purchased stock standards

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with a 2 % HNO_3 / 1 % HCl matrix. Al 500 mg/L, B 50 mg/L, Ba 50 mg/L, Ca 500 mg/L, Cu 50 mg/L, Fe 200 mg/L, Mg 500 mg/L, Mn 50 mg/L, Mo 20 mg/L, Na 1000 mg/L, Ni 20 mg/L, Se 20 mg/L, Silica 200 mg/L, Sn 20 mg/L, V 20 mg/L and Zn 20 mg/L. The standards expire according to the manufacturer's expiration dates and the standards are stored at room temperature in lab B310.

Individual element SIC checks are performed at least once every quarter. The absolute value of the concentration observed for any un-spiked analyte in the single element SIC checks must be less than two times the analyte's PQL. Export the analysis data to QC Manager and use test ID W-ICP-F and matrix, SIC. QC Manager will display a pass if the absolute value of the concentration observed for any un-spiked analyte in the single element SIC checks is less than two times the analyte's PQL and will display a fail if the result is not less than two times the analyte's PQL.

Use form MT-ICP-LIN to demonstrate the single element interference checks are within the linear range of the instrument. The acceptable recovery limits are 90 – 110 %.

NOTE: Document the analysis of the individual element SIC checks and linearity check in the instrument maintenance logbook by entering the file name of the analysis after verifying the results are acceptable. Make sure the MT-ICP-LIN form is saved to the network with the same instrument file name.

Samples with concentrations of elements higher than the SIC check must be diluted until the concentration is less than the SIC check solution.

4.12.4.3 ICS6010D: Multi-element spectral interference check standard. The standard is prepared from single element stock standards or purchased from SPEX CertiPrep. The acid matrix is 2 % HNO_3 / 1 % HCl. The standard is stored at room temperature in lab B310. The concentrations are: Al 500 mg/L, Ca 500 mg/L, Fe 200 mg/L and Mg 500 mg/L.

The multi-element solution is used daily to check that the instrument is free from interference from elements typically observed in high concentration and to check that interference corrections applied are still valid. The

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concentration measured for any target analytes must be less than +/- the PQL.

4.12.5. Instrument PQL Stock Solution – CPQLDV# INT 50X (a suffix is added to these abbreviations (e.g. 9, 10, etc.) to indicate current PQL solution used) - Prepared by a dilution of purchased single element stock standards. This intermediate solution should contain all analytes listed in Section 2.2., except SiO_2 (refer to Section 4.12.7.), at concentrations of 50X the PQL levels. Make sure the most recent PQL levels are used when making the solution. Excel files containing the current MDLs and PQLs may be found at: \\floridadep\data\Labs\Lab3\Chem_Data\Inorganic\Metals\QC Statistics.

4.12.6. Instrument PQL Solution - CPQLDV# (a suffix is added to these abbreviations (e.g. 9, 10, etc.) to indicate current PQL solution used) - Add 600 mL of DI water, 20 mL HNO_3, and 10 mL HCl to a 1 L volumetric flask. To this flask, pipette 20 mL of the Instrument PQL Stock Solution (see Section 4.12.5.). Dilute to mark with DI water.

4.12.7. Instrument SiO_2 PQL Solution - CPQLSI and IPQLSI - Add 600 mL of DI water to a 1 L volumetric flask. Add the appropriate amount of individual stock SiO_2 standard and dilute to mark with DI water. This solution does not contain acid.

4.13. Spike Solutions

The expiration dates of the prepared spike solutions will be no later than the soonest expiration date provided by the manufacturer of the purchased single element standards from which they were made. These spike solutions are used to prepare preparation batch Laboratory Fortified Blanks (LFBs) (See DEP SOP **MT-060** and DEP SOP **MT-024** for LFB preparation). The LFBs prepared at the concentrations specified in **APPENDIX B** shall also serve as the four quality control samples required for Initial or Continuing Demonstrations of Capability (DOC) for each prep technician or analyst. Acceptable analysis of a blind sample, such as a Proficiency Testing sample, may also serve as a Continuing DOC in lieu of four quality control samples, but not as an Initial DOC.

4.13.1. Digestion PQL Solution - DPQLDV# INT 50X (a suffix is added to this abbreviation to indicate the current PQL solution used (e.g. 9, 10, etc.)). This is the PQL check standard for the digested water matrix. This solution is prepared from purchased single element stock standards in 2 % HNO_3 and 1 % HCl at a concentration of 50X the final PQL. Make sure the most recent PQL levels are used when making the solution. Excel files containing the current MDLs and PQLs may be found at: \\floridadep\data\Labs\Lab3\Chem_Data\Inorganic\Metals\QC Statistics.

4.13.2. Trace Metal Spike Solution - HW6. This spike is prepared in two parts, HW6A and HW6B using the purchased second source single element

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standards. HW6A is prepared with 2 % HNO_3 and 1 % HCl while **HW6B is prepared with 4 % HNO_3**. Refer to **APPENDIX B** for spike concentrations.

4.13.3. Mineral Spike Solution - ICPMINA. For both digested and instrument spikes (digested and filtered samples) use a purchased solution from Inorganic Ventures. Refer to **APPENDIX B** for the spike concentrations. The expiration date is provided by the manufacturer.

4.13.4. Sediment Spike Solution - SEDSPK4. This spike is prepared in two parts, SED SPK4A and SED SPK4B using the second source single element standards. SED SPK4A is prepared with 2 % HNO_3 and 1 % HCl **while SED SPK4B is prepared with 4 % HNO_3**. Refer to **APPENDIX B** for spike concentrations.

4.13.5. SiO_2 Spike Solution - The second source silica stock solution is used as the spike solution. Add 200 µL of this solution to 10 mL of sample or DI water to produce a spike concentration of 20 mg/L SiO_2.

Note: The current silica stock standard may have been manufactured from sodium metasilicate in which case it cannot be combined with any standards used for sodium analysis.

4.13.6. DVPQL3052# - This is the PQL check standard for totally digested sediment samples digested according to DEP SOP **MT-063**. It is prepared at 50x the PQL concentration for totally digested sediment samples (Test ID: S-ICP-TO). A suffix is added to the DVPQL3052 abbreviation (e.g. A, B, etc.) to indicate the current PQL solution used. Dilute appropriate volumes of the single element stock standards to 1 L with 2 % HNO_3 / 1 % HCl to produce a solution at 50x the PQL for totally digested sediment samples. The current totally digested sediment PQL concentrations can be found on the Laboratory's computer network at: \\floridadep\data\Labs\Lab3\Chem_Data\Inorganic\Metals\QC Statistics. The expiration date for this standard will be no later than the soonest expiration date provided by the manufacturer of the single element stock standards from which it was made, and it is stored at room temperature in lab B411.

4.13.7. SDPQLDV# - This is the PQL check standard for digested sediment, tissue, and waste samples. It is prepared at 50x the PQL concentration for digested sediment, tissue, and waste samples. A suffix is added to the SDPQLDV abbreviation (e.g. 1, 2, etc) to indicate the current PQL solution used. Dilute appropriate volumes of the single element stock standards to 1 L with 2 % HNO_3 / 1 % HCl to produce a solution at 50x the PQL of digested sediment, tissue, and waste samples. The current digested sediment, tissue, and waste PQL concentrations can be found on the Laboratory's computer network at: \\floridadep\data\Labs\Lab3\Chem_Data\Inorganic\Metals\QC Statistics.

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The expiration date for this standard will be no later than the soonest expiration date provided by the manufacturer of the single element stock standards from which it was made, and it is stored at room temperature in lab B411.

5. SAMPLE PREPARATION PROCEDURE

5.1. Filtered Water Samples - For undigested, filtered and acidified samples, which are checked out directly from the receiving room, prepare sample matrix spikes as follows. For trace metals, pipette 200 µL of spike solution HW6 (A and B) (refer to **APPENDIX B** for spike concentrations) into 10.0 mL of sample in a centrifuge tube and mix well. For minerals spikes, pipette 200 µL of solution ICPMINA (refer to **APPENDIX B** for spike concentrations) to 10.0 mL of sample. For samples requiring silica results, pipette 200 µL of the 1000 mg/L second source SiO_2 stock standard into 10.0 mL of sample in a centrifuge tube and mix well. **Each batch must contain at least one set of duplicate matrix spikes and at least one spike for every ten samples (two different samples must be spiked for batches over 10 samples).**

5.1.1 One method blank (see Section 4.10.1.), one IPQL (see Sections 4.12.6. – 4.12.7.), and one LFB (see Sections 4.13.2. – 4.13.3.) are also required for each batch of filtered water samples.

5.1.2 Test ID W-SI-ICP indicates the sample was not filtered in the field. Filter a sample aliquot in the analysis laboratory. The filtrate is analyzed, and the comment 'Lab Filtered' is added after the sample ID in the sequence. Test ID W-SI-ICP-F indicates the sample was field filtered and the sample is analyzed by pouring an aliquot from the sample bottle. Batch samples with test IDs W-SI-ICP and W-SI-ICP-F separately.

5.1.3 If a sample is received without preservation, the sample is acidified upon receipt. The lab must wait at least 24 hours before beginning prep and will need to verify that the pH of the sample is below 2 using pH paper. The lot number and expiration date of the pH paper must be documented on the prep worksheet.

Note: If a precipitate is formed in a filtered sample during acidification, transport, or storage, the sample must be digested. Notify your supervisor immediately if a precipitate or particulates are observed in a filtered sample.

Note: If, after spiking a QC sample, the concentration of an analyte is above the instrument's calibration range, rerun the QC sample and spikes for that analyte after an appropriate dilution. The QC sample and the spikes should be diluted by the same factor.

5.2. Unfiltered (digested) water samples - See the DEP SOP **MT-024** for details on preparation.

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5.3. Solid samples (soils, sediments, and wastes) - See the DEP SOPs **MT-060** and **MT-063** for details on sample preparation.

6. INSTRUMENT START-UP/SHUTDOWN/STANDBY MODE PROCEDURE

6.1. START-UP - In the event that the instrument has been previously powered down completely, the following procedure must be used to begin operation.

6.1.1. Turn on the PolyScience chiller and allow it to equilibrate to a temperature of ~ 17 °C.

6.1.2. Toggle the AVIO 500 MAIN POWER switch, located on the right-side panel of the instrument, to the ON position.

6.1.3. Open the software as in Sections 7.1. and 7.2. below.

Note: If the instrument has been powered down for a minimal amount of time, the spectrometer will require approximately 74 minutes to become operational. However, if the instrument has been powered down for more than a few minutes it should be allowed to stabilize overnight while having everything turned on except the plasma and peristaltic pump. This will allow the optics bench and detector to reach a stable temperature. After that time, the plasma can be turned on and allowed to warm up.

6.2. SHUTDOWN - In the event that the instrument must be completely powered down, the following procedure should be followed.

6.2.1. Extinguish the plasma and turn off the pump.

6.2.2. Exit the Syngistix software.

6.2.3. Toggle the MAIN POWER switch located on the right-side panel of the instrument to the OFF position.

6.2.4. Turn off the PolyScience chiller.

6.3. STANDBY MODE - SHUT DOWN. If desired, at the end of an analysis, the instrument can be put in this mode if it is not to be used for several weeks. In Standby Mode, the argon purge gas to the detector and the detector coolant system is shut down. The command to enter this mode can be accessed two ways.

6.3.1. Manual Standby Mode Access: Click on the SYSTEM icon, then “Auto Shutdown/Start-up”, then check “Shutdown” either with “Immediately on OK” (i.e. right now!) or “At end of Automated Analysis,” then finally “Put Spectrometer into Standby” and click “ok” to apply settings.

6.3.2. Automated Standby Mode Access: Click on the AUTO icon, which brings up the Automated Analysis Control window. Under the SET UP tab, click on “Auto Shutdown, Set...” and the same screen as in Section 6.3.1. will appear. Check “Shutdown” either with “Immediately on OK” (i.e. right now!) or “At end of Automated Analysis”, then finally “Put Spectrometer into Standby” and click “ok” to apply settings.

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6.4. STANDBY MODE - START UP. If the instrument is currently in Standby Mode, the detector system will need to cool back down to operating temperature before data can be collected. To exit Standby Mode and prepare for analyses, enter the AUTOMATIC SHUTDOWN/START-UP window either via the "System, Auto Shutdown/Start-Up" path or via the AUTO icon, SET UP tab, "Auto Shutdown, Set..." box. Click on "Start-Up" and choose a time. Once the instrument begins the start-up process, it will take approximately 74 minutes before the spectrometer is ready.

7. SAMPLE ANALYSIS PROCEDURE

Note: Read the AVIO 500 Family Hardware and Software guides, and online help in Syngistix for details.

7.1. Turn on the computer, log on as "Metals" (see supervisor for password) and click on the Syngistix icon to enter the software. If the software is already loaded, there is no need to exit and re-enter.

7.2. Upon entering Syngistix, a "System Status" window will open immediately, pictorially indicating the process of checking the status of the spectrometer, plasma, and autosampler subsystems. Green colored "pipes" indicate successful connections. This window may also be seen during analyses from the main Syngistix screen under the "System, Diagnostics" path. If the instrument was powered down completely prior to this step, see note in Section 6.1.3.

7.3. Pre-Check the following:

7.3.1. Peristaltic pump tubing - Change the sample introduction (Black/Black), internal standard (Orange/Green), and pump drain tubing (Red/Red) daily. Change the rinse station pump tubing if it is flat or has visible damage. Pre-stretch the tubing before placing it around the pump to avoid slack generation and flow rate reduction later during a run.

7.3.2. Rinse water level - The rinse water should be at least one-fifth full. If it is not, prepare more (see Section 4.4.).

7.3.3. Ar gas pressure - The Ar pressure should read approximately 100 psi for the Ar flow. **DO NOT adjust the regulator at the wall. The instrument can be damaged if the pressure going to the instrument is too high!!!**

7.3.4. Nebulizer - Check the nebulizer to be sure it is clean and produces a smooth mist. Suitable nebulizers include glass Meinhard, PEEK Mira Mist, or any other nebulizers approved by the group supervisor. Normal operations utilize a PEEK Mira Mist nebulizer. If using a glass Meinhard, be sure to use a "C" type and not a "K" type. The intensities can change and cause instrumental difficulties if the wrong type is used under operating conditions for the other type.

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7.3.5. Torch - Normal operation utilizes a modified wet aerosol torch assembly. Check the following: the torch is centered in the RF coil; the slot for radial viewing is centered in the quartz window; the bonnet is clean, and the injector tip is clean. If there are deposits on the injector tip, remove the tip carefully from the bottom of the torch assembly and soak in Aqua Regia (3:1 $HCl:HNO_3$) for **no more than 30 mins.** If the inner diameter of the torch contains deposits, the torch should be cleaned in the following way: disassemble the torch, soak the torch parts in Aqua Regia (3:1 $HCl:HNO_3$) for 48 hours, rinse well with DI water, and dry thoroughly before reassembling. Refer to the AVIO 500 Family Hardware Guide from Perkin Elmer for details on removal and cleaning. The torch itself does not have to be completely clean at the top as the emission lines are viewed through the slot in the torch and/or through the end of the torch. After reassembling the torch, re-align its viewing position (Mn alignment) using the solutions in Section 4.6. and the spectrometer control option in the Syngistix software. Document the torch viewing positions and intensities in the instrument maintenance log. The intensity readings should be similar, though slightly lower than previous alignments. The radial and axial positions do not have to be exact but should be around 0.0 nm for radial viewing and 0.0, 15.0 nm for axial. Refer to the Syngistix Instrument Control Software Guide from Perkin Elmer for details on aligning the torch.

7.3.6. Spray Chamber - For normal operations, a Cyclonic Spray Chamber with inner baffle is used. The spray chamber should be visually inspected for particles or abnormalities in the glass. Once the sample/internal standard flow has started, the spray chamber should be examined for a smooth mist with no “beading” on the walls of the chamber.

7.3.7. Chiller - Ensure that the power is on, the temperature setting is 17 °C, the recirculating water pressure is ~ 60 psi, and there is enough water for cycling. If the water level is too low, fill the chiller with distilled water and a few drops of algaecide or other acceptable solution.

7.3.8. Drain line - Ensure that the condensate from the spray chamber is being pumped through its drain line in a pulsed stream.

7.3.9. Sample/Internal Standard Solution Flow Rate - When the instrument is turned on, place both the sample and internal standard probes in an acid rinse solution. Check both lines to ensure the flow rates are smooth and continuous by generating several bubbles in each line and following the passage of the bubbles all the way to the spray chamber. Ensure that the bubbles do not get stuck in the introduction lines, especially at line connections and the ‘y’ connector. The sample introduction flow rate should be smooth. The internal standard flow will pulsate somewhat, but

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this cannot be avoided. Once set, the peristaltic pump tension should not need daily adjustment.

7.3.10. Method Selection in Software - Select the desired method in the Syngistix software. It contains the associated MSF and IEC files as well as proper plasma and flow rate parameters.

Note: All instrument maintenance should be documented in the instrument maintenance log.

7.4. Torch Lighting and Warm-Up - After all pre-start checks pass inspection, perform the following steps:

7.4.1. Torch Ignition - Open the Plasma icon from the main menu and click on the "On/Off" toggle button located at upper left. The plasma ignition sequence consists of an initial 45 second gas purge, a brief stabilization period in which the pump is turned off, and then a 15-second "final purge" before ignition. Once the plasma is ignited, the pump will be turned back on automatically after ~ 15 more seconds.

7.4.2. Sippers - Manually place the sample and internal standard sippers (probes) in the rinse solution while the instrument warms up.

7.4.3. Warm-up - Allow the torch assembly/RF generator system to warm up for at least one hour to ensure that the torch and optical system are at equilibrium before starting a run. The detector system is ready to go unless the instrument was placed in "STANDBY" Mode from a previous analysis (see Section 6.3.).

7.5. Autosampler Table Set-up - While the instrument is warming up, a new "Sample Information File" can be created for a new analytical run. Create the new file as follows:

7.5.1. Click on the "SamInfo" icon at the top of the main menu to bring up the file from the most recent run.

7.5.2. The "Sample Information Editor" window will appear with the name of the file at the top. The lower section of the window displays "Parameters that vary by sample". Modify this section for each new run as follows.

7.5.2.1. The leftmost column labeled "Sample No." cannot be edited. To insert a row in the table, click on a row in this column and select "Ctrl-I" on the keyboard to insert a row before the highlighted row. To delete a row, click on the row in this column and press "Ctrl-D" to delete the highlighted row.

7.5.2.2. In the column labeled "A/S Location", type in the autosampler rack position number in which you want that sample analysis tube. Rack position number 16 is the first available entry, after the initial QC samples.

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7.5.2.3. Enter the "Sample ID" in its column and include any dilution factors, reruns, or other important notes about the sample.

Note: Only use letters and numbers in this column. Do **not** use any non-alphanumeric characters (commas, parentheses, asterisks, etc.) in the Sample ID column; these will cause errors when converting the file into QC manager.

7.5.2.4. In the column labeled "ANALYZE QCs BEFORE" and in the first row, make sure the proper sequence of QC solutions appears. See Appendix C for an example of the autosampler sequence that includes the name, rack position number, and purpose of each beginning QC. Place these QC solutions in the rack according to their position in Appendix C (these positions can also be found in the method file in the Syngistix software).

7.5.2.5. Following the initial QC set and at the end of the run, insert the QC sequence number 13, 14, 15, 16, 17 (see Appendix C or the method file) in the column. Either QC #13 (silver CCV), QC #14 (minerals CCV), or QC #15 (trace metals CCV) may be left out if none of those analytes are needed in the run.

7.5.2.6. The calibration standards will automatically appear when beginning an analysis in the Manual or Automated Analysis Control windows and are not listed in the sequence.

7.5.3. Wash Time - To add additional wash time to the preset wash time in the method (e.g. 60 seconds), type in the number of seconds in this column in the Autosampler file. Use extra wash after high-conductivity (over 20,000 µmhos/cm) samples or samples with a heavy matrix. The wash time entered in the Autosampler file will be added to the default time after the sample ID on that same row. The default wash time is preset in the Method Editor, "Sampler" bottom tab, "Autosampler" side tab.

7.6. Save and Print Autosampler Table

7.6.1. From the main menu select *File*, *Save as, Sample Information File* and assign a name in the form of *yyyymmdd-AVIO* to save the file. For example, for a run on May 1, 2018 the sample information file name would be 20180501-AVIO (the extension is automatically set to ".sif").

7.6.2. Select *File*, *Print*, *Active Window* to print the file.

7.7. Loading Samples

Pour the calibration standards, QC standards, and samples into the autosampler tubes and place them in the appropriate positions according to the sample information file. See Appendix C or the method file for the calibration and QC standard positions. Make sure there is sufficient QC solution volume in the QC tubes for the number of times they will be analyzed. The instruments usually use between 4 and 8 mL of volume depending on the analyte list and method.

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7.8. Running Samples

7.8.1. Starting the Analytical Run

7.8.1.1. From the main menu, select the *Auto* icon to bring up *the Automated Analysis Control* window. In the "Set Up" tab, make sure the proper method is displayed.

7.8.1.2. If the Sample Information File listed is not the desired one, click on OPEN and choose the appropriate file.

7.8.1.3. Choose a results data set name by clicking on OPEN and entering the desired name (the results data set name cannot be manually entered directly into its field). Create the results data set name in the format *yyyymmdd-AVIO* (e.g. 20180501-AVIO for May 1, 2018).

7.8.1.4. Make sure that the "Use Sample Info" and "Save Data" boxes are checked.

7.8.1.5. If the analyst will monitor the analytical run to its completion, skip to Section 7.8.1.8. and see Section 7.8.4. for manual shutdown of plasma. Otherwise, to set the instrument for automatic shutdown, select the "SET..." button next to "Auto Shutdown."

7.8.1.6. In the *Automatic Shutdown/Start-Up* window, check "Shutdown," "Begin at end of analysis," "Wash before shutdown" (assign at least 5 minutes time), and "Turn off Plasma and Pump."

7.8.1.7. Do not check the "Put spectrometer into Standby" option unless the instrument will be off for several days (see Section 6. above). Also, do not select the "Start-Up" menu in the lower half of the window UNLESS the Standby option has been selected. The start-up option will initiate the 74-minute stabilization period for the SCD system. Under the Start-Up menu, do NOT select "Turn on plasma and pump." Click on "OK".

7.8.1.8. Select the "Auto Wavelength Realign" and "Set..." buttons. In the *Automatic Wavelength Realign* window, select "At start of analyses" and click OK.

The Hg realignment process closes the shutter to the spectrometer and turns on the Hg lamp. It is used to align the optical signal properly on the SCD. The Hg realignment should be done at the beginning of an analytical run when the instrument has had major maintenance done or where repetitive instrument QC failures occur. When this realignment is

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performed, document the slit adjustment values and the date completed in the instrument maintenance logbook.

Note: Any adjustments made by the Hg realignment process will affect ALL analyte wavelengths. If an individual peak is found to be shifting during analyses, using the Hg realign again will not correct the problem.

7.8.1.9. Do NOT select the "Print log during analyses" box.

7.8.1.10. Select the "Analyze" tab in the *Automated Analysis Control* window.

7.8.1.11. Select the "Rebuild List" button and scroll through the sample IDs to make sure that the sample information file is correct, including proper placement of QC samples. See Appendix C for an example table.

7.8.1.12. Place the internal standard probe into a 10 mg/L Sc solution and the sample probe into the autosampler wash well. Let these solutions aspirate for at least 2 minutes to clear bubbles from the lines.

7.8.1.13. Click on the "Analyze All" button and the analysis should begin with the Hg lamp realignment as sequence #1. If the Hg realignment does not need to be completed (see Section 7.8.1.8.), **immediately** click the "Analyze All" button again to stop the run. Click the "Analyze All" button a second time to restart the run at the appropriate sequence number (not the autosampler location number).

7.8.1.14. From the main menu, select the *Results* icon to monitor the results. If you wish to monitor the four individual replicate results, select from the main menu, the *MethEd* icon, "Options" tab, and click the "Replicate Data" box under "Sample Items."

7.8.2. Calibration Procedure - Monitor the calibration standards as they are analyzed. Check that the internal standard counts in the INITIAL BLANK standard (displayed in the *Results* window) are similar in magnitude to the previous run. Also check that the precisions (RSD) of the four internal standard replicates and the four calibration standard replicates are not greater than 4 %. If the RSDs are greater than 4 %, stop the analysis and re-optimize the sample introduction system. The instrument calibration must be re-started after optimizing the sample introduction system. To monitor the calibration slope for one or more analytes, view the *Results* window immediately after the final standard has been analyzed. The AVIO 500 uses a "Linear, calculated intercept" fit whereby the calibration blank intensities (relative to the internal standard) are set at zero concentration.

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7.8.3. Check the analytical run - Ensure that recoveries of the initial QC samples are within the control limits (see DEP SOP **MT-058**).

Note: Any QC sample that was entered into the Sample Information File under the "Analyze QCs Before" column will yield a "Passed/Failed" flag displayed in the *Automated Analysis Control* window during the analytical run. More detailed information on which specific analytes passed/failed and their percent recoveries can be found in the results display window.

7.8.4. Manually extinguishing the PLASMA - If the operator is still present when the analytical run is complete, shut down the plasma by pushing the F9 key on the keyboard. If the software is hanging for some reason or communication between software and instrument is not working properly, push the red EMERGENCY PLASMA OFF button on the front of the instrument to bypass the software. This option will not harm the instrument. However, to be able to re-ignite the plasma in this case, you must reset the system by clicking on the *System* icon, and "Reset Emergency Plasma Off."

8. GENERATION OF REPORTS AND DATA ANALYSIS FILES

8.1. Printing Raw Data. The raw data, consisting of the individual replicate data for each sample analyzed, should NOT be printed unless special circumstances warrant a hard copy.

8.2. Data Report Generator. At the end of an analytical run, the raw data is to be saved both in a "Report" format and in a .csv file format using the "Export" feature. The report file format is saved to the directory: \\floridadep\data\Labs\Lab3\Chem_Data\Inorganic\Metals\ICPAESDV.

8.2.1. From the main menu in Syngistix, select *File, Utilities, Data Manager* (this application can also be accessed from the windows start menu).

8.2.2. Highlight the data set desired and click on the *Report* icon to bring up the "Data Reporting Wizard" window.

8.2.3. Select "Use existing design" and the Browse button to bring up the current list of report templates.

8.2.4. Open the template "vertical_detailed 2.rep" and click "Preview" from the Data Reporting Wizard window. Do not click on "Finish."

8.2.5. When the actual report is displayed in the Preview window, click on the icon that looks like an envelope. This will bring up the "Export" window.

Note: This "Export" window does not mean the same thing as the *EXPORT* function in Data Manager.

8.2.6. Choose "PDF" under Format, and Disk file (default). Click Okay. This will open the "Choose Export File" window.

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8.2.7. Change the destination path (Save in) to: \\floridadep\data\Labs\Lab3\Chem_Data\Inorganic\Metals\ICPAESDV. Change the file name to that of the results data set name and click 'Save'. Close the Preview window and return to the main Data Manager window by choosing "Cancel" in the "Data Reporting Wizard" window.

8.3. Export File (.csv format) Generation. The Export file (.csv) is written automatically to the directory C:\pe\Metals\Reports (but note - this is not the "report" version of the data). The Export file is then copied in 'Windows Explorer' to the directory: \\floridadep\data\Labs\Lab3\Chem_Data\Inorganic\Metals\ICPAESDV.

Note: Sections 8.3.1. - 8.3.6. only need to be completed if the results are not auto-exported or if the data was reprocessed.

8.3.1. From the main menu in Syngistix, select *File, Utilities, Data Manager*.

8.3.2. Highlight the data set desired and click on the *Export* icon to bring up the "Data Reporting Wizard" window.

8.3.3. In the "Data Exporting Wizard" window, select "use existing design" and the browse button to bring up the current list of export templates.

8.3.4. Open the "exportICP.xpt" design.

8.3.5. Click "Finish" to get to window # 8, "Export Data Set." and click "Export data".

8.3.6. Click "Finish" and exit the Data Manager program.

8.3.7. Go to Windows start menu and copy the Exported file (.csv format) from the directory: C:\pe\Metals\Reports to the directory: \\floridadep\data\Labs\Lab3\Chem_Data\Inorganic\Metals\ICPAESDV.

8.4. Exporting the Method Parameters. The method parameters for each run should be exported using the following steps:

8.4.1. Click on the MethEd tab to open the method editor.

8.4.2. Right-click in the Method Editor, select Print, and change the printer name to "Microsoft Print to PDF".

8.4.3. Save method parameters to: \\floridadep\data\Labs\Lab3\Chem_Data\Inorganic\Metals\ICPAESDV in the format *yyyymmdd-AVIO Method*.

8.5. Exporting the MSF Model. The MSF model for each run should be exported using the following steps:

8.5.1. Click on the Examine tab to open the examine spectra/MSF window in MSF mode.

8.5.2. Load current MSF file and open model from the FILE tab.

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8.5.3. Right click on the blue background and choose “MSF File Viewer/ Editor” from the dropdown menu.

8.5.4. Click “Expand All”, then “Print”.

8.5.5. Change the printer to “Microsoft Print to PDF”.

8.5.6. Save MSF model to: \\floridadep\data\Labs\Lab3\Chem_Data\Inorganic\Metals\ICPAESDV in the format of *yyyymmdd-AVIO MSF*.

8.6. Exporting the Sample Information Report. The sample information report for each run should be exported using the following steps:

8.6.1. Click on the Sample Information Editor window.

8.6.2. Right-click in the Sample Information File window, select “Print”, and change the printer to “Microsoft Print to PDF”.

8.6.3. Save sample information report to: \\floridadep\data\Labs\Lab3\Chem_Data\Inorganic\Metals\ICPAESDV in the format of *yyyymmdd-AVIO Sample Info File*.

8.7. Converting Data File. The exported (.csv) file on the network is converted and loaded in QC Manager.

8.7.1. In LIMS, follow the path “Laboratory,” “QC,” “QC Manager,” and open the program.

8.7.2. Make sure the Instrument window at upper left reads “Metals: ICP-AES-AVIO 500.” If not, select this option from the drop-down window and ensure you have selected the appropriate instrument.

8.7.3. Select the convert instrument file option, F9 function key, to convert files. This will bring up the “Select Instrument File” window. Choose the proper data set from the list and click “Open”.

8.7.4. You will immediately be taken to the “Save To LIMS” window and the .csv file name will be listed under ‘Save To LIMS as…’. Choose OK to save the data.

8.7.5. You will then be asked to either “Convert” or to “Close” the instrument file. Choose “Convert” and the .RAW data will appear in QC Manager, ready for review.

8.8. Archiving and Deleting Data. On a bi-monthly basis, archive the Syngistix Results database to a zip directory, and then delete all old data sets located in the directory.

8.8.1. Open Data Manager from outside Syngistix by selecting *Start, Programs, PerkinElmer Syngistix, Data Manager*. Close the Syngistix software.

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8.8.2. Highlight all files needed to be archived, then press the icon *Archive* and save it in the format *mmyyyy.zip* in the directory E:\\Archived data.

8.8.3. Again, highlight the same files and press the icons *Delete*, then *Pack*, then *Check* (if error appears, press *Check* again).

9. DATA PROCESSING, REVIEW, AND CALCULATIONS

The procedure for data review, cross-checking, and any calculations is summarized in DEP SOP **MT-058**, which also lists the method performance acceptance criteria for standard reference materials, matrix spikes, internal standards, and precision data. All aspects relating to tolerance limits, corrective actions for out-of-control data, and contingencies for handling unacceptable data are contained in this SOP as well as DEP SOP **LB-027**.

10. SAFETY/HAZARDOUS WASTE MANAGEMENT

10.1. Review the DEP Health and Safety Manual found on the DEAR intranet site.

10.2. Use **CAUTION** with strong irritants such as acids and bases. Avoid breathing the fumes of these irritants by using them in a hood when possible and keeping the face away from open containers of these chemicals. Avoid contact with these irritants on skin and clothing by appropriate use of gloves, apron, face mask, hood shield, etc. Safety glasses and lab coats must be worn at alltimes in the laboratory.

10.3. Store any waste that cannot be disposed of down the sink in a hazardous waste container (properly labeled with a **Hazardous Waste** label) in the hood. Make sure the bottle stays capped after use and place the bottle in the cabinet below the hood in the metals lab when it is 90 % full. When all containers are nearly full, dispose of the waste into the appropriate acidified metals hazardous waste drum located in Bldg. C.

10.4. All non-hazardous wastewater can be disposed of down the sink if the acid or base concentration is diluted to 2 % or diluted by 50 or greater. If it is not, the wastewater must be neutralized before disposing.

11. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

All samples are stored in the DEP Central Laboratory's Receiving Room. The sample pH for water matrices is checked upon arrival at the laboratory by receiving room staff to ensure it is less than 2. Samples consisting of water matrices are stored at room temperature and samples consisting of solid matrices are stored in one of the receiving room refrigerators.

12. INTERFERENCES

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See Appendix E for a list of possible interferences that can be encountered during the analysis of environmental samples.

13. REFERENCES

13.1. EPA Method 200.7, Revision 4.4, 1994

13.2. EPA Method 6010C (only S-ICP-TO) and 6010D

13.3. SM 2540 B

13.4. Optima 7000 and AVIO 500 Family Hardware Guide and ICP Syngistix Software Guide by Perkin Elmer

13.5. DEP SOP MT-024, Preparation of Water Samples for Metals Analysis by ICP-AES and ICP-MS

13.6. DEP SOP MT-055, Determination of Percent Dry Solids

13.7. DEP SOP CM-032, Calibration Of Auto-Pipettes And Dispensers Using The Check & Track Software System

13.8. DEP SOP MT-058, Procedure for Metals Data Review and Authorization

13.9. DEP SOP MT-060, Hot Block Digestion of Soil, Sediment, Waste and Tissue Samples for Total Recoverable Metals

13.10. DEP SOP MT-063, Microwave Assisted Hydrofluoric Acid Digestion of Solid Matrices for Total Metals Determinations

13.11. DEP SOP MT-069, Metals Standard and Reagent Preparation Procedure

13.12. DEP SOP LB-027, Standard Operating Procedure for Reporting Qualified Data

13.13. Laboratory Quality Manual

13.14. DEP Health and Safety Manual

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Appendix A

ICP-AES Interference Check Standard Concentrations (ICS2007 see Section 4.12.4.)

Purchased Solution	Analyte	Concentration
2007ICS #4	Al	60 mg/L
2007ICS #3	As	1 mg/L
2007ICS #3	Ag	300 µg/L
ICS #1	B	500 µg/L
ICS #3	Ba	300 µg/L
ICS #3	Be	100 µg/L
ICS #4	Ca	300 mg/L
ICS #3	Cd	300 µg/L
ICS #3	Co	300 µg/L
ICS #3	Cr	300 µg/L
ICS #3	Cu	300 µg/L
ICS #4	Fe	250 mg/L
ICS #3	K	20 mg/L
ICS #4	Mg	150 mg/L
ICS #3	Mn	200 µg/L
ICS #1	Mo	300 µg/L
ICS #4	Na	50 mg/L
ICS #3	Ni	300 µg/L
ICS #3	Pb	1 mg/L
Stock Standard	Sb	1 mg/L
ICS #3	Se	500 µg/L
ICS #1	SiO_2	230 µg/L
Stock Standard	Sn, Sr, Li	300 µg/L
ICS #1	Ti	1 mg/L
ICS #3	Tl	1 mg/L
ICS #3	V	300 µg/L
ICS #3	Zn	300 µg/L

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Appendix B

Spike Solutions

Metal	Water Spike HW6 (1/50 dilution) µg/L	Sediment Spike SEDSPK4 (1/50 dilution) µg/L	Instrument/Digested Mineral Spike ICPMINA (1/50 dilution) mg/L	SILICA Spike
Al	4000	8000	20	
As	200	400		
Sb	200	400		
B	500	400		
Ba	400	800		
Be	2	4		
Cd	10	20		
Ca	4000	8000	80	
Cr	100	400		
Co	100	200		
Cu	100	100		
Fe	4000	8000	20	
Pb	100	400		
Li	100			
Mg	4000	8000	40	
Mn	200	400		
Mo	50	200		
Ni	100	200		
K	4000	8000	10	
Se	200	400		
Ag	20*	40**		
Na	4000	8000	80	
Sr	2000	4000		
Tl	50	100		
Sn	100	400		
Ti	40	200		
V	100	200		
Zn	500	400		
U	50	50		
SiO_2				10

* Part of HW6B spike
** Part of SED SPK4B

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Appendix C

Autosampler Table Format

Automated Analysis Control Seq. #	Autosampler Rack Position #	QC[a] or Sample	Purpose	QC # (from method)[b]	"ANALYZE QCs BEFORE" sequence in Sample Information File
1	1	INITIAL BLANK	Calibration Blank		
2	2	ICPMIN	Minerals calibration standard		
3	3	ICPMET	Trace metals calibration standard		
4	13	AG-SIO2	Silver/Silica calibration standard		
5	14	AG-SIO2C	second source silver/silica calibration check	1	
6	10	ICPMETC	second source trace metal calibration check	2	
7	9	ICPMINC	second source mineral calibration check	3	
8	5	ACID-RINSE	eliminate carryover	4	
9	11	CPQLDV11	check instrument PQL levels	6	
10	12	ICS2007	interelement interference check	7	
11	6	ICPMINCCVC	initial calibration verification for minerals	8	
12	7	ICPMETCCVC	initial calibration verification for trace metals	9	
13	4	AG-SIO2CCVC	initial calibration verification for silver + silica	10	
14	5	ACID-RINSE	eliminate carryover	11	
15	1	CCB	verify no carryover exists into first sample	12	
16	15	1st Sample			1-4,6-12
17-25	16-24	2nd – 10th Samples			
26	4	AG-SIO2CCV	CCV	13	
27	6	ICPMINCCV	CCV	14	
28	7	ICPMETCCV	CCV	15	
29	5	ACID-RINSE	eliminate carryover	16	
30	1	CCB	see above	17	
31	25	11th Sample			13-17 [c]
32-40	26-34	12th - 20th samples			
41	4	AG-SIO2CCV	CCV	13	
42	6	ICPMINCCV	CCV	14	
43	7	ICPMETCCV	CCV	15	
44	5	ACID-RINSE	eliminate carryover	16	
45	1	CCB	see above	17	
46	35	21st sample			13-17 [c]
47-56	36-44	22nd - 30th samples, etc.	Run must end with CCV's and a CCB		

a For analyte concentrations, refer to Section 4.

b QC sequence numbers assigned in the Method Editor, "QC" bottom tab. These numbers are used in the Sample Information File.

c The analyst can invert the order of CCVs, skip the acid rinse (but then add extra rinse time after last CCV), or, either the ICPMETCCV, ICPMINCCV, or AG-SIO2CCV can be skipped if none of the analytes in those solutions are requested in the 20 samples surrounding this set of QC.

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Appendix D

MSF Model Preparation Notes

Note: Models should be recreated anytime the detector is adjusted or replaced.

1) Read about the MSF model in the Syngistix Instrument Control Software manual.
2) Open the MSF method from the methods option list. Click on the MethEd icon to make sure all the peak algorithms in the Peak Processing tab of the Process page are set to Peak Area.
3) Make sure there is no MSF model chosen in the Spectral Corrections tab on the Process page.
4) The peak wavelengths for all analytes need to be set to the peak maximum. Do this by displaying the most recent full analyte list run in the examine window and verifying that each wavelength is in the center of the peak. See the Syngistix Instrument Control Software manual for details.
5) Make sure that Spectral Profiling is not selected on the Settings tab on the Spectrometer page. The methods currently used do not use Spectral Profiling.
6) The scandium internal standard counts in the initial blank and all calibration standard analytes need to have RSDs less than 3 % to get the best MSF model possible.
7) Run the MSF run using single element standards for all analytes and possible interferences. Use multiple sources and concentrations when possible. Because these are approximate concentration and MSF is concentration independent, expired stock standards can be used to prepare these standards.

Note: All samples must have a different name in the Sample info file.

8) Use the examine window to create an MSF model by selecting “MSF” in the dropdown window at the upper left corner of the examine window (background should turn blue). If working on an old model, click “File” “Open” “MSF Model”.
9) Right click on blank and click “Assign global blank”. This designates the initial blank on all analytes. Display the internal standard (radial and axial) in the examine window (you can only look at one at a time), highlight the initial blank in the sample list and type “C” to clear the blank.
10) Assign individual analytes by opening a particular analyte in the examine window, highlighting the sample that corresponds with that analyte (only one concentration) and typing “A” for analyte.
11) Use the examine window to determine interfering peaks and assigning them by highlighting the sample and typing “I” for interferent. Old interference models can also be used as a basis for what the interferences for a particular analyte may be. It can be helpful to zoom in to be able to see interfering peaks.
12) Save changes to the MSF model by clicking “File” “Save” “MSF Model”.
13) Apply the new MSF model to the current method by clicking on the MethEd icon. In the Spectral Corrections tab on the Process page select the new MSF model (this needs to be reselected even if the model has the same name). Save the method.
14) Reprocess an initial calibration to determine if model is working, make changes as necessary.

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15) After the MSF model is completed, an MSF check needs to be run. This consists of 10 of each: CCB, D-BLK, DPQL, CPQL, and LFBHW. Certified standard reference materials should also be analyzed to verify proper interference correction.

IEC Model Preparation Notes

Note: Models should be recreated anytime the detector is adjusted or replaced.

1) Run an MSF run sequence using the single element stock standards following the same procedure as dictated in the MSF model preparation notes through #7.
2) View results in examine window and apply background correction points (depicted as green cross hairs along the baseline). One point if the baseline is noisy but flat across, two points if the baseline is at an angle and none if the baseline is clean. The crosshairs should be placed in a location where there are no interfering peaks or raised baselines, it is important to zoom in on the baseline when selecting base points in order to prevent false positives or false negatives due to under or over correction. To increase the number of base points type "M" to pull up the method option window and change the number of background points (none, one or two).
3) Change the integration window to include the whole peak by typing "M" to pull up the update method parameters box. Here you can change the number of points/peak, generally the number of integration points should be between 1 and 4 depending on the peak shape and width but is ultimately peak dependent. The actual pixels integrated are displayed in the examine window as small green squares along the peak lines while the large blacked out rectangle indicates the integration area.
4) Reprocess and save the MSF run as a new file with the new base points and integration windows set.
5) Select "Tools" "IEC Model Builder" and open the MSF results data set.
6) Set limits generically to 20 µg/L. Adjust accordingly based on analyte and MDL.
7) Click on the Calculate Factors tab. Set the interfering analyte to the analyte that corresponds with the sample ID (i.e. for sample ID Al 500 mg/L the interfering analyte would be Aluminum_396). Select Scandium (both axial and radial) from the analyte selection option at the top of the window and select "set to zero" for all analytes.
8) The summarize factors tab gives a table with the interference and the value calculated based on the model. Click "only non-zero factors" to view only the analytes with IEC factors.
9) Click "File" "Save" "IEC Model" and in the IEC model builder click update method. Then save the method.
10) Reprocess the initial calibration data in Syngistix off-line to check that all QC is passing. Be sure to open the appropriate method.
11) Some samples will have unnecessary IEC factors that can be eliminated without changing the results; this should be done on an analyte by analyte basis.
12) Changes can also be made to the number of integration points and the location of integration window. The yellow line indicates the peaks center and can be moved by clicking in the examine window and using the left and right arrow keys. The peak can be set by typing "P" this will shift the black

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integration window and indicate the current pixels being integrated based on the peak placement. The method parameters can be saved from this window by typing "M" and "S".

Note: A positive factor will decrease recoveries while a negative factor will increase recoveries.

13) After the IEC model is completed, an IEC check needs to be run. This consists of 10 of each: CCB, D-BLK, DPQL, CPQL, and LFBHW. Certified standard reference materials should also be analyzed to verify proper interference correction.

Appendix E

Method Parameters

Method Editor: Spectrometer Page: Settings

Spectral				
	Purge Gas Flow	High		
	Spectral Profiling	No		
	Resolution	Fixed Normal		
Read Parameters			**Min**	**Max**
	Time (sec)	Auto	2.0	20
	Delay time (sec)	25		
	Replicates	4		

Method Editor: Sampler Page: Plasma

Plasma (L/min)	15
Aux (L/min)	0.2
Neb (L/min)	0.6
Power (watts)	1500
View Distance	15
Source Equilibrium Delay (sec)	10
Plasma Conditions	Vary by Element

Method Editor: Sampler Page: Peristaltic Pump

Pump Parameters	
Sample Flow Rate (mL/min)	1.5
Flush Time (sec)	30

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Method Editor: Sampler Page: Autosampler

Wash		
Location: 0	**Frequency**	After every sample + extra time
	Rate (mL/min)	1.5
	Normal Time (sec)	60
	Extra Time (sec)	120

Analyte	Approximate Wavelength in nm	Plasma View	Possible Interferences
Al	396	Radial	
As	189	Axial	Cr, Al
Sb	207	Axial	Cr, Fe, Ti, Al, Mo
B	209	Axial	Ce, Al, Mn, W, Mo, Cr, Fe
Ba	234	Axial	Fe
Be	313	Axial	Ti, V
Cd	229	Axial	As, Ca, Fe, Ni, Mg
Ca	318	Radial	
Cr	268	Axial	
Co	229	Axial	Tl
Cu	327	Axial	Zr, Al, V, Zn, Sr, U
Fe	274	Radial	
Pb	220	Axial	Ca, Cu, Al
Mg	279	Radial	
Mn	258	Axial	Fe
Mo	202	Axial	Fe
Ni	232	Axial	Fe, Ti, Al, Zn, Ce
K	766	Radial	
Se	196	Axial	Al, Fe
Ag	328	Axial	Fe, V, Ce, Zr
Na	589	Radial	
Sr	422	Radial	Ca, Tl
Tl	191	Axial	Ti, Al
Sn	190	Axial	Ti, Zr, Fe, Sb
Ti	335	Axial	Ca, Sr
V	292	Axial	Mo, Cr, Zr
Zn	206	Axial	Cr, Ni
SiO_2	252	Radial	
Sc	357	Axial	Internal Standard
Sc	361	Radial	Internal Standard
Li	670	Axial	

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Appendix F

Method of Standard Additions

If results from TCLP samples are within 20 % of the regulatory limits and the spike recoveries are less than 50 %, the method of standard additions (MSA) must be used to quantify the samples. MSA is used to account for matrix affects in a sample. In this method the calibration standards are made in the sample matrix rather than in blank solution.

MSA requires that the calibration curve be linear up to the most concentrated addition and that all volumes be kept equal for all additions. Four identical aliquots of the sample are taken and prepared according to the chart below. All four aliquots are analyzed using CCB solution (2 % HNO_3 and 1 % HCl) as the blank.

			Unspiked Aliquot				1st Aliquot (50 % RCRA violation levels)		
	Spiking Solution		Sample	Spike Soln	CCB		Sample	Spike Soln	CCB
	mg/L		mL	mL	mL		mL	mL	mL
As	10		4	0	4		4	0.1	3.9
Ba	20		4	0	4		4	1	3
Cd	2		4	0	4		4	0.1	3.9
Cr	10		4	0	4		4	0.1	3.9
Pb	10		4	0	4		4	0.1	3.9
Se	2		4	0	4		4	0.1	3.9
Ag	10		4	0	4		4	0.1	3.9
			2nd Aliquot (100 % RCRA violation levels)				3rd Aliquot (150 % RCRA violation levels)		
			Sample	Spike Soln	CCB		Sample	Spike Soln	CCB
			mL	mL	mL		mL	mL	mL
As			4	0.2	3.8		4	0.3	3.7
Ba			4	2	2		4	3	1
Cd			4	0.2	3.8		4	0.3	3.7
Cr			4	0.2	3.8		4	0.3	3.7
Pb			4	0.2	3.8		4	0.3	3.7
Se			4	0.2	3.8		4	0.3	3.7
Ag			4	0.2	3.8		4	0.3	3.7

Complete the MSAWorksheet template (the template can be found at \\floridadep\data\DEAR\Labs\Lab5\Chemistry\Metals\TCLP analysis worksheets\MSA) by entering the spike values and sample raw results in µg/L. The worksheet will calculate the equation of the line. Fill in the X-intercept and slope boxes based on this equation. The resulting independent X axis value must be multiplied by

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2 (to account for MSA dilution) and then by 10 (to account for TCLP preparation dilution). Divide by 1000 to convert this result to mg/L.
To report the calculated result in the QCM file click on the LIMS result and change the sample result. Comment that the MSA method was used and comment if the sample results exceed the TCLP limit. Attach the MSA worksheet to the run cover page.

Appendix G

Determining Contamination in the Single Element Interference Check Standards

1. Analyze the single element interference check standards with the same software method and MSF model as used to analyze samples.
2. Examine the data and identify any detects for unspiked analytes that are above two times the instrument PQL.
3. Examine past data and the Perkin Elmer Optima 3000 Family Wavelength Tables to check if interference is a possibility.
4. Analyze the single element interference checks on the ICP-MS to determine if the detect is interference or contamination.
5. Analyze the single element interference check on the ICP-OES instrument using an additional wavelength.

Appendix H

Appendix of Significant Changes

1. The Limit of Quantitation requirement, control limits, and corrective actions were added to Section 2., Summary of Method.
2. The matrix spike frequency was added to Section 5., Sample Preparation Procedure.
3. 10/4/2010 Instrument names updated to include 7300
4. 10/4/2010 References updated to include new SOP numbers
5. 10/4/2010 Information regarding interference models was added to Appendix D.
6. 10/4/2010 Appendix F: Method of Standard Additions added to SOP
7. 10/21/2015 Lithium added as an analyte.
8. 01/21/2020 SOP updated to conform to EPA 6010D.
9. 08/12/2020 SOP updated to include AVIO 500 and remove references to the Optima 5300.
10. 06/08/2026 Grammatical and formatting changes throughout the document. Updated all network file paths. Section 4.13. was expanded to state that routine LFB concentrations also serve as the four quality

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control samples required for Initial Demonstrations of Capability and is acceptable for Continuing DOCs. Updated Reference for DEP Health and Safety Manual. Updated names and information for all PQL solutions. Removed references to TCLP and SPLP.

11. 09/08/2026 Removed all references to Optima 7300, as the instrument is now retired. Updated Section 3. regarding Avio 500 equipment. Updated Turbidimeter S/N. Grammatical and formatting changes throughout the document. Corrected headings. Updated section numbers and page numbers.

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