1.0 TITLE

Elemental Analysis by ICP-MS - EPA Methods 200.8 & 6020/6020B

2.0 LOCATION

Clean Room

3.0 SCOPE & APPLICATION

This SOP covers the analysis of trace metals and Rare Earth Elements (REEs) in waters, soil extracts, and digestates following EPA 200.8 or 6020/6020B protocols, using the Agilent 7500ce, Agilent 7900, and Thermo iCAP RQ series of ICPMS. §Table 18.11 lists those analytes approved for each method.

4.0 SUMMARY

Samples in an aqueous matrix are aspirated into the argon plasma where they are desolvated, atomized and ionized. The ions are focused by a series of electrically charged lenses before entering the quadrupole. The quadrupole selectively separates the ions according to mass to charge ratio (m/z). An electron multiplier detects each ion allowed through the mass filter and the cumulative counts of each mass of interest are acquired by a two channel detector. Polyatomic interferences are minimized by a Hydrogen (H_2) reaction mode, a He (Helium) collision mode, or an interference equation. The acquired mass spectra are then transferred to the software, where they are compared to calibration curves prepared by plotting count rates of standards similarly treated. The spectra and results are then stored in the computer and the results are uploaded to the LIMS.

Method Modifications:

4.1 For 6020/6020B analysis, ACZ designates the upper limit for analytes in the blank as <3x the existing reporting MDL (this is a modification from Method 6020B §9.7.1). Data from the quarterly IDL studies is used only to verify the instrument noise level is below ACZ's reporting MDL for each analyte. Refer to §14.2.

4.2 Due to varying state regulations ACZ is following Method 6020 (original 1994 version) and Method 6020B (revised 2014). Where the methods differ, ACZ has chosen the more rigorous of procedures or QC to follow.

4.3 The use of Ge as an internal standard (8.5) is a method modification from method 200.8. Refer to CAR455.

4.4 Method 6020B refers to the interference check QC sample as 'Spectral Interference Check' (SIC). To avoid confusion with similar methods, this QC sample will be referred to as an 'Interference Check Sample' (ICS-A or ICS-AB). All method QC requirements are met. See §8.25 in this SOP.

4.5 In this SOP the QC term 'Lower Limit of Quantitation' (LLOQ) is equivalent and interchangeable with 'Practical Quantitation Level' (PQL).

5.0 REFERENCES

5.1. J.T. Creed C.A. Brockjoff, T.D. Martin., Method 200.8, "Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma-Mass Spectroscopy (Version 5.4)," Technology Applications, Inc., and Chemistry Research Division; Environmental Monitoring and

Systems Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, OH 45268.

5.2. "Inductively Coupled Plasma-Mass Spectroscopy," M6020 SW-846, Test Methods for Evaluating Solid Waste, U.S. E.P.A., December 1994.

5.3. "Inductively Coupled Plasma-Mass Spectrometry," Method 6020B SW-846. US E.P.A., July 2014

5.3 K.E. Jarvis and A.L. Gray, "Handbook of Inductively Coupled Plasma Mass Spectrometry," Geology Department, Royal Holloway and Bedford New College, University of London, Blackie and Son Ltd. 1992.

5.4 Agilent Technologies, Inc., "Agilent 7500 ICPMS Chemstation Operator's Manual Rev. C," Agilent Technologies, Inc. 2002.

5.5 Agilent Technologies, Inc., "Agilent 7500 ICPMS Hardware Manual Rev. D," Agilent Technologies, Inc. 2002.

5.6 Agilent Technologies, Inc., "Agilent 7500 ICPMS Integrated Sample Introduction System Manual," Agilent Technologies, Inc. 2000.

5.7 Agilent Technologies, Inc., "Agilent 7500 Series ICPMS Installation Guide Rev. L.," Agilent Technologies, Inc. 2003.

5.8 Northeast Analytical, Inc. "Guide to Environmental Analytical Methods," Genium Publishing Corporation, One Genium Plaza, Schenectady, NY 12304-4690.

5.9 Agilent Technologies, Inc., "Standard Operating Procedure, US EPA Method 6020 using the Agilent 4500 and 7500 ICP-MS, Rev. 1.2" Agilent Technologies, Inc. 9/2000.Agilent Technologies, Inc., "Agilent 7900 MassHunter Help Index" Software v. 4.1 Build C.01.01 or higher

5.10 ThermoFisher Scientific, Inc., "iCAP Qnova Series ICP-MS Operating Manual Rev. B," ThermoFisher Scientific, Inc. 2017

5.11 ThermoFisher Scientific, Inc., "iCAP Q/iCAP RQ ICP-MS Software Manual Rev. C," ThermoFisher Scientific, Inc., 2018

6.0 SAMPLE COLLECTION, HANDLING & PRESERVATION

6.1 Samples for dissolved and total dissolved analysis are filtered through a 0.45um membrane filter (either by the client in the field or at the laboratory) and then preserved by the addition of nitric acid to a pH < 2. These samples are stored in a plastic bottle with a green dot. Samples for total dissolved analysis require digestion before analysis (see SOPII021). Samples cannot be analyzed until 24 hours after the time of acidification.

6.2 Samples for total and total recoverable analysis are preserved at the time of sampling or as soon after sampling as possible by addition of nitric acid to a pH < 2. These samples are stored in a plastic bottle with a red dot. Samples for total and total recoverable analysis require digestion prior to analysis (see SOPII021).

6.3 Samples for potentially dissolved and total potentially dissolved analysis are acidified at the time of sampling or as soon after sampling as possible by the addition of nitric acid to pH <2. Samples must be filtered through a 0.45um membrane filter between 8 and 96 hours after acidification. If the sample is out of hold time, a portion of the RAW sample may be acidified and filtered.

Samples for total potentially dissolved analysis require digestion before analysis (see SOPII021). All filtration of potentially dissolved samples must be done in the cleanroom to avoid contamination. See SOPWC061.

6.4 For Drinking Water (DW) matrix samples that were acidified at the lab (denoted by a pink pH adjust sticker), the analyst must determine if acidification occurred within 14 days of sampling. This can be determined by looking in LIMS → Sx Analysis → Sample Results and looking at 'Collection Date.' If the sample was acidified past 14 days qualify appropriately.

6.5 Solid samples require no additional preservation prior to analysis. There is no established hold time limit for solid samples. Solid samples require a digestion or extraction performed by the Soils dept prior to analysis.

6.6 Hold Times:

Table 6.1: Hold Times

Product	Matrix	Hold Time Starts - Ends With
Mercury	Liquids	28 days from collection to analysis
Cu-*, Pb-*	Drinking Water (DW)	14 days from collection to acidification
Approved metals*	Liquids: potentially dissolved	4 days from collection to filtration; 180 days from collection to analysis
	Liquids and solids	180 days from collection to analysis
	Solids: 1312 and TCLP extractions	180 days from collection to start of extraction; 180 days from end of extraction to analysis
	Solids: RBLP	180 days from collection to filtration; 7 days from filtration to analysis
	Solids: other extractions (e.g. AD,3050, HF, MWMT, WET)	180 days from collection to analysis

*see Table§18.11 for a full list of approved metals

7.0 APPARATUS & SUPPLIES

7.1. Agilent 7500ce or 7900 ICP-MS
7.2. Thermo iCAP RQ ICP-MS
7.3. Interfaced, network connected PC with instrument software:
  i. 7500ce - ChemStation v. B.03.04 or higher
  ii. 7900 – Mass Hunter V. 4.2 Build C.01.02 or higher
  iii. RQ – Qtegra V. 2.10 or higher
7.4. Argon supply, high purity grade (99.99%)
7.5. Helium supply, UHP grade
7.6. Hydrogen supply, UHP grade
7.7. Interfaced chiller. Operating temperature must be below 20˚C
7.8. Cetac ASX-520/560 autosampler, or equivalent
7.9. ESI PFA 100 Micro Flow or GE Micro Mist nebulizer with Teflon end cap
7.10. Quartz torch with 2.5 mm injector, Pt shield plate, and quartz bonnet
7.11. 4-place analytical balance, calibration verified daily or before use (see SOPAD013)
7.12. 0.010 to 10mL fixed or adjustable mechanical pipettes, accurate delivery verified (see SOPAD013).
7.13. 15ml polystyrene centrifuge tubes, volume certified

7.14. 50mL polypropylene digestion tubes, volume certified
7.15. Type I water source
7.16. Class A volumetric pipettes and flasks

8.0 REAGENTS & STANDARDS

NOTE: All standards are stored at room temperature in the clean room in plastic bottles. All standards must be prepared in Class A volumetric glassware or volume certified vessels. QS with Type I water. Do not store prepared standards in glass containers.

NOTE: All Class A volumetric flasks should be triple rinsed with Type I water and 1:1 HNO_3 after use. Store clean volumetrics filled with dilute HNO3 and Type I water. Class A pipettes are cleaned using the pipette washer located in the WetChem lab. Pipettes are allowed to air dry before use.

NOTE: Reagents are prepared using graduated cylinders and approximate volumes. Acids and rinse solutions can be stored in glass or plastic containers at room temperature.

NOTE: Document the creation date and time of the working level calibration, CCV, and ICV standards on each respective standard rack. (See CAR 160169)

8.1. Concentrated Nitric Acid (HNO_3), Trace Metal Grade (TMG). Observe Manufacturer expiration date.

8.2. Concentrated Hydrochloric Acid (HCl), Trace Metal Grade (TMG). Observe Manufacturer expiration date.

8.3. Standard stock solutions, ultra high purity grade. Observe manufacturer expiration date.

8.3.1. Aluminum (10,000 mg/L)
8.3.2. Antimony (1000 mg/L)
8.3.3. Arsenic (1000 mg/L)
8.3.4. Barium (1000 mg/L)
8.3.5. Beryllium (1000 mg/L)
8.3.6. Bismuth (1000 mg/L)‡
8.3.7. Boron (1000mg/L)
8.3.8. Cadmium (1000 mg/L)
8.3.9. Cerium (1000mg/L)*†
8.3.10. Cesium (1000mg/L)
8.3.11. Chromium (1000 mg/L)
8.3.12. Cobalt (1000 mg/L)
8.3.13. Copper (1000 mg/L)
8.3.14. Dysprosium (1000mg/L) *
8.3.15. Erbium (1000mg/L)* †
8.3.16. Europium (1000mg/L) *
8.3.17. Gadolinium (1000mg/L) *
8.3.18. Germanium (1000 mg/L) ‡
8.3.19. Holmium (1000mg/L) *
8.3.20. Indium (1000mg/L) ‡
8.3.21. Iron (10,000 mg/L)
8.3.22. Lanthanum (1000mg/L) *
8.3.23. Lead (1000 mg/L)
8.3.24. Lithium (1000mg/L)
8.3.25. Lithium6 ($Li^{+6}_2CO_3$), solid‡
8.3.26. Lutetium (1000mg/L) *
8.3.27. Magnesium (10,000 mg/L)
8.3.28. Manganese (1000 mg/L)
8.3.29. Mercury (1000mg/L)
8.3.30. Molybdenum (1000 mg/L)
8.3.31. Neodymium (1000mg/L) *
8.3.32. Nickel (1000 mg/L)
8.3.33. Praseodymium (1000mg/L) *
8.3.34. Samarium (1000mg/L) *
8.3.35. Scandium (1000 mg/L) * ‡
8.3.36. Selenium (1000 mg/L)
8.3.37. Silver (1000 mg/L)
8.3.38. Tellurium (1000mg/L)
8.3.39. Terbium (1000mg/L) * ‡
8.3.40. Tin (1000mg/L)
8.3.41. Thallium (1000 mg/L)
8.3.42. Thorium (1000mg/L)
8.3.43. Thulium (1000mg/L) *
8.3.44. Uranium (1000 mg/L)
8.3.45. Vanadium (1000 mg/L)
8.3.46. Ytterbium (1000mg/L) *
8.3.47. Yttrium (1000mg/L & 10,000mg/L) *†
8.3.48. Zinc (10,000 mg/L)

**Rare Earth Element (REE)*
†Tune Solution Component

‡*Internal Standard Component*

8.4. Tetra Methyl Ammonium Hydroxide (TMAH), pre-purchased solid. Used for cleaning only. Observe manufacturer expiration date.

8.5. 100 mg/L Li $^{+6}$ solution: Dissolve 0.1262 grams of $Li^{+6}_2 CO_3$ in 100mL Type I water. **Slowly** add 4.0mL of HNO_3 (Li_2CO_3 is slightly reactive) and QS to 200mL. Expires 1 year from prep date or manufacturer's expiration date, whichever is sooner.

8.6. Internal Standard Solution: Expires 1 year from prep date or manufacturer's expiration date, whichever is sooner.

8.6.1. Intermediate ISTD Solution: Add 5 ml HCl, 30mL HNO_3, 10mL each of 1000 mg/L stock solutions of indium and terbium,, 20mL each of 1000 mg/L stock solutions of bismuth, scandium and germanium, and 0.063g of lithium carbonate to a volumetric flask and QS to 1L with Type I water.

8.6.2. Working ISTD Solution for Agilent 7500 & 7900: Add 30mL TMG HNO_3 and 5mL TMG HCl and 100mL of the Intermediate ISTD Solution to a 1L volumetric flask and QS. Final concentrations are listed in §Table 18.1.

8.6.3. Working ISTD Solution for Thermo iCAP RQ: Add 15mL TMG HNO_3 and 2.5mL TMG HCl and 0.5mL of the Intermediate ISTD Solution to a 500mL volumetric flask and QS. Final concentrations are listed in §Table 18.1.

8.6.4. Working ISTD solution for REE analysis: Add 0.050mL of 1000mg/L standard of Bi, In and Ge to 50mL matrix matched water. True values are 1mg/L.

8.7. 200.8/6020 AMU Tune Check Solutions: Expires 1 year from prep date or manufacturer's expiration date, whichever is sooner.

8.7.1. Intermediate AMU Tune Check Solution: Add 2.0mL of HNO_3, 1.0mL each of 1000 mg/L stock solutions of lithium, beryllium, cobalt, indium, thallium and lead, and 0.10mL of 10,000 mg/L stock magnesium solution to a 100mL volumetric flask and QS. True value is 10.0mg/L.

8.7.2. Working AMU Tune Check Solution: Add 10mL HNO_3, 5 ml HCl, and 5.0mL of the intermediate AMU check solution to a 1L volumetric flask and QS. The true value is 0.050mg/L for all elements.

8.8. Instrument Tuning Solution: Expires 1 year from prep date or manufacturer's expiration date, whichever is sooner.

8.8.1. 7500 ICPMS Intermediate Instrument Tuning Solution: Add 30mL HNO3 and 1mL of 1000mg/L stock standards of Li, Co, Y, Ce and Tl to a 1L volumetric flask and QS. True value is 1mg/L.

8.8.2. 7500 ICPMS 10ppb Working Instrument Tuning Solution: Add 30mL HNO_3, 5mL HCl, and 10mL Intermediate Instrument Tuning Solution to a 1L volumetric flask and QS. True value is 10µg/L.

8.8.3. 7900 ICPMS Intermediate Instrument Tuning Solution: Add 1mL HNO3; 0.1mL of each 1000mg/L stock of Be, Ce, Co, In, Pb, Li, and Tl; and 0.01mL of each 10,000mg/L stock of Mg and Y to 100mL flask and QS. True value is 1mg/L.

8.8.4. 7900 ICPMS 50ppb Working Instrument Tuning Solution: Add 1mL HNO3, 0.25mL

HCl, and 2.5mL 7900 ICPMS Intermediate Instrument Tuning Solution to a 50mL tube and QS. True value is 50µg/L.

8.8.5. iCAP RQ ICPMS Intermediate Instrument Tuning Solution: Add 2mL HNO3 and 0.1mL of 1000mg/L stock standards of Ba, Bi, Ce, Co, In, Li, U, Be, Pb, Tl and 0.01mL of 10,000mg/L stock standard of Mg to a 100mL volumetric flask and QS. True value is 1mg/L.

NOTE: The Instrument Tuning Solution for the iCAP RQ also contains all analytes needed for the AMU Tunes.

8.8.6. iCAP RQ ICPMS 1ppb Working Instrument Tuning Solution: Add 10mL HNO3, 2.5mL HCl, and 0.5mL iCAP Intermediate Instrument Tuning Solution to a 500mL volumetric flask and QS. True value is 1ug/L.

8.9. Blank Solutions

8.9.1. Calibration Blank: Matrix-match the calibration blank with the associated samples to be analyzed. Dissolved and total recoverable analyses use 2% HNO3 and 0.5% HCl; Total and soils digestion analyses use 6% HNO3 and 0.5% HCl. Prepared daily.

8.9.2. Laboratory Reagent Blank/Preparation Blank. (LRB – 200.8. PBW – 6020): This sample is the same matrix as the calibration blank and is carried through the same preparation procedure as the samples.

8.9.3. Autosampler Rinse solution for Agilent instruments: 6% HNO3, 0.5% HCl in type 1 water. Autosampler Rinse solution for Thermo instrument: 2% HNO3, 0.5% HCl in type 1 water. Prepare as needed.

8.10. **Routine Analysis:** Multi-element Calibration Standards (See §8.16 – 8.19 for **Hg** standard preparation and §8.20-8.23 for **REE** standard preparation.)

8.10.1. Multi-element Calibration Standard Intermediate Solutions: There are three calibration intermediates. For each intermediate, add 1mL HNO3 and all relative stock standard solutions to a 100mL volumetric flask and QS. See §Table 18.2 for final concentrations. Prepare every 90 days or at manufacturer's expiration date, whichever is sooner.

8.10.2. Working Level Multi-element Calibration Standard: Using the Multi-element Calibration Standard Intermediate Solutions, prepare the working standards **daily** in certified 50mL centrifuge tubes as shown §Table 8.1 below. Document the creation date and time on the standard rack. Working level concentrations are shown in §Table 18.13.

Table 8.1: Multi-Element Working Standards

Standard	Final Vol. (mL)	Acid Volume (mL)	ICPMS Stock #1(mL)	ICPMS Stock #2(mL)	ICPMS Ag/Sb Stock (mL)
Cal Blank	50	Matrix match	-	-	-
L2 (PQV)*	50	Matrix match	*	*	*
L3	50	Matrix match	0.050	0.050	0.050
L4	50	Matrix match	0.250	0.250	0.250
L5	50	Matrix match	0.500	0.500	0.500
* See §8.11		(QS to 50mL with Type I water)			

8.11. Practical Quantitation Verification (PQV)/Level 2 Standard:

NOTE: The Level 2 calibration standard must be at or below the PQL concentration level as listed in §Table 18.13. If a PQL is altered, the concentration of the analyte(s) in the Level 2 calibration standard must reflect this change.

8.11.1. PQV/ L2 intermediate solution: For each intermediate, add 1mL HNO3 and all relative stock standard solutions to a 100mL volumetric flask and QS. See §Table 18.12 for final concentrations. Prepare every 90 days or at manufacturer's expiration date, whichever is sooner.

8.11.2. Working Level PQV/Level 2 standard solution: Add 0.050mL of each intermediate to a 500mL flask. Add appropriate amounts of trace metals grade HNO_3 and HCl acids to matrix match to the calibration standards, and then QS to 500mL. See §Table 18.13 for final concentrations. Prepare every 90 days or at manufacturer's expiration date, whichever is sooner.

8.11.3. For Low Level Analyses (except for ultra-low level Arsenic), add 10mL of the Working Level PQV/Level 2 standard solution (§8.11.2) to a certified 50mL tube and QS with matrix matched water. Use this standard in place of the normal L2 calibration standard when performing Low Level analysis **only**. See §Table 18.17 (Level 2 Std column) for final concentrations. Prepare daily.

8.12. Practical Quantitation Verification Prep Solution (PQVPREP).

8.12.1. PQVPREP As/Se/Cu Intermediate Solution: Add 2.38mL of the 1000mg/L Se stock standard and 0.5mLof the 1000mg/L As stock standard and 1.5mL of the 1000mg/L Cu stock standard and 0.25mL HNO3 to a 50mL volumetric flask. QS to 50mL with Type I water. Final concentration of Se = 47.5mg/L and As = 10mg/L and Cu = 30mg/L. Prepare every 90 days or at manufacturer's expiration date, whichever is sooner.

NOTE: As, Se and Cu are present in the PQV/L2 standard at lower concentrations than is required for the PQVPREP. This intermediate is used to bring the concentrations into the correct range.

8.12.2. Working Level PQVPREP

8.12.2.1. For total and total recoverable drinking water (DW) analyses, add 1mL HNO_3 and 0.020mL of the **PQV/ L2 Intermediate** solution and of the **PQVPREP As/Se/Cu Intermediate** solution to a 200mL flask and QS with Type I water. See §Table 18.10 PQL list for final concentrations. This solution must be prepared using the hot block digestion procedure detailed in SOPII021 before total or total recoverable analysis. This solution is stable for up to 90 days after digestion. Observe the expiration date for the PQV intermediate solutions.

8.12.2.2. For dissolved drinking water (DW) analyses, add 4mL HNO_3,1mL HCl, and 0.020mL of the **PQV/ L2 Intermediate** solution and of the **PQVPREP As/Se/Cu Intermediate** solution to a 200mL flask and QS with Type I water. Prepare daily, as needed.

8.13. Working Level Continuing Calibration Verification standard (CCV): Add 0.250mL of each Multi-element Calibration Intermediate Stock Solution to matrix matched water and QS to 50mL. Prepare standard fresh daily in certified 50mL centrifuge tubes. Document the creation date and time on the standard rack. This solution has the same concentration as the L4 calibration standard. See §Table 18.3 for final concentrations.

8.14. Initial Calibration Verification Solution (ICV): These solutions must be made from stocks that are from a **different source** than the calibration standards.

8.14.1. ICV Intermediate Solution 1 is purchased pre-made from SPEX (or equivalent manufacturer); see §Table 18.14 for concentrations. Expires at the manufacturer specified date.

8.14.2. ICV Intermediate Solutions 2 and 3 are made from individual stock standards; see §Table 18.14 for final concentrations. Expire 90 days from preparation or manufacturers date, whichever is sooner. ICV intermediate solution 2 is preserved with 1mL of HNO_3 to hold parameters in solution. ICV intermediate solution 3 is preserved with 1mL of HNO_3 and 0.1g tartaric acid, which helps hold Sb in solution. As there is little metals testing done on the tartaric acid reagent, when a new bottle is received, a blank solution mixed at the concentration of the analyzed ICV should be run and the results documented in the instrument logbook to check for background contamination of reagent.

8.14.3. Working Level Initial Calibration Verification Solution: Add 0.100mL of each ICV intermediate solution to matrix matched water and QS to 50mL. Prepare standard fresh daily in certified 50mL centrifuge tubes. Document the creation date and time on the standard rack. See §Table 18.3 for final concentrations.

8.15. Spike Solutions. Prepare every 90 days or at manufacturer's expiration date, whichever is sooner.

8.15.1. Spike Intermediate Solutions: Soils and Waters use different spike intermediate solutions; one set for **waters** (§Table 18.4a), and one set for **soils** (§Table 18.4b). A more concentrated version of the intermediate is prepared for soils because all soils digestates are subsequently diluted by a 5x factor prior to analysis. Spike concentrations are then at the same level at the instrument for soils and waters. To make the Spike Intermediate Solutions, add 1mL HNO3 and all relative elements to a 100mL volumetric flask and QS. See §Tables 18.5a and 5b for final concentrations.

8.15.2. Laboratory Fortified Blank, Laboratory Control Sample – Water, Laboratory Fortified Matrix, Analytical Spike and Matrix Spiking solutions (LFB/LFM/AS – 200.8, LCSW/MS/AS – 6020).

8.15.2.1. To make the LFB or LCSW, add 0.250mL of each **waters** spike intermediate solution to 50mL matrix matched water. This sample is carried through the same preparation procedure as the samples. See §Table 18.5a for final concentrations.

8.15.2.2. The LFM/D, AS/D, and MS/D are made by adding 0.250mL of each **waters** spike intermediate solution to 50mL of the analytical sample. The sample is then carried through the same preparation procedure as the samples. See §Table 18.5a for final concentrations.

8.15.2.3. The MS/D for soils digestions ONLY is made by adding 0.250mL of the **soils** Spike Intermediate solution to 50mL of analytical sample. The sample is then carried through the same preparation procedure as the samples. See §Table 18.5b for final concentrations.

8.16. **Hg** Calibration Standards:

8.16.1. **Hg** Calibration Intermediate 1: Add 0.050mL of the 1000mg/L Hg stock standard and 0.5mL TMG HNO_3 and 0.25mL TMG HCl to a 50mL volumetric flask. QS to 50mL with Type I water. Final concentration of Hg = 1mg/L. Prepare every 90 days or at

manufacturer's expiration date, whichever is sooner.

8.16.2. **Hg** Calibration Intermediate 2: Add 1.25mL of Hg Calibration Intermediate 1 and 0.25mL TMG HNO_3 to a 25mL volumetric flask. QS to 25mL with Type I water. Final concentration of Hg = 0.050mg/L. Prepare daily.

8.16.3. Working Level **Hg** Calibration Standard: Using Hg Calibration Intermediate 2, prepare the working standards daily in certified 50mL centrifuge tubes as shown in §Table 8.2 below. Document the creation date and time on the standard rack.

Table 8.2: Hg Working Standards

Standard	Final Volume (mL)	Acid Volume (mL)	Hg Calibration Intermediate 2 (mL)	Final Hg Concentration (mg/L)
Cal Blank	50	Matrix match	-	-
L2 (PQV)	50	Matrix match	0.15	0.00015
L3	50	Matrix match	0.2	0.0002
L4	50	Matrix match	1.0	0.001
L5	50	Matrix match	2.0	0.002
(QS to 50mL with Type I water)				

NOTE: The Level 2 calibration standard must be at or below the PQL concentration level as listed in §Table 18.10.

8.17. Working Level **Hg** Continuing Calibration Verification standard (CCV): Add 1.0mL of **Hg** Calibration Intermediate 2 to matrix matched water and QS to 50mL. Prepare standard fresh daily in certified 50mL centrifuge tubes. Document the creation date and time on the standard rack. Final Hg concentration is 0.001mg/L.

8.18. **Hg** Initial Calibration Verification Solution (ICV): These solutions must be made from stocks that are from a **different source** than the calibration standards.

8.18.1. **Hg** ICV Intermediate Solution 1: Add 0.050mL of the second source 1000mg/L Hg stock standard and 0.5mL TMG HNO3 and 0.25mL TMG HCL to a 50mL volumetric flask. QS to 50mL with Type I water. Final concentration of Hg = 1mg/L. Prepare every 90 days or at manufacturer's expiration date, whichever is sooner.

8.18.2. **Hg** ICV Intermediate 2: Add 1.25mL of Hg ICV Intermediate 1 and 0.25mL TMG HNO3 to a 25mL volumetric flask. QS to 25mL with Type I water. Final concentration of Hg = 0.050mg/L. Prepare daily.

8.18.3. Working Level **Hg** ICV: Add 0.5mL **Hg** ICV Intermediate 2 to matrix matched water and QS to 50mL. Prepare standard fresh daily in certified 50mL centrifuge tubes. Document the creation date and time on the standard rack. Final Hg concentration is 0.0005mg/L.

8.19. **Hg** Working Level Spike Solution: Add 0.100mL **Hg** Calibration Intermediate 2 to 10mL of sample for the AS/D or to 10mL matrix matched water for the LFB. Final Hg Concentration is 0.0005mg/L. Prepare daily.

8.20. **REE** Calibration Standards:

8.20.1. **REE** Calibration Intermediate: Add 0.500mL of each 1000mg/L stock standard listed in §Table 18.18 and 0.5mL TMG HNO_3 to a 50mL volumetric flask. QS to 50mL with Type I water. Final concentration of all REEs = 10mg/L. Prepare every 90 days or at

manufacturer's expiration date, whichever is sooner.

8.20.2. Working Level **REE** Calibration Standard: Using the REE Calibration Intermediate, prepare the working standards daily in certified 50mL centrifuge tubes as shown in §Table 8.3 below. Document the creation date and time on the standard rack.

Table 8.3: REE Working Standards

Standard	Final Volume (mL)	Acid Volume (mL)	REE Calibration Intermediate (mL)	Final REE Concentration (mg/L)
Cal Blank	50	Matrix match	-	-
L2 (PQV)	50	Matrix match	*0.25mL C5 → 50mL*	0.0005
L3	50	Matrix match	0.050	0.010
L4	50	Matrix match	0.25	0.050
L5	50	Matrix match	0.5	0.100
(QS to 50mL with Type I water)				

NOTE: The Level 2 calibration standard must be at or below the PQL concentration level as listed in §Table 18.18.

8.21. Working Level **REE** Continuing Calibration Verification standard (CCV): Add 0.250mL of the REE Calibration Intermediate to matrix matched water and QS to 50mL. Prepare standard fresh daily in certified 50mL centrifuge tubes. Document the creation date and time on the standard rack. Final REE concentration is 0.050mg/L.

8.22. **REE** Initial Calibration Verification Solution (ICV): These solutions must be made from stocks that are from a **different source** than the calibration standards.

8.22.1. **REE** ICV Intermediate Solution is purchased pre-made from SPEX (or equivalent manufacturer). Concentration for all REEs = 10mg/L. Observe manufacturer's expiration date.

8.22.2. Working Level **REE** ICV: Add 0.1mL of the REE ICV Intermediate to matrix matched water and QS to 50mL. Prepare standard fresh daily in certified 50mL centrifuge tubes. Document the creation date and time on the standard rack. Final REE concentration = 0.020mg/L.

8.23. **REE** Working Level Spike Solution: Add 0.020mL of the REE ICV Intermediate Solution to 10mL of sample for the AS/D, LFM/D, or MS/D or to 10mL matrix matched water for the LFB or LCSW. Final REE Concentration = 0.020mg/L. Prepare daily.

8.24. **Arsenic-Low Level** working level standards and QC. Prepare daily in 50mL volume certified tubes. Document the creation date and time on the standard rack.

8.24.1. 20mg/L As-LL calibration int 1: Add 1mL 1000mg/L As stock solution and 0.5mL TMG HNO3 acid to a 50mL certified tube. QS to 50m with Type I water. Or, use the existing multi-element calibration intermediates (as described in §8.10).

8.24.2. Add 0.050mL of the existing **multi-element calibration int 1 (**§Table 18.2) to a 50mL certified tube. QS to 50mL with matrix matched water. This is the Level 5 calibration std. As concentration is 0.020mg/L.

8.24.3. Add 0.025mL of the existing **multi-element calibration int 1 (**§Table 18.2) to a 50mL certified tube. QS to 50mL with matrix matched water. This is the CCV and Level 4

calibration std. As concentration is 0.010mg/L.

8.24.4. Add 5mL of the prepared solution from 8.24.2 to a 50mL certified tube. QS to 50mL with matrix matched water. This is the Level 3 calibration std. As concentration is 0.002mg/L.

8.24.5. Add 0.25mL of the prepared solution from 8.24.2 to a 50mL certified tube. QS to 50mL with matrix matched water. This is the PQL and Level 2 calibration std. As concentration is 0.0001mg/L.

8.24.6. Add 0.010mL of the second source multi-element ICV solution (See §8.14) to a 50mL certified tube. QS to 50mL with matrix matched water. This is the ICV, As concentration is 0.005mg/L.

8.24.7. Low level As LFB/Spike: Add 0.010mL of the waters spike int (See §8.15) to a 10mL sample tube. QS to 10mL with sample (for spikes) or with matrix matched diluent (LFB). As concentration is 0.010mg/L.

8.25. Interference Check solutions (ICS-A, ICS-AB – 6020/6020B). Observe manufacturer expiration date.

8.25.1. The ICS-A solution is prepared by adding 0.5mL of the SPEX Certified Interferant A standard (or equivalent) to matrix matched water, and QS to 10mL. Prepare fresh daily.

8.25.2. The ICS-AB solution is prepared adding 0.5mL of the SPEX Certified Interferant A standard, 0.020mL of the **waters** multi-element spike intermediate and 0.050mL of the **waters** Ag/Sb spike intermediate to matrix matched water, and QS to 10mL. See §Table 18.6 for final concentrations. Prepare daily.

8.26. Upper Linear Range Verification (ULRV) QC Sample. Add **1.0**mL of each Multi-Element Calibration Intermediate (§8.10) to a 15mL sample tube. QS with matrix matched water to 10mL. Prepare daily as needed. See Table 18.20.

8.27. Detectability Check Standard (DCS) QC Sample. This QC sample is to be used only for samples logged in under the Texas Risk Reduction Program (TRRP).

8.27.1. Working Level DCS: Add 1mL HNO_3 and 0.025mL of each PQV/ L2 intermediate solution to a 500mL flask and QS with Type I water. See the §Table 18.21 for final concentrations. This solution must be processed using applicable preparation procedures (e.g. hot block digestion, GeoChem extraction procedures, etc.) before analysis. Prepare daily as needed.

8.27.2. For X-MS-3050 digestions, a 5X concentrate should be prepared. Add 0.025mL of each PQV/ L2 intermediate solution to a **100mL** flask and QS with Type I water. This solution is carried through the 3050 digestion procedure and diluted 5X at the bench along with all other 3050 samples and QC. See §Table 18.21 for concentrations after 5X bench dilution.

8.28. Sample introduction cleaning solutions. Observe manufacturer expiration dates.

8.28.1. 1% TMAH: Dissolve ~0.5g Tetra Methyl Ammonium Hydroxide (TMAH) in 50mL water.

8.28.2. 30% HCl: In a fume hood, add 15ml TMG HCl to 35ml water.

9.0 SAFETY

9.1 HAZARDS

This procedure does not propose to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous.

9.2 SAFETY TECHNIQUE

9.2.1 Safety glasses are required and the use of gloves and lab coat is strongly recommended. Shorts and open-toed shoes are not allowed in the lab.

9.2.2 Always use care when working on the instrument as many parts can be hot.

9.2.3 Use care when pouring and pipetting reagents. Always add acid to water. Use caution when washing glassware.

9.2.4 Do not eat or use tobacco products in the lab.

9.2.5 Wipe up ALL spills immediately. Implement the Emergency Response Plan if necessary. See SOPAD006.

9.2.6 Do not wear gloves or lab coat outside of the laboratory. Remove gloves before using a computer, telephone, etc.

9.3 PROTECTIVE EQUIPMENT

9.3.1 Use a fume hood when there is a potential for strong fumes, and when acidifying any samples.

9.3.2 A fire extinguisher is located in each analytical laboratory.

9.3.3 An eye wash station is located next to the sonicator in the gowning room.

9.3.4 An emergency shower and eye wash station are located in the metals prep lab.

10.0 INTERFERENCES

Interferences in ICP-MS can be minimized by several different methods, including the use of interference equations, internal standard correction, collision/reaction cell (CRC) technology, and matrix matching. See below for further details on minimizing interferences.

10.1 Polyatomic Interference

10.1.1 Polyatomic ions are the main source of interference in ICPMS analysis. When two elements combine to form a single molecule, their mass may mimic that of an analyte of interest, thus causing a positive interference, or false positive result. The Agilent ICPMS uses either a collision/reaction cell or an interference equation to minimize these interferences. The two modes of collision cell operation, H_2 and He, each operate under different principles to help eliminate polyatomic interferences.

NOTE: At this point, the EPA does not allow the use of the He collision cell or H2 reaction cell for analysis of drinking water (DW) samples by method 200.8. Interference equations must be used in place of the collision/reaction cell.

10.1.1.1 For elements that are subject to interferences that originate in the Argon plasma

(e.g. [^{38}Ar ^{40}Ar] on ^{78}Se and [^{40}Ca^{16}O] on ^{56}Fe) the hydrogen mode is employed. The interferences in this mode are reacted away by protonation before entering the mass filter region. For example, [^{38}Ar ^{40}Ar] + H_2 → 2ArH. The H_2 reaction effectively eliminates the Ar interference and only ^{78}Se or is measured by the detector. For DW analysis by method 200.8, interference equations are used to minimize the interference on Se. Fe cannot be analyzed for DW analysis. See §Table 18.7 for interference equations.

10.1.1.2 For polyatomic interferences that originate in the sample matrix (e.g. [^{35}Cl^{16}O] on ^{51}V, [^{40}Ar^{12}C] on ^{52}Cr, [^{23}Na^{40}Ar] on ^{63}Cu, [^{40}Ar^{35}Cl] on ^{75}As, etc.) the He mode may be utilized. The polyatomic complexes have greater cross sectional areas than the elements of interest, and thus repeated collisions with the He atoms reduce their kinetic energy so that they are not able to reach the detector. This process is known as *kinetic energy discrimination*. For DW analysis by method 200.8, interference equations are used to minimize these interferences. See §Table 18.7 for interference equations.

10.2 Isobaric Elemental Interference

10.2.1 Isobaric interference is caused by isotopes of different elements with the same mass as an analyte of interest, and cannot be resolved by the mass spectrometer. A correction equation based on known natural abundance ratios of interfering elements is used to find the proportion of the interfering isotope on the mass of interest by comparing it to another known isotope. For example, ^{98}Ru interferes with ^{98}Mo. By measuring the amount of ^{99}Ru and using the known natural abundance ratio, all available ^{98}Ru can be subtracted, eliminating the false positive on ^{98}Mo. See §Table 18.7 for correction equations.

10.3 Physical Interference

10.3.1 These interferences are associated with the sample nebulization and transport processes, sample ionization processes in the plasma, and the transmission of ions through the plasma-mass spectrometer interface. These interferences may result in differences in instrument response between the calibration standards and the samples. Differences in matrix components, TDS, viscosity, and/or pH between samples and standards can cause a wide range of physical interferences. Internal standard correction is used to minimize these differences. The internal standards respond to such suppressions or enhancements similarly to the elements being analyzed and are chosen to bracket the mass range and ionization potential of the analytes. See §13.1 for equations used for internal standard correction, and §Table 18.15 for internal standard selection guidelines.

10.3.2 High TDS samples have also been shown to cause interference and instrument drift due to salt buildup in the nebulizer or on the sample and skimmer cones. The methods specify that overall sample TDS be restricted to 2000 mg/L and standards and samples be matrix matched to minimize these problems. Samples containing more than 2000mg/L TDS should be diluted accordingly.

10.4 Memory Interferences

10.4.1 These result when samples or standards with high concentrations of analytes are analyzed, and there is residual analyte left in the system after the normal rinse period. Sample components may be deposited on sample and skimmer cones, in the spray chamber, or in the nebulizer, and may leach back in to the system over time. Whenever a high concentration sample is analyzed, care must be taken to assure that sufficient rinse time is used between the high concentration sample and the sample analyzed immediately afterward. During analysis, if a memory effect is observed (i.e. when replicate signals

drop consecutively, evidenced by high %RSD on analytes) the analyst is to examine the previous sample concentration. The high concentration sample may require dilution and reanalysis. The sample showing the memory effect should be analyzed on its original dilution and the replicate signals observed for consistency.

11.0 PROCEDURES

11.1 Weekly Instrument Maintenance: See §4 of the Agilent Hardware Manual, the Agilent 7900 MassHunter Help index, or the Thermo iCAP Operating Manual for more details.

11.1.1. Sampling and skimmer cones: The sampling and skimmer cones should be cleaned when the sensitivity of the instrument decreases below an acceptable level or the internal standard recoveries abruptly decrease during an analytical run.

11.1.1.1. If the cones need cleaning, sonicate in Type I water for 10 minutes. Rinse thoroughly and air dry before using. Sonicate the cones in a 1% HNO3 solution for 10 minutes for deep cleaning as needed. If the orifices of the cones are in poor condition (use a magnifying glass to inspect), or if there are sensitivity or stability issues, replace the cones. Check the sampler cone o-ring (7500) or graphite gasket (7900) when reinstalling the cones. If the o-ring or gasket is visibly cracked, discolored or is “flat spotted,” replace it.

11.1.2. Nebulizers: Backpressure should be <400Kpa for routine analysis (view in instrument control ‘monitors’). A nebulizer in poor condition can affect the sensitivity, stability, and background levels.

11.1.2.1. PFA-type: Do not backflush PFA-type nebulizers as this may damage the internals. Sonicating the nebulizer may free some obstructions. If the nebulizer is in need of a thorough cleaning it should be sent to the manufacturer (ESI Inc.) for service.

11.1.2.2. MicroMist: Use care when cleaning and handling the quartz glass MicroMist nebulizer, breakage of the gas arm or orifice may occur. The nebulizer may be backflushed using a syringe or Eluo™ cleaner to free obstructions. The nebulizer can also be soaked or gently boiled in a 5% solution of FLUKA™. If the nebulizer is broken it may be repairable; send to a glass repair service such as Precision Glassblowing.

11.1.3. Sample Introduction Tubing: Peristaltic tubing should be replaced as needed. The ISIS and ISTD tubing generally last 1-2 weeks, the sample tubing lasts 2-3 days, and the waste tubing should be inspected monthly. If high %RSD or unstable ISTD recoveries are noticed, tubing should be replaced.

11.1.3.1. If there are memory effects for Ag, B, Hg, or other problem elements, the Teflon sample introduction tubing and connector Ts should be cleaned. **With the nebulizer removed from the spray chamber**, pump approx. 20mL of 1% TMAH solution, followed by 20mL 30% HCl solution, followed by 20mL of standard HNO3/HCl rinse solution through the sample introduction system from the autosampler.

11.1.4. Roughing pumps: Open the ballast valve on top of the roughing pumps for 5 minutes once a week to let the oil drain from the mist filter housing back into the pump manifold (7500 only).

11.2. Monthly Maintenance (Refer to Agilent 7500 ICP/MS Hardware Manual §4 Maintenance, Agilent 7900 MassHunter Help index, or Thermo iCAP Operating Manual).

11.2.1. Sample Introduction Glassware (Spray chamber, torch and ball joint connector): If the glassware looks cloudy, it is time for cleaning.

11.2.1.1. Rinse the glassware with 1:1 HNO3 and 1:1 HCl, followed by Type I water. If deposits do not dissolve easily, soak the glassware in a 5% ChemSolv solution for several hours. Rinse thoroughly and air dry before reinstalling the glassware.

11.2.2. Extraction lenses: These are the first components in the ion lens system and may acquire some matrix deposits during use. The lenses need to be inspected on a monthly or as needed basis to ensure that the ions will be transported properly.

11.2.2.1. When the extraction lenses require cleaning it will be observed when tuning the instrument. The signal will respond less to a given voltage change when the lenses are dirty. Clean the extraction lenses according to the Agilent 7500 ICP/MS Hardware Manual (refer to §4 Maintenance; also applicable to 7900 ICPMS).

11.2.3. Roughing Pump: The oil level and oil mist filters need to be checked for proper functioning of the roughing pumps. Change oil when it starts to change from a red color to black, or about every 3 months. Inspect mist and odor filters on an annual basis (7500 only).

11.2.4 Chiller: Each ICPMS uses a refrigerated chiller to pump cooling water to the instrument.

11.2.4.1 Check the water level at the reservoir; add de-ionized water if the system is low.

11.2.4.2 The in-line yarn filter can be visually inspected on the 7500 chillers. The 7900 has a ‘sock’-type filter accessible under the reservoir lid. When the in-line yarn filter looks discolored it should be changed. The ‘sock’-type filter can be rinsed or cleaned with soapy water and replaced.

11.2.4.3 The fiberglass mesh air filter in front of the cooling fins should be rinsed with water to remove dust accumulation (7500 only). If the dirt does not come off, cut a new filter from the stock material.

11.2.4.4 The cooling water should be drained from the system annually and replaced with de-ionized (NOT Type I) water.

NOTES: The ICPMS software will prompt the user when run times have been met on the instrument for maintenance items. These parameters should be checked and the associated maintenance performed as listed in the help manuals.

Many of the maintenance items listed need to be performed using the analyst’s discretion, not solely based on elapsed time. If instrument performance is poor, the analyst is responsible for taking the proper steps to fix the problem.

11.3. Instrument Setup & Tuning: **7500 ICPMS**

11.3.1. Begin by opening the Agilent ICPMS Top icon on the desktop (See §Fig 1).

Fig. 1

11.3.2. Click on the Instrument Control icon located at the top left corner of the screen (§Fig. 2). This brings up the instrument control with a graphic representation of the ICPMS instrument and selected meters for instrument parameters. Perform any necessary maintenance before continuing.

Fig. 2

11.3.2.1. Check that the instrument is in "Standby" mode. If not, turn the vacuum on and wait for the instrument to reach standby mode. Make sure the drain reservoirs are empty and that the pump tubing is connected correctly. See §3 in the Agilent Hardware Manual.

11.3.3. Ignite Plasma: Click on the PLASMA IGNITE icon (§Fig. 3). The instrument will begin the automated purge and ignition procedure. Watch the torch box area as the plasma ignites. If there is a 'popping' sound or the torch begins to glow red, open the torch box cover immediately to prevent glassware damage.

Fig. 3

11.3.4. Tuning for Routine Analysis: When the instrument has warmed up for approximately 20 minutes tuning may begin. Select the Instrument Tune icon (§Fig. 4):

Fig. 4

11.3.4.1. Send the autosampler probe to the 10ppb Instrument Tuning Solution vial. Wait for the tuning solution to reach the instrument.

11.3.4.1.1. Go to 'File' and 'Load tune file'. Select the norm.u tune file. Adjust the parameters (see §**Appendix A** for guidelines) until the sensitivity of the monitored masses are at acceptable levels.

NOTE: The sensitivities must be above the minimum levels described in the Agilent Technologies document §12.2 (See §5.9 in this SOP):

- Li7 > 5000cps/10ppb
- Y89 > 10,000cps/10ppb
- Tl205 > 5000cps/10ppb

If levels are below these minimum criteria perform instrument maintenance before analyzing client samples.

11.3.4.1.2. Next, select the h2.u tune file. Adjust the appropriate parameters (see §**Appendix B** for guidelines).

11.3.4.1.3. Next, select the He.u tune file. Adjust the appropriate parameters (see §**Appendix C** for guidelines).

11.3.4.1.4. Save each tune mode after the parameters are set.

11.3.4.2. When the sensitivity of the monitored masses is at an acceptable level, print an electronic copy of the tune screen (stop tuning, click file → print). Store the files in the C:/sensitivity tunes/ folder. These files will be archived by IDBA and can be used for instrument maintenance checks, training purposes, etc.

11.3.4.3. A sensitivity tune should be performed at least once per week if the instrument is running on a daily basis.

11.3.5. Setting the P/A factors: The P/A factors should be set after the sensitivity tuning procedure. These factors govern the linearity between the **P**ulse (low response) and **A**nalog (high response) modes of the detector. If these are not set regularly the calibration curves may lose linearity.

11.3.5.1. To set the P/A factors, bring down the *Tune* menu in the Instrument Tune window (see §fig 10) and select *P/A Factor*.

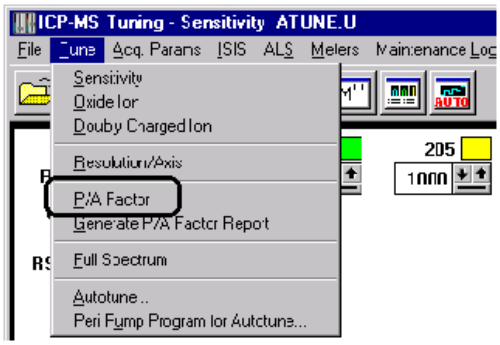


Fig. 10

11.3.5.2. Send the autosampler to the Level 3 cal std. Click on *Run* (§Fig 11 (2)).

11.3.5.3. After level 3 cal std P/A, send the autosampler to level 5 cal std and run another P/A factor. Merge the first and second P/A factor reports by clicking the radio button (§Fig 11 (3)) in the P/A factor tuning window.

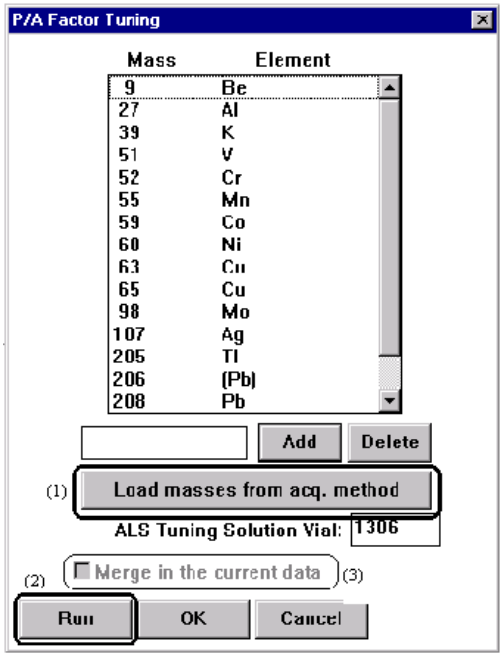


Fig. 11

11.3.5.4. Click *File* → *Print* and save a copy of the PA factor report to the C:/PA Factor/ folder for future reference. The PA factor report also contains the operating voltages for the detector which may be useful for estimating the remaining lifetime of the detector.

11.4. Instrument Setup & Tuning: **7900 ICPMS**

11.4.1. Begin by opening the Agilent MassHunter software icon  on the desktop.

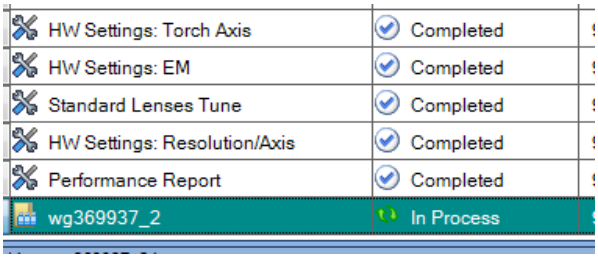
11.4.2. Perform any necessary maintenance before startup; empty drain reservoirs; turn on the chiller and tighten peristaltic pump clamps.

11.4.3. On the MassHunter main panel, click the Plasma icon  and select *Plasma On.*

11.4.4. The instrument will go through an argon purge procedure and the plasma will ignite automatically. The software will then start a 16 minute warm up timer before any analysis or tuning can begin.

11.4.5. After the warm up timer is complete, the instrument goes into a pre-programmed startup routine. The routine can be monitored by clicking the Queue button on the main panel, and checking the status of each step (Completed or In Process).

11.4.6. The startup routine optimizes: the torch position, electron multiplier voltage settings, ion lens tune, and quadrupole resolution & axis settings. The last step in the routine is the Performance Report, which runs the Agilent 7900 ICPMS 50ppb tune solution. The results from this report are stored in the software.

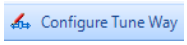


11.4.7. Tuning for Routine Analysis: The analyst may now tune the instrument for sensitivity and oxide levels. Sensitivities can be checked monthly if instrument performance has been acceptable.

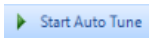
11.4.7.1. Begin by clicking on the Batch icon: 

11.4.7.2. Click *File*, *Open Batch from Template*, and select *Stune.ICPMS.Template.* When prompted save the file as *Stune[date code]*. To autotune (recommended) see §11.4.7.3. To tune manually see §11.4.7.11.

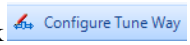
11.4.7.3. To use Autotune (recommended): Click *File, Import from Existing Batch,* and select the most recent *Stune[date code].* Import the tune mode when prompted.

11.4.7.4. Click on the 

button, and select the *Autotune* option. When the software asks *All Parameters will be reset?,* click OK. Choose *Low Matrix* from the plasma parameters list.

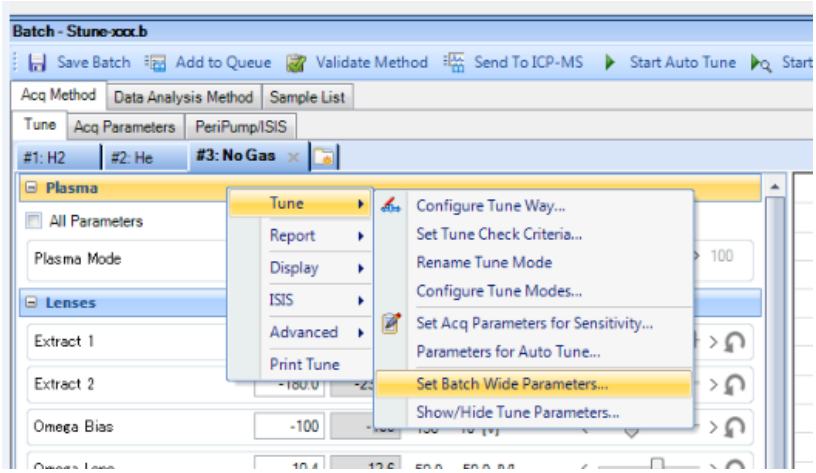
11.4.7.5. Next, click the 

button. Click OK to select *All Tune Modes*. The instrument will now go through the autotune procedure. This may take several minutes.

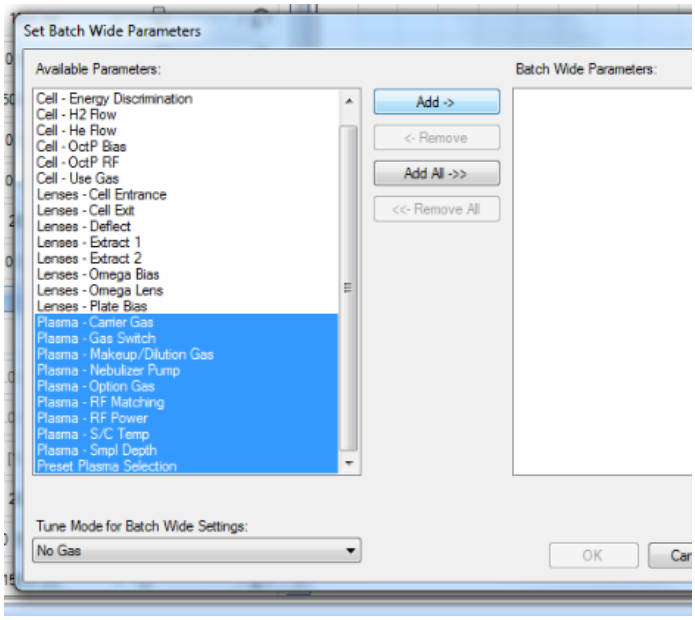
11.4.7.6. After autotune completes, click 

again, and select the *Custom Tune* option.

11.4.7.7. Now, find the Plasma header (see screen shot below), and check the *All Parameters* box. Next, right click in the Plasma header, select *Tune, Set Batch Wide Parameters.*



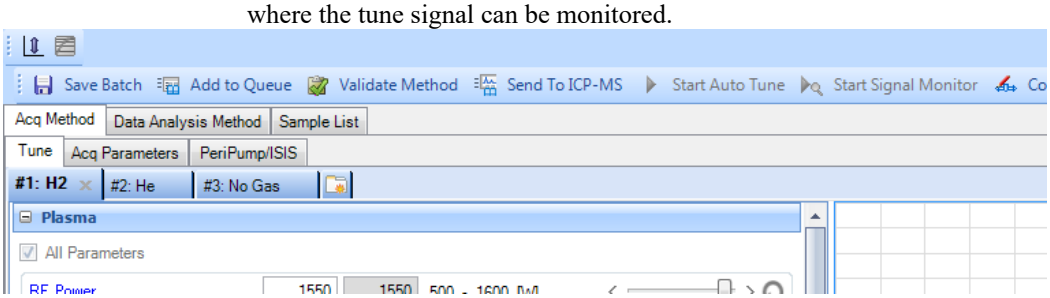
11.4.7.8. Choose all of the *Plasma* parameters, and →*Add* them to the *Batch Wide Parameters* list (see screen shot below). Click *OK*.



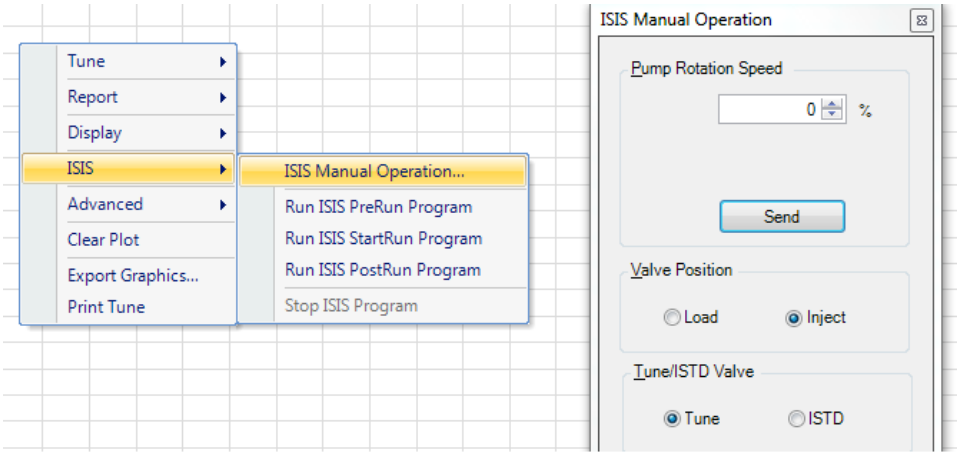
11.4.7.9. In the Plasma section of the tune screen, reset *Carrier Gas* to ~0.80L/min, and the *Make Up Gas* to ~0.20L/min. In the *H2* tab, reset the H2 gas flow to ~5.0mL/min and the *Deflect* to -2.0V; and in the *He* tab reset the Helium flow to ~4.3mL/min and the *Deflect* to -2.0V.

11.4.7.10. Save the tune when complete. To check the sensitivities after autotune and print a report, see §11.4.7.13.

11.4.7.11. **To tune manually:** On the main screen, click the *Acq Method* tab, *Tune* tab, and *#3: No Gas* tab. This will display a graph on the right side of the screen where the tune signal can be monitored.



11.4.7.12. Right click on the grid area, select *ISIS* → *Manual Operation*. On the ISIS window click the radio buttons for *Inject* and *Tune*. The instrument is now set up to run the 10ppb tune solution through the ISIS valve to the nebulizer.



11.4.7.13. Click Start Signal Monitor to start tuning. Use the MassHunter help guide to adjust parameters for optimum sensitivity and oxide levels.

11.4.7.14. After tuning levels are optimized right click on the chart, select *Report → Print Current Signal*. Save pdf files in the C:\sensitivity tune\ folder. These files will be archived by IDBA and can be used for instrument maintenance checks, training purposes, etc.

11.4.7.15. The sensitivities must be above minimum levels in order to continue with analysis. (Sensitivities on the 7900 are measure in counts per 0.1s, instead counts per second as on the 7500 ICPMS):

- Li7 > 1000counts/0.1s
- Y89 > 10,000counts/0.1s
- Tl205 > 5000counts/0.1s
- Oxides 156/140 < 1 %

If levels do not meet these minimum criteria perform instrument maintenance before analyzing client samples.

11.4.7.16. Next, select the *#2 He tab*. Adjust the appropriate parameters.

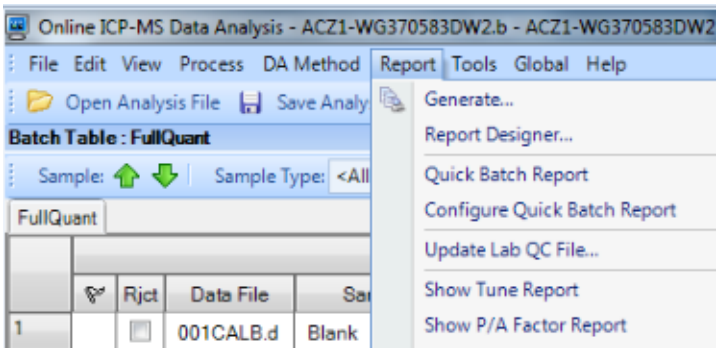
- Co59 > 2500counts/0.1s
- Mass 75 <20counts/0.1s
- Mass 51 <100counts/0.1s

11.4.7.17. Last, select the *#1 H2 tab*. Adjust the appropriate parameters.

- Y89 > 5000counts/0.1s
- Mass 78 < 5counts/0.1s
- Mass 56 <100 counts/0.1s

11.4.7.18. Click Save Batch. Refer to this batch (*Stune[date code]*) when creating subsequent analytical batches (see §11.7.4).

11.4.8. P/A factors are set automatically by the 7900 during each calibration. They do not need to be set manually after tuning. A P/A factor may be viewed by opening Offline MassHunter, and clicking *Report → Show P/A Factor.*



11.5. Instrument setup and tuning: **iCAP RQ ICPMS**

11.5.1. Begin by opening the Thermo Instrument Control software icon 

on the desktop.

11.5.2. Perform any necessary maintenance before startup; empty drain reservoir, turn on the chiller, and tighten peristaltic pump clamps.

11.5.3. Ignite plasma: Click the 'On' icon 

. The instrument will begin the automated purge and ignition procedure. Watch the torch box area as the plasma ignites. If there is a 'popping' sound or the torch begins to glow red, open the torch box cover immediately to prevent glassware damage.

11.5.4. When the instrument has warmed up for 20-30 minutes, a daily performance report may be run. This report will also contain the daily AMU tunes.

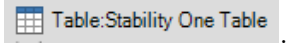
11.5.4.1. Place both the carrier and ISTD probes into the 1ppb working tune solution. Wait for the solution to reach the instrument through both lines.

11.5.4.2. Click the Performance Report icon 

. Select 'Run an existing Performance report' and click next.

11.5.4.3. Select 'Daily AMU' from the list and click next. The instrument will run a sensitivity & stability test, a mass calibration test, and will check the vacuum. When finished, select 'view report' and click next.

11.5.4.4. If the daily performance report indicates that all tests are passing, no tuning is needed and analysis of samples may proceed. All past and current performance reports may be viewed from the 'Performance Report' icon on the Views tab.


11.5.4.5. The daily AMU tunes are included within the performance report. To change the masses displayed in the 'Stability' table (representing the %RSD), open the report from the File Manager in Qtegra. Click 'Edit Report'. Select the 'Stability One Table' from the left hand menu 

. Open the drop

down 'Condition' menu and select the desired masses (7Li, 9Be, 24Mg, 59Co, 115In , 205Tl, 208Pb). Click the 'Execute Report' icon  . The report may now be saved as a PDF file.

11.5.5. Tuning for routine analysis: If any parameters in the daily performance report are failing, tuning may be needed.

11.5.5.1. Place both the carrier and ISTD probes into the 1ppb tune solution. Wait for the solution to reach the instrument through both lines.

11.5.5.2. Select the desired measurement mode (STD, KED, or KEDH).

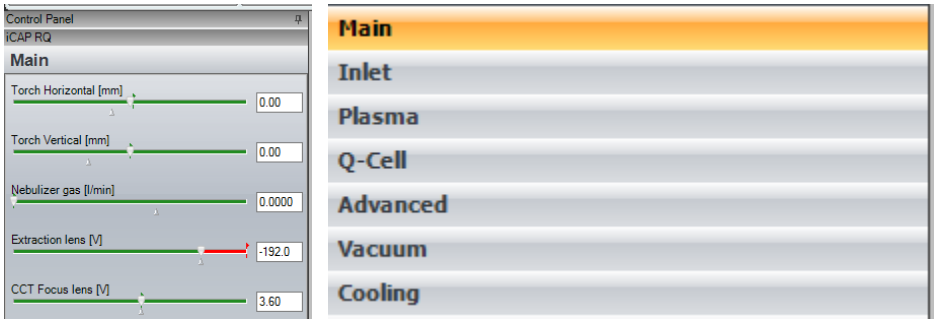
11.5.5.3. **To use Autotune**: Click the Autotune icon 

. Proceed through the steps as directed. **NOTE**: Autotune is recommended for STD mode only. KED and KEDH should be tuned manually.

11.5.5.4. If the mass calibration test is failing, a mass calibration tune may be performed. Place both the carrier and ISTD probes into the iCAP CALIBRATION solution and wait for the solution to reach the instrument through both lines. Click the Mass Calibration icon and proceed through the steps as directed.

11.5.5.5. If new P/A factors (also called "Cross Calibration") need to be applied, a detector setup tune may be performed. Place both the carrier and ISTD probes into the iCAP CALIBRATION solution and wait for the solution to reach the instrument through both lines. Click the Detector Setup icon, choose 'Detector Cross Calibration', and proceed through the steps as directed.

11.5.5.6. **To tune manually**: Parameters may be adjusted using the Control Panel on the left side of the Instrument Control window. Use the 'Run', 'Stop', and 'Restart' buttons to toggle the display of the tune signal. See §Appendix D for guidelines.



11.5.5.7. The following parameters should be evaluated when tuning STD mode:

- Li7 > 50,000 CPS
- U238 > 330,000 CPS
- Doubly charged 137++/137 <5%
- Oxides 156/140 < 3%

11.5.5.8. The following parameters should be evaluated when tuning KED mode:

- Co59 > 30,000 CPS
- KED Ratio >18

11.5.5.9. The following parameters should be evaluated when tuning KEDH mode:

- Co59 >30,000 CPS
- As75 < 100 CPS
- Se78 <100 CPS

11.5.5.10. To adjust collision cell gas flows in KED or KEDH mode, select the desired mode from the drop-down menu in the Measurement Mode window. Click on the 'Q-Cell' tab in the Control Panel. Adjust the appropriate gas (Collision gas 1 is He, Collision gas 2 is H_2) to the desired level.

11.5.5.11. See §Appendix D for additional guidelines on manual tune settings.

11.6. Generation and preparation of a workgroup for analysis.

11.6.1. Select the templates and samples of interest in LIMS and generate a workgroup for analysis. Print the bench sheet and include a standard/reagent form.

11.6.2. Label all 15ml auto sampler tubes with the sample ID and dilution factor.

11.6.3. For dissolved analyses add 0.050mL of each **waters** spike intermediate; 0.100mL of **Hg** Cal Int 2 for WGs requesting Hg; or 0.020mL of the **REE** ICV Int. for WGs requesting REEsto tubes labeled LFB or AS/D. QS to 10mL with a 2-10mL pipette using diluents (LFB) or client sample (AS/D).

11.6.4. Fill each remaining tube to approximately 10ml with sample. If a dilution is needed, add the correct aliquot of sample to an empty tube (i.e. 1ml for a 10x dilution), and QS to 10mL with matrix matched diluent using a 2-10ml calibrated pipette.

NOTE: It is not acceptable to use squirt bottles, transfer pipettes, etc. to QS the sample dilutions. Only calibrated pipettes may be used. See CAR875.

11.6.5. Record any modified dilution factors along with a comment ("organic odor," "high TDS," "color," etc.) on the WG bench sheet, and initial & date changes.

11.6.6. Transfer the sample tubes to the auto sampler rack.

11.7. Creating and running a sequence: **7500 ICPMS**

11.7.1. Open the Sequence Editor 

and select an appropriate template based on sample matrix and method. The correct calibration and analytical run QC for each method is pre-entered into the template sequences.

11.7.2. Double click on the CALIB option under sequence flow (§Fig. 14). Double click in the method column and choose an appropriate method from the list:

- ACZ.m for routine analysis of methods 200.8 or 6020/6020B
- DW.m must be used for any WGs containing Drinking Water samples
- HG.m for Hg by 200.8 analysis
- REE.m for Rare Earth Element analysis
- LowLevel.m for low level analyses

11.7.3. Next, double click on the SMPL option under sequence flow (§Fig. 14).

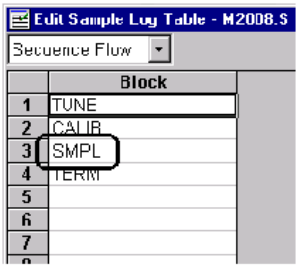


Fig. 14

11.6.3.1. Use the input file created by LIMS to upload the sample list to the Sequence Editor. Place the cursor in the top left-hand cell of the Sequence Editor spreadsheet and right click. Select *Load List from .CSV file* (§Fig. 15). The input file can be found in U:\input\icpms\WG*.

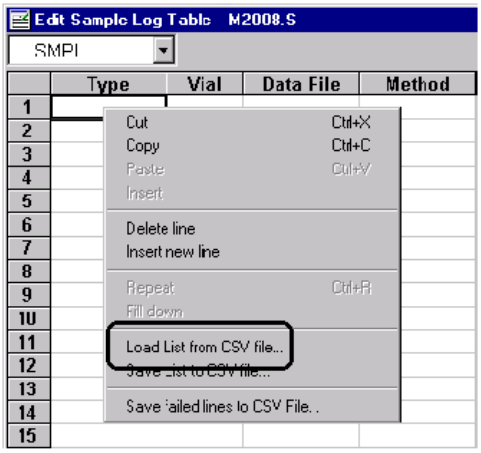


Fig. 15

11.6.3.2. Insert any updated dilution factors from the bench sheet, the appropriate method for sample analysis, and the correct sample vial locations.

11.6.3.3. When editing of the sequence is complete, save it as the associated workgroup number.

11.7.4. A chained sequence will allow the user to run single or multiple workgroups. First, all of the workgroups to be analyzed need to be created as sequences as listed in §11.6.

11.6.5.1. Click on the *Chained Sequence* menu (§Fig. 16) in ICPMS Top. Select *Edit and Run.*

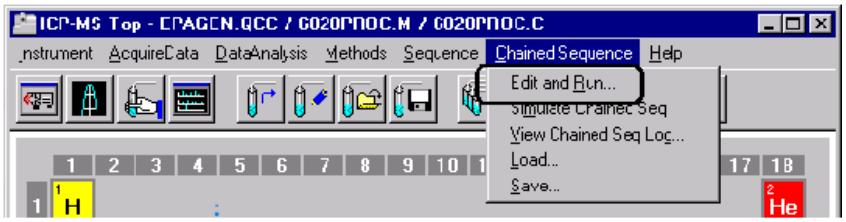


Fig. 16

11.6.5.2. Double click on the cell in the first column in row 1 (§Fig. 17) to select the desired sequence to be analyzed first in the series. Double click on the cell in the

second column in row 1 (titled *Data Batch*) and enter the data path for the analysis. Save all data to C:\ICPCHEM\1\data\WG#. Double click in the third column (titled *Tune File*), select the tune file *norm.u*.

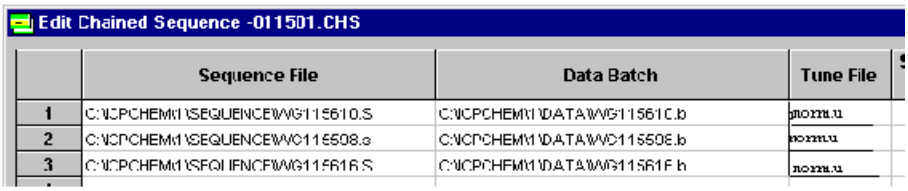


Fig. 17

11.6.5.3. Once per 24 hours, run the 200.8/6020 AMU tune checks and make sure that they are passing (see §Table 18.9 for criteria). Open the proper sequence file (i.e. *2008tune*), and save with the following format: YYMMDDat, YYMMDDbt, etc. These can be run any time within 24 hours of client samples as long as changes are not made to the detector or quadrupole parameters.

11.6.5.4. Repeat this process until all of the workgroups to be analyzed are entered into the chained sequence. If the instrument should shut down after the last WG, select 'standby' as the last sequence.

11.6.6 Make sure that the all rinse cups are topped off, standard cups are uncapped and that the sample vials are in the correct locations. Click on *Run* in the Chained Sequence screen and calibration and analysis will begin.

11.8. Creating and running a batch: **7900 ICPMS**

11.8.1. Click on the 

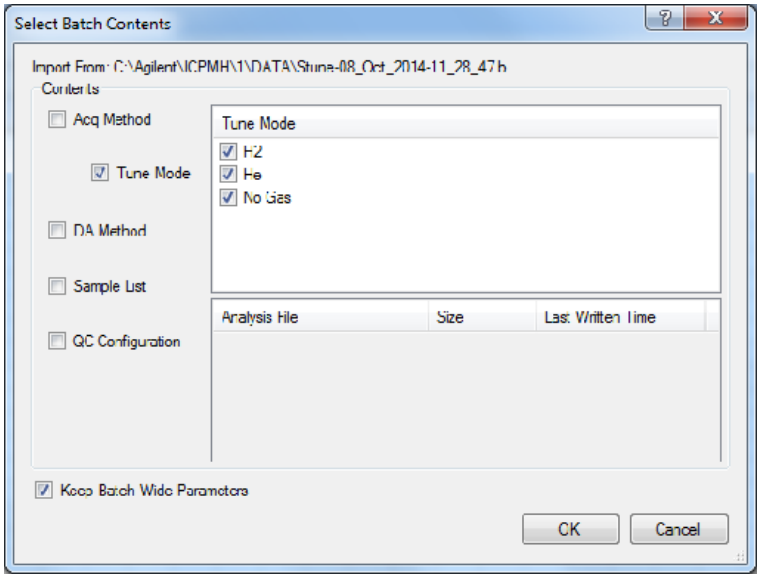
icon to start a new batch. Each batch contains pre-assigned calibration and QC samples.

11.8.2. Click *File → Open Batch from Template*. Select the desired template based on the type of WG that will be run.

- *ACZ2%.ICPMS.template* (2% HNO3 matrix, normal list)
- *ACZ6%.ICPMS.template* (6% HNO3 matrix, normal list)
- *ACZ_DW.ICPMS.template* (For DW matrix samples)
- *ACZ_HG.ICPMS.template* (Hg analysis)
- *2008tune.ICPMS.template* (For daily 200.8 AMU check tune)
- *6020tune.ICPMS.template* (For daily 6020/6020B AMU check tune)

11.8.3. When prompted, save the file as the WG# or as the software generated date code for daily tunes (example: *2008tune-19_Sep_2014-11_13_48.b*).

11.8.4. Next the instrument tune parameters need to be set. Click *File → Import from Existing Batch*. Select the S*tune[date code]* batch created in §11.4.7.10. Import **only** the *Tune Mode* section.



11.8.5. To import the sample input file from LIMS, click Import Sample List in the batch screen. Select the WG# from the U:\Input\ICPMS\ folder.

11.8.6. In the *Sample* List tab, assign the proper location of the samples in the *Vial #* column. If any dilution factors were changed at the bench, update them in the *Dilution* column.

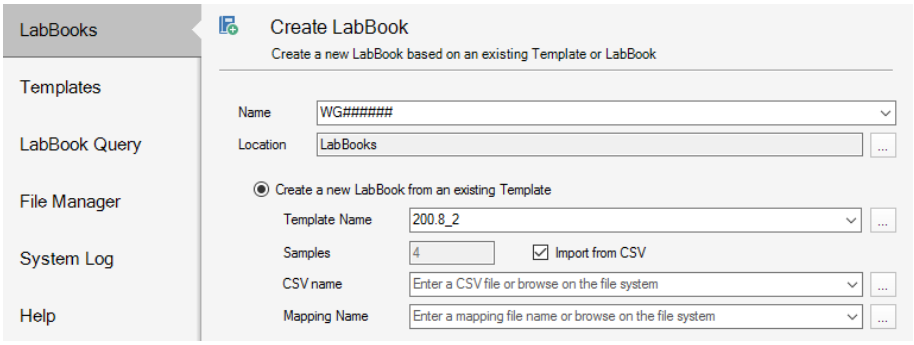
11.8.7. Click Save Batch after all changes have been made. Last, click Add to Queue and the batch will begin.

11.8.8. In Queue click if the ICPMS should enter standby mode after analysis is complete.

11.9. Creating and running a LabBook: **iCAP RQ ICPMS**

11.9.1. Open the Qtegra software. Qtegra

11.9.2. Click the 'LabBooks' tab. Select 'Create a new LabBook from an existing Template'. Enter the WG# as the name. Select the desired Template from the drop down menu and check the 'Import from CSV' box. In the 'CSV Name' box, browse to the desired input file from U:/input/ICPMS7. In the 'Mapping Name' box, select 'mapping' from the drop down menu. Click the 'Create LabBook' button.



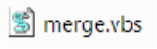
11.9.3. Update any dilution factors which need to be changed in the 'Dilution Factor' column. Scroll to the right and enter the correct Rack and Vial positions for all samples (reference the ASX-560 icon 

for a rack numbering diagram).

11.9.4. Once all necessary changes have been made, click the 'Save' disk icon in the upper left corner. Click the green 'Play' arrow  in the upper left corner to add the LabBook to the Scheduler.

11.9.5. Click the green 'Play' arrow in the lower left (at the top of the Scheduler) to begin running the queue. Additional LabBooks may be added to the queue as the instrument is running. If the plasma should shut off when the Scheduler is finished, click the Scheduler Options icon  . Select 'Closedown on an empty queue' from the Closedown drop down menu.

11.10. Reviewing and uploading data after analysis: **7500 ICPMS**.

11.10.1. All raw data is printed electronically to the C:/pdftemp/ folder. Cut and paste all of the replicate files for an individual WG to the C:/pdfmerge/ folder. Double click the 

icon in the C:/pdfmerge/ folder to merge the files into one pdf file. The raw data is now available for review in P:/pdfmerge/ICPMSx/.

11.10.2. Review the raw data for the following: ICV and CCV failures, recoveries for internal standards (ISTD) that are not within method limits, analytes of interest that are above the calibration range, %RSD discrepancies that may indicate a missed sample cup or incorrect sample uptake.

11.10.3. Select the *Offline Data Analysis* icon on the desk top: 

11.10.3.1. Click on the load method icon:  . Open the C:/ICPCHEM/1/DATA/ folder and double click on the desired WG (§Fig 20). Double click on the correct method on the left half of the screen. Click "OK" to load the corresponding calibration file.

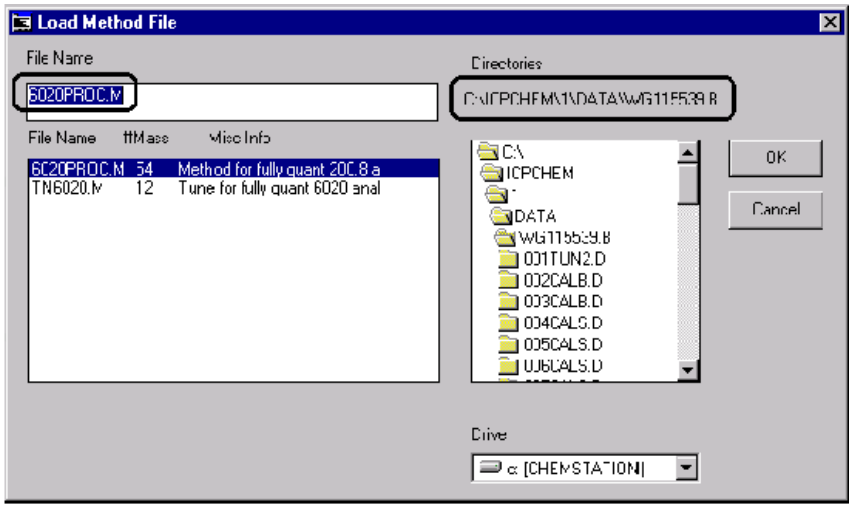


Fig. 20

11.10.3.2. For each WG print a calibration correlation (r^2) sheet. In Offline Analysis, click on *FullQuant* → *Edit Custom Report.* Click the printer icon. Attach the r^2 sheet to the WG.

11.10.3.3. Click on the Calibration Table icon (§Fig. 21) if data needs to be reprocessed for QC failures.

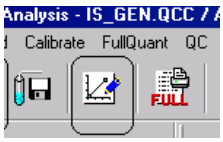


Fig. 21

11.10.3.4. Once in the calibration table, select the element that needs to be reprocessed by using the drop down menu labeled *step mass element*. Select an alternate ISTD (see §Table 18.15 for acceptable ISTDs) from the *ISTD* drop down menu (§Fig 22)

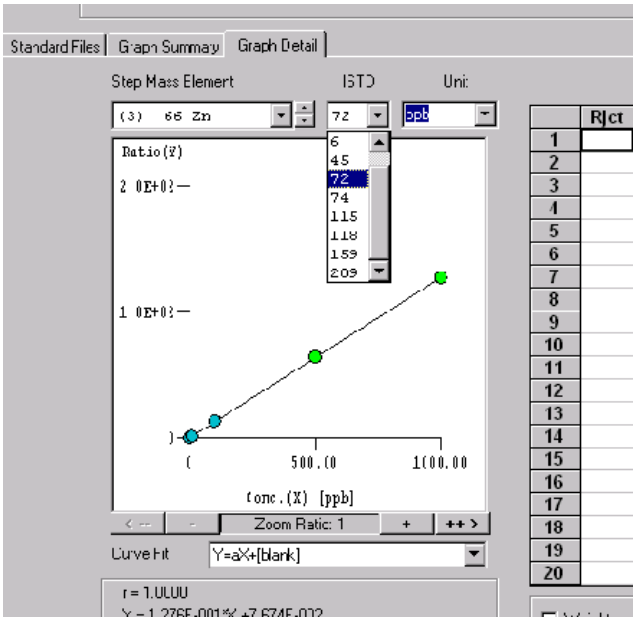


Fig. 22

11.10.3.5. When the calibration file has been updated with the appropriate internal standard, the data may be recalculated. Click the *Tools* menu (§Fig 23) and select *DoList.*

Fig. 23

11.10.3.6. Select the *QC REPORT-Recalculate then Print* option. Click on *GO.*

11.10.3.7. Select the appropriate workgroup and associated data for recalculation (see (1) §Fig 25). Click on the *ADD* button ((2) §Fig. 25). The data files will now be displayed in the Files Selected for window. Click on the *PROCESS* button ((3) §Fig. 25). The data will be reprocessed using the new internal standard and printed to the C:*pdftemp* folder. Re-merge the data as in §11.8.1.

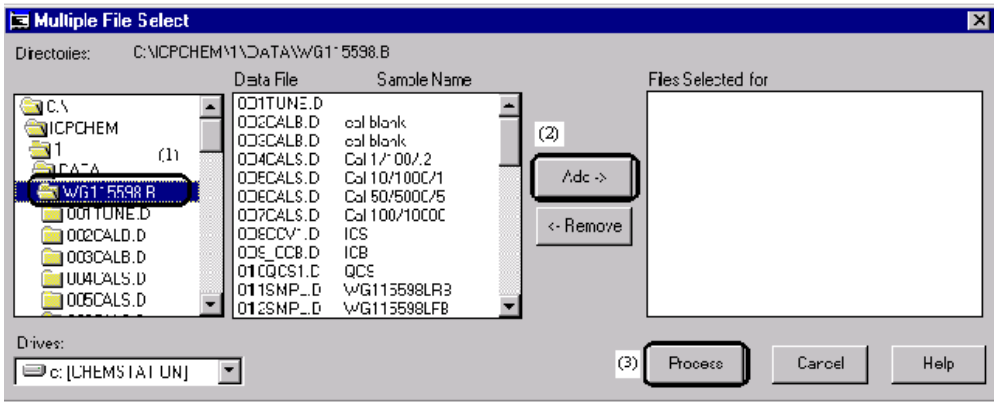


Fig. 25

11.10.4. Exporting data to the LIMS:

11.10.4.1. Click on the 

icon on the desktop

11.10.4.2. Select the appropriate directory and workgroup file (see (1) §Fig 26). Highlight the samples and QC to be exported in area (2) §Fig. 26. Click on the arrow ((3) §Fig. 26). Click on *Process* ((4) §Fig 26).

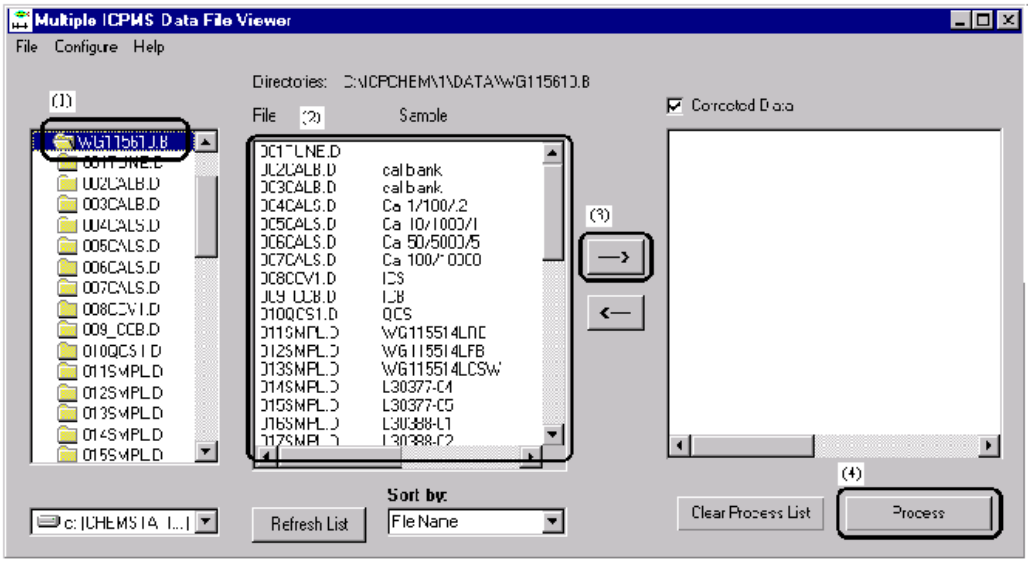


Fig. 26

11.10.5. A new spreadsheet screen will be displayed. Click the *concentration*  icon, then click the *Transpose*  icon. Bring down the *Tools* menu (§Fig. 30). Click on *Copy Selected Area to CSV file* (§Fig. 30).

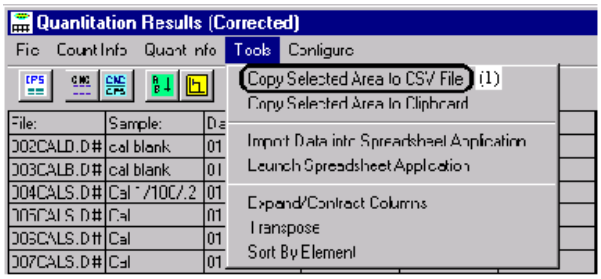
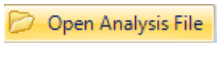


Fig. 30

11.10.6. Save the WG to the U:/autoload/ICPMSx/ directory. The workgroup is now exported to the LIMS and is ready for AREV. See §15 for data review procedure.

11.11. Reviewing and uploading data after analysis: **7900 ICPMS**.

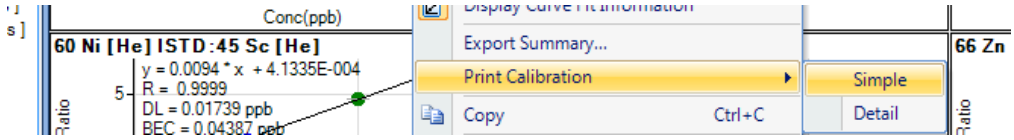
11.11.1. Select the 

icon from the main screen and open a copy of *Offline Data Analysis.* Click 

in Offline Data Analysis and select the WG# from

the C:\Agilent\ICPMH\1\data\ folder.

11.11.2. For each calibration print a calibration correlation coefficient (r^2) report. Right click in the bottom right part of the screen, and select *Print Calibration* → *Simple* from the menu. Print the file that displays on the screen and submit it with the associated WG.



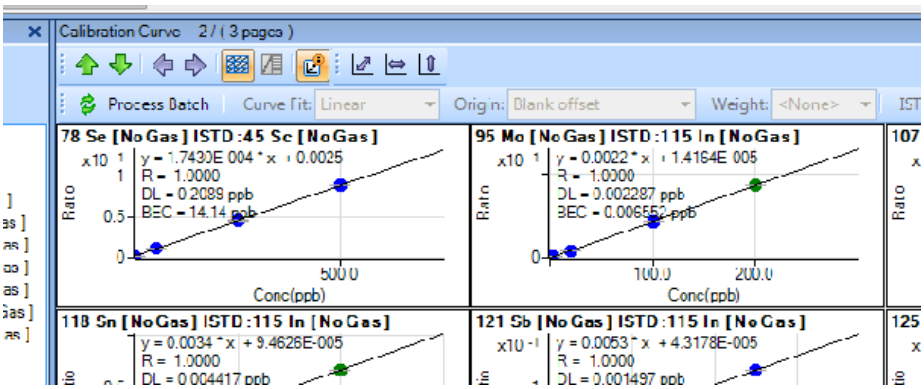
11.11.3. Right click on the internal standard graph and select *Print*. Include a copy of the ISTD graph in the WG package.

11.11.4. The top half of the screen in Offline Data Analysis will show the samples and QC in tabular form. If any of the parameters (QC check standards, Internal Standards, %RSDs, etc.) are out of pre-determined limits, a icon will appear at the left side. If icons are not present move on to §11.9.5.

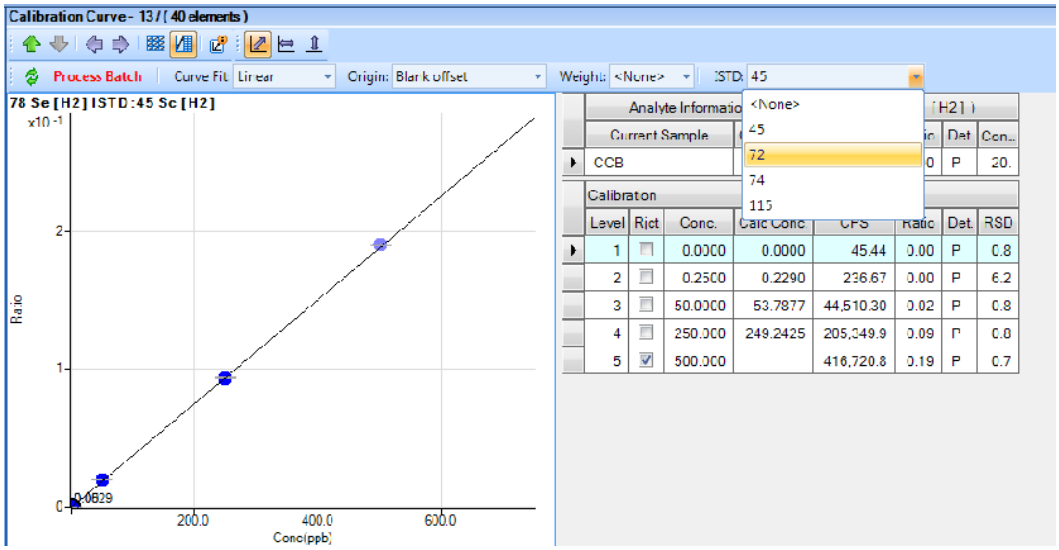
11.11.4.1. Alternate internal standards can be chosen or high standards me be dropped in order to fix QC failures.

NOTE: If a high calibration standard is dropped it must be noted on the review sheet, and the high limit for the analyte must be lowered to the next highest calibration point. Mid-level calibration standards may not be dropped.

11.11.4.2. In the bottom right side of the Offline Data Analysis screen, double click on the calibration plot of the analyte that needs to be fixed.



11.11.4.3. The screen will zoom in on the selected element. To drop a high calibration point single click on it. It will 'gray out' and the plot to the right will have a check mark in the *Rjct* column. To change the internal standard click on the *ISTD* drop down menu and select an alternate ISTD (see §Table 18.15 for accepted alternate ISTDs).



11.11.4.4. When all of the desired changes have been made click the Process Batch button and the changes will be made to all samples and QC. Click the Save Analysis File button to save changes.

11.11.4.5. To print raw data after the WG file has been modified, click *Report* → *Generate*. The raw data files will print to the C:\pdftemp\folder.

11.11.5. All raw data is printed electronically to the C:\pdftemp\ folder. Cut and paste all of the replicate files for an individual WG to the C:\pdfmerge\ folder. Double click the merge.vbs icon in the C:\pdfmerge\ folder to merge the files into one .pdf file. The raw data is now available for review in P:\pdfmerge\ICPMSx\.

11.11.6. To export data to LIMS, Click *Report* → *LIMS* → *Export Selected Samples.* All samples in the WG will automatically be converted to a .csv file and saved to the U:\Autoload\ICPMS6\ folder.

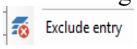
11.11.7. Data is now ready for review. See §15 for data review procedure.

11.12. Reviewing and uploading data after analysis: **iCAP RQ ICPMS**

11.12.1. Raw data on the 'Concentrations' tab of the completed LabBook should be reviewed for the following: ICV and CCV failures, recoveries for internal standards (ISTD) that are not within method limits, analytes of interest that are above the calibration range, %RSD discrepancies that may indicate a missed sample cup or incorrect sample uptake. Also check that all dilution factors are correct, as these are applied in the software and cannot be corrected after data upload.

11.12.2. Alternate internal standards may be chosen or high standards may be dropped in order to fix QC failures.

11.12.2.1. To change an internal standard: click on 'Quantification' under 'Method Parameters' from the left hand menu. Choose the new internal standard from the drop down menu for the desired analyte. Returning to the 'Concentrations' tab will automatically reprocess all data for that analyte.

11.12.2.2. To drop a high standard: right click on the standard to be dropped and select 'Exclude entry' 

. That standard will now appear grayed out. To re-add a high standard, right click and select 'Include entry'. Calibration and sample data will be reprocessed automatically as these changes are made.

11.12.3. When all necessary changes have been made, a raw data report may be printed. Click on 'Reports' from the left hand menu and then choose 'ACZ' 

. Once the report has rendered, click on 'Edit Report'. In the 'Name' box, enter the WG# and then click the 'Execute' icon  . The report may now be saved as a PDF to the P:\pdfmerge\ICPMS7 folder.

11.12.4. Save a copy of that day's performance report as "WG######-PR" to P:\pdfmerge\ICPMS7 also. This contains the daily AMU tune and will be merged with the raw data file at SREV.

11.12.5. To export data to LIMS, click 'Query' on the left hand menu. Select the correct preset from the drop down menu at the top. Click the 'Export' icon  . Choose 'Query CSV Export' from the drop down menu and choose U:\autoload\icpms7 for the pathway. Enter the WG# as the filename and click 'Export'.

NOTE: If a CSV file is subsequently opened from U:\uploads\ICPMS7, it should be saved using 'Save As' to ensure that it remains in CSV format.

Data is now ready for AREV. See §15 for data review procedure.

12.0 QUALITY CONTROL

Quality control parameters and corrective actions for QC failures are outlined in §Table 18.9.

13.0 DATA CALCULATIONS, DATA REPORTING & ARCHIVING

13.1 ICPMS Calibration and Quantitation Equations.

NOTE: ICPMS custom worksheet may be used to calculate slope, intercept, COD, and concentrations. See technical director for use of "ICPMS cal worksheet" (QA049).

13.1.1 Calibration Model: The ICPMS ChemStation uses an un-weighted linear regression model. Internal standard correction is used by setting the y-axis as a *response factor* and thus normalizing all samples and calibration standards. The curve is not forced through the origin so any background noise is accounted for.

Y = mx + [blank]

Where:
Y = instrument response ratio = ([cps of sample or std]/ [cps of ISTD])*(conc. of ISTD)
ISTD=internal standard cps=counts per second
x = concentration (mg/L) of std or sample
m = slope
[blank] = intercept of the linear line through the Y axis, instrument response ratio of calibration blank =([([cps of cal blank]/ [cps of ISTD])*(conc. of ISTD)

13.1.2 Slope (m) = $\frac{\sum_i^n x_i(Y_i - [blank])}{\sum_i^n x_i^2}$

Where:
i→n = calibration points in order of increasing concentration
x_i = concentration for the i[th] calibration standard (C_x)
Y_i = response ratio (cps ratio*internal standard conc.)for the i[th] $\left(\frac{A_x}{A_{is}} \times C_{is}\right)$
[blank] = instrument response ratio for the calibration blank = intercept through y-axis $\left(\frac{A_{blank}}{A_{is}} \times C_{is}\right)$

13.1.3 Calibration Coefficient (R)= $\frac{\left(\sum_i^n w_i \times \sum_i^n x_i Y_i\right) - \left(\sum_i^n x_i \times \sum_i^n Y_i\right)}{\sqrt{\left(\left(\sum_i^n w_i \times \sum_i^n x_i^2\right) - \left(\sum_i^n x_i\right)^2\right) \times \left(\left(\sum_i^n w_i \times \sum_i^n Y_i^2\right) - \left(\sum_i^n Y_i\right)^2\right)}}$

Where:
w_i = weighting factor for the i[th] calibration standard (=1)
i→n = calibration points in order of increasing concentration
x_i = concentration for the i[th] calibration standard (C_x)
Y_i = response ratio (cps ratio*internal standard conc.) for the i[th] $\left(\frac{A_x}{A_{is}} \times C_{is}\right)$

13.1.4 Coefficient of Determination = R^2

Where: R = Calibration Coefficient

13.1.5 Concentration (x) = $\frac{Y - [blank]}{m}$

Where:
x = concentration (mg/L) of target ion (C_x)
Y = response ratio (cps ratio*internal standard conc.) of target ion $\left(\frac{A_x}{A_{is}} \times C_{is}\right)$
m = slope, coefficient "a" in calibration curve
[blank] = intercept of calibration curve, response ratio of calibration blank

13.2 Relative Percent Difference / Relative Standard Deviation Calculation:

RPD = [x-y]/[Average[x,y]]

RSD = [SD[x,y,z,…]]/[Average[x,y,z,…]]

13.3 Additional information for calibration, concentration, and internal standards are discussed in Appendix B of the Agilent 7500 ICP-MS ChemStation Operator's Manual.

13.4 Archived Data:

13.4.1 All data is archived automatically using the IDBA system. Data is saved for 10 years. Once data is verified to be on the server, it can be deleted from the instrument PC.

13.4.1.1 To restore archived data back to the instrument PC go to the proper archive server:
Saloon:\instrument\ ICPMSx\ICPCHEM\1\data\ **(7500)** *or*
Saloon:\instrument\ ICPMSx\Agilent\ICPMH\1\data\ **(7900)*or***
Saloon:\instrument\ICPMSx\ProgramData\Thermo\Qtegra\ (iCAP RQ)

13.4.2 Save the folder with the data of interest onto the instrument PC in the C:\ICPCHEM\1\Data\ (7500) or the C:\Agilent\ICPMH\1\data\ (7900) or the C:\ProgramData\Thermo\Qtegra\ (iCAP RQ) directory. Data can now be reprinted or reprocessed, and calibration curves can be recreated using the Offline Data Analysis software.

13.4.3 To find raw counts per second (cps) of QC or client samples:

13.4.3.1 On the 7500 ICPMS, follow the above procedure to restore data to the instrument PC. Once restored, open the data file in the FileView 32 software and click 'process'. The cps are listed for each element and sample selected.

13.4.3.2 On the 7900 ICPMS, open the data file in *Offline Data Analysis* after it has been restored to the PC. Right click on the desired sample in the chart displayed on the screen, and select *Details*. The software will now display detailed information for each sample including CPS, counts for individual replicates, etc. Right click again in the *Details* screen and the values can be exported or printed if needed.

13.4.3.3 On the iCAP RQ ICPMS, open the data file in Qtegra after it has been restored to the PC. Click on 'Intensities' in the left hand Content menu. Click the '+' next to the desired sample to see CPS for each individual replicate. Right click anywhere in the results screen and choose 'Export to Excel' to generate a spreadsheet of all CPS values.

13.4.4 After verifying that IDBA is functioning properly, periodically delete all folders in the C:\ICPCHEM\1\Data\ (7500) or the C:\Agilent\ICPMH\1\data\ (7900) or the C:\ProgramData\Thermo\Qtegra (iCAP RQ) directory older than 28 days.

13.5 See §Table 18.10, §Table 18.17, and §Table 18.18 for MDL and PQL levels.

13.6 Instrument Detection Limit (IDL) calculation. Run for method 6020B. 10 replicates of a blank solution are analyzed and IDLs are calculated by: adding the mean result of the 10 reps to three times the standard deviation of the 10 reps. I

IDL = [MEAN conc. of 10 reps] + [3x(STDEV of 10 reps)]

13.7 For any dilutions that may be performed, the only calculation required would be a dilution factor. The dilution factor (DF) is calculated based on the final volume (V_f) and the volume of the analytical sample (V_s). Dilution factors must be documented on the workgroup bench sheet: $DF = V_f / V_s$

14.0 METHOD PERFORMANCE/DETECTION LIMITS

14.1 Method 200.8 MDL Studies:

NOTE: The 8 replicates of the MDL study must be performed over 3 different days for Drinking Water analysis by 200.8.

14.1.1 Prepare 8 replicates of a MDL solution fortified at 1-5 times the MDL of each element (See Table §18.10 and §Table 18.16) following the total digestion procedure described in SOPII021. Sample analysis for the MDL calculation may be made over a period of three days to include day-to-day variation as an additional source of error. The analysis must include a passing calibration, ICV/ICB, and CCV/CCB. Calculate the MDL by multiplying the standard deviation of all of the replicates by the appropriate student t value for each individual analyte (t=2.998 for 8 replicates). Use FRMAD031 and FRMAD094 for additional analytes to calculate MDL values.

14.1.2 A MDL study is required for M200.8 only and must be performed whenever, in the judgment of the analyst, a change in analytical performance caused by either a change in instrument hardware or operating conditions would dictate the MDL be re-determined. Refer to SOPAD001 for more detail.

14.1.3 A passing MDL study for the analytes listed in §Table 18.16 is required as part of the IDOC package for each new analyst that prepares or analyzes samples that are a Drinking Water matrix. The training MDL needs be performed on only one instrument.

14.1.4 An MDL verification must be performed annually for each instrument. Prepare a solution at 1-4 times the MDL listed in §Table 18.10 and §Table 18.18. All analytes must have positive confirmation above the MDL, along with passing run QC. Run only one replicate of the MDL Verification. Use FRMAD095 to calculate MDL Verifications.

14.2 An Instrument Detection Limit (IDL) study must be performed each quarter on each instrument (Method 6020/6020B requirement). The IDL is used to evaluate the instrument signal to noise ratio, and to ensure that the reported detection limit for each analyte is greater than the measured instrument detection limit.

14.2.1 Prepare 10 replicates of a matrix matched blank solution. The solution does not need to be carried through the hot block prep steps. True value of each analyte <<MDL.

14.2.2 Calibrate the instrument, include a passing ICV/ICB, followed by the 10 IDL reps, and a passing closing CCV/CCB.

14.2.3 Calculate the IDL by adding the mean of the 10 replicates to three times the standard deviation . Replicates that have values > 3x[±MDL] may not be used for IDL calculations. IDL = [MEAN of 10 reps]+[3*STDEV of 10 reps]

14.2.4 Submit a completed IDL package using FRMII025 to the supervisor for review. The QA/QC dept. keeps IDLs on file.

14.3 Lower Limit of Quantittion (LLOQ) study and verification:

14.3.1 Each instrument must have a **LLOQ Study** performed once to establish limits. Prepare a PQV solution (See Table 18.13, Level 2 Std) using the Total Hot Plate digestion procedure (SOPII024). Analyze 8 replicates. The mean recovery and %RSD must be within +/-35% and <20%, respectively. This study will be kept on file by QA/QC.

14.3.2 Each ICP-MS must have a **Ongoing LLOQ Verification** analyzed at the frequency of 1

replicate per quarter. This may be prepared in a clean test matrix and does not need to be prepared by hot block digestion. This QC sample may be run along with the quarterly IDL study described in § 14.2. Recovery for all elements must be within +/-30%.

14.4 Demonstration of Capability (DOC):

14.4.1 A successful Initial Demonstration of Capability (**IDOC**) must be completed and approved by the QA/QC department for each analyst prior to independent generation of client data for both aqueous and solid analyses. A passing MDL study must be performed by each new analyst for the drinking water analytes listed in §Table 18.16. See §14.1 for details. A Continuing Demonstration of Capability (**CDOC**) must be performed on an annual basis.

14.4.2 A separate IDOC/CDOC is required for aqueous and solid matrices. All three ICPMS instruments are identical in operation, so DOCs need only be performed on one ICPMS.

- For the aqueous **IDOC** run four aliquots of a single blind solution made from a source independent of the calibration. The solution may be obtained from a reputable vendor, prepared by the department supervisor, or prepared by another analyst approved by the QA/QC department to perform the procedure. The IDOC solution must have an SCN or PCN and the IDOC documentation must state who prepared the solution.

- For the aqueous **CDOC**, run four aliquots of a solution made from a source independent of the calibration. The CDOC solution must have a SCN or PCN.

- For the solid **IDOC and CDOC** analyze four aliquots of the 3050 digestate of the ERA Metals in Soils SRM (or equivalent) AND four replicates of the MRad Soil Radionuclides SRM (or equivalent, for Uranium). Digestions will be performed by the geochemistry dept.

- For Rare Ear**th Element an**alysis **IDOC** and **CDOC** analyze 4 reps of a second source standard.

- Complete the following forms before submitting to QA: DOC calculators FRMAD023 and FRMAD093 for additional analytes; FRMQA047 General Lab Practice Training Form, FRMQA004 Initial Method Training Form, and FRMQA050 Method Calibration Training Form. Attach all raw data and any other supporting documentation. Refer to SOPAD001 for more detail.

14.5 Linear Dynamic Range (LDR) study and verification (Method 200.8 only): Results above the high calibration point may be reported without qualifiers if it is shown that each analyte is within 10% of an established LDR value. An initial LDR Study and subsequent annual LDR verifications are required for each ICPMS. See Table 18.19 for current LDR values**.**

NOTE: Method 6020/6020B must have the LDR verified with each calibration. A Upper Linear range Verification (ULRV) QC sample is run with each 6020/6020B calibration.

14.5.1 LDR Study: The Linear Dynamic Range for each instrument must be established by performing a LDR study. Submit a full data package to QA for approval.

- Prepare a solution that is at least 10% greater than the desired LDR. Calibrate the instrument and run all associated QC (ICV, ICB, etc.). Analyze a single replicate of the prepared solution. Results for each analyte must be +/-10% of the true value.

- The established LDR for each analyte is then calculated as the [True Value of LDR Study Solution]*90% = [Established LDR]. The Established LDR may be set equal to or less than the above calculated value. For example, for Cobalt, the LDR study is analyzed at 2400mg/L. [2400mg/L]*0.9=2160mg/L. The LDR limit can be rounded down and set at 2000mg/L for Co.

14.5.2 LDR Verification: The Linear Dynamic Range of each instrument must be verified annually in order to report results above the high calibration standard.

- Prepare a solution at the established LDR for each analyte. Analyze a single replicate of the prepared solution. Results for each analyte must be +/-10% of the true value. If results are not within limits, a new LDR must be established using the procedure in §14.5.1.

15.0 DOCUMENTATION

15.1 Use the LIMS Create PCN/SCN functions to record all standards or reagents used in making standards. Reagents used for rinse or carrier solutions may be recorded on reagent sheets.

15.2 Make sure the following information is included with the Workgroup (either electronically or in hard copy):

- Dilution factors
- Analysis date
- Analytical method used
- Analyst's initials
- Standard/Reagent form
- Any remarks about analysis or samples
- Observed matrix effects and the associated actions for reanalysis
- Calibration Correlation Coefficients for associated elements
- Initial tune analysis
- All raw data, including calibration, QC, and samples

15.3 Label each prepared standard or reagent with the following information:

- standard name
- SCN (or other unique ID)
- preparer's initials
- expiration date
- prep date

15.4 Fill out a data review sheet (FRMII012) detailing any QC that is not within acceptance limits and the associated action needed to complete the analysis of samples.

15.5 If an "OCAL" alert appears in LIMS, set the analyte to REDO and re-run on appropriate dilution. In general, dilute OCALs to the approximate middle of the calibration range; do not use the Linear Dynamic Range limit to determine dilution factors. This is subject to change based on client requests or analyst discretion.

15.6 If a "LOW" alert appears in LIMS and the sample is analyzed on a 1x bench dilution, set the analyte to REDO and re-run on a 2x dilution to minimize matrix effects. If the sample is on a bench dilution and a "LOW" alert appears, qualify the analyte appropriately.

15.7 If an OCAL alert appears in LIMS for Ag by total or total recoverable analysis, the sample must be sent to REDX and (re)prepped on a dilution so that Ag concentration in the prepped digestate is <0.050mg/L. In general, prepping on 5x will be sufficient. Ag has been shown to precipitate at

concentrations above 0.100mg/L, and bench level dilutions may deliver biased low data. See CAR1115 for more details.

15.8 Review the data in the LIMS (AREV) and set any QC failures to FAIL and the associated analytical samples to REDO or REDX, or edit a footnote on the review sheet and WG as to the reason why the data may be accepted with failing QC criteria (data must be appropriately flagged).

15.9 Data is automatically backed up using the IDBA system. Refer to SOPAD044.

16.0 WASTE MANAGEMENT/POLLUTION PREVENTION

Refer to ACZ's Waste Management Plan for appropriate disposal details for this method.

17.0 DEFINITIONS

See §Table 18.9 for QC definitions.

18.0 TABLES & DIAGRAMS

18.1 Figures:
Fig. 1 – Fig. 11: Instrument set up
Fig. 14 – Fig. 17: Sequence creation
Fig. 18 – Fig. 30: Data Analysis

18.2 Tables:
Table 6.1: Hold Times
Table 8.1: Multi-Element Working Standards
Table 8.2: Hg Working Standards
Table 8.3: REE Working Standards

Table 18.1: Internal Standard Solution for Routine Analysis

Element	Concentration (mg/L) (Agilent 7500 & 7900)	Concentration (mg/L) (Thermo iCAP RQ)
Bismuth	2.00	0.02
Germanium	2.00	0.02
Indium	1.00	0.01
Lithium	6.00	0.06
Scandium	2.00	0.02
Terbium	1.00	0.01

Table 18.2: Multi-element Calibration Standard Intermediate Solutions

ICPMS Stock #1		ICPMS Stock #2		ICPMS Ag/Sb Stock	
Element	**Conc. (mg/L)**	**Element**	**Conc. (mg/L)**	**Element**	**Conc. (mg/L)**
Aluminum	100	Boron	2	Silver	5
Arsenic	20	Tin	20	Antimony	2.5
Beryllium	20	Selenium	50	Thorium	20
Cadmium	20	Thallium	20		
Chromium	20	Uranium	20		
Cobalt	20	Vanadium	20		
Copper	50	Tellurium	20		

Iron	100				
Lead	50				
Manganese	20				
Molybdenum	20				
Nickel	50				
Zinc	100				
Cesium	20				

Table 18.3: 200.8 and 6020/6020B ICV and CCV concentrations

Element	CCV Conc. (mg/L)	ICV Conc. (mg/L)
Aluminum	0.500	0.100
Antimony	0.0125	0.020
Arsenic	0.100	0.050
Barium	0.250	0.050
Beryllium	0.100	0.050
Boron	0.010	0.020
Cadmium	0.100	0.050
Cesium	0.100	0.050
Chromium	0.100	0.050
Cobalt	0.100	0.050
Copper	0.250	0.050
Iron	0.500	0.100
Lead	0.250	0.050
Manganese	0.100	0.050
Molybdenum	0.100	0.020
Nickel	0.250	0.050
Selenium	0.250	0.050
Silver	0.025	0.020
Tellurium	0.100	0.050
Thallium	0.100	0.050
Thorium	0.100	0.050
Tin	0.100	0.050
Uranium	0.100	0.050
Vanadium	0.100	0.050
Zinc	0.500	0.050

Table 18.4a: Waters

Multi-Spike Intermediate Solution (mg/L)		Ag/Sb/Th Spike Intermediate (mg/L)	
Aluminum	10	Antimony	2
Arsenic	10	Silver	2
Barium	10	Thorium	10
Beryllium	10		
Boron	2		

Table 18.4b: Soils

Multi-Spike Intermediate Solution (mg/L)		Ag/Sb Spike Intermediate (mg/L)	
Aluminum	50	Antimony	10
Arsenic	50	Silver	10
Barium	50		
Beryllium	50	**Th Spike Intermediate (mg/L)**	
Boron	10	Thorium	25

Cadmium	10		
Chromium	10		
Cesium	10		
Cobalt	10		
Copper	10		
Iron	10		
Lead	10		
Manganese	10		
Molybdenum	10		
Nickel	10		
Selenium	10		
Thallium	10		
Tellurium	10		
Tin	10		
Uranium	10		
Vanadium	10		
Zinc	10		

Cadmium	50		
Chromium	50		
Cesium	25		
Cobalt	50		
Copper	50		
Lead	50		
Manganese	50		
Molybdenum	50		
Nickel	50		
Selenium	25		
Thallium	50		
Tellurium	25		
Tin	50		
Uranium	25		
Vanadium	50		
Zinc	50		

Table 18.5a: Analytical/Matrix Spike for Water

Element	Concentration (mg/L)
Aluminum	0.050
Antimony	0.010
Arsenic	0.050
Barium	0.050
Beryllium	0.050
Boron	0.010
Cadmium	0.050
Cesium	0.050
Chromium	0.050
Cobalt	0.050
Copper	0.050
Iron	0.050
Lead	0.050
Manganese	0.050
Molybdenum	0.050
Nickel	0.050
Selenium	0.050
Silver	0.010
Tellurium	0.050
Thallium	0.050
Thorium	0.050
Tin	0.050
Uranium	0.050
Vanadium	0.050
Zinc	0.050

Table 18.5b: Analytical/Matrix Spike for Soils

Element	Concentration (mg/L)
Aluminum	0.250
Antimony	0.050
Arsenic	0.250
Barium	0.250
Beryllium	0.250
Boron	0.050
Cadmium	0.250
Cesium	0.125
Chromium	0.250
Cobalt	0.250
Copper	0.250
Lead	0.250
Manganese	0.250
Molybdenum	0.250
Nickel	0.250
Selenium	0.125
Silver	0.050
Tellurium	0.250
Thallium	0.250
Thorium	0.125
Tin	0.250
Uranium	0.125
Vanadium	0.250
Zinc	0.250

Table 18.6: ICS-A / ICS-AB				
Interferant Elements	**Conc. (mg/L)**		**Analyte Elements**	**Conc. (mg/L)**
Aluminum	50		Antimony	0.01
Calcium	150		Arsenic	0.02
Carbon	100		Barium	0.02
Chloride	1000		Beryllium	0.02
Iron	125		Cadmium	0.02
Magnesium	50		Chromium	0.02
Molybdenum	1		Cobalt	0.02
Phosphorus	50		Copper	0.02
Potassium	50		Lead	0.02
Sodium	125		Manganese	0.02
Sulfur	50		Nickel	0.02
Titanium	1		Selenium	0.02
			Silver	0.01
			Thallium	0.02
			Thorium	0.05
			Uranium	0.02
			Vanadium	0.02
			Zinc	0.02
			Boron	.004
			Tin	0.02
			Cesium	0.02
			Tellurium	0.02

Table 18.7: Interference Equations	
Mass	**Equation**
**6Li	-0.073067*7Li
*51V	51cps – 53cps*(51ClO/53ClO)[53cps – (53Cr/52Cr)52cps] Or (51)*1 – (53)*3.127 + (52)*0.353351
**51V	-3.0556*37Cl.16O + 0.3616*52Cr + -0.1803*13C
**52Cr	-0.299387*13C
**59Co	-0.00103*43Ca
**60Ni	-.002401*43Ca
**63Cu	-0.006974*47Ti
**65Cu	-0.0029*47Ti
**66Zn	-0.002536*47Ti
*75As	75cps – (75ArCl/77ArCl)[(77cps - 77Se/82Se[(82cps) – 83Kr(82Kr/83Kr)]] Or (75)*1 – (77)*3.127 + (82)*2.736 – (83)*2.76
**75As	-2.9522*40Ar.37Cl + 2.184*82Se + -2.186*83Kr + -0.006347*79Br
*82Se	82cps – 83cps*(82Kr/83Kr) Or (82)*1 – (83)*1.009
**82Se	-1.00087*83Kr – 0.002906*79Br
98Mo	98cps – 99cps*(98Ru/99Ru)

	Or (98)*1 – (99)*0.146
111Cd	111cps – 95MoO/92MoO[108cps – (108Cd/106Cd)106cps) Or (111)*1 – (108)*1.073 + (106)*0.763976
208Pb	208Pb + 207Pb + 206Pb Or (206)*1 + (207)*1 + (208)*1
202Hg	199Hg + 200Hg + 201Hg + 202Hg Or (199)*1 + (200)*1 + (201)*1 + (202)*1
**40Ar.37Cl	-0.739788*82Se
**37Cl.16O	-0.118339*52Cr
	where cps = counts per second. (xxx) denotes cps of particular mass.
	* = Used only for DW analysis by 200.8 **=Interference equations provided by Thermo for the iCAP RQ. Used only for DW analysis by 200.8

Table 18.8: Monitored Analytical Isotopes	
27	Aluminum
121	Antimony
75	Arsenic
137	Barium
9	Beryllium
11	Boron
111	Cadmium
140	Cerium
133	Cesium
52	Chromium
59	Cobalt
63*, 65†	Copper
163	Dysprosium
166	Erbium
153	Europium
157	Gadolinium
165	Holmium
56	Iron
139	Lanthanum
175	Lutetium
206, 207, 208	Lead
55	Manganese

Table 18.8: Monitored Analytical Isotopes	
199, 200, 201, 202	Mercury
98	Molybdenum
146	Neodymium
60	Nickel
141	Praseodymium
147	Samarium
45	Scandium
78*, 82†	Selenium
107	Silver
125	Tellurium
159	Terbium
205	Thallium
232	Thorium
169	Thulium
118	Tin
238	Uranium
51	Vanadium
172	Ytterbium
89	Yttrium
66	Zinc
Isotopes recommended for analytical determinations are underlined	
†Used for DW analysis by 200.8 only *Used for non-DW analysis by 200.8/6020	

Table 18.9: ICPMS QC			
(200.8)			
Type	**Definition**	**Analysis**	**QC Limits and Corrective Action**

Mass Tune	AMU Check Tune. Verifies that the detector is seeing the correct Atomic Mass Unit, and that the resolution is acceptable.	Analyzed every 24. 5 replicates of 50 ppb solution of Be, Mg, Co, In, and Pb.	RSD <5% Resolution must be <0.75 AMU at 5% peak height. Mass Calibration within 0.1 AMU of target mass.
Calibration	Calibration Correlation Coefficient. Shows that the linearity of the multi-point calibration is acceptable.	Analyzed prior to each analytical workgroup.	If the correlation coefficient for the element of interest is not greater than 0.995, then the instrument must be recalibrated and all of the associated samples for that element must be reanalyzed.
CCV	Continuing Calibration Verification. Run every ten samples to show that calibration is still valid.	Analyzed after every ten samples, and the end of the analytical run.	If recovery is not within +/- 10% all associated samples must be reanalyzed since the last compliant CCV. If CCV recovery was high, 'U' samples can be qualified and passed.
ICB/ CCB	Initial and Continuing Calibration Blank Verification. Run after the ICV and/or CCV to show that the blank levels for each analyte are less than 3X the MDL. The ICB serves as the LRB in dissolved analyses, and must be < 2.2 times the MDL to be considered passing.	Analyzed after calibration (ICB), after every ten samples (CCB) and the end of the analytical run (CCB). Run every 20 client samples for dissolved analyses.	If the blank is > 3 times the MDL of the associated analyte, or >2.2 times the MDL for dissolved 200.8 analyses, reanalyze all associated samples that are < 10X the blank and > zero since the last compliant CCB. Recalibrate if ICB is outside of acceptance criteria.
ICV	Initial Calibration Verification (Same as QCS). Made from a different source or lot number than the calibration standards. Verifies the calibration.	Analyzed immediately after each calibration; must be prepared from second source.	The ICV may be re-run once. If recovery is not within +/- 10% recalibrate and reanalyze samples.
LRB	Laboratory Reagent Blank. The LRB is carried through the prep process to account for any systematic contamination.	Carried through the entire sample preparation process with each batch of 20 or fewer samples of the same matrix. In dissolved analysis the ICB serves as the LRB.	If the LRB is > 2.2 times the MDL of the associated analyte, re-prep and reanalyze all associated samples that are < 10X the LRB and > zero
LFB	Laboratory Fortified Blank. The LFB is carried through the prep process to demonstrate acceptable recovery of analytes.	An LRB that is fortified with multi-element stock standards. Run with every batch of 20 samples.	If recovery is not within +/- 15% the samples must be re-prepped and reanalyzed. If the LFB recovery is high, 'U' samples may be qualified and passed.
AS	Analytical Spike. A client sample is spiked with a known amount of analytes. % recovery checks for potential matrix effects.	A sample spiked with the same multi-element stock standard as the LFB for each batch of ten samples.	If recovery is not within +/- 30% and sample is not >4 times the spike concentration, then matrix interference is suspect and the data is qualified accordingly.
ASD	Analytical Spike Duplicate. Same as AS. Used to check the reproducibility of the spike recovery.	A secondary analytical sample spiked with a known amount of multi-element analytes for comparison to the AS sample for %RPD calculation.	If %RPD is not within 20%, samples must be re-prepped and reanalyzed. It is acceptable to pass high RPD for Ag samples due to low solubility in the presence of chloride.
LFM	Laboratory Fortified Matrix. A client sample is spiked with a known amount of analytes and then carried through the prep process. % recovery checks for potential matrix effects.	A sample spiked with the same multi-element stock standard as the LFB, prior to digestion, and for each batch of ten samples.	If recovery is not within +/- 30% and sample is not >4 times the spike concentration, then matrix interference is suspect and the data is qualified accordingly.

LFMD	Laboratory Fortified Matrix Duplicate. Same as LFM. Used to check the reproducibility of the spike recovery.	A secondary analytical sample spiked with a known amount of multi-element analytes, prior to digestion, for comparison to the LFM sample for %RPD calculation.	If %RPD is not within 20%, samples must be re-prepped and reanalyzed. Ag must have passing RPD in digested samples.
PQV	Practical Quantitation Verification standard. Run after the ICV/ICB to verify the reporting limit in sample batches containing Drinking Water (DW) samples run by method 200.8 only.	A reagent blank fortified with the PQV intermediate solutions. Run after the ICV/ICB with every batch containing DW samples. This sample is not prepped, and is used for dissolved analyses only.	If recovery is not within +/- 30%, Drinking Water samples must be re-analyzed for failing parameters.
PQVPREP	An aliquot of reagent water into which the method analytes are added at the quantitation level. The PQVPREP is prepped and analyzed exactly like a sample. This QC sample is required for Drinking Water (DW) matrices only.	This sample must be prepped according to SOPII021 when run with TR or THP DW samples. It is not batch QC. At a minimum, one passing PQVPREP is required per day when DW samples are analyzed.	If recovery is not within +/- 30%, Drinking Water samples must be re-analyzed for failing parameters. If failing upon re-run, re-prep and re-analyze the PQVPREP only to obtain passing results.
DCS	Detectability Check Standard. Used for projects logged in for TRRP reporting only. An aliquot of reagent water into which the method analytes are added at 2-3x the MDL. The DCS is prepped and analyzed exactly like a sample.	Analyzed at a frequency of 1 per 20 or less TRRP samples.	Recovery must be > MDL for each analyte of interest. If results are < MDL, associated samples must be reanalyzed or re-prepped for affected analytes.
Internal Standard	A known, constant amount of elements not normally found in environmental samples added on line to all standards, QC, and samples. Used as a reference for evaluating, controlling, and normalizing physical and chemical interferences, and instrument drift.	Added during instrument analysis to all samples, calibration standards, and QC.	If the internal standard is not within 60—125% of the response in the calibration blank, recalculate the data using an alternative internal standard. If no alternative internal standard meets the 60—125% criteria, set the sample to REDO and reanalyze on a 2X greater dilution. If samples are 'U' and ISTD recovery is high, the data may be qualified. If the sample is put on a dilution and ISTD are still out of limits, data may be qualified. NOTE: If internal standards fails in a spike do not put all associated samples to REDO. Only samples that have failing internal standards need to be reanalyzed.

ICPMS QC (6020/6020B)

Type	Definition	Analysis	QC Limits and Corrective Action
Mass Tune	AMU Check Tune. Verifies that the detector is seeing the correct Atomic Mass Unit, and that the resolution is acceptable.	Analyzed every 24. 4 replicates of a 50 ppb solution of Li, Co, In, and Tl.	RSD < or 5% Resolution must be <0.9 AMU at 10% peak height. Mass Calibration within 0.1 AMU of target mass.
Calibration	Calibration Correlation Coefficient. Shows that the linearity of the multi-point calibration is acceptable.	Analyzed prior to each analytical workgroup.	If the correlation coefficient for the element of interest is not greater than 0.995, then all of the associated samples for that element must be reanalyzed.

ICV/ CCV	Initial and Continuing Calibration Verification. Made from a different source or lot number than the calibration standards. Verifies the calibration.	Analyzed after calibration (ICV), after every ten samples (CCV), and the end of the run (CCV).	Recalibrate if ICV is not within +/- 10%. Redo all associated samples since the last compliant CCV if CCV is not +/- 10%. If CCV recovery was high, 'U' samples can be qualified and passed.
ICB/ CCB	Initial and Continuing Calibration Blank Verification. Run after the ICV and/or CCV to show that the blank levels for each analyte are less than 3X the MDL.	Analyzed after calibration (ICB), after every ten samples (CCB) and the end of the analytical run (CCB).	If the blank is > 3 times the MDL of the associated analyte, reanalyze all associated samples that are < 10X the blank and > zero since the last compliant CCB. Recalibrate if ICB is outside of acceptance criteria.
LLOQ	Lower Limit of Quantitation, equivalent to PQVPREP in this SOP. Analyzed at the quantitation limit for each element.	Once per quarter per instrument.	Recovery within +/-30%. PQL must be raised if LLOQ cannot be verified.
PQV	Practical Quantitation Verification standard. Run after the ICV/ICB to verify the reporting limit for all 6020/6020B matrices.	A reagent blank fortified with the PQV intermediate solutions. Run after the ICV/ICB. This QC sample does not need to be prepped.	Recovery within +/- 30%. Recalibrate and REDO analytes outside acceptance range.
ICSA	Interferant Check Sample A. Contains known interferants, and is meant to check the efficacy of the interference equations and collision/reaction cell.	Analyzed after the ICV/ICB. Checks for positive interference.	Analytes with known mass interferences must recover < PQL. Recalibrate and reanalyze if the ICSA is failing. Analytes with no known major interferences are not evaluated in the ICSA. [1]
ICSAB	Interferant Check Sample A & B. An ICSA spiked with known amount of analytes. Used to check the efficacy of the interference equations and collision/reaction cell.	Analyzed after the ICV/ICB. Checks for positive and negative interference.	Recovery of analyte elements should be within +/- 20%. Upon failure the associated analytes should be reanalyzed.
ULRV	Upper Linear Range Verification. A QC sample run after each calibration to verify concentrations reported above the normal calibration range. If *not* run, results may *not* be reported above the high calibration standard.	Analyzed any time after the calibration to verify results outside of the calibration range.	Recovery must be within 90-110% or concentrations above the high calibration standard may not be reported. If the ULRV is *not* run, results are only valid within the calibration range.
PBW	Preparation Blank (Water). The PBW is carried through the prep process to account for any systematic contamination.	A reagent blank sample carried through the same preparation procedure as the samples.	If the PBW is > 3 times the MDL of the associated analyte, re-prep and reanalyze all associated samples that are < 10X the LRB and > zero
PBS	Preparation Blank (Soil). The PBS is carried through the prep process to account for any systematic contamination.	A reagent blank sample carried through the same preparation procedure as the samples.	If the PBS is > 3 times the MDL of the associated analyte, re-prep and reanalyze all associated samples that are < 10X the LRB and > zero
LCSW	Laboratory Control Sample (Water). The LCSW is carried through the prep process to demonstrate acceptable recovery of analytes.	A water matrix standard that is carried through the same preparation procedure as the samples.	If recovery is not within +/- 20% the samples must be re-prepped and reanalyzed.

LCSS (soil)	Laboratory Control Sample Solid (soil). The LCSS is a soil matrix QC sample that is carried through the entire prep process to demonstrate acceptable recovery of analytes.	LCSS QC samples are added by the Soils Dept, at the frequency of 1 per 20 or fewer client samples. They are prepared and analyzed using the same procedures as the client samples.	Observe vendor limits where available. Default limits are ±20% of the assigned value. If recovery is outside of limits associated samples should be re-prepped and re-analyzed unless; the LCSSD and RPD are within limits *or* the assigned value after applicable dilutions is < 3x the PQL. Data may be passed and appropriately qualified in these cases.
LCSSD	Laboratory Control Sample Solid Duplicate (soil). Duplicate of the LCSS. Used to check the reproducibility of the analyte recovery.	LCSSD QC samples are added by the Soils Dept, at the frequency of 1 per 20 or fewer client samples. They are prepared and analyzed using the same procedures as the client samples.	See QC limits and description for LCSS (soil). RPD must be ≤ 20% or sample should be re-prepped and reanalyzed.
LCSS (tissue)	Laboratory Control Sample Solid (tissue). The LCSS is a tissue matrix QC sample that is carried through the entire prep process to demonstrate acceptable digestion of analytes.	One per tissue preparation batch of 20 or less samples. The LCSS shall resemble the sample origin (e.g. fish tissue, shellfish, or plant material) as closely as possible.	Limits are ±20%, except Al which is control charted. Control chart limits are stated on the associated PCN report. Re-prep and re-analyze associated samples if recovery is outside acceptance limits. If the assigned value after applicable dilutions is < 3x the PQL, data may be passed and appropriately qualified.
LFB (tissue)	Laboratory Control Sample (tissue). The LFB consists of Teflon beads spiked with all target analytes. It is used to subsidize the LCSS because SRM's are not available with all elements at quantifiable levels.	One LFB/LFBD per tissue preparation batch.	If recovery is not within +/- 20% the samples must be re-prepped and reanalyzed.
LFBD (tissue)	Same as LFB. Used to check the reproducibility of the analyte recovery.	One LFB/LFBD per tissue preparation batch.	If %RPD is not within 20%, samples must be re-prepped and reanalyzed.
ASD	Analytical Spike Duplicate. Same as AS. Used to check the reproducibility of the spike recovery.	A secondary analytical sample spiked with a known amount of multi-element analytes for comparison to the AS sample for %RPD calculation.	If %RPD is not within 20%, samples must be re-prepped and reanalyzed.
DCS	Detectability Check Standard. Used for projects logged in for TRRP reporting only. An aliquot of reagent water into which the method analytes are added at 2-3x the MDL. The DCS is prepped and analyzed exactly like a sample.	Analyzed at a frequency of 1 per 20 or less TRRP samples.	Recovery must be > MDL for each analyte of interest. If results are < MDL, associated samples must be reanalyzed or re-prepped for affected analytes.
MS	Matrix Spike. A client sample is spiked with a known amount of analytes and then carried through the prep process. % recovery checks for potential matrix effects.	An analytical sample spiked prior to digestion with a known amount of multi-element analytes for each batch of 20 or less client samples.	If recovery is not within +/- 25% and sample is not >4 times the spike concentration, then matrix interference is suspect and the data is qualified accordingly.

MSD	Matrix Spike Duplicate. Same as MS. Used to check the reproducibility of the spike recovery.	A duplicate analytical sample spiked with a known amount of multi-element analytes for comparison to the MS sample for %RPD calculation.	If %RPD is not within 20%, solid matrix samples may be qualified for non-homogeneity if the LCSS/D RPD is acceptable.
DUP	Matrix Duplicate. A second portion of the client sample is prepped and analyzed to evaluate the precision of the system.	A duplicate analytical sample for determination of precision. The value of the DUP is compared to the value of the sample.	If %RPD is not within 20%, the data may be qualified for non-homogeneity if the LCSS/D RPD is acceptable.
Internal Standard	A known, constant amount of elements not normally found in environmental samples added on line to all standards, QC, and samples. Used as a reference for evaluating, controlling, and normalizing physical and chemical interferences, and instrument drift.	Added during instrument analysis to all samples, calibration standards, and QC.	If the internal standard is not within 30—120% of the response in the calibration blank, recalculate the data using an alternative internal standard. If no alternative standard meets the 30—120% criteria, set the sample to REDO and reanalyze on a 5X greater dilution. If samples are 'U' and ISTD recovery is high, the data may be qualified. If the sample is put on a dilution and ISTD are still out of limits, data may be qualified. NOTE: If internal standards fails in a spike, do not put all associated samples to REDO. Only samples that have failing internal standards need to be reanalyzed.
[1]Analytes without known mass interferences and/or analytes that are added as interferants to the ICSA are not evaluated. ICSA standards are not commercially available with all the desired elements below the required detection limits.			

Table 18.10: Method MDL and PQLs

200.8/ & 6020/6020B

Element	MDL (mg/L)	PQL (mg/L)
Aluminum	0.005	0.015
Antimony	0.0004	0.002
Arsenic non-DW *Arsenic DW only*	0.0002 *0.0005*	0.001 *0.002*
Barium	0.0005	0.0025
Boron	0.001	0.005
Beryllium	0.00008	0.00025
Cadmium	0.00005	0.00025
Cesium	0.0002	0.001
Chromium	0.0005	0.002
Cobalt	0.00005	0.00025
Copper *Copper DW only*	0.0008 *0.002*	0.002 *0.005*
Iron	0.007	0.020
Lead	0.0001	0.0005
Manganese	0.0004	0.002
Mercury	0.00006	0.00015
Molybdenum	0.0002	0.005
Nickel	0.0004	0.001

Selenium non-DW *Selenium DW only*	0.0001 0.001	0.00025 0.005
Silver	0.0001	0.0005
Thallium	0.0001	0.0005
Tellurium	0.001	0.005
Tin	0.0008	0.0025
Thorium	0.001	0.005
Uranium	0.0001	0.0005
Vanadium	0.0005	0.002
Zinc	0.006	0.015

Table 18.11: Approved Elements for 6020/6020B and 200.8

6020/6020B	**200.8**
Aluminum (Al)	Aluminum (Al)
Antimony (Sb)	Antimony (Sb)
Arsenic (As)	Arsenic (As)
Barium (Ba)	Barium (Ba)
Beryllium (Be)	Beryllium (Be)
Cadmium (Cd)	Cadmium (Cd)
Chromium (Cr)	Chromium (Cr)
Cobalt (Co)	Cobalt (Co)
Copper (Cu)	Copper (Cu)
Lead (Pb)	Iron (Fe)
Manganese (Mn)	Lead (Pb)
Nickel (Ni)	Manganese (Mn)
Silver (Ag)	Molybdenum (Mo)
Thallium (Tl)	Nickel (Ni)
Zinc (Zn)	Selenium (Se)
	Silver (Ag)
	Thallium (Tl)
	Thorium (Th)
	Uranium (U)
	Vanadium (V)
	Zinc (Zn)
	Mercury (Hg)

Table 18.12: PQV Intermediate for Calibration Standard

Element	Stock Volume* (mL)	Final Volume (mL)	Final Concentration (mg/L)
Beryllium	0.250	100	2.50
Boron	5.000	100	50.0
Aluminum*	1.50	100	150.0
Vanadium	2.000	100	20.0
Chromium	2.000	100	20.00
Manganese	2.000	100	20
Iron*	2.000	100	150.0
Cobalt	0.250	100	2.50
Nickel	3.000	100	10
Copper	2.000	100	20
Zinc*	1.50	100	100.0

	Arsenic	1.000	100	10.0	
	Selenium	0.250	100	2.5	
	Molybdenum	2.500	100	5	
	Silver	0.500	100	5.00	
	Cadmium	0.250	100	2.500	
	Tin	2.50	100	25.0	
	Antimony	2.000	100	20.0	
	Cesium	1.000	100	10.00	
	Barium	2.500	100	25.00	
	Thallium	0.500	100	5.00	
	Lead	0.500	100	5.00	
	Thorium	5.00	100	50.0	
	Uranium	0.500	100	5.00	
	Tellurium	5.00	100	50.0	
***All stock concentrations are 1,000 mg/L, except Al, Fe and Zn at 10,000 mg/L**					

Table 18.13: ICPMS Calibration Concentration Levels (mg/L)

Element	PQV / L2 Std	Level 3	Level 4	Level 5
Beryllium	0.00025	0.020	0.100	0.200
Boron	0.005	0.002	0.010	0.020
Aluminum	0.015	0.100	0.500	1.00
Vanadium	0.002	0.020	0.100	0.200
Chromium	0.002	0.020	0.100	0.200
Manganese	0.002	0.020	0.100	0.200
Iron	0.020	0.100	0.500	1.00
Cobalt	0.00025	0.020	0.100	0.200
Nickel	0.001	0.050	0.250	0.500
Copper	0.002	0.050	0.250	0.500
Zinc	0.015	0.100	0.500	1.00
Arsenic	0.001	0.020	0.100	0.200
Selenium	0.00025	0.050	0.250	0.500
Molybdenum	0.0005	0.020	0.100	0.200
Silver	0.0005	0.005	0.025	0.050
Cadmium	0.00025	0.020	0.100	0.200
Tin	0.0025	0.020	0.100	0.200
Antimony	0.002	0.0025	0.0125	0.025
Barium	0.0025	0.050	0.250	0.500
Tellurium	0.005	0.020	0.100	0.200
Cesium	0.001	0.020	0.100	0.200
Thallium	0.0005	0.020	0.100	0.200
Lead	0.0005	0.050	0.250	0.500
Thorium	0.005	0.020	0.100	0.200
Uranium	0.0005	0.020	0.100	0.200

Table 18.14: ICV Intermediate Solutions

ICV Intermediate Soln 1		ICV Intermediate Soln 2		ICV Intermediate Soln 3	
Element	**Concentration (mg/L)**	**Element**	**Concentration (mg/L)**	**Element**	**Concentration (mg/L)**
Be	25	Fe	50	Sb	10

B	10	Mo	10	Sn	25
Al	50	Ag	10		
V	25				
Cr	25				
Mn	25				
Co	25				
Ni	25				
Cu	25				
Zn	25				
As	25				
Se	25				
Cd	25				
Te	25				
Cs	25				
Ba	25				
Tl	25				
Pb	25				
Th	25				
U	25				

Table 18.15: Acceptable Internal Standards for Methods 200.8 and 6020/6020B

Analyte	ISTD mass
Be	6, 45
B	6, 45
Al	45, 72, 74, 115
Sc	72
V	45, 72, 74, 115
Cr	45, 72, 74, 115
Mn	45, 72, 74, 115
Fe	45, 72, 74, 115
Co	45, 72, 74, 115
Ni	45, 72, 74, 115
Cu	45, 72, 74, 115
Zn	45, 72, 74, 115
As	45, 72, 74, 115
Se	45, 72, 74, 115
Y	72, 115
Mo	72, 74, 115, 159, 209
Ag	72, 74, 115, 159, 209
Cd	72, 74, 115, 159, 209
Sn	72, 74, 115, 159, 209
Sb	72, 74, 115, 159, 209
Cs	72, 74, 115, 159, 209
Te	72, 74, 115, 159, 209
Ba	72, 74, 115, 159, 209
La	115, 209
Ce	115, 209
Pr	115, 209
Nd	115, 209
Sm	115, 209
Eu	115, 209
Gd	115, 209
Tb	115, 209
Dy	115, 209
Ho	115, 209
Er	115, 209
Tm	115, 209
Yb	115, 209
Lu	115, 209
Hg	115, 159, 209
Tl	115, 159, 209
Pb	115, 159, 209
Th	115, 159, 209
U	115, 159, 209

Table 18.16: Maximum Contaminant Levels (MCL)

Drinking Water Analytes	MCL (trigger level), mg/L
Sb	0.006
As	0.01
Ba	3

Be	0.004
Cd	0.005
Cr	0.1
Cu	1.3
Pb	0.015
Ni	None
Se	0.05
Ag	None
Tl	0.002
U	0.03

Table 18.17: Low Level Method MDL and PQLs

Element	MDL (mg/L)	PQL (mg/L)	Level 2 Std Conc. (mg/L)
Antimony	0.0002	0.001	0.0004
Barium	0.0001	0.0005	0.0005
Chromium	0.00005	0.0004	0.0004
Molybdenum	0.0001	0.0005	0.0001
Nickel	0.0002	0.001	0.0002
Thallium	0.00005	0.00025	0.0001
Vanadium	0.00005	0.00025	0.0002
Arsenic*	0.00002	0.0001	0.0001
*See §8.24 for As standard preparation			

Table 18.18: REE MDL/PQL

Rare Earth Element	MDL (mg/L)	PQL (Mg/L)
Ce	0.0001	0.0005
Dy	0.0001	0.0005
Er	0.0001	0.0005
Eu	0.0001	0.0005
Gd	0.0001	0.0005
Ho	0.0001	0.0005
La	0.0001	0.0005
Lu	0.0001	0.0005
Nd	0.0001	0.0005
Pr	0.0001	0.0005
Sc	0.0001	0.0005
Sm	0.0001	0.0005
Tb	0.0001	0.0005
Tm	0.0001	0.0005
Y	0.0001	0.0005
Yb	0.0001	0.0005

**Table 18.19:
ICPMS Linear Dynamic Range (LDR) Limits [M200.8 only] (mg/L)**

Element	Linear Dynamic Range (mg/L)
Beryllium	2.0
Boron	0.2
Aluminum	10
Vanadium	2.0
Chromium	2.0
Manganese	2.0
Iron	10
Cobalt	2.0
Nickel	5.0
Copper	5.0
Zinc	10
Arsenic	2.0
Selenium	5.0
Molybdenum	2.0
Silver	0.05*
Cadmium	2.0
Tin	0.2*
Antimony	0.25
Tellurium	2.0
Cesium	2.0
Barium	5.0
Thallium	2.0
Lead	5.0
Thorium	2.0
Uranium	2.0
*LDR = high cal point	

Table 18.20:
ICPMS Upper Linear Range Verification (ULRV) QC Sample (Method 6020/6020B)
(mg/L)

Element	Conc. (mg/L)
Beryllium	2.0
Boron	0.2
Aluminum	10
Vanadium	2.0
Chromium	2.0
Manganese	2.0
Iron	10

Cobalt	2.0
Nickel	5.0
Copper	5.0
Zinc	10
Arsenic	2.0
Selenium	5.0
Molybdenum	2.0
Silver	0.5
Cadmium	2.0
Tin	2.0
Antimony	0.25
Tellurium	2.0
Cesium	2.0
Barium	5.0
Thallium	2.0
Lead	5.0
Thorium	2.0
Uranium	2.0

Table 18.21:
Detectability Check Standard (DCS)

Element	mg/L
Be	0.000125
B	0.0025
Al	0.005
V	0.001
Cr	0.001
Mn	0.001
Fe	0.005
Co	0.000125
Ni	0.0005
Cu	0.001
Zn	0.005
As	0.0005
Se	0.000125
Mo	0.00025
Ag	0.00025
Cd	0.000125
Sn	0.00125

Sb	0.001
Te	0.0025
Cs	0.0005
Ba	0.00125
Tl	0.00025
Pb	0.00025
Th	0.0025
U	0.00025

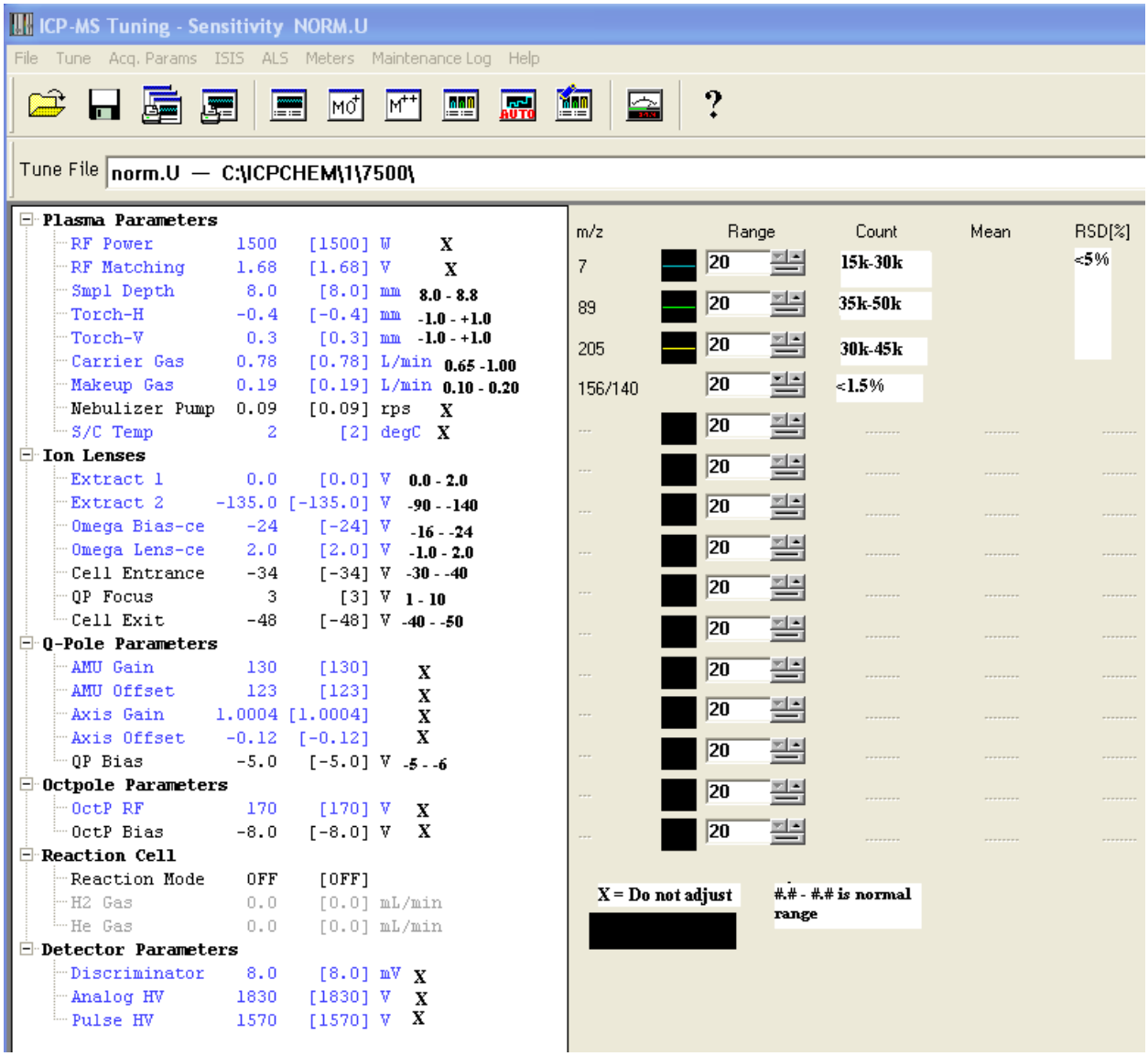
19.0 CORRECTIVE ACTION

19.1 For QC samples that do not meet the method acceptance criteria, refer to §Table 18.9. For retests that will occur past the method hold time, check first with the department supervisor to determine if the reanalysis should be conducted.

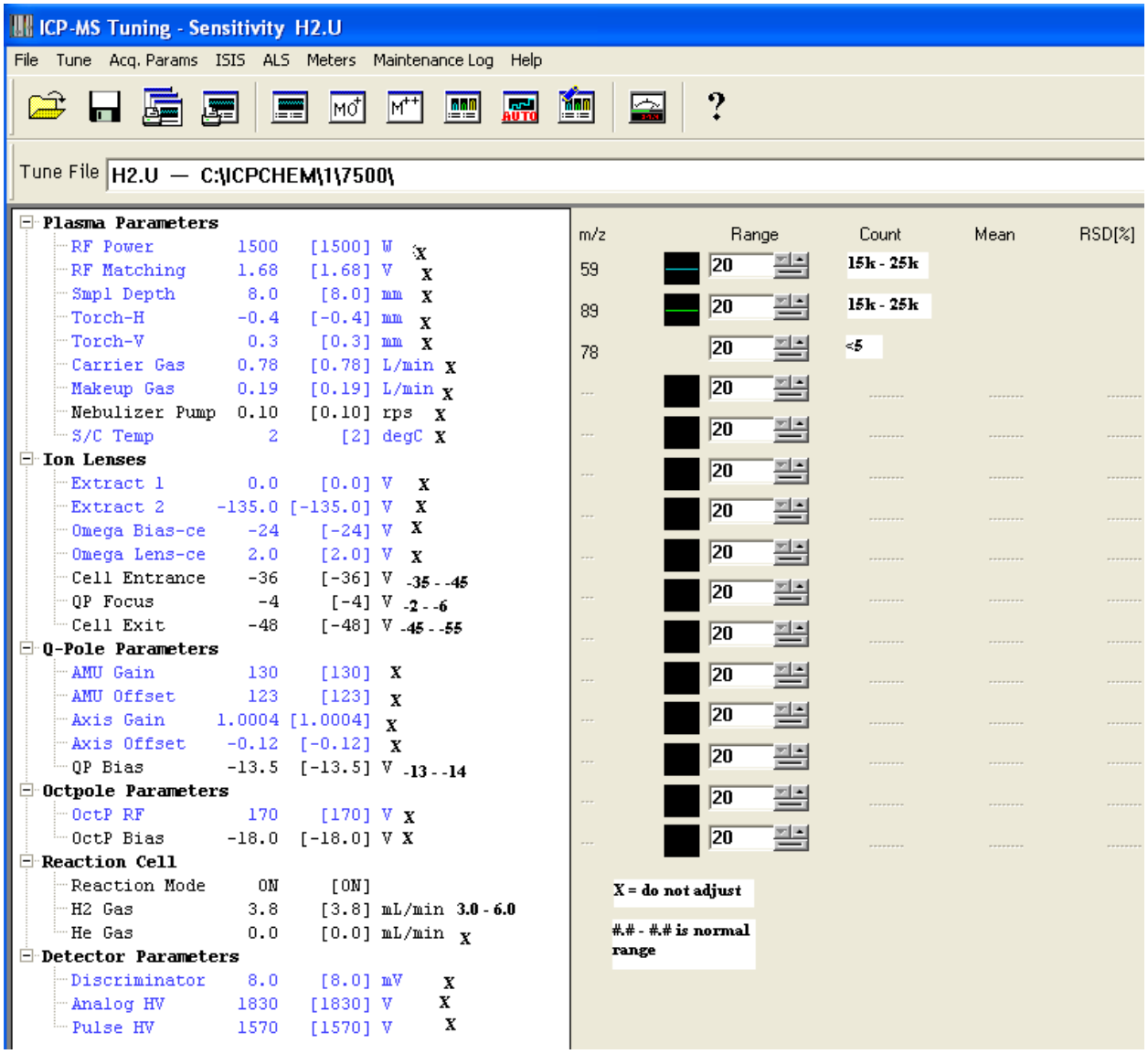
19.2 For any SOP/method deviation fill out §1 of a corrective action report (FRMQA001). If necessary, the department supervisor and/or project manager may provide additional information in the appropriate sections; however, QA/QC does not need to close a minor corrective action. Attach a copy of the minor corrective action report to all workgroups affected. A minor corrective action is for documentation purposes –any SOP or method deviation may be noted on the data review checklist or on the workgroup bench sheet in lieu of using FRMQA001.

19.3 For any system failure a major corrective must be opened and the problem investigated. Consult the QA department to open a major corrective action. The corrective action will be assigned a unique tracking number by the QA/QC Officer (or designee) and will be closed by the QA/QC Officer (or designee) once the failure has been resolved. Use FRMQA001.

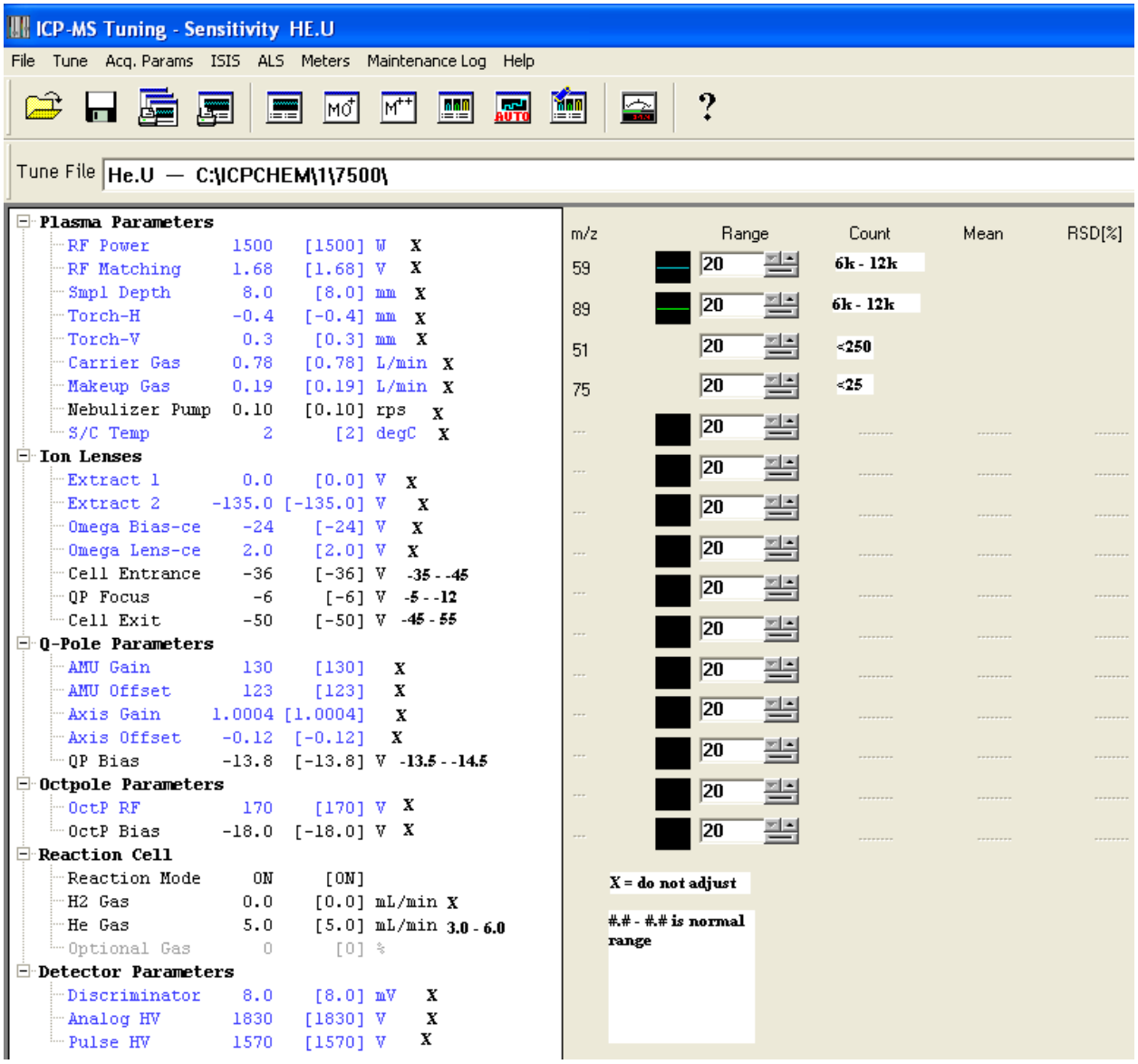
Appendix A



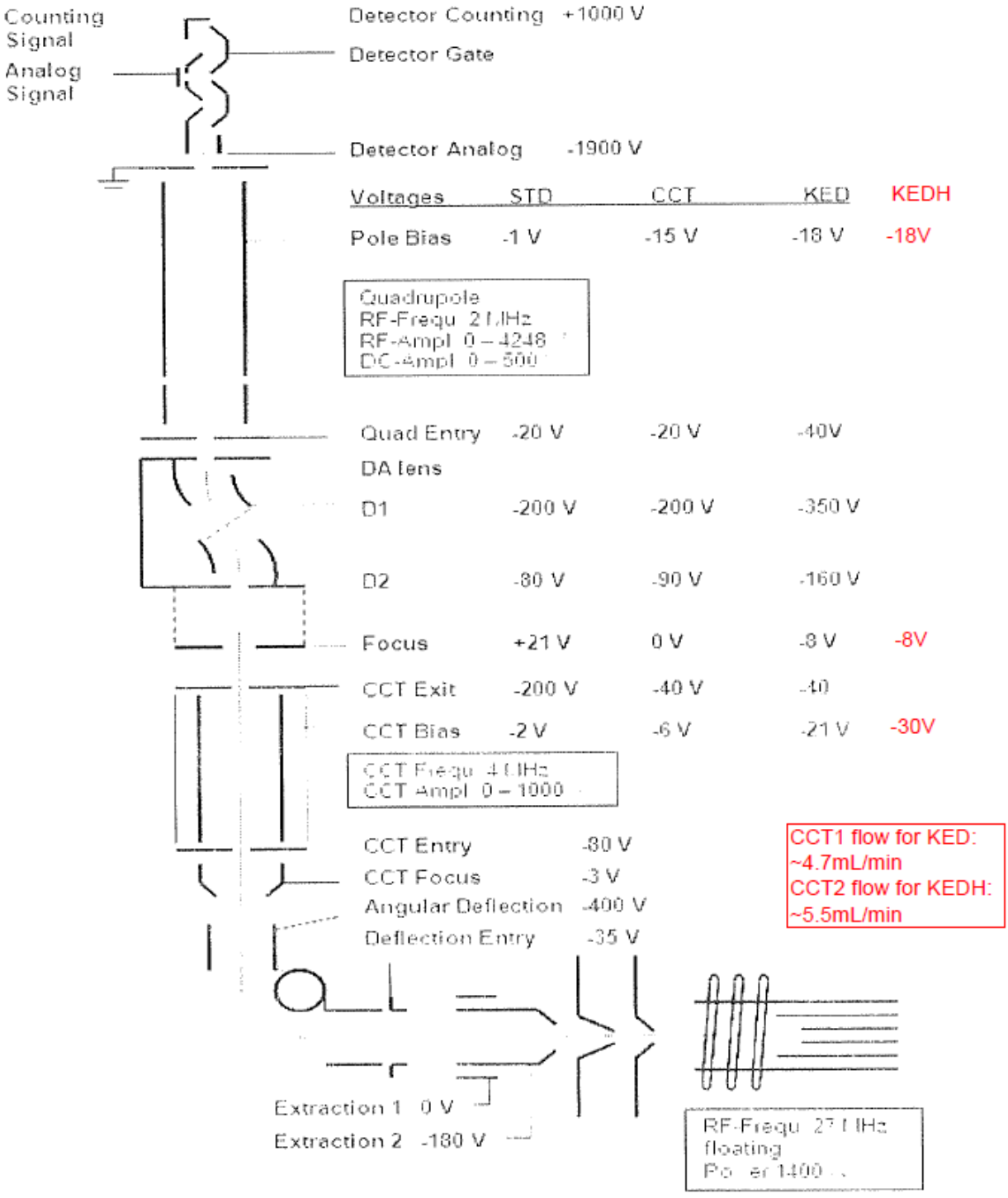
Appendix B



Appendix C



APPENDIX D


Counting Signal
Analog Signal
Detector Counting +1000 V
Detector Gate
Detector Analog -1900 V
Voltages STD CCT KED KEDH
Pole Bias -1 V -15 V -18 V -18V
Quadrupole
RF-Frequ 2 MHz
RF-Ampl 0 – 4248
DC-Ampl 0 – 500
Quad Entry -20 V -20 V -40V
DA lens
D1 -200 V -200 V -350 V
D2 -80 V -90 V -160 V
Focus +21 V 0 V -8 V -8V
CCT Exit -200 V -40 V -40
CCT Bias -2 V -6 V -21 V -30V
CCT Frequ 4 MHz
CCT Ampl 0 – 1000
CCT Entry -30 V
CCT Focus -3 V
Angular Deflection -400 V
Deflection Entry -35 V
CCT1 flow for KED:
~4.7mL/min
CCT2 flow for KEDH:
~5.5mL/min
Extraction 1 0 V
Extraction 2 -180 V
RF-Frequ 27 MHz
floating
Po er 1400
iCAP Q Ion Optics

APPENDIX E

Appendix E - Quick Reference Sheet

			mg/L								
Element	Mass	Default ISTD	ACZ MDL	ACZ PQL	PQV	L3	L4/CCV	L5	LDR	Spike Conc	Element
Be	9	Li 6	0.00008	0.00025*	0.00025	0.02	0.1	0.2	2.0	0.05	Be
B	11	Li 6	0.001	0.005	0.005	0.002	0.01	0.02	0.20	0.01	B
Al	27	Ge 72	0.005	0.015*	0.015	0.1	0.5	1	10.0	0.05	Al
V	51	Sc 45	0.0005	0.002*	0.002	0.02	0.1	0.2	2.0	0.05	V
Cr	52	Sc 45	0.0005	0.002*	0.002	0.02	0.1	0.2	2.0	0.05	Cr
Mn	55	Ge 72	0.0004	0.002	0.002	0.02	0.1	0.2	2.0	0.05	Mn
Fe	56	Sc 45	0.007	0.02*	0.020	0.1	0.5	1	10.0	0.05	Fe
Co	59	Ge 72	0.00005	0.00025	0.00025	0.02	0.1	0.2	2.0	0.05	Co
Ni	61	Sc 45	0.0004	0.001*	0.001	0.05	0.25	0.5	5.0	0.05	Ni
Cu	63	Sc 45	0.0008	0.002*	0.002	0.05	0.25	0.5	5.0	0.05	Cu
Cu[DW]	65	Sc 45	0.002	0.005*	0.002	0.05	0.25	0.5	5.0	0.05	Cu
Zn	66	Ge 72	0.006	0.015*	0.015	0.1	0.5	1	10.0	0.05	Zn
As	75	Sc 45	0.0002	0.001	0.001	0.02	0.1	0.2	2.0	0.05	As
As[DW]	75	Sc 45	0.0005	0.002*	0.001	0.02	0.1	0.2	2.0	0.05	As
Se	78	Sc 45	0.0001	0.00025*	0.00025	0.05	0.25	0.5	5.0	0.05	Se
Se[DW]	82	Sc 45	0.001	0.005	0.00025	0.05	0.25	0.5	5.0	0.05	Se
Mo	98	In 115	0.0002	0.0005*	0.0005	0.02	0.1	0.2	2.0	0.05	Mo
Ag	107	In 115	0.0001	0.0005	0.0005	0.005	0.025	0.05	0.05	0.01	Ag
Cd	111	In 115	0.00005	0.00025	0.00025	0.02	0.1	0.2	2.0	0.05	Cd
Sn	118	In 115	0.0008	0.0025*	0.0025	0.02	0.1	0.2	0.20	0.05	Sn
Sb	121	In 115	0.0004	0.002	0.002	0.0025	0.0125	0.025	0.25	0.01	Sb
Te	125	In 115	0.001	0.005	0.005	0.02	0.1	0.2	2.0	0.05	Te
Cs	133	In 115	0.0002	0.001	0.001	0.02	0.1	0.2	2.0	0.05	Cs
Ba	137	In 115	0.0005	0.0025	0.0025	0.05	0.25	0.5	5.0	0.05	Ba
Hg	202	Bi 209	0.00006	0.00015*	0.00015	0.0002	0.001	0.002	0.002	0.0005	Hg
Tl	205	Bi 209	0.0001	0.0005	0.0005	0.02	0.1	0.2	2.0	0.05	Tl
Pb	208	Bi 209	0.0001	0.0005	0.0005	0.05	0.25	0.5	5.0	0.05	Pb
Th	232	Bi 209	0.001	0.005	0.005	0.02	0.1	0.2	2.0	0.05	Th
U	238	Bi 209	0.0001	0.0005	0.0005	0.02	0.1	0.2	2.0	0.05	U
				* = PQL < 5x MDL							

x

Appendix F: CAR1309 Memo

This appendix addresses issues related to tissue certified reference materials (e.g. LCSS) used in ICP and ICPMS analysis first extracted by the soils department. For more details, refer to CAR1309. ACZ's 3050 extraction does not recover aluminum to the method specified 80-120% acceptance criteria, so aluminum limits are control charted. As such, limits for certain CRMs (e.g. DOLT-5 LCSS) must be entered in LIMS as hi/lo limits in mg/Kg. The standard % recovery configuration is not sufficient. Document control is not aware of special cases where CRMs require limits, but have none listed on the certificate of analysis. It is the responsibility of the department supervisor to ensure that proper limits are entered for tissue CRMs, when required.

Limits should be entered during PCN validation, which is required before any PCN may be used in a workgroup. Supervisors have the permissions required to enter limits using the LIMS PCN edit tool.

1) Contact the soils supervisor to ensure that aluminum limits have been control charted.
    a. QA will log in 4 test samples, which will be digested by the soils department and analyzed by the metals department. Use these four values to control chart new limits at 2σ (default). Control charts should be updated once more data are available (preferably >20 data points):
        i. Find the sample mean (x) and sample standard deviation (σ)
            1. Lower limit = x-2σ
            2. Upper limit = x+2σ
2) All limits need to be converted to mg/Kg prior to entry. Verify acceptance recovery in the analytical SOP (e.g. 80-120%) and enter the converted values in LIMS using the PCN edit tool. See figure 3 for example conversions.

Figure 1: Example DOLT-5 COA, with 80-120% limits converted to mg/Kg

Element	Mass fraction, mg/kg	lo limit	hi limit	units
Arsenic (b,d)	34.6 ± 2.4	27.7	41.5	mg/Kg
Cadmium (a,d)	14.5 ± 0.6	11.6	17.4	mg/Kg
Calcium (c)	550 ± 80			
Cobalt (b,d)	0.267 ± 0.026			

As a preventative measure, CAR1309 implemented an alert in LIMS to notify analysts if limits are required, but have not yet been entered. Limits should be entered during PCN validation, but if they are missed, you will see error messages similar to those in figures 2 and 3 during analytical workgroup creation. Please contact the metals supervisor, and follow steps 1 and 2 above to ensure that limits are properly entered before proceeding with WG analysis.

Figure 2: LIMS limits alert 1

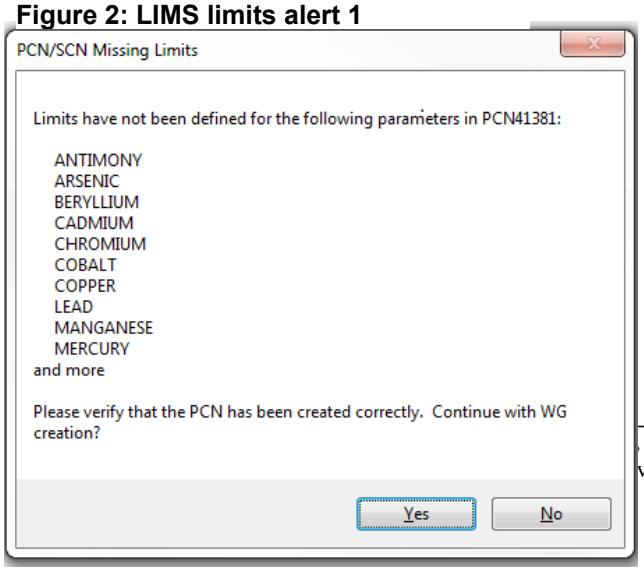
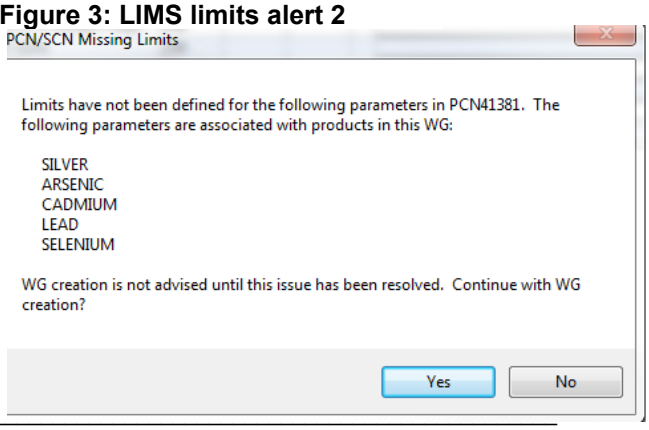


Figure 3: LIMS limits alert 2



, the SOP revision # must match the latest SOP revision # in
ved from all points of use or clearly marked to indicate the