STANDARD OPERATING PROCEDURE FOR THE INDUCTIVELY COUPLED PLASMA MASS SPECTROMETER (ICP-MS) WITH COLLISION CELL TECHNOLOGY (CCT) AND KINETIC ENERGY DISCRIMINATION (KED)

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1. SCOPE AND APPLICATION

1.1 Samples and sample digestates are analyzed for trace metals utilizing a Thermo Elemental X Series II ICP-MS with collision cell technology and kinetic energy discrimination and a Thermo Elemental X Series (upgraded to XII specifications) ICP-MS with collision cell technology and kinetic energy discrimination.

1.2 The Florida Department of Environmental Protection (FDEP) analyzes for 21 analytes using EPA method 200.8 (Revision 5.4) for test ID's W-ICPMS and W-ICPMS-F in aqueous and saline/estuarine matrices.

	Analyte	Method	NELAP approval	Matrices
1	Al	200.8 Rev. 5.4	Yes	aqueous, saline/estuarine
2	Sb	200.8 Rev. 5.4	Yes	aqueous, saline/estuarine
3	As	200.8 Rev. 5.4	Yes	aqueous, saline/estuarine
4	Ba	200.8 Rev. 5.4	Yes	aqueous, saline/estuarine
5	Be	200.8 Rev. 5.4	Yes	aqueous, saline/estuarine
6	B	200.8 Rev. 5.4	No	aqueous, saline/estuarine
7	Cd	200.8 Rev. 5.4	Yes	aqueous, saline/estuarine
8	Cr	200.8 Rev. 5.4	Yes	aqueous, saline/estuarine
9	Co	200.8 Rev. 5.4	Yes	aqueous, saline/estuarine
10	Cu	200.8 Rev. 5.4	Yes	aqueous, saline/estuarine
11	Gd	200.8 Rev. 5.4	No	aqueous, saline/estuarine
12	Pb	200.8 Rev. 5.4	Yes	aqueous, saline/estuarine
13	Mn	200.8 Rev. 5.4	Yes	aqueous, saline/estuarine
14	Mo	200.8 Rev. 5.4	Yes	aqueous, saline/estuarine
15	Ni	200.8 Rev. 5.4	Yes	aqueous, saline/estuarine
16	Se	200.8 Rev. 5.4	Yes	aqueous, saline/estuarine
17	Sr	200.8 Rev. 5.4	No	aqueous, saline/estuarine
18	Ag	200.8 Rev. 5.4	Yes	aqueous, saline/estuarine
19	Tl	200.8 Rev. 5.4	Yes	aqueous, saline/estuarine
20	Zn	200.8 Rev. 5.4	Yes	aqueous, saline/estuarine
21	U	200.8 Rev. 5.4	No	aqueous, saline/estuarine

1.3 Samples are also analyzed using EPA Method 6020A for 16 analytes for tests W-ICPMS-R, S-ICPMS, T-ICPMS, TCLP-ICPMS, SPLP-ICPMS, and S-ICPMS-TO in aqueous, biological tissue, chemical waste, and solids matrices.

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	Analyte	Method	NELAP approval	Matrices
1	Sb	6020A	Yes*	aqueous, biological tissue, chemical waste, solids
2	As	6020A	Yes*	aqueous, biological tissue, chemical waste, solids
3	Ba	6020A	Yes*	aqueous, biological tissue, chemical waste, solids
4	Be	6020A	Yes*	aqueous, biological tissue, chemical waste, solids
5	Cd	6020A	Yes*	aqueous, biological tissue, chemical waste, solids
6	Cr	6020A	Yes*	aqueous, biological tissue, chemical waste, solids
7	Co	6020A	Yes*	aqueous, biological tissue, chemical waste, solids
8	Cu	6020A	Yes*	aqueous, biological tissue, chemical waste, solids
9	Pb	6020A	Yes*	aqueous, biological tissue, chemical waste, solids
10	Mn	6020A	Yes*	aqueous, biological tissue, chemical waste, solids
11	Mo	6020A	Yes*	aqueous, biological tissue, chemical waste, solids
12	Ni	6020A	Yes*	aqueous, biological tissue, chemical waste, solids
13	Se	6020A	Yes*	aqueous, biological tissue, chemical waste, solids
14	Ag	6020A	Yes*	aqueous, biological tissue, chemical waste, solids
15	Tl	6020A	Yes*	aqueous, biological tissue, chemical waste, solids
16	Zn	6020A	Yes*	aqueous, biological tissue, chemical waste, solids

*Not NELAP approved for the biological tissue matrix.

2. SUMMARY OF THE METHOD

2.1 The ICP-MS uses inductively coupled plasma as a source for metal cations, which are introduced into a quadrupole mass spectrometer. This results in an instrument capable of detecting a wide variety of metals at very low concentrations.

2.2 The detection limits for ICP-MS are comparable to those of graphite furnace atomic absorption spectroscopy (GFAAS). Although ICP-MS data is acquired sequentially, ICP-MS has the capability of determining all the metals of interest in the time it would take GFAAS methods to determine one analyte. Internal standards are used to compensate for changes in instrumental sensitivity and mass transport phenomena.

2.3 The calibration range for each analyte is demonstrated to be within the linear operating range of the instrument at the beginning of each and every analytical run. The instrument is calibrated with 3 standards (see sections 5.4.1 – 5.4.3) of varying concentrations and a blank and the calibration is forced through the blank. The correlation coefficient for the first order linear plot of the calibration curve should be 0.998 or greater. The validity of the curve is then further tested with a solution (CCMSMETC3, section 5.4.4) prepared from standards purchased from a vendor that is different from the one used to prepare the calibration standards. The CCMSMETC3 solution verifies the calibration curve, serving as the initial

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calibration verification, and instrument performance. The analytes present in the second source standard (CCMSMETC3) are the same as those the instrument was calibrated for. If the determined concentration for any analyte in this standard (CCMSMETC3) is less than 90% or greater than 110% of the stated value then the data for that analyte are considered invalid and cannot be used, unless appropriately qualified. Data are not reported for samples with concentrations of analytes outside of the established calibration range without qualification. The range may be extended by dilution.

3. INTERFERENCES

3.1 The primary interferences in ICP-MS are molecular ions such as oxides, doubly charged ions, and isobaric interferences. The interference check solution, IC6020C (see Appendix G), is used to assess the effects of a variety of molecular interferences. The acceptable recovery limit for trace metals in IC6020C is 85 – 115 %. The table below lists common interferences observed in environmental samples.

Target Analyte	Common Interference	Monitor	Correction Based On
$^{9}Be^{+}$			
$^{11}B^{+}$			
$^{27}Al^{+}$			
$^{52}Cr^{+}$	$^{40}Ar^{12}C^{+}$, $^{35}Cl^{16}O^{1}H$		
$^{55}Mn^{+}$			$^{54}Fe^{+}$
$^{59}Co^{+}$			
$^{60}Ni^{+}$			
$^{65}Cu^{+}$	$^{49}Ti^{16}O^{+}$, $^{25}Mg^{40}Ar^{+}$	$^{46}Ti^{+}$	
$^{66}Zn^{+}$	$^{50}Ti^{16}O^{+}$	$^{46}Ti^{+}$	
$^{75}As^{+}$	$^{40}Ar^{35}Cl^{+}$	$^{77}Se^{+}$, $^{78}Se^{+}$	
$^{78}Se^{+}$	$^{156}Gd^{2+}$		
$^{88}Sr^{+}$			
$^{95}Mo^{+}$			
$^{107}Ag^{+}$	$^{91}Zr^{16}O^{+}$		
$^{111}Cd^{+}$	$^{95}Mo^{16}O^{+}$	$^{95}Mo^{+}$	$^{95}Mo^{+}$
$^{121}Sb^{+}$			
$^{137}Ba^{+}$			
$^{158}Gd^{+}$			
$^{205}Tl^{+}$			
$^{208}Pb^{+}$	Abundance	$^{206}Pb^{+}$, $^{207}Pb^{+}$	$^{206}Pb^{+}$, $^{207}Pb^{+}$
$^{238}U^{+}$			

3.2 Collision Cell Technology with Kinetic Energy Discrimination (CCT-KED): This component of the instrument selectively reduces argon based polyatomic interferences as a result of colliding and reacting the interfering ions with a 7% H_2

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/ 93% He gas mixture in an enclosed cell within the lens system and ion path of the ICPMS. Kinetic energy discrimination is created by running the quadrupole bias slightly less negative than the hexapole bias. Polyatomic ions generated within the plasma have larger atomic radii than analyte ions of similar mass. These larger polyatomic ions undergo more collisions in the cell, in which they lose increasingly more energy, and are then excluded from the quadrupole mass filter by the kinetic energy barrier.

3.3 Correction equations for isobaric interferences are listed in Appendix B.

4. APPARATUS AND EQUIPMENT

4.1 Thermo Electron X Series II ICP-MS, serial number 1065C, with third generation collision cell technology and Xt interface. Purchased in 2007.

4.2 Thermo Electron X Series ICP-MS, serial number X0366. Purchased in 2004, upgraded to X Series II specifications in April 2007.

4.3 Interface: Nickel sample cone (part # 3600812) and a Nickel skimmer cone (part # 3600811)

4.4 Nebulizer: Pneumatic Burgener PEEK Mira Mist Nebulizer.

4.5 Spray Chamber: Peltier-cooled standard quartz spray chamber.

4.6 Collision Cell mixed gas: A mixture of 7% hydrogen, 93% helium with a purity greater than 99.996% delivered with a high quality two stage regulator. The max delivery pressure to the instrument is 1 bar.

4.7 Cetac autosampler, which has an on-board peristaltic pump for the rinse station.

4.8 A three-channel peristaltic pump was provided with the instrument. Separate channels are used for sample and internal standard introduction, and the spray chamber drain. The pump tubing used is as follows:

Sample	Orange-Yellow	0.508 mm ID
Internal Standard	Orange-Green	0.38 mm ID
Drain	Red-Red	1.14 mm ID

4.9 Samples and standards are aspirated from 17 x 100 mm polypropylene round-bottom test tubes arranged in the autosampler. Rinse with deionized (DI) water and allow to dry prior to use. Use a Kimwipe to prevent dust from entering the tubes as they dry.

4.10 A THERMO NESLAB M75 Refrigerated Recirculator is coupled to the instrument to keep the cooling water temperature constant at 19 °C +/- 1 °C. The chiller operates at 40 to 60 psi during normal operation.

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4.11 Argon is supplied to the instruments from the laboratory's MicroBulk argon delivery system. The delivery pressure to the instrument should be 85 – 95 psi.

4.12 Class A volumetric flasks

4.13 Pipettes:

4.13.1 Class A volumetric glass pipettes

4.13.2 100 µL Eppendorf

4.13.3 100 – 1000 µL Eppendorf

4.13.4 2 – 10 mL Finnpipette

4.14 HF Scientific Inc. MicroTPW Portable Turbidimeter; SN: 201205062.

5. REAGENTS AND CHEMICALS

Note: Be careful not to contaminate solutions with trace metals or minerals during preparation and use. Be sure to mix all solutions thoroughly after they are prepared. Store standard solutions in Teflon bottles. Preparation of all metals standards must be documented in the LIMS standard prep tracker. Label all bottles containing standards according to DEP SOP MT-069, Metals Standard and Reagent Preparation Procedure. Metals standards used for quantitation of sample results must not be used past the expiration date given by the manufacturer. Laboratory DI water, trace metal grade nitric acid (HNO_3), and trace metal grade hydrochloric acid (HCl) are used to prepare all standards.

5.1 Probe Rinse Solution – 4% HNO_3 / 3% HCl: dilute 400 mL of HNO_3 and 300 mL of HCl to 10 L with DI water.

5.2 Internal Standard Solution - Prepare a solution of 200 µg/L – ^6Li, 750 µg/L – Sc, 1000 µg/L – Ga, 100 µg/L – Rh, Tb, and Bi. This solution can be used past the manufacturer's expiration date as long as the analytical signal produced by the solution is stable for an analytical run.

5.3 Calibration Blank, Continuous Calibration Blank (CCB), Rinse - Dilute 20 mL of HNO_3 and 10 mL of HCl to 1 L using DI water. Use this solution for dilution of samples, calibration blanks, CCBs, and rinse.

5.4 Calibration Standards and SRMs:

5.4.1 CCMSMET 200 µg/L Calibration Standard. This standard has the following analytes: Sb, As, B, Be, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, Se, Ag, U, and Zn at 200 µg/L, Ba at 300 µg/L, Tl at 30 µg/L, Sr at 1000 µg/L, and Al at 1500 µg/L in 2% HNO_3 and 1% HCl solution.

5.4.2 CCMSMET 100 µg/L Calibration Standard, MSCCV2. This standard has the following analytes: Sb, As, B, Be, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, Se, Ag, U, and Zn at 100 µg/L, Ba at 150 µg/L, Tl at 15 µg/L, Sr at 500 µg/L, and Al at 750 µg/L in 2% HNO_3 and 1 % HCl solution. This solution is

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used as the mid-level calibration standard and the continuing calibration verification (CCV) standard.

5.4.3 CCMSMET 50 µg/L Calibration Standard. This standard has the following analytes: Sb, As, B, Be, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, Se, Ag, U, and Zn at 50 µg/L, Ba at 75 µg/L, Tl at 7.5 µg/L, Sr at 250 µg/L, and Al at 375 µg/L in 2% HNO_3 and 1% HCl solution.

5.4.4 CCMSMETC3 100 µg/L Calibration Check Solution or Second Source. This standard has the following analytes: Sb, As, Ba, B, Be, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, Se, Sr, Ag, U, and Zn at 100 µg/L, Tl at 10 µg/L, and Al at 750 µg/L in 2% HNO_3 and 1% HCl solution.

Note: The commercial source(s) of the calibration check solution (5.4.4) must be different from those used in the preparation of the calibration standards (5.4.1 - 5.4.3).

5.4.5 Calibration and Instrument PQL Solution (CPQLCCT# and IPQLCCT#). This practical quantitation limit (PQL) solution is prepared by diluting appropriate volumes of single element stock standards to 1 L with 20 mL HNO_3 and 10 mL HCl. See current MDL/PQL calculations for exact value of the PQL solution. Current instrument MDLs and PQLs can be found at \\FLDEP1\DEAR\LABS\LAB5\Chemistry\Common\MDLs_Control_Limits\Metals_Mercury\.

5.4.6 Digestion PQL Solution (DPQLCCT#). The digestion PQL spike solution is prepared by diluting appropriate volumes of single element stock standards to 1 L with 20 mL HNO_3 and 10 mL HCl. This spike solution is subsequently diluted 1/50 by the preparation group to produce a solution with the current method PQLs. Current instrument MDLs and PQLs can be found at: \\FLDEP1\DEAR\LABS\LAB5\Chemistry\Common\MDLs_Control_Limits\Metals_Mercury\.

5.4.7 Interference Check Solution (IC6020C). Dilute appropriate volumes of single element stock standards that result in a solution containing 2120 mg/L Cl; 300 mg/L Ca; 250 mg/L Fe and Na; 200 mg/L C; 100 mg/L Al, Mg, P, K, and S; 2 mg/L Mo and Ti; 100 µg/L Mn; 20 µg/L As, Cd, Cr, Co, Cu, Ni, Se, Ag, and Zn in a 1% HCL and 2% HNO_3 matrix. See also Appendix G.

5.4.8 Tuning Solution (20 µg/L). Dilute the appropriate volumes of single element stock standards to 1 L with 20 mL HNO_3 to produce a solution with 20 µg/L Li, Be, Co, Ni, In, Ba, Ce, Pb, Bi and U and 250 µg/L of Al and Cu. This solution is used for: a) daily performance check b) instrument tuning (lens voltage adjustment, X-Y-Z alignment and nebulizer flow rate optimization) c) mass and resolution calibration d) hydrogen/helium CCT tuning. However, it is NOT used in the

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quantitation of any analytical sample results. This solution can also be used past the manufacturer's expiration date as long as the analytical signal produced by the solution is stable.

5.4.9 CROSS CAL Solution. Dilute the appropriate volumes of single element stock standards to produce a 400 µg/L solution of Al, Sb, As, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Se, Ag, Na, Tl, V, Zn, In, Li and U to 1 L with 20 mL HNO_3. This solution is used to set detector pulse and analogue voltages and perform a dual detector calibration. However, it is NOT used in the quantitation of any analytical sample results. This solution can also be used past the manufacturer's expiration date as long as the analytical signal produced by the solution is stable.

6. SAMPLE PREPARATION PROCEDURE

Note: Silver is only slightly soluble in the presence of chloride unless there is a sufficient chloride concentration to form the soluble chloride complex. Therefore, low recoveries of silver may occur in samples analyzed by direct analysis. The total recoverable sample digestion procedure, DEP SOP MT-024, is suitable for determination of silver in aqueous solutions up to 0.1 mg/L. For samples with concentrations higher than 0.1 mg/L the sample should be redigested using a sample volume that will result in a silver concentration in the digestate of less than 0.1 mg/L.

Solid or waste samples prepared according to DEP SOP MT-060 that contain silver concentrations greater than 0.5 mg/L should be treated similarly.

6.1 Sample Preparation:

6.1.1 Filtered Water Samples - For undigested, filtered and acidified samples, which are checked out directly from the custody room, prepare matrix spikes and laboratory fortified blanks (LFBs) by pipetting 50 µL of the high water spike (HW6A and HW6B) into a 10 mL centrifuge tube containing 9.9 mL of either sample (matrix spike) or the blank solution of 2% HNO_3/1% HCl (LFB). Mix thoroughly. Each batch must contain at least one matrix spike for every 10 samples (two different samples are spiked for batches over 10 samples) and one set of matrix spike duplicates. Each batch has a maximum of 20 samples per batch. See DEP SOP MT-061 for HW6A and HW6B preparation details.

6.1.2 Unfiltered (digested) water samples - See DEP SOP MT-024 for preparation details.

Note: Where EPA Method 200.8 Rev. 5.4 is approved for the determination of metals in drinking water, samples may be analyzed directly without acid digestion if the samples have been properly preserved with acid and have turbidity of < 1 NTU at the time of analysis. This includes aluminum, antimony, arsenic, barium, beryllium, cadmium, chromium, copper, lead, manganese, nickel, selenium, thallium and zinc.

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6.1.3 Solid samples (soils, sediments, and wastes) - See DEP SOPs MT-060 for details of total recoverable metals preparation and DEP SOP MT-063 for details of total metal determination preparation.

6.1.4 TCLP and SPLP samples - See DEP SOP MT-068 for TCLP extractions and SPLP extractions.

6.2 Internal Standards - The internal standard solution and sample solution are mixed in-line using a T-connector prior to nebulization. The ratio of sample to internal standard is 1.33:1.

7. SAMPLE ANALYSIS PROCEDURE

Note: Read the operator's guide as supplementary material to assist in the operation of the ICP-MS.

7.1 Instrument Startup: The ICPMS instrument is typically left in 'Vacuum Ready' mode when not in use. When in 'Vacuum Ready' mode, the spectrometer vacuum is maintained and all electronics are on. The vacuum pressure is typically 9 - 10 x 10^{-8} mbar after the instrument has been in 'Vacuum Ready' mode for several hours. If the instrument is in 'Vacuum Ready' mode, skip to section 7.2. To startup the instrument from 'Shutdown' mode, follow steps 7.1.1 – 7.1.2.

7.1.1 When in 'Shutdown' mode, the instrument electrical breakers and embedded PC may be on or off. If the electrical breakers and embedded PC are on, then click 'On' to go from 'Shutdown' to Vacuum Ready'.

7.1.2 If the instrument electrical breakers or embedded PC are off, follow the procedure below.

7.1.2.1 Remove the instrument hood and place it carefully on the floor or the bench adjacent to the instrument.

7.1.2.2 Locate the breakers on the left hand front of the instrument.

7.1.2.3 Turn on the breakers in the following sequence. Wait a few seconds between turning on each breaker.

1st Electronics, embedded PC, rotary pump, turbo pump

2nd Peltier spray chamber cooling

3rd Plasma RF generator

7.1.2.4 Turn on the embedded PC (green switch under the instrument cover on the back left side). Allow two minutes for the embedded PC to boot up.

7.1.2.5 Turn on the user interface (bench) PC and start the Plasma Lab software. The Plasma Lab Service (MS icon in system tray) starts automatically when turning on the PC. The Plasma Lab Service in

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the Windows Services may need to be manually restarted (or started if set to manual) before the two computers will communicate after an instrument restart.

7.2 Daily Instrument Maintenance:

7.2.1 Peristaltic pump tubing - Change the sample and internal standard tubing daily. Drain tubing can be changed every other day.

7.2.2 Probe Rinse solution level - The rinse solution supply should be at least one quarter full. If it is not, prepare more and fill (See 5.1).

7.2.3 Waste container - The waste container should be emptied when it is filled to 3/4 of the container, to prevent overflow. The acidic waste can be poured down the sink while flushing with tap water.

7.2.4 Ar pressure - The argon supply pressure should be about 85-95 psi when the plasma is on. If the supply argon pressure falls below it, a safety interlock automatically shuts off the plasma.

7.2.5 Chiller temperature, pressure, and water level - The temperature should be regulated at 19 ± 1 ºC. Check the current temperature on the chiller to ensure it is within this range. Check the inlet cooling water pressure, which must be between 40 and 60 psi. Check the fluid bag filter and condenser filter weekly (See Appendix I for details).

7.2.6 Nebulizer - Check the nebulizer to be sure it is clean and the capillary is not clogged.

7.2.7 Torch - Inspect the torch visually to make sure it is clean and does not have any deposits on it. If it is dirty, remove the metal clamp connecting it to the spray chamber, disconnect the metal clamp from the white torch holder, disconnect the gas lines, and remove the torch. Soak the torch overnight in a 50% aqua regia solution in the fume hood of the metals lab, B310.

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

7.3.1 Autosampler Probe - Send the autosampler probe to the rinse position by selecting the following buttons: Instrument, Tune, Accessories window, Autosampler, Connect and initialize autosampler and Go to rinse station.

7.3.2 Torch Ignition - Click on the "On" button located at the top left of the Plasma Lab window to initiate the Torch Ignition Sequence, which takes a little over 2 minutes to complete.

Note: Do not attempt to ignite plasma when the analyzer vacuum pressure exceeds 4×10^{-7} mbar!

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7.3.3 Warm-Up - Allow instrument to warm-up for at least an hour to ensure the torch, interface, and spray chamber are at equilibrium, and the peristaltic pump tubing has completely stretched. Make sure that the nebulizer pressure is 2 to 3 bar, the expansion pressure is 2 to 3 mbar and the analyzer pressure is $7 – 8 \times 10^{-7}$ mbar (1×10^{-6} mbar in CCT-KED mode).

7.4 Daily Optimization Procedures, Performance Report. The instrument performance which includes mass calibration verification, sensitivity at low, medium and high masses, background counts at low, medium and high masses, CeO/Ce and Ba^{++}/Ba ratios must be verified on a daily basis before the start of analytical sequence:

7.4.1 Performance Report Xt Mode - The Xt mode is for running samples for beryllium and boron, and for performing cross calibrations and mass calibrations. The collision cell gas is not on during Xt mode.

Select left hand icon named instrument to view the following tabs.



Select the Configurations tab to see what mode the instrument is currently in. Select the latest Xt lens tune.

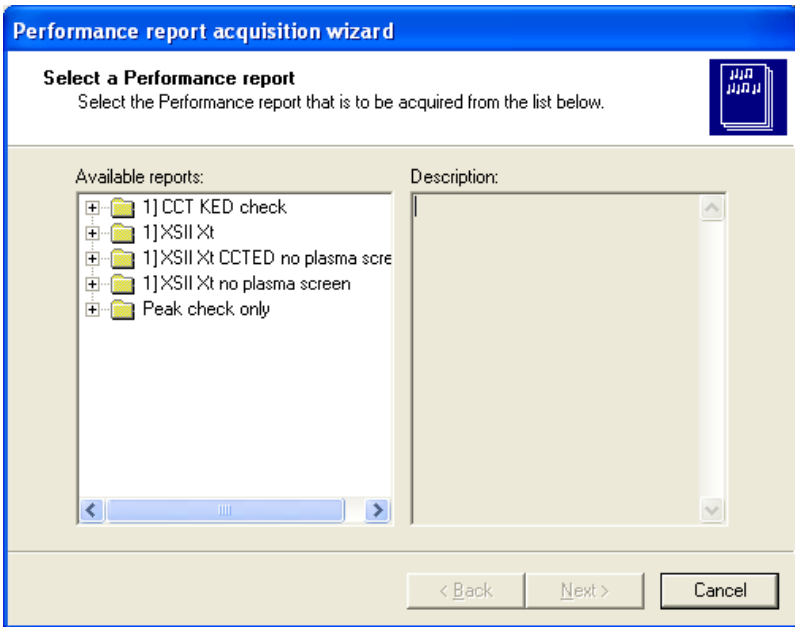
Instrument settings

	Use	Date	User	Description
	☐	1/9/2007 11:46:38 AM	XSeries	1] Xt CCTED
	☐	1/8/2007 10:38:06 AM	XSeries	1] Xt CCTED
	☐	1/5/2007 5:15:56 PM	Autotune	1] STAGE TUNE ONLY x,y,z
	☑	1/5/2007 3:07:06 PM	XSeries	1] Xt lens tune only
	☐	1/5/2007 3:05:33 PM	XSeries	1] Xt lens tune only
	☐	1/5/2007 11:51:18 AM	XSeries	1] Xt CCTED
	☐	1/5/2007 11:50:23 AM	XSeries	1] Xt CCTED
	☐	1/5/2007 11:48:35 AM	XSeries	1] Xt CCTED
	☐	1/5/2007 11:48:19 AM	XSeries	1] Xt CCTED
	☐	1/5/2007 11:48:04 AM	XSeries	1] Xt CCTED
	☐	1/5/2007 11:44:38 AM	XSeries	1] Xt CCTED

Place the probe in the 20 µg/L tuning solution. Looking at Real Time Display make sure that the solution has reached the plasma, select the button that has a green sheet of paper with musical notes in the top left corner named, “Start performance report wizard,” in order to acquire a performance report.

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Click the next button to get to the following window:



Select the folder named "XSII Xt no plasma screen", click Next, select "I want to introduce the sample manually" and then follow the directions on the subsequent windows.

If the performance report generated passes for all criteria, then the instrument is ready for calibration and analysis of samples in Xt mode (no CCT-KED).

Note: The performance report may be labeled as failing if the ratios analyte/background is infinitely large. If the performance report has failed but the reason is for an "INF" value for one of these ratios, then the instrument is ready for analysis. Save the performance report in \\FLDEP1\DEAR\Labs\Lab3\Chem_Data\Inorganic\Metals\ICP-MS-X2\ folder.

If the performance report is reported as failing, the instrument needs tuning (see section 7.4.3). If after tuning performance report fails again notify your supervisor or the individual providing training for the instrument before proceeding.

7.4.1.1 The performance report limits listed below are general guidelines that are subject to change based on instrument condition.

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Performance Report Limits (Xt Mode)

Mass Calibration Verification

Sweeps: 10
Dwell: 1.0 mSecs
Point Spacing: 0.05 amu
Peak Width measured at 5 % of peak max

Analyte	Limits		
	Max Width	Min Width	Max Error
27 Al	0.85	0.65	0.10
65 Cu	0.85	0.65	0.10
115 In	0.85	0.65	0.10
238 U	0.85	0.65	0.10

Sensitivity and Stability Results

Sweeps: 70

Analyte	Limits		
	Dwell (mSec)	% RSD	Counts / s
5 Bkg	100		<1
7 Li	10	2.0 %	>15000
56 ArO	10		
59 Co	10		
137 Ba ++	30		
138 Ba ++	30		
101 Bkg	100		<1
115 In	10	2.0 %	>50000
137 Ba	10		
138 Ba	10		
140 Ce	10		
156 CeO	30		
220 Bkg	100		<1
238 U	10	2.0 %	>80000

Ratio Results

Analyte	Ratio Limit
137 Ba++/137 Ba	<0.04
115 In/ 220 Bkg	
156 CeO/ 140 Ce	<0.02

7.4.2 Performance Report **CCT-KED** mode.

Follow the same procedure as the performance report for Xt mode, but select the latest 'Xt CCT-KED lens only' tune in the configurations tab. After checking the box next to the latest 'Xt CCT-KED lens only' tune, the instrument is now running in CCT-KED mode.

After placing the probe in the 20 µg/L tuning solution select the folder named "XSII Xt CCT-KED no plasma screen", click Next, select "I want

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to introduce the sample manually" and then follow the directions on the subsequent windows.

If the performance report generated passes for all criteria, then the instrument is ready for calibration and analysis of samples in CCT-KED mode. Save the performance report at \\FLDEP1\DEAR\Labs\Lab3\Chem_Data\Inorganic\Metals\ICP-MS-X2. If the performance report is reported as failing the instrument needs tuning (see section 7.4.3). If after tuning the performance report fails again, notify your supervisor or the individual providing training for the instrument before proceeding.

7.4.2.1 The performance report limits listed below are general guidelines that are subject to change based on instrument condition:

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Performance Report Limits (CCT-KED Mode)

Mass Calibration Verification

Sweeps: 20
Dwell: 3.0 mSecs
Point Spacing: 0.05 amu
Peak Width measured at 5 % of peak max

Analyte	Limits		
	Max Width	Min Width	Max Error
27 Al	0.85	0.65	0.10
65 Cu	0.85	0.65	0.10
115 In	0.85	0.65	0.10
238 U	0.85	0.65	0.10

Sensitivity and Stability Results

Sweeps: 100

Analyte	Limits		
	Dwell (mSec)	% RSD	Counts / s
5 Bkg	10		<1
27 Al	10	2.0 %	>4000
63 Cu	10		
65 Cu	10		
137 Ba ++	10		
138 Ba ++	10		
78 Se	10		<20
80 Se	10		<4500
101 Bkg	10		<1
115 In	10	2.0 %	>35000
137 Ba	10		
138 Ba	10		
140 Ce	10		
156 CeO	10		
220 Bkg	10		<1
238 U	10	2.0 %	>60000

Ratio Results

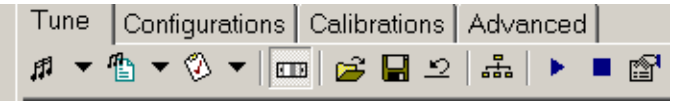
Analyte	Ratio Limit
63 Cu/ 65 Cu	>1.85
137 Ba++/137 Ba	<0.04
115 In/ 220 Bkg	
156 CeO/ 140 Ce	<0.03

7.4.3 Tuning of the instrument – The instrument needs to be tuned if the daily performance report will not pass or instrument maintenance was performed (such as cones, torch, spray chamber or nebulizer replacement - see Thermo Electron Corporation *X*-Series ICP-MS Getting Started Guide for details).

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Choosing which tune is needed depends on any instrument maintenance that has been performed recently. If no instrument maintenance has been performed since the last tune, just the lenses need to be tuned. This is due to deposits building up on the extraction lens and L1 lens resulting in more voltage needing to be applied to optimize the ion path. If cones or torch is changed, then perform a stage tune which tunes the x,y,z position of the torch. If the nebulizer is changed, a nebulizer tune should be performed to find the optimal gas flow rate for the nebulizer. The nebulizer can typically be fine-tuned manually.

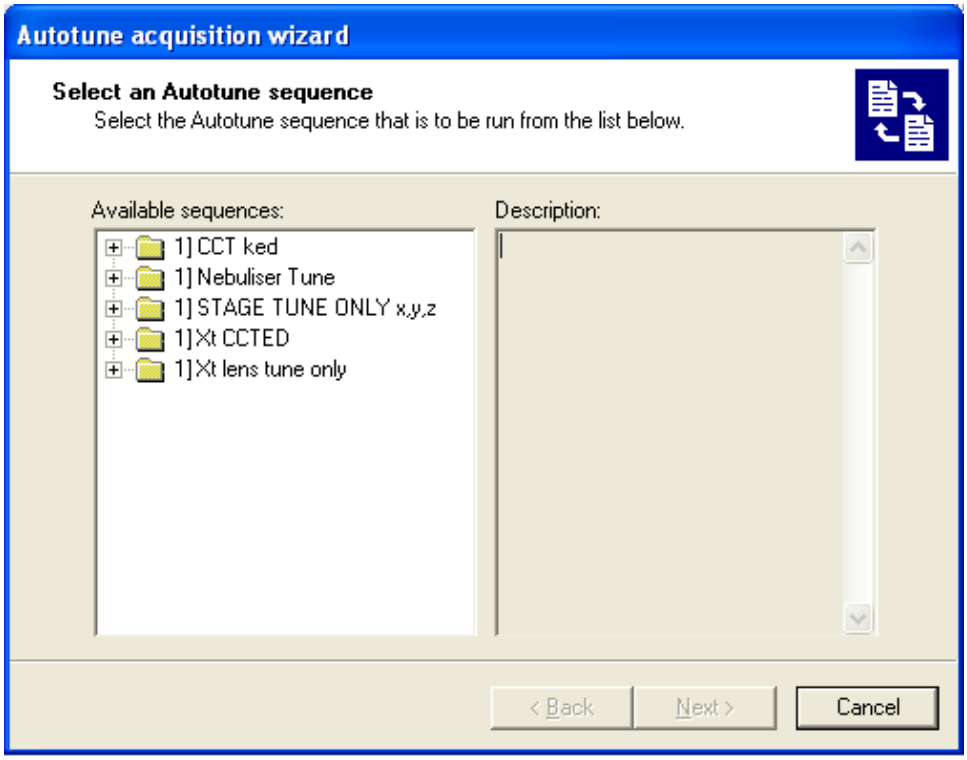
7.4.3.1 Lens Tuning in Xt Mode - The lens tune optimizes only the lenses used to form the ion path. Select left hand icon named instrument to view the following tabs.



Place the probe in the 20 µg/L tuning solution. Looking at Real Time Display make sure that the solution has reached the plasma, select the button that has black musical notes in the top left corner named, “Start autotune report wizard,” in order to acquire an autotune report.

Click the next button to get to the following window:

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Select the folder named 'Xt lens tune only', click Next, select 'I want to introduce the sample manually' and then follow the directions on the subsequent windows. In the configurations tab, a new tune is listed with the date and time it was done, the box next to it is automatically checked indicating the instrument is currently in that mode.

7.4.4 Tuning procedure in CCT-KED mode - The tuning of the CCT-KED mode is generally based on how the Xt mode was tuned. Most of the voltage settings on the lenses will be the same in both modes. The lenses that do have different voltage settings are the Focus, Pole Bias, and Hex Bias. The collision cell gas is turned on during CCT-KED mode; this should be tuned to maximize ^{115}In CPS, while keeping ^{78}Se CPS less than 20, mass 80 cps less than 4500, and keeping the CeO/Ce ratio less than 3%.

To use the CCT-KED autotune, go through the same procedure as the Lens Tuning. Check the box next to the latest CCT-KED tune in the configurations tab, the instrument is now in CCT-KED mode, then click on the button with the black musical notes to open the autotune wizard. Make sure probe is in 20 µg/L tune solution. Select the Xt CCT-KED folder and click Next.

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This optimization is described in detail in part 4 of Thermo Electron Corporation *X*-Series ICP-MS Training Course Lectures, (pages 7-13) for the hydrogen/helium gas mixture.

7.5 Complete Optimization - If the cones or torch is removed and replaced, a stage tune and a nebulizer tune should be performed.

7.5.1 Stage Tune: The stage tune optimizes the x, y, and z positions of the torch to make sure it is centered, maximizing ^{115}In cps. To perform this tune, make sure the instrument is in Xt mode on the configurations tab, then click on the black musical notes button, make sure probe is in 20 µg/L tune solution, and select the stage tune folder and click next.

7.5.2 Nebulizer Tune: The nebulizer tune adjusts the gas flow to the nebulizer, optimizing it for maximum ^{115}In cps while keeping the CeO/Ce ratio to a minimum. To perform this tune, make sure the instrument is in Xt mode on the configurations tab, then place the probe in 20 µg/L tune solution, click on the button with black musical notes, and select the nebulizer tune and click next.

7.5.3 Detector Setup: The detector setup adjusts the voltage of the detector and performs a cross calibration between the analogue portion of the detector and the pulse counting portion of the detector. This should be performed when the sensitivity is low. However, low sensitivity can come from other factors, such as very dirty cones or an improperly working nebulizer; these factors should be examined first, before performing a detector setup.

To perform a detector setup, make sure the instrument is in Xt mode on the configurations tab, make sure the probe is in the 400 µg/L cross calibration solution, and click on the button with the red check on a piece of paper, which is to the right of the performance report button. The Detector Setup wizard gives the user the option of performing a detector voltage setup, a cross calibration, or both at the same time. While a cross calibration can be performed without doing a detector setup, the detector setup should always be followed by a cross calibration. When the procedure is done, write the new voltages down in the maintenance log. If the procedure 'passed', the new cross calibration will be set as the current calibration, which can be viewed in the Calibrations tab of the Instrument page.

7.5.4 Mass Calibration: The mass calibration calibrates the analyte mass defined in the database and the actual mass at which peak sensitivity is found.

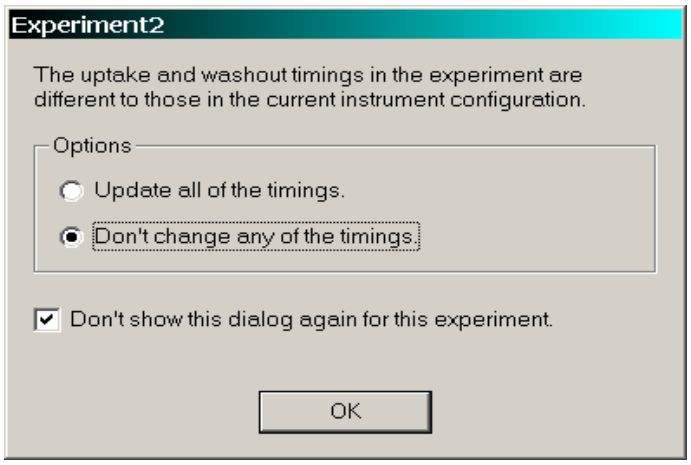
This should be performed when the performance report shows the mass calibration failed. To perform the mass calibration, click on the button with the red check on the white piece of paper. Click on mass calibration in the drop down menu. The 20 µg/L tune solution is used for this

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calibration. See the flowchart in Appendix J for further instruction on mass calibration failures.

7.6. Running Samples - After Warm-Up is complete and the performance report has passed, perform the following steps to collect a dataset:

7.6.1 Create new experiment - Select File/New/Experiment from Template and select the appropriate template for the samples to be analyzed. The following window should appear:

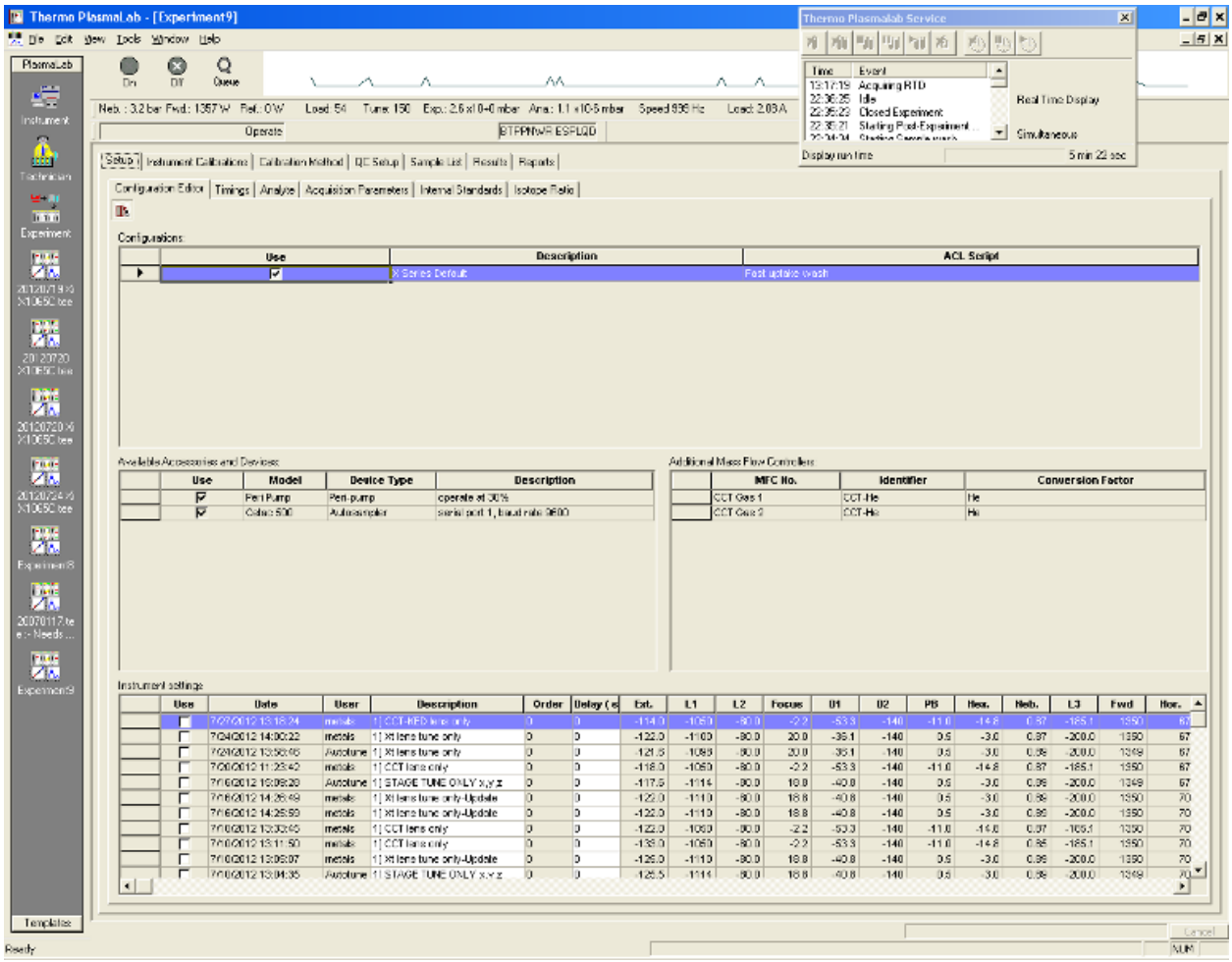


Select, 'Don't change any of the timings' and 'Don't show this dialog again for this experiment' and click 'OK'.

For beryllium or boron experiments (Xt mode) select the 'Be ONLY experiment.tet' template. For CCT-KED experiments select 'CCT-KED current template experiment.tet' template.

7.6.2 Verify the experiment settings are correct - The following window should be displayed:

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This is the configuration editor of the experiment page. It looks very similar to the configuration tab on the instrument page. The tune highlighted in blue is the tune that is checked on the configuration tab of the instrument page. This window allows the analyst to choose which modes the instrument shall run samples in. If only Xt mode is needed (no CCT-KED mode), check the box with the latest dated tune, this should be the one highlighted in blue. If only CCT-KED mode is needed, check the box next to the latest CCT-KED tuning, this should be highlighted in blue. If both modes are needed for one experiment, check the box next to the latest Xt mode first, then check the box next to the latest CCT-KED tune, the Xt mode should be highlighted in blue. A delay must be used because the instrument switches between modes while running the same sample and a settle time is needed after the switch from Xt mode to CCT-KED mode. A delay of 55 s is appropriate.

Note: More sample volume will be used when analyzing samples with Xt and CCTED mode in the same analysis.

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7.6.3 Verify that Acquisition Parameters are Correct – If more than one mode is selected make sure that on the Acquisition Parameters page each analyte has the right setting (for example, Be is scheduled to be analyzed in Xt mode, As - in CCT-KED mode, etc.). If only one mode is selected all the acquisition parameters are automatically set to only that mode.

7.6.4 Begin Automated Analysis - The instrument calibration and sample sequence is located on the 'Sample List' tab of the experiment window. The sample list can be edited before and after the 'Queue' button is selected and the experiment has begun. Place all calibration standards, calibration check solutions, and samples in the autosampler according to the sample list. Click on the 'Queue' button to begin analysis. A prompt will appear to save the file. Save it at Program Files/Thermo Fisher/PlasmaLab/data/Runs/Current Experiments.

Note: Don't forget to place the internal standard probe in the bottle of internal standard.

7.6.4.1 Monitor Initial QC - Check the calibration blank results for signs of contamination and the rest of the calibration and initial QC results for signs of problems. Periodically check instrument to make sure it is operating smoothly. Do not continue on to samples if the calibration checks fail, contact supervisor.

7.6.4.2 After the experiment has completed - The plasma can be extinguished by clicking the 'Off' button in PlasmaLab. Aspirate the rinse solution for five minutes prior to extinguishing the plasma. The peristaltic pump tubing may be loosened, place caps on the standard autosampler tubes and turn the computer monitor off.

7.6.4.3 Automatic Shutdown - If analysis will not be completed until after hours, set the instrument's 'Queue empty action' to Vacuum. This will return the instrument to 'Vacuum Ready' automatically when analysis is complete. The Queue empty action can be set while the instrument is analyzing samples.

7.7 To completely turn off the instrument – After the plasma has been extinguished and the instrument is in 'Vacuum Ready' mode, follow the steps below:

7.7.1 Click 'Shutdown'

7.7.2 Turn off the desktop computer.

7.7.3 Remove the instrument hood and place it carefully on the floor or the bench adjacent to the instrument.

7.7.4 Turn off the onboard instrument computer (green switch on the back left side of the instrument).

7.7.5 Locate the breakers on the left hand front of the instrument

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7.7.6 Turn off the breakers in the following sequence: Wait a few seconds between turning off each switch.

1st Plasma RF generator

2nd Peltier spray chamber cooling

3rd Electronics, Embedded PC, Rotary pump, Turbo pump

8. DATA ARCHIVAL

8.1. Archive Data:

8.1.1 Go to the page Experiment/Results/Numerical Results/Analyte Dilution Conc. and click the refresh button. The time column must be showing before exporting. Click the far left icon that appears as a clock to show the time column.

8.1.2 Place the mouse pointer in the middle of the data display field and press the right mouse button. Select 'Export CSV file'.

8.1.3 A 'Save as' window will open. Change the 'Save in' folder on top of the 'Save as' window to \\FLDEP1\DEAR\Labs\Lab3\Chem_Data\Inorganic\Metals\ICP-MS-X2\ and make the file name the date with the year first followed by the month and then the day and include the instrument serial number. YYYYMMDD –X****.

8.2. Defaulting the Database on the Thermo XII ICPMS:

The service technician will typically perform this during preventative maintenance. When the .tei file on the instrument becomes too large, around 100 MB, the instrument software will start to freeze and become unresponsive. In this situation the database needs to be defaulted as follows:

1: Print performance report for settings.

2: Export autotunes and performance report templates.

3: Stop Services.

4: Change extension of the Instrument.tei file to .old.

5: Edit ACL script to remove stop command for peristaltic pump.

6: Redo all calibrations.

9. QUALITY CONTROL

9.1 QC Data Processing: The procedure for data review and cross-checking is summarized in the DEP SOP MT-058, which also lists the acceptance criteria for

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standard reference materials, matrix spikes, internal standards, and precision data. Contingencies for out of control QC data are listed in DEP SOP LB-027 as well as DEP SOP MT-058.

9.2 Internal Standards:

9.2.1 Internal Standard intensities are used to normalize the effects of mass transport phenomena and instrument drift. An internal standard intensity must remain between 60% and 125% of its initial value for analysis of water matrices and between 70% and 130% for solid and waste matrices, as well as water samples analyzed according to the Resource Conservation and Recovery Act (RCRA), which will have test ID W-ICPMS-R. This instrument allows the use of an interpolated form of internal standard correction as well as a direct assignment of analyte masses to internal standard masses. Using the interpolation form for internal standard correction, the effect of an internal standard on an analyte is weighted according to proximity of the surrounding internal standards. If an internal standard is outside of the acceptance limits, samples requiring any analytes at lower or higher masses up to the next passing internal standard must be rerun with proper dilution in attempts to minimize the matrix affects, or rerun using another analytical technique (e.g. ICP-AES) if acceptable.

9.2.2 Changes in internal standard intensity should not be more than 10% from one sample to the next unless the change is an attenuation that appears to be due to a matrix effect.

9.2.2.1 Samples containing a significant amount of dissolved solids suppress the instrument sensitivity. Although the constituents of a sample also play a role, generally the higher the dissolved solids the more the signal is suppressed. Samples containing 0.5% solids attenuate the signal by about half. This effect should be approximately the same for internal standards as well. It is normal to observe a sudden decrease in the internal standard intensity for samples known to contain or are suspected of containing significant dissolved solids.

9.2.2.2 Sudden increases in internal standard intensity can be the result of signal attenuation by a matrix effect or due to contamination. The latter of which usually yields an increase in the intensity of individual internal standards, rather than in all of them as would be the result for the former case.

9.2.3 All internal standard intensities should be checked to see that the above criteria are met. If these criteria are not met, the samples must be rerun or appropriately qualified. If the reason a sample does not meet these criteria appears to be excessive attenuation due to the matrix, the sample must be

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diluted and rerun. If a sample appears to be significantly contaminated by an internal standard it should be reprocessed using another suitable internal standard, rerun diluted, or rerun using alternative analytical instrumentation (e.g. ICP-AES):

9.2.3.1 When an analysis result has utilized an internal standard that is outside the control limits, reprocessing with a different internal standard may result in acceptable data. Choose an uncontaminated internal standard as close in mass as possible to the affected analytes. Edit the experiment to define the new internal standards and use the Save As option under the Files menu to **save the new experiment file under a different name**. Refresh the numerical results and export the CSV file for QC Manager and review the resulting dataset for potential upload.

10. DATA REVIEW AND CALCULATIONS

The procedure for data review, crosschecking, 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.

11. TROUBLESHOOTING

Note: See 'X-Series ICP-MS Getting Started Guide' section 'G: Maintenance and Troubleshooting'.

Communication Errors: Occasionally, a software error will cause a loss of communication between the embedded-PC, instrument electronics, and desktop-PC. The instrument may need to be turned off and then back on to regain communication. See sections 7.1 and 7.7.

12. SAFETY / HAZARDOUS WASTE MANAGEMENT

12.1 Review the Health and Safety Plan located at https://www.fldepnet.org/system/files/Division-of-Environmental-Assessment-and-Restoration/governing-documents/Health%20%20Safety%20Plan_0.docx.

12.2 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. Avoid contact of these irritants with skin and clothing by appropriate use of gloves, apron, facemask, safety glasses, hood shield, etc.

12.3 Store any wastes that cannot be disposed of down the sink (See Laboratory Health and Safety Plan) in the appropriate plastic waste container properly labeled with

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Hazardous Wastes Labels. These wastes include used vacuum pump oil and aqueous solutions known to contain trace metals at concentrations that exceed the violation limit for those metals. Vacuum pump oil waste must be stored separately from acidic aqueous waste. Empty full bottles of wastes into containers in the appropriate waste storage room on an AS FILLED basis. The limits for discharging inorganics are: As < 132 µg/L, Cd < 79 µg/L, Cr < 2.898 mg/L, Cu < 852 µg/L, CN < 1.252 mg/L, Pb < 540 µg/L, Hg < 38 µg/L, Ni < 1428 µg/L, Se < 353 µg/L, Ag < 3.19 mg/L, Zn < 2.73 mg/L.

13. 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 as many of these samples also require organic analyses, which require refrigeration.

14. REFERENCES

14.1 Thermo Electron Corporation *X*-Series ICP-MS Getting Started Guide

14.2 Thermo Electron Corporation *X*-Series ICP-MS Training Course Lectures

14.3 EPA Methods 200.8 Revision 5.4 and 6020A

14.4 DEP SOP MT-007, Procedure for Cleaning Metals Labware.

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

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

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

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

14.9 DEP SOP MT-061, Analysis of Selected Metals by Dual View Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES).

14.10 DEP SOP MT-063, Microwave Assisted Hydrofluoric Acid Digestion of Solid Matrices for Total Metals Determinations (Adapted from EPA Method 3052 for the Milestone Ethos EZ microwave system).

14.11 DEP SOP MT-068, Toxicity Characteristic Leaching Procedure (EPA Method 1311) and the Synthetic Precipitation Leaching Procedure (EPA Method 1312).

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

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14.13 Quality Manual, Bureau of Laboratories, DEP.

14.14 Laboratory Health and Safety Plan.

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APPENDIX A

Acquisition Parameters

Survey Scan
Sweeps: 10
Acquisition time: 14 s

Start Mass	End Mass	Dwell (ms)	Channels (AMU)	Resolution	Instrument Mode
5.59	10	5	10	high	Xt
26	27.41	0.6	10	high	Xt
44	54	0.6	10	high	Xt
57	78.64	0.6	10	high	Xt
81	245.5	0.6	10	high	Xt

Main Scan
Sweeps: 50
Acquisition time: 37 s

Analyte / Mass	Abundance (%)	Dwell (ms)	Channels	Separation AMU	Resolution	Instrument Mode
^{6}Li	7.5	10	1	0.02	Standard	Xt
^{9}Be	100	100	3	0.02	Standard	Xt
^{10}B	19	10	1	0.02	Standard	Xt
^{11}B	81	10	1	0.02	Standard	Xt
^{27}Al	100	10	1	0.02	Standard	CCT-KED
^{45}Sc	100	10	1	0.02	Standard	Xt / CCT-KED
^{47}Ti	46.9	10	1	0.02	Standard	CCT-KED
^{52}Cr	83.8	20	1	0.02	Standard	CCT-KED
^{54}Fe	5.8	10	1	0.02	Standard	CCT-KED
^{55}Mn	100	10	1	0.02	Standard	CCT-KED
^{59}Co	100	10	1	0.02	Standard	CCT-KED
^{60}Ni	26.2	20	1	0.02	Standard	CCT-KED
^{63}Cu	69.2	20	1	0.02	Standard	CCT-KED
^{65}Cu	30.8	20	1	0.02	Standard	CCT-KED
^{66}Zn	27.9	10	1	0.02	Standard	CCT-KED
^{71}Ga	39.9	10	1	0.02	Standard	CCT-KED
^{75}As	100	50	1	0.02	Standard	CCT-KED
^{77}Se	7.5	50	1	0.02	Standard	CCT-KED
^{78}Se	23.8	100	1	0.02	Standard	CCT-KED
^{83}Kr	11.6	10	1	0.02	Standard	CCT-KED
^{88}Sr	82.6	10	1	0.02	Standard	CCT-KED
^{91}Zr	11.2	10	1	0.02	Standard	CCT-KED
^{92}Mo	15	10	1	0.02	Standard	CCT-KED
^{94}Zr	17.4	10	1	0.02	Standard	CCT-KED

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Analyte / Mass	Abundance (%)	Dwell (ms)	Channels	Separation AMU	Resolution	Instrument Mode
^{95}Mo	15.9	10	1	0.02	Standard	CCT-KED
^{103}Rh	100	10	1	0.02	Standard	CCT-KED
^{106}Cd	1.22	10	1	0.02	Standard	CCT-KED
^{107}Ag	51.8	10	1	0.02	Standard	CCT-KED
^{108}Cd	0.89	10	1	0.02	Standard	CCT-KED
^{111}Cd	12.8	20	1	0.02	Standard	CCT-KED
^{121}Sb	57.4	10	1	0.02	Standard	CCT-KED
^{137}Ba	11.2	10	1	0.02	Standard	CCT-KED
^{158}Gd	24.9	10	1	0.02	Standard	CCT-KED
^{159}Tb	100	10	1	0.02	Standard	CCT-KED
^{205}Tl	70.5	10	1	0.02	Standard	CCT-KED
^{206}Pb	24.1	10	1	0.02	Standard	CCT-KED
^{207}Pb	22.1	10	1	0.02	Standard	CCT-KED
^{208}Pb	52.4	10	1	0.02	Standard	CCT-KED
^{209}Bi	100	10	1	0.02	Standard	CCT-KED
^{238}U	99.3	10	1	0.02	Standard	CCT-KED

APPENDIX B

Corrective Equations

Mass/ Analyte	Interference equation
9Be	
27Al	
45Sc	
52Cr	
55Mn	-A(54Fe)
59Co	
60Ni	
63Cu	
65Cu	
66Zn	
75As	
78Se	
89Y	
95Mo	
107Ag	
109Ag	
111Cd	- B(95Mo)
121Sb	
137Ba	

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Mass/ Analyte	Interference equation
159Tb	
205Tl	
206Pb	
207Pb	
208Pb	208Pb + 1.0(206Pb) + 1.0(207Pb)
209Bi	

A = 100ppm Fe solution [55Mn cps / 54Fe cps]
B = 2ppm Mo solution [111Cd cps / 95Mo cps]

APPENDIX C

Calibrated Elements:

Symbol	Method
Be	Fully Quant
Al	Fully Quant
Sc	Internal Standard
Cr	Fully Quant
Mn	Fully Quant
Co	Fully Quant
Ni	Fully Quant
Cu	Fully Quant
Zn	Fully Quant
As	Fully Quant
Se	Fully Quant
Ga	Internal Standard
Mo	Fully Quant
Rh	Internal Standard

Symbol	Method
Ag	Fully Quant
Cd	Fully Quant
Sb	Fully Quant
Ba	Fully Quant
Tb	Internal Standard
Tl	Fully Quant
Pb	Fully Quant
Bi	Internal Standard
B	Fully Quant
Sr	Fully Quant
Gd	Fully Quant
U	Fully Quant
Ti	Semi Quant

'Internal Standard' – Used as an internal standard.
'Fully Quant' – Results quantitated.
'Semi-quantified' – Concentrations estimated based on the mass response curve of the instrument instead of the use of calibration standards.

APPENDIX D

Internal Standardization techniques:

Symbol	Technique	1st ionization potential
9Be	Interpolate	9.322
10B	Interpolate	8.298
11B	Interpolate	8.298

Symbol	Technique	1st ionization potential
95Mo	Interpolate	7.099
106Cd	Interpolate	8.993
107Ag	Interpolate	7.576

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Symbol	Technique	1st ionization potential
27Al	Interpolate	5.986
52Cr	Interpolate	6.766
55Mn	Interpolate	7.435
59Co	Interpolate	7.860
60Ni	Interpolate	7.635
63Cu	Interpolate	7.726
65Cu	Interpolate	7.726
66Zn	Interpolate	9.394
75As	Interpolate	9.810
78Se	Interpolate	9.752
88Sr	Interpolate	5.695
92Mo	Interpolate	7.099

Symbol	Technique	1st ionization potential
108Cd	Interpolate	8.993
109Ag	Interpolate	7.576
111Cd	Interpolate	8.993
121Sb	Interpolate	7.850
123Sb	Interpolate	7.850
137Ba	Interpolate	5.212
158Gd	Interpolate	6.140
205Tl	Interpolate	6.108
206Pb	Interpolate	6.108
207Pb	Interpolate	6.108
208Pb	Interpolate	6.108
238U	Interpolate	6.080

APPENDIX E

Example Sample List. Unused columns are left out of the example for clarity.

#	Label	Type	QC Type	Rack	Row	Column	Height (mm)	Survey Runs	Main Runs	User Pre-dilution
1	Rinse (IS 19972 no HCl)	Unknown		0	1	1	144	1	5	1
2	BLK	Blank		0	1	1	144	1	5	1
3	CCMS MET 50 19165	Fully Quant Standard		0	1	2	144	1	5	1
4	CCMS MET 100 19642	Fully Quant Standard		0	1	3	144	1	5	1
5	CCMS MET 200 19167	Fully Quant Standard		0	1	4	144	1	5	1
6	I-BLK	Unknown		0	1	1	144	1	5	1
7	I-BLK	Unknown		0	1	1	144	1	5	1
8	CPQLCCT1 19226	Unknown		0	1	10	144	1	5	1
9	MSMETC 100 19168	Unknown		0	1	7	144	1	5	1
10	IC6020 19271	Unknown		0	1	9	144	1	5	1
11	ICSA 19330	Unknown		4	1	1	144	1	5	1
12	MSCCV	QC Sample	CCV	0	1	3	144	1	5	1
13	CCB	QC Sample	CCB	0	1	1	144	1	5	1
14	D-BLK MW-040712-B	Unknown		1	1	1	144	1	5	1
15	765873 EB	Unknown		1	1	2	144	1	5	1
16	765885 EB	Unknown		1	1	3	144	1	5	1
17	DPQLCCT1	Unknown		1	1	4	144	1	5	1
18	LFB LW3	Unknown		1	1	5	144	1	5	1
19	765882 A	Unknown		1	1	6	144	1	5	1
20	765882 B	Unknown		1	1	7	144	1	5	1
21	765882 S1	Unknown		1	1	8	144	1	5	1
22	765882 S2	Unknown		1	1	9	144	1	5	1
23	765869	Unknown		1	1	10	144	1	5	1
24	MSCCV	QC Sample	CCV	0	1	3	144	1	5	1
25	CCB	QC Sample	CCB	0	1	1	144	1	5	1

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APPENDIX F

Spike Levels (µg/L)

Analyte	Water Spike (LW6)	Sediment Spike (SEDSPK4)
Al	800	8000
Sb	40	400
As	40	400
Ba	80	800
Be	0.4	4
B	100	400
Cd	2	20
Cr	20	400
Co	20	200
Cu	20	100
Gd	10	N/A
Pb	20	400
Mn	40	400
Mo	10	200
Ni	20	200
Se	40	400
Ag	4	40
Sr	400	4000
Tl	10	100
Zn	100	400
Fe	800	8000
K	800	8000
Mg	800	8000
Ti	8	200
Sn	20	400
V	20	200
Ca	800	8000
Na	800	8000
U	10	50

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APPENDIX G

ICPMS Interference Check Solution (IC6020C)

Component	Interferences	Analytes A	Interferes with	Interferences
27Al	100 mg/L	0	NA	13C14N
40 Ca	300 mg/L	0	59Co, 60Ni	NA
Fe	250 mg/L	0	Mn resolution check	NA
25Mg	100 mg/L	0	65Cu	NA
23Na	250 mg/L	0	63Cu	NA
31P	100 mg/L	0	65Cu	NA
39K	100 mg/L	0	NA	NA
32S	100 mg/L	0	52Cr, 65Cu, 66Zn, 51V	NA
12C	200 mg/L	0	52Cr	NA
35Cl, 37Cl	2120 mg/L	0	75As, 52Cr, 55Mn, 51V	NA
98Mo	2 mg/L	0	111Cd	98Ru
48Ti	2 mg/L	0	NA	NA
75As	0	20 µg/L	NA	40Ar35Cl
111Cd	0	20 µg/L	NA	95Mo16O, 94Mo17O
52 Cr	0	20 µg/L	NA	40Ar12C, 36Ar16O, 35Cl17O, 34S18O
59Co	0	20 µg/L	NA	43Ca16O
65Cu	0	20 µg/L	NA	25Mg40Ar, 33S16O2, 31P17O2, 32S16O17O, 31P16O18O
55Mn	0	100 µg/L	NA	37Cl18O, 40Ar15N, 40Ar14N1H, Fe
60 Ni	0	20 µg/L	NA	44Ca16O
107Ag	0	20 µg/L	NA	NA
66Zn	0	20 µg/L	NA	34S16O2, 32S17O2
78Se	0	20 µg/L		
51V	0	0	NA	35Cl16O, 1H34S16O
82Se	0	0	NA	82Kr, 1H81Br

NA: Not Applicable

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APPENDIX H

Lens Settings (Example)

Date	1/10/2005	12/19/2006			1/8/2007		Notes
User	Default	Xseries					
Description	Default settings	Xt default install	**fixed Xt**	**fixed CCT**	**Copper in seawater** CCTED only		
Order	0	0	1	2			Xt mode 1, CCT mode 2
Delay	0	0	0	55s	0		Instrument needs 55s to settle after switching from CCT mode to Xt mode.
Ext	-125	-106			-141		Changes daily, as the extraction lens gradually gets dirty from the ion beam, more voltage must be applied.
L1	-1000	-1200			-1230		1st lens after extraction, changes slightly for the same reason as the extraction lens.
L2	-80	-80	-80	-80	-80		Lens behind L1, **set.**
Focus	11	12.9			4.1		Different setting for Xt and CCT, changes slightly
D1	-40.8	-41.6	-39.2	-39.2	-39.2		Lens before ion path bends, **set.**
D2	-140	-140	-140	-140	-140		Lens after ion path bends, **set.**
PB	0.2	-0.5	0.5	-9	-7		Pole Bias. Xt mode, -0.5; CCT mode, -10; CCTED mode, -7
Hex.	-4	-3	-3	-12	-10		Xt mode, -3.0; CCT mode, -5; CCTED mode, -10
Neb.	0.9	0.89			0.94 (glass)		**Set.** Only optimize after installing new nebulizer
L3	-195.3	-195.3	-195.3	-195.3	-195.3		Lens right after hexapole. **Set.**
Fwd	1400	1400	1400	1400	1400		**Set.**
Hor.	80	70			76		**Set.** Only optimize after changing torch.
Vert.	405	422			409		**Set.** Only optimize after changing torch.
DA	-25.1	-39.2	-35.3	-35.3	-35.3		
Cool	13	13	13	13	13		**Set.**
Aux.	0.8	0.75	0.75	0.75	0.75		**Set.**
Depth	150	110	100	100	100		**Set.**
CCT He	0	0			2.8		Adjust for CPS.

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APPENDIX I

Maintenance

Daily:

- Replace sample and drain peristaltic pump tubing
- Check air filters and clean if necessary.

Monthly:

- Check rotary pump oil level
- Check oil mist filters
- Check chiller water level in reservoir

See The X-Series ICP-MS Getting Started Guide for more information.

Maintenance Tips

Cleaning of Cones:

The cones need to be cleaned as part of regular instrument maintenance. Some indications that it is time to clean the cones are low sensitivity, repeated instrument PQL recovery problems, salt water SRM recovery problems, internal standard recoveries not responding as expected and spike recoveries bias low (especially in mid-mass elements). Visual inspection is a good method to determine if there is too much build-up on the cones.

The cones are very delicate, especially the tip around the orifice. Be very careful not to bump the tip on anything, dropping the cone will result in an unusable cone. There are various ways to clean the cones. If they are not very dirty, just running the cones under DI water will rinse off loose build up. If, after rinsing with DI water, there is still considerable build up, prepare a small bath with 10 % HNO_3 and 1 % HCl. Place the cone in the acid solution and allow to soak for just a few minutes. The buildup should start to dissolve and a q-tip can be used to gently scrub the sides of the cone.

Note: **Do not leave the cone in an acid solution for longer than 10 minutes or it will start to dissolve the metal.**

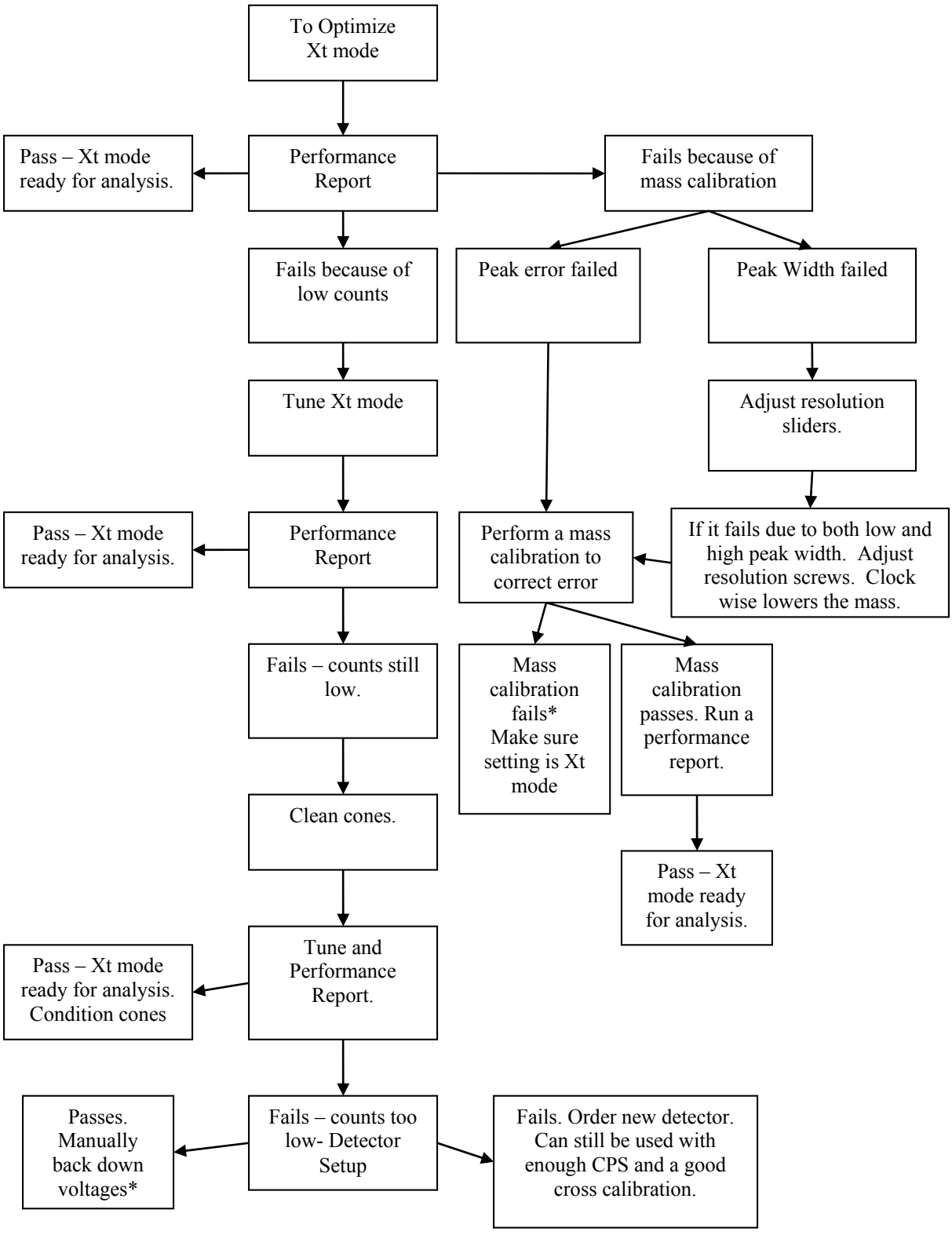
Chiller Filter Cleaning:

Fluid Filter Bag: To clean, remove the filter by gently pulling up on the plastic funnel housing to remove it and simply pull the bag out of the unit. Gently scrub with a brush and soap.

Condenser Filter: Clean the filter through the grill using a vacuum with a soft-bristle brush. Failure to clean the condenser filter will cause a loss of cooling capacity and lead to premature failing of the cooling system.

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APPENDIX J, Xt mode Optimization flowchart



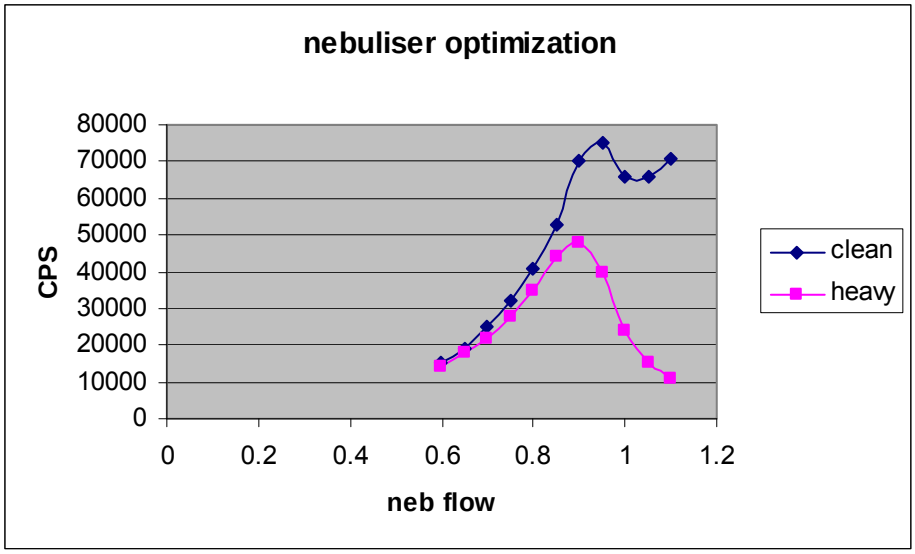
* Consult supervisor. May not do this every time

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APPENDIX K

Nebulizer Optimization

Neb flow	CPS clean matrix 20 µg/L In	CPS heavy matrix 20 µg/L, In	Difference
0.6	15000	14000	1000
0.65	19000	18000	1000
0.7	25000	22000	3000
0.75	32000	28000	4000
0.8	41000	35000	6000
0.85	53000	44000	9000
0.9	70000	48000	22000
0.95	75000	40000	35000
1	66000	24000	42000
1.05	66000	15000	51000
1.1	71000	11000	60000



This chart was made by first varying the nebulizer flow while observing In CPS in the 20 µg/L tune solution in CCT-KED mode. Next, a solution of 20 µg/L In was prepared in a matrix similar to the IC6020C (heavy matrix) solution. The nebulizer gas flow was then set at different points while observing the In CPS in the 20 µg/L In heavy matrix solution in CCT-KED mode. As seen in the chart, the maximums (neb flow 0.90) are separated by approximately 25,000 CPS. By setting the nebulizer flow lower, around 0.80, there will be less internal standard suppression on saltwater samples.

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APPENDIX L

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% HNO3 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 (10 0% 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 (can be found at \\FLDEP1\DEAR\LABS\LAB5\Chemistry\Metals\TCLP analysis worksheets\Multiphasic

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Samples\) 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 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 of Significant Changes

1. All sections: Updated concentrations of metals solutions used in lab.
2. Section 6: Added limits for performance reports.
3. Appendix B: Added arsenic interference equation.

08/04/2009

1. Updated argon supply from four argon Dewars to MicroBulk argon delivery system.
2. Added MDL/PQL location on the network to section 4.4
3. Updated the concentration of the tune solution used in the lab
4. Reference to prep SOPs added to section 5.1
5. Section 6.4: Reorganized to reduce redundancy and updated performance report limits.
6. Corrected internal standard recoveries for sediments and wastes in section 8.3.1.

07/16/2015

1. All hyperlinks updated.
2. Standard and reagent labeling procedure referred to MT-069.
3. Chiller filter cleaning procedure added to Appendix I.

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