1.0 TITLE

Elemental Analysis by ICP-AES using EPA M200.7/6010B/6010D

2.0 LOCATION

Inorganic Instrument Laboratory

3.0 SCOPE & APPLICATION

Inductively coupled plasma-atomic emissions spectrometry (ICP-AES) determines trace elements in aqueous solutions including soil, sludge, sediment, and biota extracts and digestions; surface water, ground water, waste water, drinking water, and leachates. Digestion or filtration is required for all matrices, including drinking water; refer to the applicable preparation SOPs for details about the digestion or filtration processes. Table §18.3 lists the elements approved for both methods.

4.0 SUMMARY

EPA Method 200.7 is utilized for samples regulated under the Safe Drinking Water Act (SDWA) and the Clean Water Act (CWA). Method 6010B/6010D from the SW-846 guidelines is used for the analysis of samples regulated under the Resource Conservation and Recovery Act (RCRA). Both methods describe a technique for the simultaneous determination of trace elements in solution. The basis of each method is the measurement of atomic emissions from ionized elements by an optical spectrometer and detector system.

Samples in an aqueous solution are nebulized. The aerosol is transported to the argon plasma where it is desolvated, atomized and ionized, resulting in light emissions at characteristic wavelengths for each element. The emitted light enters a spectrometer where adjustable grating is used to separate the wavelengths. The different wavelengths are detected by a Charged Injection Device (CID). This measurement is directly proportional to the concentration of each element in the sample. The measured intensities are transferred to the interfaced PC and compared to calibration curves to yield elemental concentrations.

Modifications:

1) In the case where a calibration blank is failing above the acceptance criteria, samples analyzed by Method 200.7 are accepted if the value is > 10x the ICB or CCB.

2) Due to varying state regulations ACZ is following Method 6010B (revised 1996) and Method 6010D (revised 2014). Where the methods differ, ACZ has chosen the more rigorous of procedures or QC to follow.

3) Because samples are analyzed in small batches, the SIC for Method 200.7 is analyzed only at the beginning of each analysis. One full workgroup takes ~ 2.5 hours, including calibration and QC samples.

4) The Thermo iTEVA v.9.5 software cannot run 4 replicates of the ICV solution as required by Method 200.7. This has been verified by the manufacturer. ACZ's solution is to run two sequential analyses of the ICV solution, with each containing two replicates, for a total of four ICV replicates. SAGE will perform calculations to report average % recovery and %RSD for these four replicates. These values will be displayed in the converted upload file, in the SAGE AREV/SREV screen, and run approval report. It will still be possible to view the four replicates in the raw data file attached to each WG.

5) Method 6010D 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.

5.0 REFERENCES

5.1 "Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometric," Method 200.7, ed. by Theodore D. Martin and John F. Koop, Physical and Chemical Methods Branch, Environmental Monitoring and Support Laboratory, U.S. E.P.A. O.R.D., Cincinnati, OH 45268, v. 4.4, May 1994.

5.2 "Inductively Coupled Plasma-Optical Emission Spectrometry," M6010D SW-846 Update V, Test Methods for Evaluating Solid Waste, U.S. E.P.A, July, 2014; Revision 4.

5.3 "Appendix C to Part 136 -- Inductively Coupled Plasma -- Atomic Emission Spectrometric Method for Trace Element Analysis of Water and Wastes Method 200.7," Code of Federal Regulations.

5.4 Standard Methods for the Examination of Water and Wastewater, 20th Edition, pp. 2-35, Method 2340B, (1999).

6.0 SAMPLE HANDLING & PRESERVATION

6.1 Samples for dissolved metals analysis are filtered through 0.45µm membrane filter and then preserved by the addition of nitric acid to a pH < 2. §Qualtrax ID: 1481. Samples must be filtered and acidified for at least 24 hours before prep or analysis can begin. These samples are stored in plastic bottles with a green dot in the inorganic storage room. When properly preserved they can be stored at room temperature for up to 6 months.

NOTE: If a "green" sample is not available then a new green bottle must be created, logged in, filtered, and acidified. New samples cannot be run until 24 hours after acidification.

6.2 Samples for potentially dissolved metals are acidified and then filtered. Samples must be filtered between 8 and 96 hours after acidification. These samples are stored in plastic bottles in the Cleanroom. Samples are stable for up to 6 months after filtration. §Qualtrax ID: 1274 for additional information.

6.3 Samples for total or total recoverable analysis are preserved with nitric acid to pH < 2 at the time of sampling or as soon as possible after sampling. Samples are stored in plastic bottles with red dots in the inorganic storage room. When properly preserved they can be stored at room temperature for up to 6 months.

NOTE: If a "red" sample is not available then a "raw" sample (unfiltered, unpreserved) may be used. Document the substitution on the workgroup bench sheet.

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 SAGE → 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 for solid samples. They require digestion or extraction prior to analysis and are prepared by the Soils Department.

6.6 Hold Times are set for individual products based on the table below:

Table 6.1: Hold Times

Parameter Description	Matrix	Hold Time Starts – Ends With
Approved metals*	Liquids	180 days form collection to analysis
	Liquids: potentially dissolved	4 days from collection to filtration; 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: other extractions (e.g. AD, 3050, HF, MWMT, WET)	180 days from collection to analysis
	Solids: RBLP	180 days from collection to filtration; 7 days from filtration to analysis
Cu-*, Pb-*	Drinking Water (DW)	14 days from collection to acidification

*see Table §18.3 for a full list of approved metals

7.0 APPARATUS AND SUPPLIES

7.1 Thermo iCAP ICP
- 7.1.1 Interfaced PC with iTEVA software
- 7.1.2 Interfaced chiller
- 7.1.3 Thermo high solids nebulizer, or equivalent
- 7.1.4 High solids, wide bore torch or equivalent
- 7.1.5 Cyclonic spray chamber with knockdown baffle

7.2 Interfaced autosampler
7.3 Peristaltic pump tubing in various sizes
7.4 Argon gas supply, welding-grade or better
7.5 8mL autosampler tubes
7.6 Class A volumetric flasks and pipettes in various sizes
7.7 Fixed and adjustable volume pipettes, accurate delivery verified, §Qualtrax ID: 1522
7.8 Analytical balance, calibration verified before use §Qualtrax ID: 1522
7.9 Type I water system, 18MΩ or greater. Verify daily §Qualtrax ID: 1522

8.0 REAGENTS AND STANDARDS

NOTES:
- Prepare standards using Class A volumetric flasks and Type I water unless otherwise noted. Clean flasks with 1:1 HNO_3:H_2O and rinse with Type I water 3 times before and after each use. Volumetric pipettes are cleaned in a pipette washer using DI H_2O for 2 hours.
- Volumes may be dispensed with Class A volumetric pipettes or mechanical pipettes.
- Always add acid to water to avoid reactions.
- Trace metal grade (TMG) acid is used unless otherwise stated.

- Prepared standards are stored in plastic containers at room temperature in the inorganic instrument lab.

8.1 Concentrated Nitric Acid (HNO_3), Trace Metals Grade (TMG), observe manufacturer's expiration date.

8.2 Concentrated Nitric Acid (HNO_3), ACS Grade, observe manufacturer's expiration date.

8.3 Concentrated Hydrochloric Acid (HCl), Trace Metals Grade (TMG), observe manufacturer's expiration date.

8.4 Concentrated Hydrochloric Acid (HCl), ACS Grade, observe manufacturer's expiration date.

8.5 Single and Multi-element stock standards of varying concentrations, ultra high purity ICP/ICPMS. Observe manufacturer's expiration date.

8.5.1 Aluminum (10,000mg/L)
8.5.2 Antimony (10,000mg/L and 1000mg/L)
8.5.3 Arsenic (10,000mg/L and 1000mg/L)
8.5.4 Barium (1000mg/L)
8.5.5 Beryllium (1000mg/L)
8.5.6 Bismuth (10,000mg/L and 1000mg/L)
8.5.7 Boron (1000mg/L and 10,000mg/L)
8.5.8 Cadmium (1000mg/L
8.5.9 Calcium (10,000mg/L)
8.5.10 $CaCl2 \cdot 2H_2O$ (27.26% Ca) solid
8.5.11 Chromium (1000mg/L)
8.5.12 Cobalt Cal Stock (1000mg/L)
8.5.13 Cobalt ICV Stock (1000mg/L)
8.5.14 Copper (1000mg/L)
8.5.15 Gallium (1000mg/L and 10,000mg/L)
8.5.16 Iron (10,000mg/L)
8.5.17 Lead (10,000mg/L and 1000mg/L)
8.5.18 Lithium (1000mg/L)
8.5.19 Magnesium (10,000mg/L)
8.5.20 $Mg(NO_3)_2 \cdot 6H_2O$ (9.48% Mg) solid
8.5.21 Manganese (10,000mg/L and 1000mg/L)
8.5.22 Molybdenum (1000mg/L)
8.5.23 Nickel Cal Stock (1000mg/L)
8.5.24 Nickel ICV Stock (1000mg/L)
8.5.25 Phosphorous Cal Stock (10,000mg/L)
8.5.26 Phosphorous ICV Stock (10,000mg/L)
8.5.27 Potassium (10,000mg/L)
8.5.28 KCl (52.44% K) solid
8.5.29 Scandium (10,000mg/L and 1000mg/L)
8.5.30 Selenium (10,000mg/L)
8.5.31 Silicon (10,000mg/L)
8.5.32 Silver Cal Stock (1000mg/L)
8.5.33 Silver ICV Stock (1000mg/L)
8.5.34 Sodium (10,000mg.L)
8.5.35 NaCl (39.34% Na) solid
8.5.36 Strontium (1000mg/L)
8.5.37 Sulfur Cal Stock (10,000mg/L)
8.5.38 Sulfur ICV Stock (10,000mg/L)

8.5.39 Thallium (10,000mg/L)
8.5.40 Tin (1000mg/L)
8.5.41 Titanium (1000mg/L)
8.5.42 Vanadium (1000mg/L)
8.5.43 Yttrium (10,000mg.L)
8.5.44 Zinc (10,000mg/L and 1000mg/L)
8.5.45 SPEX Custom Assurance Multi Element Solution for ICV/CCV (See Table §18. 20)

8.6 Tetramethyl-Ammonium Hydroxide Pentahydrate (TMAH) solid: Observe manufacturer's expiration date.

8.6.1 Nebulizer cleaning solution - 1% (m/v) TMAH: 10g of TMAH. QS to ~1L with Type I water in plastic container. Observe manufacturer's expiration date.

8.7 Triton X-100 wetting agent. Observe manufacturer's expiration date.

8.8 Autosampler Rinse Solution: ~ 3.4L Type I water + 400mL ACS grade HNO_3 + 200mL ACS grade HCl + 2-3 mL of Triton X-100 wetting agent in a 4L plastic bottle. Mix thoroughly. Prepare as needed. Expires on the earliest expiration date of the acids or wetting agent.

8.9 Aqua Regia glassware cleaner: **Prepare under a hood immediately before use**. In a beaker, carefully add three volumes of concentrated HCl to one volume of concentrated HNO_3. Discard into drain under hood immediately after use. Prepare as needed using acids that have not expired.

8.10 Calibration Blank/Diluent Solutions: Prepare every 90 days or at manufacture's expiration date, whichever is sooner.

8.10.1 **1% HNO_3 + 5% HCl** (for Dissolved and Total Recoverable): Add 10 mL HNO_3 and 50 mL HCl to ~ 800 mL Type I water. QS to 1L in bottle with Type I water and mix.

8.10.2 **10% HNO_3 + 5% HCl (**for Total): Add 100 mL HNO_3 and 50 mL HCl to ~ 800 mL Type I water. QS to 1L in bottle with Type I water and mix.

8.11 10mg/L Yttrium Internal Standard Solutions: Prepare every 90 days or at manufacture's expiration date, whichever is sooner.

8.11.1 Add 2mL of 10,000mg/L Y stock, 200mL of TMG HNO_3 acid, and 100mL of TMG HCl acid to ~1L Type I water. QS to 2L with Type I water.

NOTE: Prepare §8.12 - §8.18 in the same acid matrices as the calibration blank solutions (§8.10).

8.12 Initial Calibration Verification solution (ICV): Add 10mL of each of the Spex Custom Assurance Multi Element Solutions + appropriate amounts of elemental Ag, Co, Ni, P, and S to ~500mL Type I water. QS to 1000mL. See Table §18.11 for final concentrations. Prepare every 90 days or at manufacture's expiration date, whichever is sooner.

8.13 Continuing Calibration Verification (CCV) solution: Add 5mL of each of the Spex Custom Assurance Multi Element Solutions + appropriate amounts of elemental Ag, Co, Ni, P and S to ~500mL Type I water. QS to 1000mL. See Table §18.17 for final concentrations. Prepare every 90 days or at manufacture's expiration date, whichever is sooner.

8.14 Practical Quantitation Verification Check Standard (PQV):

Intermediates: Prepare in 5% Nitric acid:

8.14.1 PQV Intermediate: See Table §18.12 for final concentrations. Prepare every 90 days or at manufacture's expiration date, whichever is sooner.

8.14.2 Ag PQV Intermediate: Refer to Table §18.13 for final concentration. Prepare every 28 days or at manufacture's expiration date, whichever is sooner.

Working Solution:

8.14.3 Pipette 0.5mL of each PQV intermediate into a 50mL volumetric flask. QS to 50mL with the matrix matched calibration blank solution. Prepare fresh daily. See Table §18.3 for PQV concentrations.

PQV Prep for TR and THP Workgroups with Drinking Water (DW) matrices only:

Add 0.5mL of each PQV intermediate to 50mL Type I water and prep according to § Qualtrax ID: 1268. This hot block prepped solution is stable to the expiration of the PQV intermediates.

8.15 Method 6010B/6010D Interference Check Standard (ICSAB): Prepare every 90 days or at manufacture's expiration date, whichever is sooner.

8.15.1 Prepare using appropriate amounts of elemental stock standards. QS to 1000mL with Type I water. Refer to Table §18.14 for final concentrations.

8.16 Method 200.7 Spectral Interference Check (SIC) Standard:

8.16.1 Prepare the SIC intermediate in 5% HNO_3 using appropriate amounts of elemental stock standards. See Table §18.15 for final concentrations. Prepare every 90 days or at manufacture's expiration date, whichever is sooner.

8.16.2 For the working level SIC add 10mL of PQV Intermediate, 10mL of SIC intermediate and appropriate amounts of elemental standards. QS to 1000mL with Type I water. Prepare every 90 days or at manufacture's expiration date, whichever is sooner. See Table §18.16 for final concentrations.

8.17 Matrix Spike/LFB/LCSW:

8.17.1 Intermediate Solutions: There are four intermediate solutions used to make the working level spike. Refer to Tables §18.6 – §18.10 for final concentrations. Prepare spikes 1-3 every 90 days, and the Ag/Sc spike monthly, or at manufacture's expiration date, whichever is sooner. Prepare spikes 1-3 and the Ag/Sc spikes in 5% HNO_3.

8.17.2 Working Level Solutions: Add 0.100mL of each intermediate to a 10mL Class A volumetric flask and QS with either client sample (matrix spike) or matrix matched reagent water (LFB/LCWS). See Table §18.19 for final concentrations. Prepare as needed.

8.18 Calibration Standards:

8.18.1 Calibration standards are prepared from single element stock solutions from a different source then the ICV/CCV standards. Prepare every 90 days or at manufacture's expiration date, whichever is sooner. See Tables §18.4 – §18.5 for final concentrations.

8.19 Upper Linear Range Verification (ULRV) Solution:

8.19.1 Prepare a working ULRV solution with concentrations as listed in Table §18.22. Add applicable standards to a 1000mL flask, add 50mL TMG HNO3 and QS. Prepare every 90 days or at manufacture's expiration date, whichever is sooner.

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 Use care when pouring and pipetting reagents. Always add acid to water. Use the proper method when washing glassware.

9.2.3 Do not use tobacco products in the lab. Do not eat in the lab.

9.2.4 Wipe up ALL spills immediately. Implement the Emergency Response Plan if necessary.

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

9.2.6 Do not conduct "experiments" unrelated to the analysis.

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 emergency shower and eye wash station is located in the metals prep lab, and an eye wash bottle in the metals lab.

10.0 INTERFERENCES

10.1 Spectral Interference

10.1.1 Spectral interferences are a result of the principles of detection used in the polychromator. These interferences can cause positive or negative bias on analytes of interest. Forms of spectral interference are:

1) Overlap of a spectral emission from another element.

2) Unresolved overlap of molecular band spectra.

3) Background contribution from continuous or recombination phenomena.

4) Background contribution from stray light from the line emission of high concentration elements.

10.1.2 Overlap of spectral emissions is minimized by utilizing a mathematical correction on the data. Spectral overlaps are investigated and Interelement Correction Factors (IECs) are determined for each instrument. Spectral overlap was carefully considered in selecting the wavelengths used for each analyte. Background effects are compensated for by the use of background correction points adjacent to the analyte line.

10.1.2.1 There is always the possibility that an unexpected and/or uninvestigated element may be present in a given sample and could impact data quality. The IECs are only valid for analytes that are part of ACZs parameter list.

10.2 Physical Interference

10.2.1 Physical interference is generally associated with sample nebulization and sample transport processes. Differences in physical properties such as surface tension, viscosity, density, and total dissolved solids (TDS) from calibrations standards to samples can cause inaccuracies. In high TDS samples there is also the possibility that salt buildup may occur inside the nebulizer, which can cause instrument sensitivity drift and sample carryover, or “memory.”

10.2.2 The primary techniques for minimizing physical interferences is by matrix matching standards to samples as closely as possible, digestion of samples as described in EPA method 200.2/SM3030F, and dilution of samples. Samples with TDS>2000mg/L should be diluted before analysis. Samples with other obvious physical properties (odor, reactivity, color) should be diluted at the analyst’s discretion.

10.3 Chemical Interference

10.3.1 Chemical interferences usually occur within the plasma. They include molecular compound formation, ionization effects, and solute vaporization effects.

10.3.2 Chemical interference is not usually pronounced in ICP, but can occur. When observed, it can be minimized by careful selection of operating conditions (RF power, torch position, etc.), matrix matching or sample buffering procedures. These interferences are highly dependent on the matrix type and the specific analyte of interest.

11.0 PROCEDURES

11.1 **Instrument Set-Up and Maintenance**

11.1.1 Pump tubing should be replaced weekly. Periodically check the pump tubing for pre-maturewear and tear and replace with new tubing if necessary. Worn pump tubes will look flattened. Adjust pump cassettes so solution flows smoothly.

11.1.2 Pull the nebulizer from the spray chamber and disconnect the nebulizer gas line and the sample introduction tubing. Insert the nebulizer into the Teflon® syringe and clean by flushing once with 1%TMAH, once with 1:1 nitric acid, and three times with Type I water.

NOTE: If the nebulizer is not coming clean with the above method, prepare a 25:75 mixture of Fluka® to Type I water. Carefully boil the nebulizer in the solution for 30 minutes in a beaker with a boiling chip under the hood, or soak overnight. Rinse with Type I water, and clean using above method.

11.1.3 Inspect the torch for salt build-up. If observed on the inner injector, clean the torch by boiling in aqua regia for at least 15 minutes or by soaking overnight. **Do not remove the aqua regia solution from the hood!** Rinse the torch thoroughly with Type I water and then with methanol. Allow to dry completely. A hair dryer can be used to speed the drying.

NOTE: The torch can also be cleaned by soaking it in a ChemSolv solution. Consult the bottle for instructions.

11.1.4 Install the torch according to the manufacturer's guideline.

11.1.5 Clean the spray chamber if there is noticeable residue. . Clean with 1:1 HNO_3 and rinse thoroughly with Type I water. 1% TMAH or Formula 409® can also be used prior to the 1:1 HNO_3 if necessary.

NOTE: Use only 409 All-Purpose Cleaner®. Other all-purpose cleaners have been shown to contain contaminates.

11.1.6 Install the spray chamber, insert the nebulizer and reconnect the gas, sample, and waste lines.

11.1.7 Open the iTEVA Analyst instrument control software:

11.1.7.1 Click on the desktop icon, and choose admin as the user name.
11.1.7.2 Click on the analyst icon. Make sure that the most current database is displayed at the top of the method selection screen.
11.1.7.3 Select a method and click OK.

11.1.8 iTEVA has three main components seen in tabs in the lower left hand corner:

11.1.8.1 The 'Method' section controls all analytical operating conditions including method set-up, calibration, QC samples and parameters.

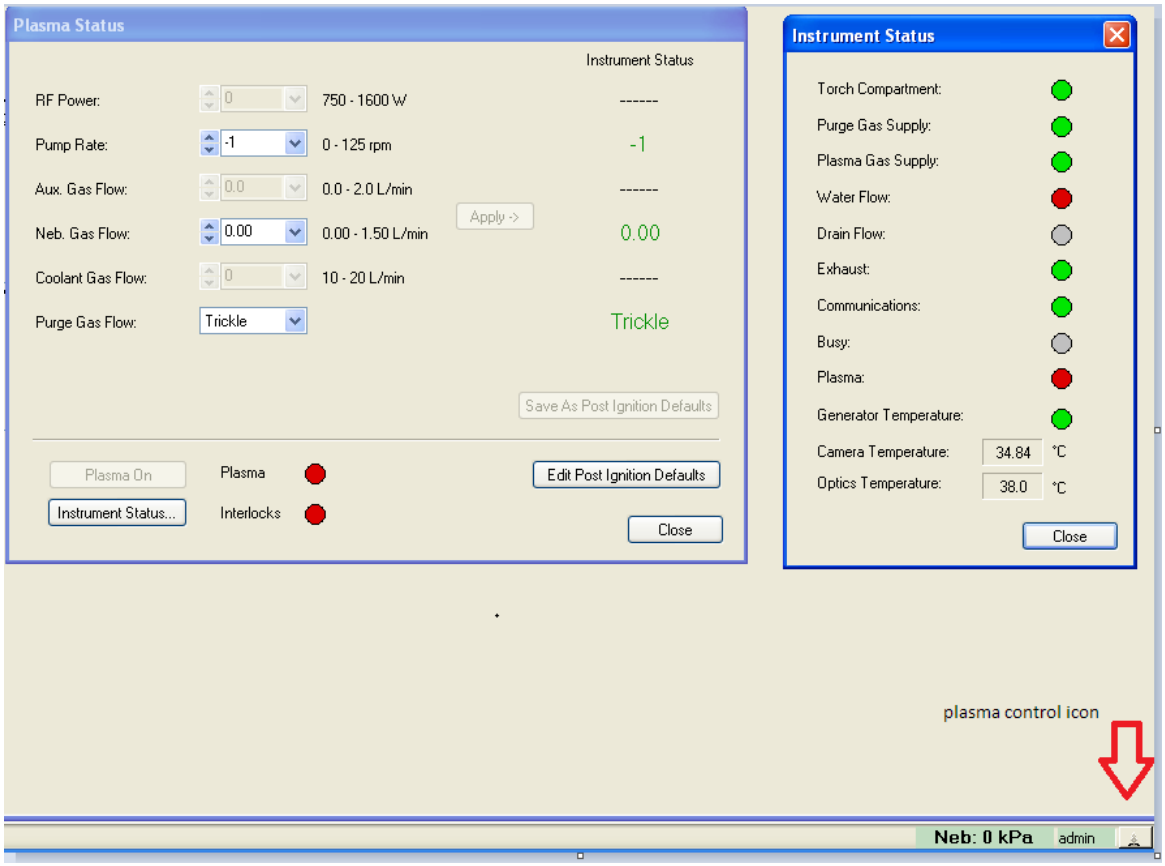
11.1.8.2 The 'Sequence' section controls the run sequence of the samples.

11.1.8.3 The 'Analysis' section is where results are viewed and reports are generated. In addition, other useful components such as scans and recalculations that can aid in instrument troubleshooting are located in this section.

11.2 **Thermo iCAP Start Up**

11.2.1 Turn on the chiller. Wait for temperature to reach the set point.

Figure 11.1: Thermo iCap Start Up



11.2.2 Click the 'Plasma On' button (Figure §11.1) and wait for plasma to ignite.

11.2.3 Ensure proper flow through all pump tubing. Check to see that the spray chamber is being emptied by the waste line. Check rinse solution, and internal standard levels.

11.2.4 Immediately after the plasma ignites the instrument's spectrometer optimizes. The spectrometer will also optimize at the beginning of each analysis. The settings are recorded in the software log and do not need to be entered in the logbook.

11.2.5 Approximately every 6 months or if a new element is added to the method, perform an auto peak adjust.

11.2.5.1 In the 'Analysis' tab, click 'Instrument' → 'Perform Auto Peak.' The software will ask the user to introduce a calibration standard, and will auto align all wavelengths.

11.2.6 Before proceeding with analysis, it is vital that the analyst confirms that the most recent method revision is active. Data run under old revisions is invalid.

11.2.6.1 At the top of the iTEVA Analyst software, there is a banner that displays the method name (such as '200.7') and the active revision (such Rev 3). Confirm that this is the latest revision by consulting the logbook.

11.2.6.2 If the analyst is unsure if the most recent method revision is open, simply close and then re-open iTEVA Analyst. The software will list only the most recent method(s).

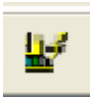
11.2.6.3 If ANY change is made to a method (rinse time change, added element, IEC update, etc.), the change must be clearly described in the logbook. After the change has been made the software requires that the method be saved, and will automatically bump the revision number up. Record the new revision number in the right margin of the logbook.

11.2.6.4 Only after confirming that the most recent revision is active can analysis proceed.

11.2.7 Let the instrument stabilize for 30 minutes before proceeding with analysis.

11.3 **Analysis set-up for Thermo iCAP:**

11.3.1 In the 'Sequence' tab, click 'Auto-Session' → 'New Autosampler.' Choose the default rack configuration (*Cetac Extra Stds 3x7 15x6*).

11.3.2 Click on the initialize autosampler icon  . This will allow manual movement of the autosampler and will establish communication with the PC.

11.3.3 Click 'Sequence' → 'Add' and choose either 200.7, 6010B, or RadBa depending on which method type the WG will be.

11.3.4 Click on the grid format icon  . This will present the autosampler in row/column format.

11.3.5 Next, click the import icon  . Select the desired WG# from the drop down menu. Change any dilution factors or run order at this point. RadBa workgroup sample identification numbers need to be manually entered.

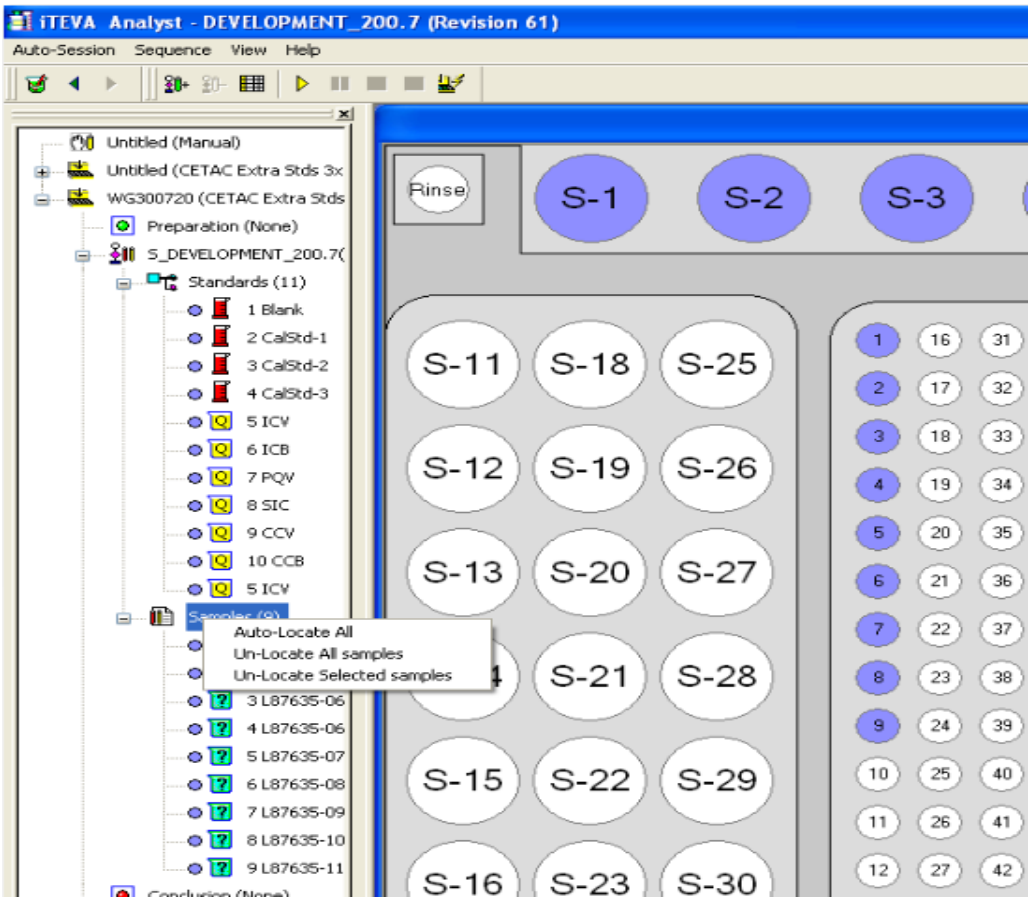
11.3.6 Switch back to the normal view of the sequence table by clicking on the grid format icon again.

11.3.7 While holding down the Shift key, click and drag the 'Standards' to the desired locations. Right click on 'Samples' and select 'Auto-Locate All.'

11.3.7.1 Check that the assigned locations for ALL standards and samples are correct.

11.3.7.2 To change the location of standards or samples, right click and choose 'Un-locate Selected Samples.' While holding down the Shift key, click and drag to the desired location.

Figure 11.2: Analysis set-up for Thermo iCAP



11.3.8 To add additional Workgroups to the sequence, click 'Sequence' → 'Add' and choose the desired method. Follow §11.3.7 to locate standards and samples.

11.3.9 Load the samples for the workgroups into the autosampler. Confirm that the samples are in the correct location by cross checking the software with the physical locations in the autosampler rack.

11.3.10 Click the  icon to start the analysis. Click the 'Analysis' tab to see real time results and to verify QC is passing for the desired elements.

11.3.11 If the plasma needs to shut down at the end of the sequence, click 'Auto-Session' → 'Modify.' Click the 'Shut Down plasma' option.

11.4 Workgroup Set-Up

11.4.1 Using Workgroup Wizard in SAGE, create a workgroup.

NOTE: SAGE will automatically assign a dilution factor for samples with TDS > 2000mg/L and EC > 3130µS/cm due to physical interferences.

NOTE: SAGE will apply prep dilution factors automatically. Check for accuracy.

11.4.2 Label each sample tube with the log-in number and the dilution factor.

11.4.3 Prepare LFB, LCSW and AS/D according to §8.17.2. Cover with parafilm and mix by inverting the flask at least three times. Transfer the solution to the proper sample tube.

11.4.4 For bench level dilutions, make a check mark next to the dilution factor on the bench sheet to indicate the dilution was made.

11.4.4.1 Prepare dilutions greater than 2X in a 10mL class A volumetric flask. Add the appropriate amount of sample (i.e. 1mL for a 10X dilution), and dilute to the mark with the appropriate calibration blank and mix well.

11.4.4.2 Prepare a 2X dilution in the sample tube using equal parts sample and calibration blank. Invert the tube at least three times to mix thoroughly.

NOTE: Any 2X dilution requires a second check mark next to the dilution factor on the bench sheet to indicate the sample was thoroughly mixed.

11.4.5 If any sample requires a dilution greater than what is listed on the bench sheet, document the new dilution factor and reason for the dilution on the bench sheet. Possible reasons for dilutions are color, sediment, odor, reactivity with acid, apparent TDS, etc. Initial and date the change. Make a check mark next to the dilution factor on the bench sheet to indicate the dilution was made – it is imperative that values reported for client and QC samples reflect the correct dilution factor.

11.4.6 For 6010B/6010D analyses prepare the SDL by pipetting 2mL of client sample into a 10mL volumetric flask (DF = 5X). If the client sample has a bench dilution, dilution factor is multiplied by 5X. QS with the appropriate calibration blank solution and mix.

11.4.7 Analyze soils extracts, leachates, and digestions with all QC prepared by the Soils department.

11.4.7.1 Digest TCLP, 1312, and MWMT workgroups adding the appropriate amount of spikes prior to digestion. §Qualtrax ID: 1268.

NOTE: Add 1mL Ba to LFB, MS, and MSD in TCLP workgroups, and upload using the IITCLPSPIKE SCN to reflect added Ba.

11.4.7.2 All other workgroups received from soils should be run with a MS/MSD and a SDL for every 20 samples.

NOTE: SP are prepared only with a DUP for every 20 samples. No additional QC is necessary.

11.4.7.3 Dilute AD extracts at a 5X. Dilute 3052s and non-DI WETs at a 10X to minimize possible matrix effects.

11.4.8 Pour off samples into appropriately labeled tubes.

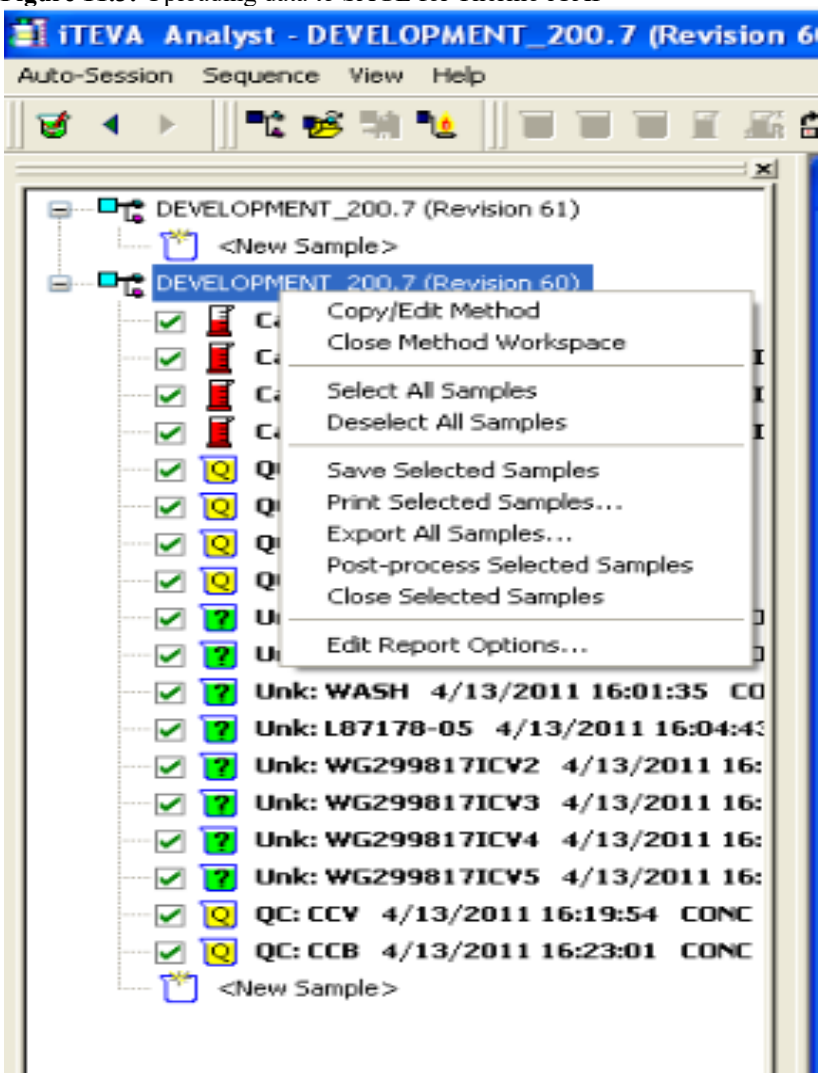
11.5 **Uploading data to SAGE for Thermo iCAP:**

11.5.1 Open the iTEVA Analyst software.

11.5.2 The results should be displayed in the 'Analysis' tab. If the software has shut down or you are trying to access previously run workgroups that are not displayed, click 'Results' → 'Open.' Click 'Search' in the pop up window. Highlight the data that needs to uploaded and click the check box. Click 'OK.' Data will show up in the analysis tab (Figure §11.3).

11.5.3 Right click at the top of the sequence that is to be uploaded. Choose 'Export All Samples' (Figure §11.3). Enter the WG# and click OK.

Figure 11.3: Uploading data to SAGE for Thermo iCAP

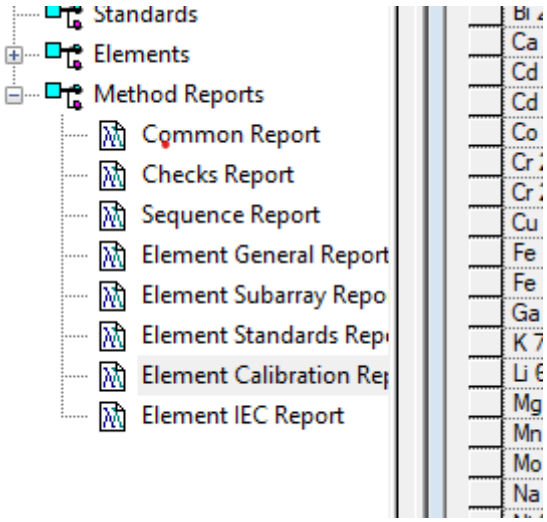


11.5.3.1 Print the workgroup to PDF Creator. Right click at the top of the sequence and select 'Print Selected Samples.' If the default printer is not set to PDF Creator, make sure to select it prior to clicking OK.

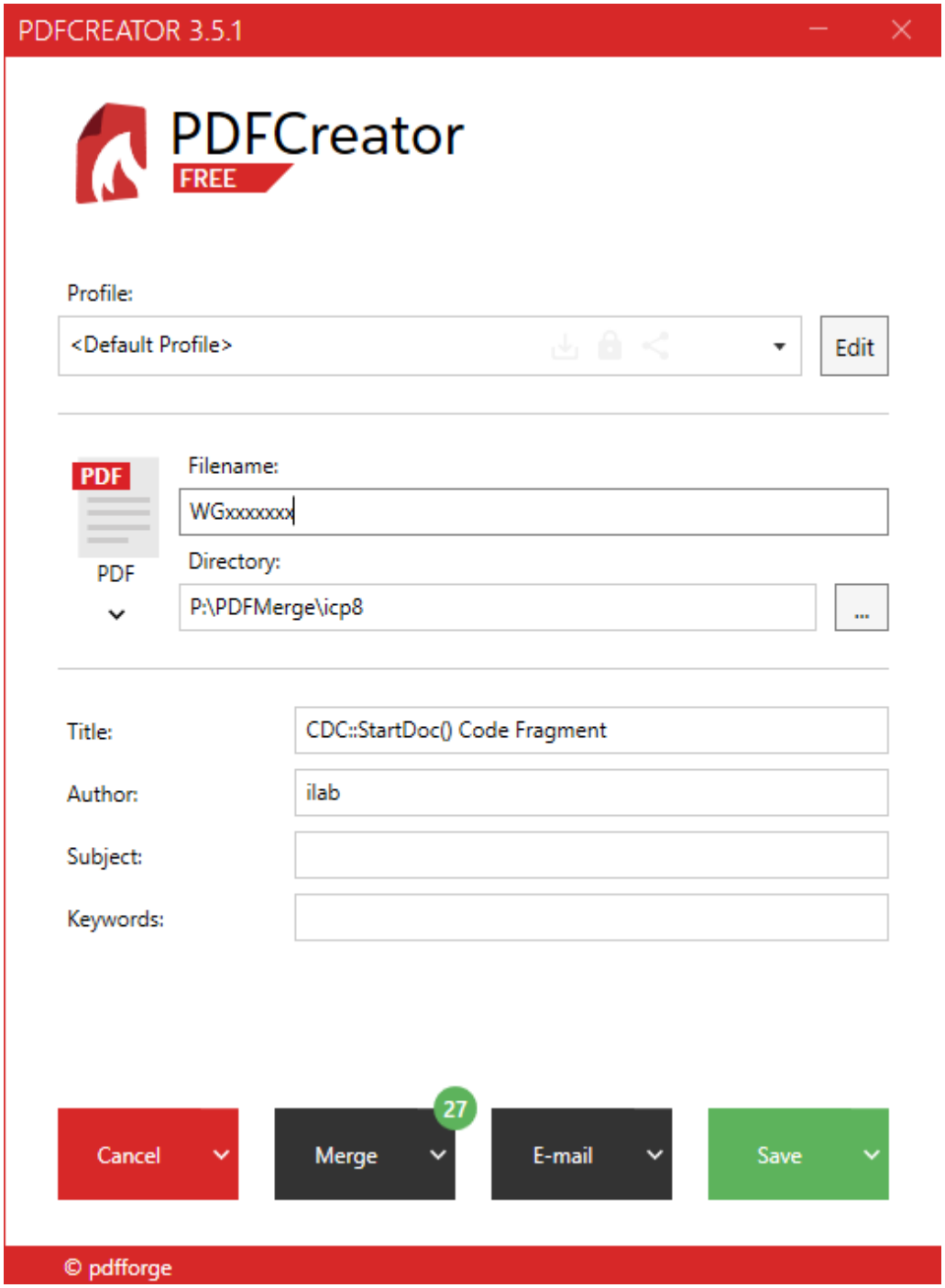
11.5.3.2 The samples will be electronically printed as individual files and sent to the P:\PDFmerge\icpX folder associated with the instrument PC.

11.5.3.3 Print a copy of the most current reagent sheet to the PDF Creator printer.

11.5.3.4 Print a copy of the calibration report to the PDF Creator printer. Calibration report can be found by clicking the method tab, select 'Method Reports', and click on Element Calibration Report. Right click on the report and print.



11.5.3.5 Once the PDF Creator screen pops up with all associated files, enter the WG# in the Filename box and click the ∨ in the merge box and select 'Merge All'. Once merged enter the WG# in the Filename box and click save when finished.

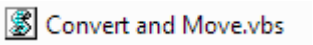


11.5.3.6 Files will be merged and sent to the P:/PDFmerge/ICPx/ folder.

11.5.4 Check the workgroup for saturation. If there is saturation go to the U:/input/ICP7/WG#.txt file, or access it from the (W:) drive. Find the sample/s that saturated and edit the values that came up as ***** and ----- with dummy numbers. Remove all the ^ symbols and '*S*'s. The k flags do not have to be removed for the workgroup to upload properly. Document

the sample number on the bench sheet noting that dummy numbers were entered prior to uploading.

11.5.5 Convert and move the samples to automatically upload into SAGE.

11.5.5.1 Double click the 'OLD' 

icon on the desktop. Enter the WG# when prompted and click OK.

NOTE: The 'convert and move' function combines the two separate ICV analyses to meet Method 200.7 requirements. See §4.3 for details. If more than 2 ICVs are uploaded in a WG, an error message will appear.

11.6 **Data Review**

11.6.1 If dilutions were not entered prior to analysis / upload then they must be corrected. Open the upload file found in U:/input/ICP7/, or the (W:) drive. Correct the dilution factor(s) in the 'Custom ID2' line and save the file. Make sure WG is at WIP and double click convert and move icon. Enter WG# and press Enter.

11.6.2 Review data in SAGE (AREV). Complete a data review checklist §Qualtrax ID: 1138 detailing any problem or QC failure and document the associated action(s) needed to successfully complete the analysis of samples. See
11.6.3 Table 18. 1 and Table 18. 2 for corrective actions for QC failures.

11.6.4 Set any QC failures to FAIL and update the status of the associated analytical samples to REDO or REDX. If data will be qualified, note the failures on the review sheet and the appropriate qualifier(s) used.

11.6.5 Any sample that OCALs' must be retested on an appropriate dilution. Estimate the final concentration of the diluted sample so that the value is within the calibration range and well above the PQL. If the data uploads with a "B" or "U" qualifier, then retest the sample on a smaller dilution or provide an explanation to indicate the reason for accepting the data.

11.6.6 If the Yttrium internal standard is out of range, the sample should be put to REDO. Y uploads to SAGE and will alert for samples or QC if it is outside the 80-120% limits. Dilute sample based on the recovery of the Y to prevent failures upon re-run. If a sample cup was missed, the Y will recover very high (>200%), visually verify that the sample was missed. If the sample cup was missed, do not dilute the sample for the re-run.

NOTE: SAGE calculates the Yttrium recovery based on the limits of the QC. This can cause false alerts on the initial QC and spike recoveries. As long as the recovery is within 80-120%, QC is acceptable.

11.6.7 If a LOW alert appears in SAGE, then the sample must be reanalyzed on a dilution. Go up one dilution factor from the original dilution (1X → 2X, 2X → 5X etc.). This reduces matrix interference.

11.6.8 If an OCAL alert appears in Sage for Ag by a digested analysis, the sample must be sent to REDX and (re)prepped on a dilution so that the Ag concentration in the prepped digestate is <1mg/L. Ag has been shown to precipitate at concentrations above 2mg/L,

and bench level dilutions may deliver biased low data. See CAR1460/Qualtrax CAR5142.

11.6.9 If a sample saturates, dilute the sample at least 2 factors up from the original dilution (1X → 5X, 2X → 10X etc.). If the analytes of interest have a 'k' qualifier in the raw data, it needs to go to REDO. Samples with no 'k' qualifier can be passed.

11.6.10 Samples analyzed on a 2X must be inspected for proper mixing following analysis.

11.6.10.1 Access the PDFMerge file in the P drive (P:/PDFMerge/ICP#) and find the appropriate workgroup.

11.6.10.2 Use Control F to cycle through all 2X dilutions and verify that the %RSD for Ca (commonly found in high concentrations) is below 10%. If Ca has a low concentration in the sample then check the %RSD of other cations or elements that routinely have a higher concentration.

11.6.10.3 If not properly mixed, set all analytes to REDO in SAGE.

11.6.11 Attach all supporting documentation and turn in the complete data package for SREV.

12.0 QUALITY CONTROL

To ensure data validity and quality, a series of QC samples are analyzed with each workgroup. These are required by the method or by other regulatory agencies. Refer to Table §18.1 and Table §18.2 for specific QC types, frequency, and acceptance criteria.

12.1 Calibrate the instrument before each workgroup.

12.2 Determination of Upper Linear Range (ULR), Method 200.7:

12.2.1 Perform ULR verification whenever IECs are run (Bi-annually). Also, perform an ULR study when a change in analytical performance caused by a change in instrument hardware or operating conditions dictates they be redetermined. The data collected from IEC determination can be used, or use the following procedure:

12.2.2 Prepare single-element solutions at the ULR. Prepare each in 10% HNO_3 + 5% HCl. Prepare Ag solutions right before they are to be analyzed. Record all PCNs used.

12.2.3 Calibrate the instrument and verify the calibration (ICV/ICB). Use 10% limits for the ICV and ± 3X the MDL for the ICB. Run each ULR standard, followed by a CCV/CCB at the end of the analysis.

12.2.4 Use form §Qualtrax ID:1146 to calculate the percent recoveries.

12.2.5 Recoveries must be ± 10%. Redo any analyte that does not meet this criterion, remake solution if necessary. If any retest is not successful then the upper limit for the analyte(s) needs to be reconsidered.

12.2.5.1 Remake the solution at a slightly higher concentration then you think the ULR should be.

12.2.5.2 Analyze the solution.

12.2.5.3 If it passes within ± 10% of true value, calculate new ULR.

12.2.5.3.1 Multiply the true value of analyte run by 0.1.

12.2.5.3.2 Subtract answer from true value. This is the new ULR for the analyte.

12.2.5.3.3 Round down to a whole number with a factor of five.

12.2.6 Submit the data to the department supervisor, including a reagent sheet with ICV/CCV SCNs, the PCN of the standard used, a copy of the raw data, and all calculations performed. The QA/QC Department will maintain all raw data for ULR studies.

12.3 Determining IECs for Thermo iCAP

NOTE: Determine IEC factors every six months for method 6010B/6010D.

12.3.1 Change all pump tubing, Fluka® nebulizer, clean the spray chamber, clean the POP window, and aqua regia torch to optimize the sample introduction.

12.3.2 Archive current database. Refer to section §13.6.

12.3.3 Use Method 200.7 to run IECs.

12.3.4 Delete all current IEC factors stored in the 'Method' tab of the iTEVA Analyst software. Click on 'Elements' in the tree on the left side of the screen, and under each element delete the IEC k1 factors. In addition, uncheck the 'Use IECs' box for each element.

12.3.5 Set up the automated single element IEC run. (See Figure §12.1)

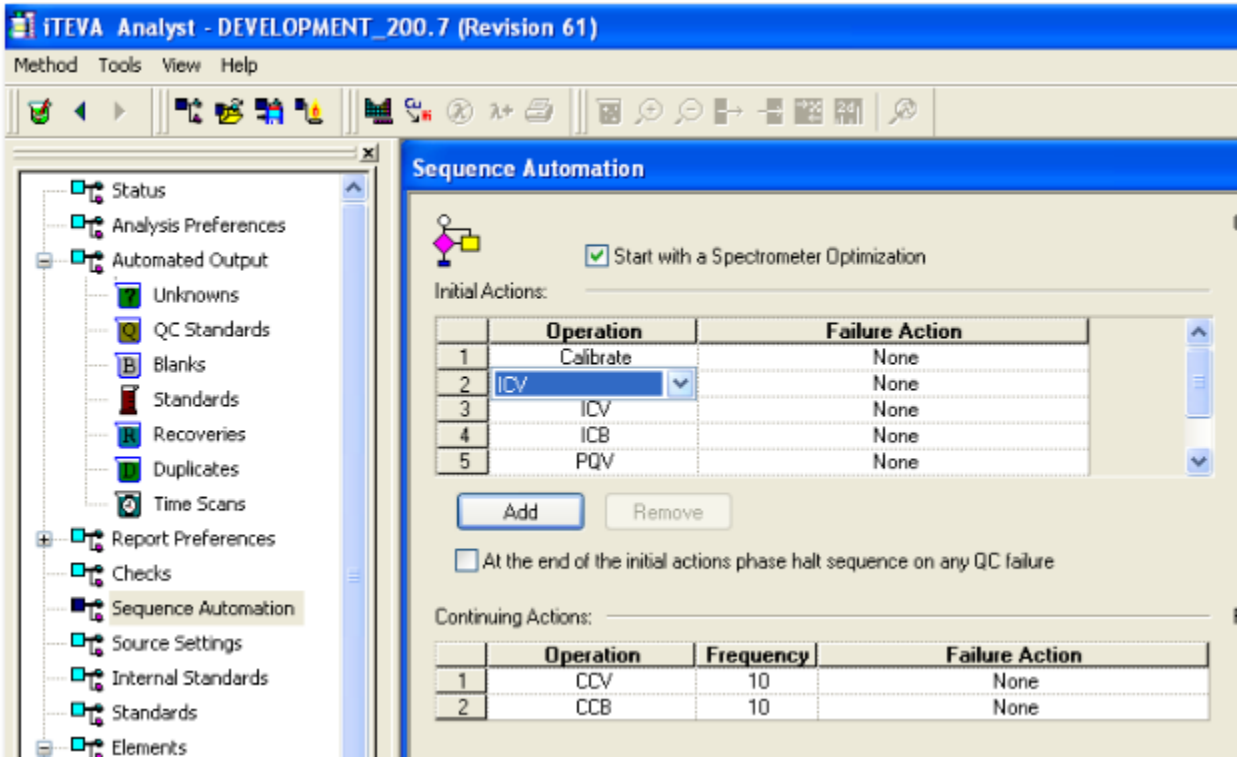
12.3.5.1 In the 'Method' tab, select 'Sequence Automation.'

12.3.5.2 Remove 1 ICV, PQV, SIC and WASH from the 'Initial Actions'.

12.3.5.3 Remove the CCV and CCB from the 'Continuing Actions'.

12.3.5.4 Using the drop down menu 'Add' each single element to this list (Ag, Al, etc.), in the order which they will run, to the 'Initial Actions'.

Figure 12.1: Single Element IEC Run set up



12.3.5.5 Change the rinse time to 180 seconds.

12.3.5.6 After making all the changes to the Sequence Automation, save the method and record the revision number in the logbook.

NOTE: If you leave the page before method is saved, changes will be lost and you have to start over.

12.3.6 Following §11.3, set up a sequence to run the single element standards. Place the calibration standards and the 50mL digestion tubes used to make single element solutions in designated locations and press play to begin the analysis. Some of the ULR standards will overlap cups, make sure to switch out prior to analysis.

12.3.6.1 Set up the Fe225 and Zn213 ULR standards as samples to be analyzed in the sample rack.

12.3.7 Once the calibration is completed, confirm the ICV and ICB are passing within Method 6010B/6010D limits before continuing on to the single element standards.

12.3.8 Confirm that the single element standards are passing within 10% of the true value. The data will indicate if the found value is outside the limits.

If the ULR is not within 10% of the true value, or the CCV/CCB is failing for any analytes, do not autocalc IECs for failinganalyte/s. Failing analytes will need to be re-run under a new calibration after IECs for passing analytes have been calculated.

12.3.9 Print a copy of the raw data into the C:/pdftemp/ folder, along with a copy of the reagent sheet. Do not merge data until all analytes are passing and all required forms are included.

12.3.10 Next, IEC factors need to be calculated and stored for all passing elements before recalibrating for remaining elements. Skip this step for any elements that did not have a passing ULR or had a failing ICV/ICB or CCV/CCB.

12.3.10.1 Click on the 'Analysis' tab.

12.3.10.2 Click on the first single element standard (Ag for example).

12.3.10.3 Click on 'Results' → 'QC Actions' → 'Autocalc IECs.'

12.3.10.4 Select the interfering element from the drop down list. Make sure that the element matches the element from §12.3.10.2

12.3.10.5 Repeat for all passing elements. IEC factors will calculate and be stored in the software.

12.3.10.6 Save the method and record the revision number in the logbook.

12.3.11 Set up a sequence for the remaining elements that did not pass, if any, using the new revision with the saved IECs just calculated. If all elements passed contine to step§12.3.11.7

12.3.11.1 In the 'Method' tab, select 'Sequence Automation.'

12.3.11.2 Using the drop down menu "Remove" each single element that passed initially from this list.

12.3.11.3 After making the changes to the Sequence Automation, save the method and record the revision number in the logbook.

12.3.11.4 Following §11.3, set up a sequence to run the remaining single element standards that did not pass. Locate the calibration standards and the 50mL digestion tubes used to make single element solutions in designated locations and press play to begin the analysis.

12.3.11.4.1 If Fe or Zn were among the failing elements, be sure to set up the Fe225 and/or the Zn213 ULR standards as samples to be analyzed in the sample rack.

12.3.11.5 Start the analysis. Once the calibration is completed, confirm the ICV and ICB are passing within Method 6010B/6010D limits for needed elements before continuing on to the single element standards.

12.3.11.6 Repeat steps §12.3.8 through §12.3.11.5 until all elements are passing and IECs have been autocalced for all elements.

12.3.11.7 Check the "Use IEC" box for each element.

12.3.11.8 Correct the IEC values for SiO_2 by copying the values directly from the Si values. This is due to the SiO_2 line being multiplied by 2.14.

12.3.11.9 Save the method and record the revision number in the logbook.

12.3.12 Print an IEC report to the PDF temp folder after Autocalc IECs is finished. From the 'Method' tab click on 'Method Reports' → 'Element IEC Report.'

12.3.13 Restore the method to original settings.

12.3.13.1 Remove all single elements from the initial actions.

12.3.13.2 Add 1 ICV, PQV, SIC, ICSAB (will be removed later), ULRV (will be removed later), and 2 WASHes to initial actions, 1 that will be removed later.

12.3.13.3 Add CCV and CCB to continuing actions.

12.3.13.4 Change rinse time to 75 seconds.

12.3.13.5 Save the method and record the revision number in the logbook.

12.3.14 Copy the IEC factors to the 6010B method. Make sure method 200.7 is active.

12.3.14.1 Click on 'Method' at the top left of the screen and choose 'Save As'.

12.3.14.2 Click the 'Overwrite method and bump revision number' button.

12.3.14.3 Type the method name you want to save as and click 'OK'. Save the method and record the revision number in the logbook.

12.3.14.4 Remove 1 ICV and the SIC from the initial actions and add in the ULRV and an additional WASH. Save the method and record the revision number in the logbook.

12.3.14.5 Change number of reps to 3 under 'Analysis Preferences' and save the method and record the revision number in the logbook.

12.3.15 Copy the IEC factors to the RadBa method. Make sure method 200.7 is active.

12.3.15.1 Click on 'Method' at the top left of the screen and choose 'Save As'.

12.3.15.2 Click the 'Overwrite method and bump revision number' button.

12.3.15.3 Type the method name you want to save as and click 'OK'. Save the method and record the revision number in the logbook.

12.3.15.4 Remove 1 ICV, PQV, SIC, ICSAB, and WASH from the initial actions.

12.3.15.5 Remove the CCV and CCB from the continuing actions. Save the method and record the revision number in the logbook.

12.3.16 Restore 200.7 method by removing the ICSAB and the ULRV from the initial actions. Save the method and record the revision number in the logbook.

12.3.17 Submit an electronic copy of the all supporting raw data, the IEC report, and ULR verification spreadsheet§Qualtrax ID: 1146, to the department supervisor. The QA/QC department will maintain all data. Include a cover sheet, a standard reagent sheet, ICV/CCV SCNs, all calculations, and all elemental standard PCNs.

12.4 If there are systematic failures of analyte(s) in the SIC, use the following steps to fix the interferences. These failures are usually attribute to drifting interferences from the high concentration SIC elements (Al, Ca, Fe, Mg, Mn).

12.4.1 Prepare single element solutions at the SIC or ULR concentration for each of the following elements: Al, Ca, Fe, Mg, Mn. These are found in high concentrations in the SIC and cause the most interference. If interfering element is known, just prepare the one that is needed.

12.4.2 With IECs on, calibrate the instrument and run an ICV/ICB to confirm calibration.

12.4.3 Run single element solutions with a 180 second rinse time between samples with a continuing calibration check (CCV/CCB) after.

12.4.4 Review data. If any of the analytes of interest are outside of the MDL range a new IEC factor needs to be calculated.

12.4.5 Calculate a new correction factor manually:

12.4.5.1 Uncheck the 'use IECs' box for the element needing to be corrected, and zero out the factor that needs to be changed. Remove the PQV and SIC from initial actions, and change rinse time to 180 seconds. Record new revision in logbook.
12.4.5.2 Re-run the high concentration element/s that interfere with the analyte of interest.
12.4.5.3 Calculate a new IEC factor by dividing the concentration of the analyte of interest by the interfering element.
12.4.5.4 Enter the new factor in manually and recheck the 'use IECs' box. Add PQV and SIC back into initial actions. Change rinse time to 75 seconds.
12.4.5.5 Save the method and record revision in logbook.
12.4.5.6 Change the other active methods IEC factors and save revisions in logbook
12.4.5.7 Document calculations in logbook.

13.0 DATA CALCULATIONS, DATA REPORTING & ARCHIVING

13.1 Instrument Standardization Calculations

13.1.1 In the iTEVA 'Analyst' software select the 'Method' tab and click on 'Elements' in the tree. Select the 'Fit' tab to see a graphical and mathematical display of the calibration curve.

13.1.2 A multi-point linear calibration is used. Correlation must be > 0.995. *A0(offset)* denotes the intercept (b) and *A1(gain)* denotes the slope (m).

13.1.3 Corrected intensities are not stored with raw data packages. Corrected intensities may be found by:

13.1.3.1 Activating the database of interest in the Analyst software (see §13.7).

13.1.3.2 Opening the 'Publisher' software from the iTEVA Control Center. Select 'Report' → 'New Report' and then 'intensity_report.tpl' under the Customized Report Templates column.

13.1.3.3 Select the data to be reported. Click OK and a report with all corrected intensities and intensity ratios will be created. Use these intensities to re-create a calibration.

1) EXTERNAL STANDARD LINEAR CALIBRATION

NOTE: Refer to §Qualtrax ID: 2323 to calculate slope, intercept, COD, and concentration. Use the worksheet titled "ESTD EW".

y=mx+b

Where: y= intensity of analyte (A_x)
m=slope
x= concentration of analyte (C_x)
b=intercept

$$\textbf{Slope (m)} = \frac{\left(\sum_i^n x_i y_i \times \sum_i^n w_i\right) - \left(\sum_i^n x_i \times \sum_i^n y_i\right)}{\left(\sum_i^n w_i \times \sum_i^n x_i^{\,2}\right) - \left(\sum_i^n x_i\right)^2}$$

$$\textbf{Intercept (c)} = \frac{\left(\sum_i^n x_i^{\,2} \times \sum_i^n y_i\right) - \left(\sum_i^n x_i \times \sum_i^n x_i y_i\right)}{\left(\sum_i^n w_i \times \sum_i^n x_i^{\,2}\right) - \left(\sum_i^n x_i\right)^2}$$

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: (variables for **slope (m)**, **intercept (c)**, **calibration coefficient (R)**)
x_i= concentration for the i^{th} calibration standard
y_i= intensity for the i^{th} calibration standard

w_i = weighting factor for the i^{th} calibration standard (=1)
i→n = calibration points in order of increasing concentration

Coefficient of Determination = R^2

Where: R = Calibration Coefficient

Inter-element Correction Factor (IEC) = C_j / C_{IEC}

Where: C_j(mg/L)= the apparent element *j* concentration resulting from the Interferent (at analyte wavelength).
C_{IEC}(mg/L)= the concentration of the interferent in the IEC standard (containing only the interferent).

Corrected Concentration $C_{j(true)} = C_{j(raw)} - \sum_{j=0}^{n}(IEC_{jk} \times C_{k(raw)})$

where: $C_{j(true)}$ (mg/L)= IEC corrected concentration for element *j*
$C_{j(raw)}$ (mg/L)= calculated concentration for element *j*, $\left(\frac{Ax_j - b_j}{m_j}\right)$
Ax_j= intensity of element *j*
m_j = slope of element *j*
b_j =intercept of element *j*
IEC_{jk} = IEC coefficient of element *k* on element *j*
$C_{k(raw)}$ (mg/L)= calculated concentration for element *k*, $\left(\frac{Ax_k - b_k}{m_k}\right)$
Ax_k= intensity of element *k*
m_k = slope of element *k*
b_k =intercept of element *k*
n = number of IEC correction on element *j*

2) INTERNAL STANDARD LINEAR CALIBRATION

NOTE: Refer to §Qualtrax ID: 2323 to calculate slope, intercept, COD, and concentration. Use the worksheet titled "ISTD EW".

y=mx+b

Where: y= intensity ratio, $\frac{analyte\ response}{internal\ standard\ response} = \left(\frac{Ax}{Ais}\right)$
m=slope
x=concentration ratio, $\frac{analyte\ concentration}{istd\ concentration} = \left(\frac{Cx}{Cis}\right)$
b=intercept

Slope (m) $= \dfrac{\left(\sum_i^n x_i y_i \times \sum_i^n w_i\right) - \left(\sum_i^n x_i \times \sum_i^n y_i\right)}{\left(\sum_i^n w_i \times \sum_i^n x_i^{\,2}\right) - \left(\sum_i^n x_i\right)^2}$

$$\textbf{Intercept (c)} = \frac{\left(\sum_i^n x_i^{\,2} \times \sum_i^n y_i\right) - \left(\sum_i^n x_i \times \sum_i^n x_i y_i\right)}{\left(\sum_i^n w_i \times \sum_i^n x_i^{\,2}\right) - \left(\sum_i^n x_i\right)^2}$$

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: (variables for **slope (m)**, **intercept (c)**, **calibration coefficient (R)**)
x_i= concentration ratio for the i^{th} calibration standard (Cx/Cis)
y_i= intensity ratio for the i^{th} calibration standard (Ax/Ais)
w_i = weighting factor for the i^{th} calibration standard (=1)
i→n = calibration points in order of increasing concentration

Coefficient of Determination = R^2

Where: R = Calibration Coefficient

Inter-element Correction Factor (IEC) = C_j / C_{IEC}

Where: C_j (mg/L)= the apparent element *j* concentration resulting from the Interferent (at analyte wavelength).
C_{IEC} (mg/L)= the concentration of the interferent in the IEC standard (containing the interferent only).

Corrected Concentration $C_{i(true)} = C_{i(raw)} - \sum_{j=0}^{n} (IEC_{ij} \times C_{j(raw)})$

Where: $C_{j(true)}$ (mg/L)= IEC corrected concentration for element *j*
$C_{j(raw)}$ (mg/L)= calculated concentration for element *j*, $\left(\frac{(Ax_j/Ais) - b_j}{m_j}\right)$
Ax_j= intensity of element *j*
m_j = slope of element *j*
b_j=intercept of element *j*
IEC_{jk} = IEC coefficient of element *k* on element *j*
$C_{k(raw)}$ (mg/L)= calculated concentration for element *k*, $\left(\frac{(Ax_k/Ais) - b_k}{m_k}\right)$
Ax_k= intensity of element *k*
m_k = slope of element *k*
b_k =intercept of element *k*
n = number of IEC correction on element *j*

3) <u>Calculation for Total Hardness:</u>

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

13.2 Raw data can be accessed on P:/PDFMerge/ICP#/. Files are automatically linked with the scanned workgroup, and data is appended to the end of the workgroup PDF. Raw data can be found in the archive link on the labweb page once the WG has been scanned.

13.3 Results are reported in mg/L. A "U" qualifier indicates the sample value is < MDL. A "B" qualifier indicates the result is between the MDL and PQL and is an estimated value.

13.4 A complete explanation must be documented on the workgroup bench sheet or data review checklist any time a workgroup is re-uploaded.

13.5 Calculations for % Recovery, %RPD, %RSD are listed in ACZ's QAP.

13.6 Instrument Backup and Archiving.

13.6.1 Archive Thermo iTEVA data approximately every week.

13.6.1.1 Restart the PC before archiving data.

13.6.1.2 Copy the most recent database files:
13.6.1.3 For either ICP, copy the files from C:/users/public/iTEVA/Andata/ folder (saved as YYMMDDthermo.udl, .ldf, and .mdf) to the P:/instruments/raw/ICPX/ folder.

13.6.1.4 The IDBA system will back the files up to the archive server from this location only; <u>data is not backed up until it is archived.</u>

13.6.1.5 Periodically delete databases from the C:/ drive that are older than 28 days.

13.6.2 Create a new database after archiving:

13.6.2.1 Open the iTEVA Control Center software. Click 'Tools' → 'Options' and select the 'Application Database' tab. (See Figure §13.1).

13.6.2.2 Click 'Run Database Wizard.'

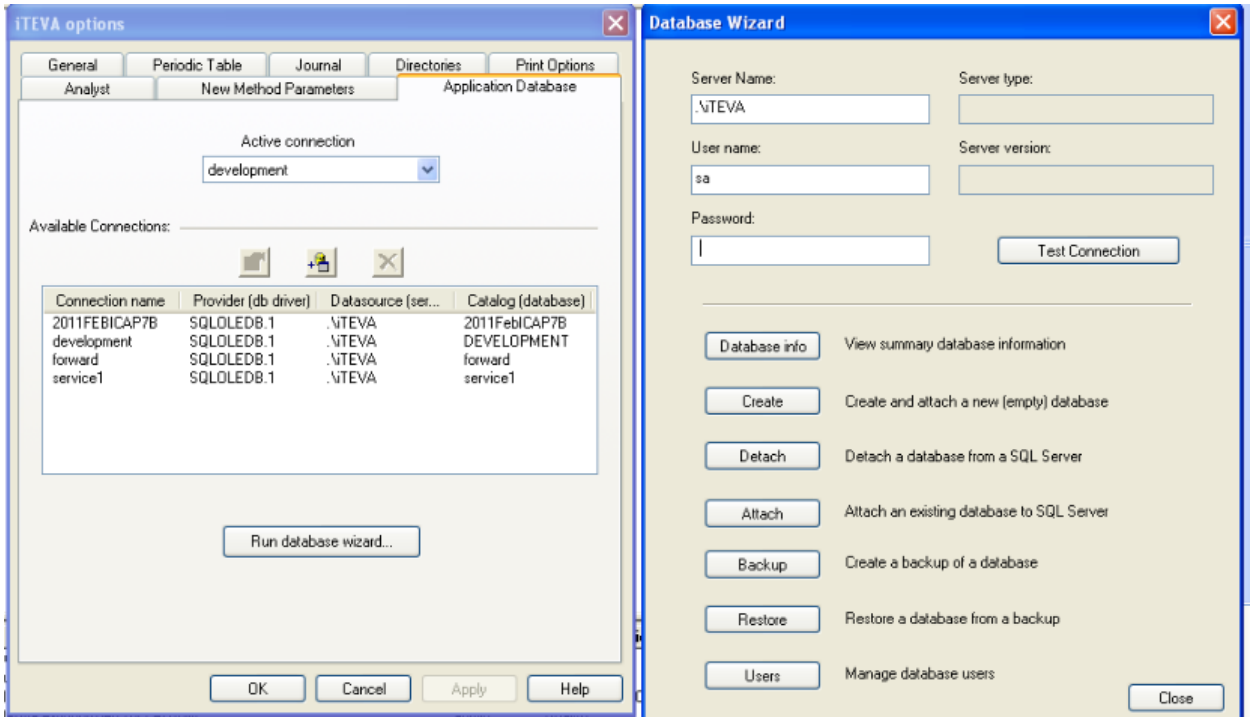
13.6.2.2.1 ICP7: Enter password 'Thermo-123' when prompted.
13.6.2.2.2 ICP8: Enter password 'Thermo-12345' when prompted.

13.6.2.3 Click 'Create' to make a new database.

13.6.2.4 Enter the new database name in the format 'YYMMDDthermo.' Click OK and exit the database wizard.

13.6.2.5 In the 'Application Database' tab click the  icon to connect the new database to the SQL server. Enter the appropriate password when prompted and select new database from dropdown menu. Type in new database when prompted to establish the connection. (See Figure §13.1).

Figure 13.1: Instrument Backup and Archiving



13.6.2.6 Open the iTEVA Analyst software. Select one of the current methods and click on the 'Copy To' button. Select the new database from the drop down menu. Copy any other current methods to the new database. Close the Analyst software.

13.6.2.7 In the 'Application Database' tab select the new database from the 'Active Connection' drop down menu.

13.6.2.8 The new database is now active.

13.7 Restoring archived data to the instrument PC on the Thermo iCAP ICP8.

13.7.1 Restart the PC

13.7.2 Find the Saloon://instrument/ICP8/instruments/Raw/ICP8/ directory (for data 0-5 years old).

13.7.3 Copy and save the files of interest to the instrument PCs:

13.7.3.1 Save to the C:/users/public/iTEVA/Andata/ folder.

13.7.4 Make sure to copy and save the .mdf, .ldf, and .udl files for each database to be unarchived.

13.7.5 In the iTEVA Control Center software, click on 'Tools' → 'Options' → 'Application Database' tab. Select the unarchived database from the 'Active Connection' drop down menu.

13.7.6 Re-open the analyst software. The unarchived database is now active and includes all method revisions, data, calibrations, IECs, etc. that were created while the database was active.

13.7.6.1 Print a workgroup that was analyzed the previous quarter by following § 11.5.2-§11.5.3.6. Once finished submit the WG# and the re-created upload file to the supervisor.

13.7.7 To restore the most current database, follow §13.7.5 and select the current database.

13.8 Restoring archived data to the instrument PC in Thermo iCAP ICP7

13.8.1 Restart the PC.

13.8.2 Find the Saloon://instrument/ICP7/instruments/Raw/ICP7/ directory (for data 0-5 years old).

13.8.3 Copy and save the files of interest to the instrument PCs

13.8.4 Make sure to copy and save the .mdf, .ldf, and .udl files for each database to be unarchived.

13.8.5 In the iTEVA Control Center software, click on 'Tools' → 'Options' → 'Application Database' tab. Click 'Run Database Wizard' → Enter Thermo-123 for the password → Attach → Click the '…' button → Select the database of interest → Change database name (example – change the 1 to a 2) → Click OK → Ignore error message that pops up → Click OK → Close → Add Connection → Enter password → Select Database with newest name → Click OK → Enter newest name → Click Active connection → Select the newest name from the drop down menu.

13.8.6 Re-open the analyst software. The unarchived database is now active and includes all method revisions, data, calibrations, IECs, etc. that were created while the database was active.

13.8.6.1 Print a workgroup that was analyzed the previous quarter by following § 11.5.2-11.5.3.6. Once finished submit the WG# and the re-created upload file to the supervisor.

13.8.7 To restore the most current database, follow §13.7.5 and select the current database.

14.0 METHOD PERFROMANCE / DETECTION LIMITS

14.1 Method Detection Limit Study, Method 200.7:

14.1.1 An MDL must be established as part of the initial method set-up and whenever, in the judgment of the analyst, a change in analytical performance caused by a change in instrument hardware or operating conditions would dictate the MDL be re-determined.

14.1.2 Spike at least eight aliquots of reagent blank at 1-4X MDL and process according to the THP procedure. Calibrate the instrument and verify the calibration with an ICV/CCV using 200.7method requirements. Run the prepped samples with an adequate rinse time.

14.1.3 Use MDL Calculator/Verification Spreadsheet §Qualtrax ID: 2267 and §Qualtrax ID: 1692 to evaluate all criteria stated in §Qualtrax ID: 1518. If any criteria fail, rerun at a different concentration or reconsider the MDL value. Attach all raw data and supporting documentation. Submit the data package to the department supervisor for review. Include

all raw data, a reagent sheet, any SCNs/PCNs used, and copies of the forms. See §Qualtrax ID: 1518 for additional information.

14.2 Quarterly QA MDL Samples:

14.2.1 Each quarter, two QA samples will be logged in for ICP Analysis. Prep and analyze according to the method and this SOP, by spiking reagent blank at the PQL or the agreed upon spiking level determined by QA and the Supervisor.. These samples can be pulled into workgroups containing other client samples and passed through SAGE as a normal workgroup. Refer to §Qualtrax ID: 1518 for additional information.

14.3 Instrument Detection Limit (IDL) study:

14.3.1 An IDL must be established for each ICP upon setup, at the discretion of the analyst, and/or after major instrument maintenance. Use Method 6010B/6010D QC limits.

14.3.2 Prepare 10 replicates of a matrix-matched reagent blank solution. Calibrate the instrument and anlyze. Re-run any elements with failing QC.

14.3.3 Calculate the IDL by multiplying the standard deviation of the 10 replicates by the appropriate student *t* value (*t*=2.8214 for 10 replicates). Replicates that have values > 3x[±MDL] may not be used for IDL calculations.

14.3.4 Submit a completed IDL package using §Qualtrax ID: 1149 to the supervisor for review. The QA/QC dept. keeps IDLs on file.

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

14.4.1 Each instrument must have a **LLOQ Study** performed once to establish limits. Prepare a PQVPREP solution (See § 8.14.4) using the Total Hot Plate digestion procedure §Qualtrax ID: 1268. 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.

14.4.2 Each ICP 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. Recovery for all elements must be within +/-30%.

14.5 Demonstration of Capability (DOC): A successful initial DOC (IDOC) must be completed and approved by the QA/QC department for each analyst prior to independent generation or review of client data. Continued proficiency must be demonstrated and documented annually (CDOC). §SOPAD001 (§Qualtrax ID: 1518) for additional information.

14.5.1 Aqueous DOC: Analyze four individual aliquots of the LCSW solution. Include a passing calibration, ICV/ICB and CCV/CCB. Also include a passing PQV and SIC. The average of the replicates must be within ± 15% and the RSD must be ≤ 20%. Complete forms(§Qualtrax ID:2268 and §Qualtrax ID: 1691) and attach all raw data and supporting documentation, and turn in to the department supervisor for review.

14.5.2 Solid DOC: Analyze four individual aliquots of the LCSS. Include a passing calibration, ICV/ICB and CCV/CCB. Also include a passing PQV and ICSAB. The average of the replicates must be within vendor's limits and the RSD must be ≤ 20%. Complete forms §Qualtrax ID:2268 and §Qualtrax ID: 1691 and attach all raw data and supporting documentation, and turn in to the department supervisor for review.

15.0 DOCUMENTATION

15.1 Fill out the instrument logbook daily. At a minimum the logbook must contain the following: date, operator's initials, routine set-up steps or maintenance performed, and workgroup number(s). Record any malfunctions, as well as any maintenance and service repairs performed. Attach a copy of any service receipt in the logbook.

15.2 Record the appropriate information for all standards and reagents in SAGE and/or on the reagent form.

15.3 Document any SOP deviation(s) on the workgroup bench sheet or data review form.

15.4 Label each standard or reagent with the following information:

- Standard name
- SCN (or other unique ID)
- Concentration
- Preparer's initials
- Expiration date
- Prep date
- Storage requirement

15.5 Make sure the following information is included as part of the Workgroup:

- Correct ID of instrument used
- Dilution factors
- Analysis date
- Analyst's initials
- Any remarks about analysis or samples.
- Completed data review checklist form.
- Current standard/reagent form.
- *ANY OTHER PERTINENT INFORMATION*

15.6 Document the file backup/archiving in the instrument logbook.

16.0 WASTE MANANGEMENT / POLLUTION PREVENTION

16.1 Waste from the ICP and samples poured off for analysis may be disposed of down any sink connected to ACZ's neutralization tank.

17.0 DEFINITIONS

Refer to Tables §18.1 and §18.2.

18.0 TABLES & DIAGRAMS

Table 18. 1: QC Types, Limits, and Corrective Action

ICP Method 200.7				
QC Type	**Definition**	**Analysis**	**QC Limits**	**Corrective Action**
ICV	Initial Calibration Verification. Solution containing known concentrations of method	Run immediately after each calibration.	95-105% RSD of 4 reps < 3%	Recalibrate or update status of client samples to REDO at AREV. Remake any

	analytes. Prepared from a different source or lot number than calibration standards. Same as QCS from method 200.7.			calibration standard if necessary.
ICB	Initial Calibration Blank. Same solution as calibration blank. Confirms the absence of background contamination in calibration blank, or carryover from calibration standards.	Run immediately after ICV.	± 3X MDL [SX] > 10X ICB	Recalibrate or update status of client samples to REDO at AREV. Sample values > 10X ICB, may be accepted and qualified if ICB fails high.
PQV	Practical Quantitation Verification. Required for any instrument using a single-point calibration to verify accuracy of PQL. Per NELAC Chapter 5, a standard at the lowest quantitation level must be analyzed with each analytical batch.	Run immediately after ICB.	70-130%	Update status of client samples to REDO at AREV. If repetitive failures occur, examine instrument carefully for problems. A new MDL study may be necessary.
SIC	Spectral Interference Check. A solution of known interferents at elevated concentrations and target analytes at low concentrations. Ensures the correctness of the inter-element correction factors.	Run immediately after PQV, followed by a wash to minimize carryover.	80-120%	Update status of client samples to REDO at AREV. If consistently out of range, determine cause and change inter-element correction factor if necessary.
CCV	Continuing Calibration Verification. Solution containing method analytes of known concentrations, different than the ICV. Confirms instrument stability and verifies more than one point on the calibration curve.	Run every ten samples, and at the end of each workgroup.	90-110%	Update status of client samples to REDO at AREV. All client and control samples (LRB, LFB, PBW, LCS) must be bracketed by passing CCVs. Samples < MDL may be accepted and qualified if CCV fails high.
CCB	Continuing Calibration Blank. Same as calibration blank. Detects baseline drift or carryover.	Run every ten samples, immediately after CCV.	± 3X MDL [SX] > 10X CCB	Update status of client samples to REDO at AREV. All client and control samples (LRB, LFB, PBW, LCS) must be bracketed by a passing CCB. Sample values > 10X CCB or < MDL may be accepted and qualified if CCB fails high.
PQVPREP	The same solution as the PQV. An aliquot of reagent water to which the method analytes are added at the quantitation level. Prepped and analyzed exactly like a sample according to §SOPII018 For TR and THP workgroups with drinking water (DW) matrix samples only.	One per 20 samples for WG containing DW samples.	70-130%	Update status of all DW analytes to REDO. If failing upon re-run, reprep the PQVPREP only (sxs need not be reprepped), or run a previously passing PQVPREP that has not expired. NOT considered batch QC.

LRB	Laboratory Reagent Blank. A reagent blank carried through the entire prep process. Treated exactly like a sample to confirm absence of contamination during prep process.	Run one every 20 or less prepped samples.	± 2.2X MDL	Reanalyze client samples if carryover is suspected. Update to REDX at AREV if contamination is confirmed. Sample values > 10X LRB or < MDL may be accepted and qualified if LRB fails high.
LFB	Laboratory Fortified Blank. A reagent blank to which known concentrations of method analytes are added. Treated exactly like a sample to confirm methodology control and accuracy and precision of laboratory measurements.	Run one every 20 or less client samples.	85-115%	Update status of dissolved samples to REDO at AREV. Update status of prepped samples to REDX at AREV after confirming out of range. If LFB fails high, samples < MDL may be accepted and appropriately qualified.
LFM/LFM D	Laboratory Fortified Matrix and Duplicate. A client sample to which known concentrations of method analytes are added. Carried through prep process to confirm appropriateness of prep process to samples. Estimates accuracy of method and matrix effects.	Run one every 10 or less prepped client samples.	70-130% RPD ≤ 20%	If recovery is out of range, the data may be appropriately qualified. If the RPD ≥ 20% samples must be reprepped and reanalyzed. Ag must have passing RPD in digested samples.
AS/ ASD	Analytical Spike and Duplicate. A client sample to which known concentrations of method analytes are added. Analyzed exactly like a sample to determine if matrix interference is present.	Run one every 10 or less client samples.	85-115% RPD ≤ 20%	If recovery is out of range, the data may be appropriately qualified. If the RPD ≥ 20% samples must be reprepped and reanalyzed. It is acceptable to pass high RPD for Ag samples due to low solubility in the presence of chloride.

Table 18. 2: QC Types, Limits, and Corrective Action

ICP Method 6010B/6010D				
QC Type	**Definition**	**Analysis**	**QC Limits**	**Corrective Action**
ICV	Initial Calibration Verification. Solution containing known concentrations of method analytes. Prepared from different source/lot number than calibration standards.	Run immediately after each calibration.	90-110% recovery; RSD of 3 reps < 5%	Recalibrate or update status of client samples to REDO at AREV. Remake any calibration standard if necessary.
ICB	Initial Calibration Blank. Same solution as calibration blank. Confirms the absence of background contamination in calibration blank, or carryover from calibration standards.	Run immediately after ICV.	±3X MDL [SX] > 10X ICB	Recalibrate or update status of client samples to REDO at AREV. Sample values > 10X ICB may be accepted and qualified if ICB fails high.
PQV	Practical Quantitation Verification. Required for any instrument using a single-point calibration to verify accuracy of	Run immediately after ICB	70-130%	Update status of client samples to REDO at AREV. If repetitive failures occur, examine instrument carefully

	PQL. Per NELAC Chapter 5, a standard at the lowest quantitation level must be analyzed with each analytical batch.			for problems. A new MDL study may be necessary.
ICSAB	Interference Check Solution A + B. A solution of known interferents at elevated concentrations and target analytes at low concentrations. Ensures the correctness of the inter-element correction factors.	Run immediately after PQV, followed by a wash to minimize carryover.	80-120%	Update status of client samples to REDO at AREV. If consistently out of range, determine cause and change inter-element correction factor if necessary.
ULR	Upper Linear Range Verification. A solution fortified above the high calibration standard concentration for select elements. Required for Method 6010D only.	Run after the ICSAB. Follow with a wash sample to avoid carryover into subsequent samples.	90-110%	If not within QC limits, element concentrations cannot be reported above the high calibration point. Set samples to REDO if > C3.
CCV	Continuing Calibration Verification. Solution containing method analytes of known concentrations, different than the ICV. Confirms instrument stability and verifies more than one point on the calibration curve.	Run every ten samples, and at the end of each workgroup.	90-110%	Update status of client samples to REDO at AREV. All client and control samples (LRB, LFB, PBW, LCS) must be bracketed by a passing CCV. Samples < MDL may be accepted and qualified if fails high.
CCB	Continuing Calibration Blank. Same as calibration blank. Detects baseline drift or carryover.	Run every ten samples, immediately after CCV.	± 3X MDL	Update status of client samples to REDO at AREV. All client and control samples (LRB, LFB, PBW, LCS) must be bracketed by a passing CCB. Sample values > 10X CCB or < MDL may be accepted and qualified if fails high.
PBW/PBS	Preparation Blank Water/Soil. Reagent blank carried through entire prep process to confirm absence of systematic contamination.	Run one every 20 or less prepped samples.	± 3X MDL	Reanalyze client samples if carryover is suspected. Update to REDX at AREV if contamination is confirmed. Sample values > 20X PBW/S or < MDL may be accepted and qualified if PBW/S fails high.
LCSW	Laboratory Control Sample Water. A reagent blank to which known concentrations of method analytes are added. Treated exactly like a sample to confirm methodology control and accuracy and precision of laboratory measurements.	Run one every 20 or less client samples.	80-120% for waters.	Update status to REDX at AREV after confirming out of range. If LCSW fails high, samples < MDL may be accepted and appropriately qualified.
LCSS/D	Laboratory Control Sample Soils. A matrix matched standard of known concentrations of method analytes carried through entire	Run one every 20 or less client samples.	Vendor supplied. RPD<20%	Update status to REDX at AREV if both LCSS and LCSSD fail; otherwise appropriately qualify.

	prep process. Confirms acceptability of prep process to the matrix and analytes.			
LCSS (Tissue)	Laboratory Control Sample (tissue). The LCSS is carried through the prep process to demonstrate acceptable digestion of analytes. LCSS is made from a second source	One per tissue preparation batch. The LCSS shall resemble the sample origin (e.g. fish tissue, shellfish, or plant material) as closely as possible.	80-120%, 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.
LFB/D (Tissue)	Laboratory Control Sample (tissue). The LFB consists of Teflon beads spiked with all target analytes. It is used to supplement the LCSS because SRMs are not available with all elements at quantifiable levels.	One LFB/LFBD per tissue preparation batch.	80-120%	Re-prep and re-analyze associated samples if recovery is outside acceptance limits.
MS/MSD	Matrix Spike and Duplicate. A client sample to which known concentrations of method analytes are added. Carried through prep process to confirm appropriateness of prep process to samples. Estimates accuracy of method and matrix effects.	Run one every 20 or less samples.	75-125% RPD ≤ 20%	If recovery is out of range the data may be appropriately qualified. If RPD is out of range for solid matrices data may be accepted and appropriately qualified.
AS/ASD	Analytical Spike and Duplicate. A client sample to which known concentrations of method analytes are added. Analyzed exactly like a sample to determine if matrix interference is present.	Run one every 20 or less client samples.	75-125% RPD ≤ 20%	If recovery is out of range, the data may be appropriately qualified. If the RPD ≥ 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.
DUP	Matrix Duplicate. A second aliquot of client sample prepped and analyzed as samples. Demonstrates the precision of the procedure.	Run one every 20 or less client samples. Solids matrix only.	RPD ≤ 20% if [sx] is > 10X MDL.	For solid matrices, the data may be accepted and appropriately qualified.
SDL	Serial Dilution. Tests for possible physical or chemical interferences by diluting a client sample by 5X.	Run one every 20 or less client samples.	RPD ≤ 10%	Data may be accepted and appropriately qualified.

Table 18.3

Method MDLs and PQLS		
Element	**MDL (mg/L)**	***PQL (mg/L)**
Aluminum	0.05	0.25
Antimony	0.03	0.15

Arsenic	0.04	0.2
Bismuth	0.04	0.2
Barium	0.007	0.035
Beryllium	0.01	0.05
Boron	0.03	0.1
Cadmium	0.008	0.025
Calcium	0.1	0.5
Chromium	0.02	0.05
Cobalt	0.02	0.05
Copper	0.01	0.05
Gallium	0.1	0.5
Iron	0.06	0.15
Lead	0.03	0.15
Lithium	0.008	0.04
Magnesium	0.2	1
Manganese	0.01	0.05
Molybdenum	0.02	0.1
Nickel	0.008	0.04
Phosphorous	0.1	0.5
Potassium	0.2	1
Scandium	0.05	0.2
Selenium	0.05	0.25
Silica (SiO_2 = Si * 2.14)	0.214	1.07
Silicon	0.1	0.5
Silver	0.01	0.025
Sodium (588.9)	0.2	1
Strontium	0.009	0.045
Sulfur	0.25	1.25
Thallium	0.1	0.5
Tin	0.04	0.2
Titanium	0.005	0.025
Vanadium	0.01	0.025
Zinc	0.02	0.05

*PQL(mg/L) = PQV(mg/L)

Table 18.4

Calibration Standard 2 (Standard 1 is a 2X dilution of Standard 2)	
Element	**Final Concentration (mg/L)**
Aluminum	10
Antimony	2
Arsenic	5
Barium	2
Beryllium	2
Bismuth	5
Boron	5
Cadmium	2
Calcium	5
Chromium	5
Cobalt	2
Copper	2

Gallium	2
Iron	5
Lead	5
Lithium	2
Magnesium	10
Manganese	2
Molybdenum	2
Phosphorous	5
Potassium	10
Scandium	2
Selenium	5
Silica (SiO_2)	10.7
Silicon	5
Silver	1
Sodium	2
Strontium	2
Sulfur	5
Thallium	10
Tin	5
Titanium	1
Vanadium	1
Zinc	2

Table 18.5

Calibration Standard 3	
Element	**Final Concentration (mg/L)**
Calcium	100
Magnesium	100
Nickel	2
Potassium	100
Sodium	100
Sulfur	50

Table 18.6

Spike 1 Working Solution	
Element	**Final Concentration (mg/L)**
Arsenic	100
Barium	50
Beryllium	50
Boron	50
Cadmium	50
Chromium	50
Cobalt	50
Copper	50
Iron	100
Lead	100
Manganese	50
Nickel	50
Phosphorous	100

Silica (SiO_2)	2140
Silicon	1000
Thallium	200

Table 18.7

Spike 2 Working Solution			
Element (Concentration)	**Amount Used**	**Final Volume (mL)**	**Final Concentration (mg/L)**
Aluminum (10,000)	5mL	500	100
Antimony (10,000)	10mL	500	200
Calcium ($CaCl_2 \cdot 2H_2O$) 27.26% Ca	~12.47 g	500	~6800*
Magnesium ($Mg(NO_3)_2 \cdot 6H_2O$) 9.48% Mg	~26.37 g	500	~5000*
Molybdenum (1000)	25mL	500	50
Potassium (KCl) 52.44% K	~9.53 g	500	~10000*
Selenium (10,000)	5mL	500	100
Sodium (NaCl) 39.34% Na	~12.71 g	500	~10000*
Strontium (10,000)	2.5mL	500	50
Vanadium (1000)	25mL	500	50
Zinc (10,000)	2.5mL	500	50
* Concentration may vary depending on exact weight and composition of salts			

Table 18.8

Spike 3 Working Solution	
Element	**Final Concentration (mg/L)**
Bismuth	100
Gallium	100
Lithium	100
Sulfur	500
Tin	100
Titanium	100

Table 18.9

Spike 4 Working Solution	
Element	**Final Concentration (mg/L)**
Scandium	100
Silver	50

Table 18.11

ICV	
Element	**Final Concentration (mg/L)**
Aluminum	2
Antimony	4
Arsenic	4
Barium	2
Beryllium	2
Bismuth	2

Boron	2
Cadmium	2
Calcium	100
Chromium	2
Cobalt	2
Copper	2
Gallium	2
Iron	2
Lead	4
Lithium	2
Magnesium	100
Manganese	2
Molybdenum	2
Nickel	2
Phosphorous	5
Potassium	20
Scandium	2
Selenium	4
Silica (SiO_2)	42.8
Silicon	20
Silver	1
Sodium	100
Strontium	2
Sulfur	50
Thallium	4
Tin	2
Titanium	2
Vanadium	2
Zinc	2

Table 18.12

PQV Intermediate	
Element	**Final Concentration (mg/L)**
Aluminum	25
Antimony	15
Arsenic	20
Barium	3.5
Beryllium	5
Bismuth	20
Boron	10
Cadmium	2.5
Calcium	50
Chromium	5
Cobalt	5
Copper	5
Gallium	50
Iron	15
Lead	15
Lithium	4
Magnesium	100

Manganese	5
Molybdenum	10
Nickel	4
Phosphorous	50
Potassium	100
Scandium	20
Selenium	25
Silica (SiO_2)	107
Silicon	50
Sodium	100
Strontium	4.5
Sulfur	125
Thallium	50
Tin	20
Titanium	2.5
Vanadium	2.5
Zinc	5

Table 18.13

Ag PQV Intermediate	
Element	**Final Concentration (mg/L)**
Silver	2.5

Table 18. 14

ICSAB	
Element	**Final Concentration (mg/L)**
Aluminum	500
Calcium	500
Iron	200
Magnesium	500

Table 18.15

SIC Intermediate	
Element	**Final Concentration (mg/L)**
Barium	6.5
Beryllium	5
Cadmium	7.5
Chromium	5
Cobalt	5
Copper	5
Lithium	6
Nickel	6
Strontium	5.5
Titanium	7.5
Vanadium	7.5
Zinc	5

Table 18.16

SIC Working Solution	
Element	**Final Concentration (mg/L)**
Aluminum***	200
Antimony*	0.15
Arsenic*	0.2
Barium**	0.1
Beryllium**	0.1
Bismuth*	0.2
Boron*	0.1
Cadmium**	0.1
Calcium***	200
Chromium**	0.1
Cobalt**	0.1
Copper**	0.1
Gallium*	0.5
Iron***	200
Lead*	0.15
Lithium**	0.1
Magnesium***	200
Manganese***	50
Molybdenum*	0.1
Nickel**	0.1
Phosphorous*	0.5
Potassium*	1
Scandium*	0.2
Selenium*	0.25
Silica (SiO_2)*	1.07
Silicon*	0.5
Silver	0.1
Sodium*	1
Strontium**	0.1
Sulfur*	1.25
Thallium*	0.5
Tin*	0.2
Titanium**	0.1
Vanadium**	0.1
Zinc**	0.1
*Added as PQV intermediate	
**Added as PQV intermediate and SIC intermediate	
***Added as PQV intermediate and as individual element standard	

Table 18.17

CCV	
Element	**Final Concentration (mg/L)**
Aluminum	1
Antimony	2
Arsenic	2
Barium	1

Beryllium	1
Bismuth	1
Boron	1
Cadmium	1
Calcium	50
Chromium	1
Cobalt	1
Copper	1
Gallium	1
Iron	1
Lead	2
Lithium	1
Magnesium	50
Manganese	1
Molybdenum	1
Nickel	1
Phosphorous	2.5
Potassium	10
Scandium	1
Selenium	2
Silica (SiO_2)	21.4
Silicon	10
Silver	0.5
Sodium	50
Strontium	1
Sulfur	25
Thallium	2
Tin	1
Titanium	1
Vanadium	1
Zinc	1

Table 18.18

Upper Linear Range(ULR) Method 200.7	
Element/ wavelength	**ICP7/8(mg/L)**
Ag328.068	10
Al396.152	900
As189.042	50
B208.959	150
Ba455.403	25
Be313.107	25
Bi223.061	100
Ca315.887	800

Cd214.441	50
Cd226.502	50
Co228.615	100
Cr205.552	100
Cr267.716	100
Cu324.754	100
Fe240.489	500
Fe259.940	225
Ga294.364	100
K766.491	1000
Mg279.078	1000
Li670.784	50
Mo202.030	100
Mn257.610	100
Na589.952	1000
Ni231.604	100
P214.914	100
Pb220.353	200
S182.034	500
Sc361.383	50
Sb206.833	50
Se196.090	100
Sn189.991	100
Si251.611	90
Sr421.552	18
Ti334.941	50
Tl190.864	100
V292.401	100
Zn206.200	280
Zn213.856	90

Table 18.19

Working Level Spike Concentrations (mg/L)	
Element	**Final Concentration (mg/L)**
Aluminum	1
Antimony	2
Arsenic	1
Barium	0.5
Beryllium	0.5

Bismuth	1
Boron	0.5
Cadmium	0.5
Calcium	~ 68
Chromium	0.5
Cobalt	0.5
Copper	0.5
Gallium	1
Iron	1
Lead	1
Lithium	1
Magnesium	~ 50
Manganese	0.5
Molybdenum	0.5
Nickel	0.5
Phosphorous	1
Potassium	~ 100
Scandium	1
Selenium	1
Silica (SiO_2)	21.4
Silicon	10
Silver	0.5
Sodium	~ 100
Strontium	0.5
Sulfur	5
Thallium	2
Tin	1
Titanium	1
Vanadium	0.5
Zinc	0.5

Table 18. 20

Spex Assurance Multi-Element ICV/CCV Intermediate Solutions	
Element	**Int. Conc. (mg/L)**
Aluminum	200
Antimony	400
Arsenic	400
Bismuth	200

Barium	200
Beryllium	200
Boron	200
Cadmium	200
Calcium	10000
Chromium	200
Copper	200
Gallium	200
Iron	200
Lead	400
Lithium	200
Magnesium	10000
Manganese	200
Molybdenum	200
Potassium	2000
Scandium	200
Selenium	400
Silicon	2000
Sodium	10000
Strontium	200
Thallium	400
Tin	200
Titanium	200
Vanadium	200
Zinc	200

Table 18.21

Internal Standard	% Recovery Limits
Yttrium (Y)	80-120%

Table 18.22

6010B/6010D Upper Linear Range Verification Solution(mg/L)	
Aluminum	250
Barium	25
Boron	25
Cadmium	25

Calcium	500
Copper	25
Iron	500
Lead	50
Magnesium	250
Manganese	100
Phosphorous	100
Silica (SiO_2)	107
Sodium	500
Strontium	10
Titanium	25
Zinc	50

19.0 CORRECTIVE ACTION

19.1 For QC samples that do not meet the method acceptance criteria, refer to Tables §18.1 and §18.2. For retests that will occur past the method hold time, check first with the department supervisor to determine if the reanalysis should be conducted.

For any SOP/method deviation or system failure, notify department supervisor so that they can assess the need for corrective action. If deemed necessary, QA personnel will open a corrective action, classify the corrective action as minor or major, specify which elements of the corrective action process must be executed, and assign a deadline for completion. Refer to §Qualtrax ID: 1524.

APPENDIX A – QUICK REFERENCE SHEET

Element	Spike (mg/L)	MDL (mg/L)	PQL (mg/L)	200.7 ULR (mg/L)	6010 ULR (mg/L)	PQV (mg/L)	SIC (mg/L)	ICSAB (mg/L)	ICV (mg/L)	Cal (mg/L)	Spike Int #	Element
									CCV = 1/2	*C2/C3 C1 = (1/2) C2*		
Ag	0.5	0.01	*0.025	10	1	*0.025	0.1		1	1	4	**Ag**
Al	1	0.05	0.25	900	250	0.25	200	500	2	10	2	**Al**
As	1	0.04	0.2	50	5	0.2	0.2		4	5	1	**As**
B	0.5	0.03	0.1	150	25	0.1	0.1		2	5	1	**B**
Ba	0.5	0.007	0.035	25	25	0.035	0.1		2	2	1	**Ba**
Be	0.5	0.01	0.05	25	2	0.05	0.1		2	2	1	**Be**
Bi	1	0.04	0.2	100	5	0.2	0.2		2	5	3	**Bi**
Ca	68	0.1	0.5	800	500	0.5	200	500	100	5/100	2	**Ca**
Cd_214	0.5	0.008	*0.025	50	25	*0.025	0.1		2	2	1	**Cd_214**
Cd_226	0.5	0.008	*0.025	50	25	*0.025	0.1		2	2	1	**Cd_226**
Co	0.5	0.02	0.05	100	2	0.05	0.1		2	2	1	**Co**
Cr_205	0.5	0.02	0.05	100	5	0.05	0.1		2	5	1	**Cr_205**
Cr_267	0.5	0.02	0.05	100	5	0.05	0.1		2	5	1	**Cr_267**
Cu	0.5	0.01	0.05	100	25	0.05	0.1		2	2	1	**Cu**
Fe_240	1	0.06	*0.15	500	500	*0.15	200	200	2	5	1	**Fe_240**
Fe_259	1	0.06	*0.15	225	500	*0.15	200	200	2	5	1	**Fe_259**
Ga	1	0.1	0.5	100	2	0.5	0.5		2	2	3	**Ga**
K	100	0.2	1	1000	100	1	1		20	10/100	2	**K**
Li	1	0.008	0.04	50	2	0.04	0.1		2	2	3	**Li**
Mg	50	0.2	1	1000	250	1	200	500	100	10/50	2	**Mg**
Mn	0.5	0.01	0.05	100	100	0.05	50		2	2	1	**Mn**
Mo	0.5	0.02	0.1	100	2	0.1	0.1		2	2	2	**Mo**
Na	100	0.2	1	1000	500	1	1		100	2/100	2	**Na**
Ni	0.5	0.008	0.04	100	2	0.04	0.1		2	0/2	1	**Ni**
P	1	0.1	0.5	100	100	0.5	0.5		5	5	1	**P**
Pb	1	0.03	0.15	200	50	0.15	0.15		4	5	1	**Pb**
S	5	0.25	1.25	500	50	1.25	1.25		50	5/50	3	**S**
Sb	2	0.03	0.15	50	2	0.15	0.15		4	2	2	**Sb**
Sc	1	0.05	*0.2	50	2	*0.2	0.2		2	2	4	**Sc_361**
Se	1	0.05	0.25	100	5	0.25	0.25		4	5	2	**Se**
Si	10	0.1	0.5	90	50	0.5	0.5		20	5	1	**Si**
SiO2 (=2.14*Si)	21.4	0.214	1.07	192.6	107	1.07	1.07		42.8	10.7	1	***SiO2***
Sn	1	0.04	0.2	100	5	0.2	0.2		2	5	3	**Sn**
Sr	0.5	0.009	0.045	18	10	0.045	0.1		2	2	2	**Sr**
Ti	1	0.005	0.025	50	25	0.025	0.1		2	1	3	**Ti_334**
Tl	2	0.1	0.5	100	10	0.5	0.5		4	10	1	**Tl**
V	0.5	0.1	*0.025	100	1	*0.025	0.1		2	1	2	**V**
Zn_206	0.5	0.02	*0.05	280	50	*0.05	0.1		2	2	2	**Zn_206**
Zn_213	0.5	0.02	*0.05	90	50	*0.05	0.1		2	2	2	**Zn_213**

* [PQL] ≠ 5x[MDL]

SPECIAL SCNs

H20 @ PREP	Soils @ BENCH
II2XWATER	II2XSOIL
II5XWATER	II5XSOIL
II10XWATER	II10XSOIL
II20XWATER	II20XSOIL
etc.	etc.

CEC/SP/NH4 (meq/L)
IICECSPIKE

TCLP (Ba added)
IITCLPSPIKE
(reference Ba PCN on prep benchsheet)
II5XTCLPSPIKE
II10XTCLPSPIKE

Appendix B: 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 SAGEas 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 SAGEPCN 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 SAGEto 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:SAGE limits alert 1

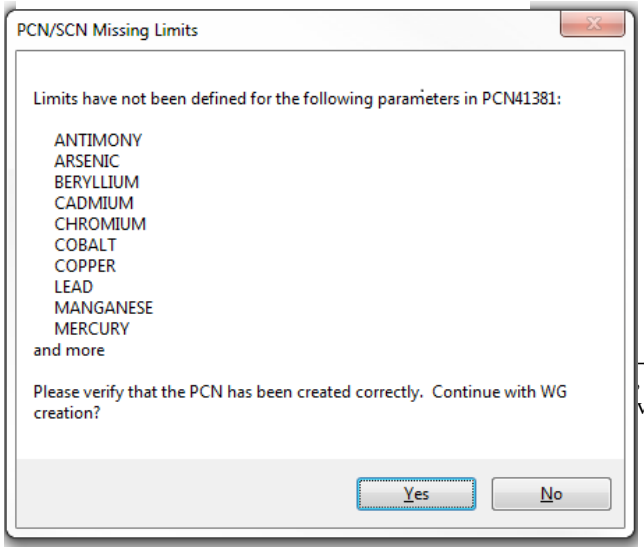
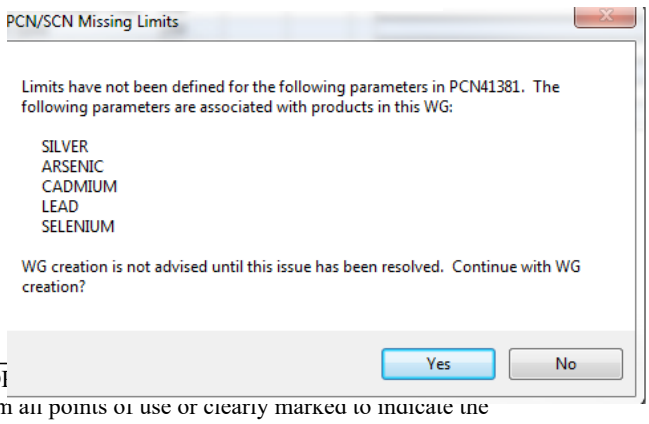


Figure 3:SAGE limits alert 2



the SOI
ved from all points of use or clearly marked to indicate the