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CCP-TP-182

Revision 1

CCP
Determination of Metals by ICP-AES for TRU Waste Characterization

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RECORD OF REVISION

Revision Number	Date Approved	Description of Revision
0	05/02/2007	Initial Issue.
1	01/26/2009	Revised to add instructions for analysis using simultaneous Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) instrumentation.

1. ABSTRACT

This Central Characterization Project (CCP) procedure provides instruction for the determination of total metals by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) per the requirements of the Waste Isolation Pilot Plant (WIPP) Waste Analysis Plan (WAP).

2. APPLICABILITY

This procedure functions as an Idaho Cleanup Project (ICP) Use Type 2 document for performing operations in the Analytical Laboratories Department (ALD) facilities.

Personnel performing this procedure will be trained and qualified in accordance with CCP-QP-002, *CCP Training and Qualification Plan*, prior to performing this procedure.

2.1 Regulatory Basis

Instructions in this method are based upon Method 6010B from the EPA publication, *Test Methods for Evaluating Solid Waste* (SW-846). This method also implements requirements and quality assurance objectives defined in the WIPP WAP. Additional quality control elements in Chapter One of SW-846 are also implemented.

2.2 Analytes Determined

The method is applicable to the target analytes listed in Appendix A.

2.3 Sample Types Analyzed and Sample Pretreatment

This method is applicable to homogeneous solids and soil/gravel. These matrices require pretreatment prior to analysis according to CCP-TP-183, *CCP Microwave Assisted Digestion of Homogeneous Solids and Soil/Gravel*.

2.4 Interferences

Several types of interference effects may contribute to inaccuracies in the determination of trace elements by ICP-AES. These effects are described in the following paragraphs.

Spectral interferences may be caused by one or more of the following:

A. Overlap of a spectral line from another element.
B. Unresolved overlap of molecular band spectra.
C. Background contribution from continuum or recombination phenomena.
D. Background contribution of stray light from the line emission of high-concentration elements.

Spectral overlap can be compensated for by computer-correcting the raw data after monitoring and measuring the interfering element. Unresolved overlap requires selection of an alternate wavelength. Background contribution and stray light can usually be compensated for by background correction adjacent to the analyte line.

Physical interferences are effects associated with the sample nebulization and transport processes. Properties such as changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by application of internal standard correction and/or diluting the sample.

In the internal standard technique, fixed concentrations of one or more elements are added to the samples, standards, and blanks. Elements which do not interfere with analytes and are not expected to be in samples, such as yttrium or lutetium, are chosen for internal standards. The ratio of analyte intensity to the intensity of the added element (the internal standard) is used to create calibration curves and quantify samples. Internal standard correction is typically performed only with simultaneous instruments.

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

2.5 Range of Method, Wavelengths & Estimated IDLs

Generally the lower range of the method is the Instrument Detection Limit (IDL) that is experimentally determined.

The upper linear range is limited to the concentration of the high calibration standard unless a Documented Linear Range (DLR) has been demonstrated as described in Section 7.35. This upper range may be further extended by analyzing sample dilutions.

Appendix A lists IDLs typically obtained. IDLs are re-determined periodically and vary with time and with instrument operating conditions.

The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be chosen due to analytical considerations such as spectral interference, sensitivity, and background. Adequate IDLs and Interelement Corrections (IECs) must be demonstrated and documented for all wavelengths and analytes before they are used to obtain reported data.

2.6 Precision Attainable

The precision of the method is expected to be ±10% or better when measured results exceed the IDL by a factor of ten or more.

3. DISCUSSION

Samples must be in an acidified, aqueous form and should contain minimal suspended particulate material prior to analysis by ICP-AES. Homogeneous solids and soil/gravel are prepared as directed in CCP-TP-183.

When all necessary pretreatment is complete, sample and standard solutions are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific atomic line emission spectra are produced by a radio frequency inductively-coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the lines are measured by photo-multiplier tubes. Background-corrected analyte intensities measured from samples are compared to analyte intensities measured from solutions of known metal concentrations. Results of this comparison are printed and stored in a computer file.

3.1 Method Limitations

The concentration of silver which can be determined by this procedure is limited by solubility during digestion. The digestion method used for this procedure utilizes excess hydrochloric acid to complex silver as $(AgCl_2)^{1-}$ and $(AgCl_3)^{2-}$ and is reliable for the silver concentrations up to 5 mg/L. Digestion methods which do not add excess chloride are subject to precipitation loss of silver by traces of chloride typically present in wastes, waste waters, and natural waters.

Instructions in this method deviate from verbatim implementation of cited reference documents, as described in Section 3.2.1. These modifications are allowed by the inherent flexibility of EPA methods, as discussed in SW-846 Chapter Two.

3.2 Modifications to SW-846 Method 6010B Protocol

3.2.1 Section 7.5 of Method 6010B states: ". . . The rinse time will be one minute. Each laboratory may establish a reduction in this rinse time through a suitable demonstration. . ." The minimum rinse times for this method is one minute which meets the intent of Method 6010B §7.5. Additional information in Method 6010B §3.4 makes it clear that the rinse time cited in Method 6010B §7.5 was NOT intended to preclude longer rinse times.

3.3 Sequential and Simultaneous Analysis

3.3.1 This method contains instructions for analysis using either a sequential or a simultaneous ICP-AES system. For the sequential systems, a limited set of interferents are routinely quantified and corrections are

applied; qualitative sample surveys are performed to identify additional interferents which are quantified and corrected only when surveys indicate their presence at interfering levels. For the simultaneous systems, all identified potential interferents are quantified in all samples and corrections are applied.

4. SAFETY PRECAUTIONS

4.1 Chemical Hazards

4.1.1 Handle all chemicals per MCP-3635, "Chemical Hygiene Plan."

4.1.2 Wear the following standard laboratory PPE in the lab:

A. Lab coat
B. Safety glasses with side shields
C. Substantial footwear
D. Appropriate gloves.

4.1.3 Change gloves immediately upon chemical contact.

4.1.4 Handle corrosives per ACLP-0.27, "Routine Handling of Corrosives."

4.1.5 Handle all spills per ACLP-0.24, "Laboratory Spill Cleanup."

4.2 Radiological Hazards

4.2.1 Perform all work under an applicable Radiological Work Permit (RWP) per MCP-7, "Radiological Work Permit."

4.2.2 Handle nonroutine samples per ACLP-0.21, "Work Control Procedure for the Analysis of Nonroutine Samples."

4.3 Cryogenic Hazards

4.3.1 Handle cryogens per MCP-3635.

4.4 Electrical Hazards

4.4.1 Operate 208 to 480 V circuit breakers and disconnect switches in accordance with Host site procedures.

4.5 Waste Disposition and Pollution Prevention

4.5.1 Manage all waste generated per ACLP-0.40, "Analytical Laboratories Waste Management."

5. APPARATUS AND REAGENTS

5.1 Apparatus

5.1.1 Spectrometer: Computer-controlled inductively coupled plasma source emission spectrometer with background correction capability:

5.1.1.1 Sequential JY-138 Ultrace®.

OR

5.1.1.2 Simultaneous Perkin-Elmer Optima 4300, or equivalent.

5.1.2 Computer: Industry standard computer with color monitor, hard disk drive and printer.

5.1.3 Adjustable-speed peristaltic pump, external or incorporated into the instrument, two or more channels.

5.1.4 Polyvinyl chloride (PVC) peristaltic pump tubing. Typical sizes:

- Intake: 0.030” (0.76 mm) I.D., color code Black-Black
- Waste: 0.045” (1.14 mm) I.D., color code Red-Red
- Waste: 0.035” (0.89 mm) I.D., color code Orange-Orange

NOTE: *Alternate peristaltic pump tubing sizes are allowed. Use of intake tubing sizes other than those listed above are documented in the instrument maintenance log or on the documentation for IDL determinations.*

5.1.5 Argon, welders grade or better.

5.1.6 Compressed air, filtered, oil-free.

5.1.7 Nitrogen, welders grade or better.

5.1.8 Mechanical Pipets, 0.010- to 10.0-mL with disposable tips verified according to ACLP-0.255, “Mechanical Pipetor Calibration Verification.”

5.1.9 Pipets for dispensing reagents, 1.0- to 10.0-mL with disposable tips, or equivalent.

5.1.10 Balance, resolution ≤1 mg and 100 g minimum capacity.

5.1.11 High density polyethylene (HDPE) bottles, assorted sizes.

5.1.12 Spatula.

5.1.13 Disposable syringes, 10- to 60-mL or other appropriate volumes.

5.1.14 Syringe filters (Nalgene®, or equivalent), 0.45-micron pore size.

5.1.15 Autosampler, computer-controlled (optional).

5.1.16 Autosampler tubes, 15- and 50-mL, approximate volumes (if autosampler is used).

5.2 Reagents

NOTE: *Reagent volumes other than specified may be prepared by using appropriate ratios of components.*

Use trace metals grade acids throughout this procedure unless another grade is specified. Use Analytical Reagent Grade or better chemicals for other reagents.

Use ASTM Type II water (with respect to conductivity) or better for preparation of all reagents and samples.

5.2.1 Nitric acid (concentrated). Trace Metal Grade or equivalent.

5.2.2 Nitric acid (1+1). Add 500 mL concentrated Trace Metal Grade nitric acid to approximately 400 mL water and dilute to 1 liter.

5.2.3 Hydrochloric acid (concentrated). Trace Metal Grade or equivalent.

5.2.4 Hydrochloric acid (1+1). Add 500 mL concentrated HCl to approximately 400 mL water and dilute to 1 liter.

NOTE: *The following primary standards, secondary standards, and QC solutions are provided by the Quality Control Laboratory (QCL) per ACLP-1.01, "Preparation of Reagents and Standards" and tracked and used by the Spectrochemistry Group (SCG) per ACLP-2.05, "Control, Distribution and Use of Spectrochemical Standards." Instructions for preparing working standards from these standards and solution are provided in Section 7.3.*

5.2.5 Stock Standard Solutions. Solutions containing known concentrations traceable to the NIST for each analyte required. These solutions, which may contain one or more analytes, are used individually or in combination to prepare calibration standards. All stock standard solutions used for this method must be plasma grade or better.

5.2.6 Calibration Stock Solution(s) (CalSt). Primary or secondary standard used to prepare calibration standards. Typically the CalSt concentration is 200 times the desired high calibration standard concentration for each analyte. The CalSt solution concentration is typically 1000 mg/L for all target analytes. Do NOT add internal standard elements to CalSt.

5.2.7 Initial Verification Stock Solution(s) (ICVSt). Used to make the ICV working solution, and may also be used to make the Continuing Calibration Verification (CCV) working solution. All primary standards used to make the ICVSt solution must be independent of those standards used to make the CalSt. Typically the ICVSt analyte concentration is such that a 40-fold dilution of the ICVSt will yield a solution in which all analytes are present at approximately half the concentration of the high calibration standard. The ICVSt solution concentration is typically 100 mg/L for all target analytes. Do NOT add internal standard elements to ICVSt.

5.2.8 Internal Standard Stock Solutions (ISSt). Prepare ISSt at concentrations which are 100 times the desired internal standard final concentration. Lutetium or yttrium are used as internal standards. Prepare in a minimum 5% (v/v) nitric acid matrix. Include other acids when needed for increased solution stability.

NOTE: *ISSt is required only when internal standard correction is applied to the calibration.*

5.2.9 ICSA Solution. Interference Check Solution A (ICSA) contains interfering elements at approximately the following concentrations: 500 mg/L Al, Ca, and Mg; and 200 mg/L Fe and U. If internal standard is included, then ICSA also contains 1 mL of ISSt per 100 mL ICSA.

5.2.10 ICSAB Stock Solution(s). Interference Check Solution B (ICSAB) stock solution is used to make the ICSAB working solution. The ICSAB stock solution contains concentrations of all target analytes. Typically analyte concentrations in the ICSAB <u>stock</u> solution(s) are 100 times the concentration desired in the ICSAB <u>working</u> solution. <u>Working</u> ICSAB solution analytes should be present at the nominal concentrations listed in the Appendix A. If internal standard is included, then ICSAB Stock Solution also contains 1 mL of ISSt per 100 mL ICSAB stock solution.

6. SAMPLE HANDLING

6.1 Store digested samples at room temperature until analysis.

6.2 Prepare and analyze samples within 180 days of sample collection.

6.3 Group samples into analytical batches. The analytical batch is a suite of samples of similar matrix that are processed as a unit, using the same analytical method

within a specific time period. An analysis batch must not exceed 20 samples, all of which must be received by the laboratory within 14 days of the validated time of sample receipt (VTSR) of the first sample of the batch.

7. PROCEDURES

NOTE 1: *Sections 7.2, 7.3, 7.4, 7.5, 7.6, 7.7 and 7.8 provide general instructions to be used concurrently with other procedure sections.*

NOTE 2: *Data recording instructions are provided in CCP-TP-188, CCP Analytical Data Recording, Review and Reporting.*

7.1 Labware Cleaning

Clean all reusable labware according to ACLP-0.25, "Labware Cleaning for Environmental Analyses," before use in this procedure. Subsequent cleaning to ACLP-0.25 is not required when labware is reused for identical QC or rinse solutions.

NOTE: *It is suggested that the ASTM Type II water rinse be repeated on stored glassware just prior to use.*

7.2 General Instructions for Standard Preparation and Analysis

NOTE: *This procedure includes instructions for the preparation of specific volumes of standards and other solutions. In all cases, alternate volumes may be prepared if the proportions of reagents within the solution are maintained as specified.*

7.2.1 Reagent Control

Various chemicals used in this procedure contain trace amounts of metals that show up as a consistent level of contamination in the analysis. Treat all solutions in the batch with the same reagents so that the contribution of this contamination to sample results can be estimated. For this reason, check that a single container of each chemical with enough for the entire batch is available before adding it to any samples and standards.

7.2.2 Standard Control

7.2.2.1 Control all primary, secondary, and working standards per ACLP-2.05.

7.2.2.2 Prepare working solutions daily.

7.2.3 Sample Analysis Requirements

7.2.3.1 Document on the raw data corrective actions taken for data not within control limits. Include a description of the deficiency and the corrective action taken.

7.2.3.2 Contact supervision for directions if this procedure is not compatible with the sample or sample matrix received.

7.2.3.3 Determine Interelement Correction Factors (IECs) for the instrument and operating conditions according to Section 7.32 or 7.33 of this procedure before samples are analyzed.

NOTE: *The value of the high calibration standard is the linear range unless another* DLR *has been established (see Section 7.35).*

7.2.3.4 IF internal standard correction was used for the determination of IDLs and IECs,
THEN add internal standard solution to standards and samples and use internal standard correction during sample analysis.

7.3 Preparation of Calibration, Verification, and Rinse Solutions

NOTE: *The following instructions are based on use of a 1000 mg/L CalSt and 100 mg/L ICVSt solutions. Stock standard volumes added for preparation of calibration standards and ICV solutions may be other than those specified in these instructions. In all cases identifiers and actual stock solution volumes added are recorded in the standard preparation log.*

7.3.1 Non-Zero Calibration Standard Preparation

7.3.1.1 Prepare calibration standards daily by adding approximately 50 mL of water to 100-mL volumetric flasks. Add nitric acid, hydrochloric acid, and, if applicable, Internal Standard Stock Solutions (ISSt) to the flasks according to the following table:

Table 7.3.1.1: Acid Matrix

Volume of Conc. HNO_3 added per 100 mL of Standard (mL)	Volume of Conc. HCl added per 100 mL of Standard (mL)	Volume of ISSt added per 100 mL of Standard (mL), if applicable	Matrix
12	10	1	12% HNO_3, 10% HCl

7.3.1.2 Pipet 0.50 mL of Calibration Stock Solution(s) (CalSt) into the flask.

7.3.1.3 Bring to volume with water.

7.3.2 Calibration Blank Preparation

7.3.2.1 Prepare the calibration blank daily by filling a marked or graduated plastic bottle or container with approximately 50 mL of water.

7.3.2.2 Add HNO_3, HCl, and ISSt to the bottle as directed in Table 7.3.1.1 above.

7.3.2.3 Add water to the 100-mL mark.

7.3.3 Initial Calibration Verification (ICV) Standard Preparation

7.3.3.1 Prepare the ICV daily by adding approximately 50 mL of water to a 100-mL volumetric flask.

7.3.3.2 Add HNO_3, HCl, and ISSt according to Table 7.3.1.1, matching the acid concentrations for the ICV with that of the calibration standards.

7.3.3.3 Pipet 2.5 mL of ICVSt into the volumetric flask.

7.3.3.4 Bring to volume with water.

7.3.4 Low Level Concentration (LLC) Standard Preparation

7.3.4.1 Prepare the LLC daily by adding approximately 50 mL of water to a 100-mL volumetric flask.

7.3.4.2 Add HNO_3, HCl, and ISSt according to Table 7.3.1.1, matching the acid concentrations of this standard with that of the calibration standards.

7.3.4.3 Pipet 0.20 mL of ICVSt into the volumetric flask.

7.3.4.4 Bring to volume with water.

7.3.5 Continuing Calibration Verification (CCV) Standard Preparation

The ICV solution may also serve as the CCV solution. Alternately, prepare the CCV daily by following the instructions for ICV preparation, substituting the CalSt for ICVSt. Because CalSt is typically 10 times the concentration of ICVSt, the volume of CalSt added will be one tenth the volume for ICVSt.

NOTE: *It is recommended that the ICV and CCV be the same solution.*

7.3.6 Probe Wash Solution Preparation

Prepare the probe wash solution by adding nitric and hydrochloric acids to water in the proportions list below in Step 7.3.6.2. Alternate probe wash solution compositions may be used if required due to analytical considerations such as sample matrix and minimization of memory effects.

NOTE: *Probe wash solution is replaced whenever significant contamination is suspected.*

7.3.6.1 Fill a 500-mL marked or graduated plastic bottle or container with approximately 250 mL of water.

7.3.6.2 Add HNO_3 and HCl to the bottle as directed in the following table.

Concentrated HNO_3, mL	Concentrated HCl, mL	Matrix
60	50	12% HNO_3, 10% HCl

7.3.6.3 Add water to the 500-mL mark.

7.3.7 Interference Check Solution A (ICSA) Preparation

7.3.7.1 IF internal standard correction is NOT to be applied OR if the ICSA was prepared with internal standard,
THEN analyze the ICSA Solution (See Item 5.2.9) undiluted for the target analytes.

7.3.7.2 IF internal standard correction is to be applied AND internal standard was not added to the ICSA solution,
THEN prepare the ICSA by adding 0.1 mL ISSt to a measured 10-mL volume of the ICSA solution.

7.3.7.3 Do not apply a dilution factor to compensate for internal standard addition.

NOTE: *Internal standard correction compensates for the 1% dilution due to addition of ISSt.*

7.3.8 Interference Check Solution B (ICSAB) Preparation

7.3.8.1 IF internal standard correction is NOT to be applied OR if the ICSA and ICSAB were prepared with internal standard,
THEN prepare the ICSAB solution daily by making a 100-fold dilution of the ICSAB Stock Solution (See Item 5.2.10) using ICSA Solution as diluent.

7.3.8.2 IF internal standard correction is to be applied AND internal standard was not added to the ICSA and ICSAB solutions, THEN prepare the ICSAB by adding 0.1 mL ISSt and 0.1 mL ICSAB Stock Solution (See Item 5.2.10.) to a measured 10-mL volume of the ICSA solution (See Item 5.2.9).

7.3.8.3 Do not include the volume of ISSt added when calculating the ICSAB dilution factor.

NOTE: *Internal standard correction compensates for the 1% dilution due to addition of ISSt.*

7.4 Instrument Setup

7.4.1 Computer Startup

7.4.1.1 Computer Startup, Sequential

7.4.1.1.1 IF the computer has been turned off, THEN turn on the computer and wait for the Windows Desktop© to appear.

7.4.1.1.2 IF the computer was left in the DOS mode, THEN type “WIN” and press <Enter> from the DOS prompt and wait for the Windows Desktop© to appear.

7.4.1.2 Computer Startup, Simultaneous

7.4.1.2.1 IF the computer has been turned off, THEN turn on the computer and wait for the Windows Desktop© to appear.

7.4.2 Spectrometer Startup

7.4.2.1 Spectrometer Startup, Sequential

7.4.2.1.1 IF the argon gas supply is not on, THEN turn on the argon gas supply.

7.4.2.1.2 Ensure that the nitrogen purge gas supply is on and is set to 30 ± 2 psi.

7.4.2.1.3 Activate the cooling water by opening the valve or turning on the cooling water system.

7.4.2.1.4 Access the plasma control icon from the Windows Desktop©.

NOTE: *The plasma control icon may be located directly on the Windows Desktop© or located through the JY-138 Ultratrace icon.*

7.4.2.1.5 Change the displayed plasma parameter settings, if necessary, to agree with the following table.

Plasma Start Up Parameters

Parameter	Setting
Power	1100 ± 200 W
Plasma Gas	15.0 ± 5 lpm
Auxiliary Gas	0.2 ± 0.2 lpm
Sheath Gas	0.2 ± 0.2 lpm
Power Asserv	Checked
Power Reflected	Checked
Argon Humidifier	Checked

7.4.2.1.6 After the settings are correct click *Start.*

7.4.2.1.7 IF the plasma control screen indicates successful ignition,
THEN GO TO Step 7.4.2.1.9.

NOTE: *It is not unusual to need 2 or 3 attempts for starting.*

7.4.2.1.8 IF the plasma control screen indicates ignition failure,
THEN perform one or more of the following steps:

7.4.2.1.8.1 Click the *Controls* box then click *Start,*

7.4.2.1.8.2 Repeat Step 7.4.2.1.6,

OR

7.4.2.1.8.3 Repeat Steps 7.4.2.1.1 through 7.4.2.1.6.

7.4.2.1.9 Allow at least 30 minutes after plasma ignition before proceeding with the auto-search process.

NOTE: *The Analytical Method may be selected at any time after plasma ignition and prior to Auto Search (see Step 7.5.2). Plasma conditions used for analytical measurements are set when the Analytical Method is selected.*

7.4.2.1.10 From the ICP SYSTEM menu, press <Shift> and <F2> simultaneously to activate the normal starting mode and perform the zero order search.

7.4.2.2 **Spectrometer Startup, Simultaneous**

7.4.2.2.1 Click the spectrometer icon to start the spectrometer control software.

NOTE: *System checks will be performed and the results listed on the screen.*

7.4.2.2.2 IF system check results indicate components not in a ready state,
THEN perform the actions necessary to bring the system to ready state.

7.4.2.2.3 Open the plasma menu item and click the 'ON' icon to ignite the plasma.

7.5 Sample Analysis Overview and Instrument Set-Up

7.5.1 Perform all calibration and analysis steps using the conditions under which IDLs and IECs were obtained. Use background correction and a minimum of two replicate measurements.

7.5.2 Sample Analysis Overview and Instrument Set-Up, Sequential

7.5.2.1 Perform these tasks in the following sequence:

A. Select Analytical Method
B. Auto Search
C. Auto Attenuate
D. Auto Search (Optional)
E. Acquire Sample Profiles
F. Calibrate
G. Analyze.

7.5.3 Sample Analysis Overview and Instrument Set-Up, Simultaneous

7.5.3.1 **Torch Viewing Position Optimization**

NOTE: *Torch viewing alignments are performed, at a minimum, whenever the torch is repositioned, removed, or replaced, and when changes are made to the nebulizer or spray chamber. Radial and axial alignments can be performed in any order.*

7.5.3.1.1 Click on spectrometer control in the tools menu to bring up the torch alignment window.

7.5.3.1.2 Aspirate an appropriate solution containing Mn and click the axial button to begin the axial torch alignment.

7.5.3.1.3 WHEN the alignment is complete, THEN aspirate an appropriate solution containing Mn and click the radial button to begin the radial torch alignment.

7.5.3.2 **Wavelength Alignment**

NOTE: *Wavelength alignment is performed daily, and may be performed as part of the instrument performance check.*

7.5.3.2.1 Click on spectrometer control in the tools menu to bring up the torch alignment window.

7.5.3.2.2 Click Hg realign.

NOTE: *Instrument status messages will indicate the progress of the alignment. The internal mercury lamp will be turned on, allowed to warm up, and measured intensities will be automatically aligned to known mercury wavelengths.*

7.5.3.3 **Wavelength Alignment and Instrument Performance Check**

NOTE: *Wavelength alignments followed by atom/ion ratio performance checks are performed daily. Alternate/equivalent software commands may be used to complete these tasks.*

7.5.3.3.1 Open the daily performance workspace.

7.5.3.3.2 Click the automatic analysis icon and go to the analysis page. Click the 'rebuild' button.

NOTE: *A wavelength alignment using the internal mercury lamp will automatically be added to the run sequence if a wavelength alignment has not yet been performed.*

7.5.3.3.3 Place an appropriate solution containing 5 ppm Mg in the autosampler location indicated for the instrument performance check.

7.5.3.3.4 Click 'analyze all.'

7.6 Analytical Run Sequence

Appendix D, Typical Analytical Run Sequence, specifies the run sequence of the analysis procedure. Instructions for the completion of each task are included in the indicated step.

The term *analytical sample* includes any solution or media introduced into the instrument on which an analysis is performed, excluding instrument calibrations, initial calibration verifications, and continuing calibration verifications. Note that the following are all defined as analytical samples: samples, diluted samples, spiked samples, LCSs, low level concentration (LLC) solution, interference check solutions (ICSA and ICSAB), and laboratory blanks. Re-analysis of any analytical sample is counted as an additional analytical sample. However a rinse typically does NOT count as an analytical sample because no analysis is performed on the rinse.

When multiple analytical batches are combined in one run, it is suggested that the sequence start at "ICV Analysis" for each analytical batch.

7.7 ICP Rinse Sequence

NOTE: *Multiple probe wash compositions may be used; however, the rinse sequence must include a minimum 60-second rinse in calibration blank or in a probe wash solution which matches the acid matrix of the calibration blank.*

7.7.1 Place the probe in the probe wash after removing it from any sample or non-zero QC solution. An intermediate probe dip in water is allowed.

7.7.2 When a rinse sequence is specified, aspirate probe wash or Calibration Blank Solution for a minimum total rinse time of 60 seconds.

NOTE: *The fast pump speed setting may be activated during the rinse sequence.*

7.7.3 Place the probe in probe wash or water during warm-up and whenever there is a break in the analytical run sequence.

7.8 Solution Introduction Sequence

7.8.1 Perform Section 7.7, ICP Rinse Sequence.

7.8.2 Aspirate the solution to be measured for at least 60 seconds.

NOTE: *The fast pump speed setting may be activated during sample introduction. Return to the analytical pumping rate for at least 10 seconds of sample introduction before initiating the data acquisition step.*

7.8.3 Activate the computer data acquisition sequence.

7.8.4 When sample data acquisition is complete, place the probe in probe wash.

7.9 Auto Search, Sequential

NOTE: *The Auto Search routine locates the position of the element lines relative to their theoretical positions prior to entering the analysis routine. Auto Search is applicable to sequential spectrometers only.*

7.9.1 Select an analytical method program for the analyte set to be determined.

7.9.2 Include the following elements in addition to the target analytes (see Appendix A):

A. Aluminum
B. Calcium
C. Iron
D. Magnesium
E. Uranium.

7.9.3 Include any other elements identified as interferents according to Section 7.13 or quantify these additional interferents in a separate analytical run.

NOTE: *Analyte wavelengths and background correction offsets must be identical to those contained in the template method used for interelement interference and IDL studies.*

7.9.4 From the MAIN MENU, select "**P**reparation".

7.9.5 Select "Auto **S**earch."

7.9.6 Aspirate the high calibration standard.

7.9.7 Use the arrow keys to highlight "small" and press <F10> or <Enter> to accept.

7.9.8 IF during the search routine the element line is not located, THEN select the "large" window option and repeat the Auto Search function. Once the line is located, perform the Auto Search with the small window option.

7.9.9 Press <F10> to search all highlighted elements,
OR to search specific elements, press <F5> or <F9> to scroll through the method elements. To select an element, press <F5> while the element symbol is blinking. Press <F9> to de-select the element. When only the desired elements are highlighted, press <F10> to initiate the AutoSearch routine.

NOTE: *The AutoSearch routine produces a graph of wavelength versus intensity. The element name, wavelength, intensity in total counts, and the current position of the motor in nm are displayed. The dotted yellow vertical line identifies the center of the search window; the dotted brown line, the theoretical position; and the full white line, the limit of the range. When a peak is located, the curve will remain displayed for a few seconds and then will continue on to the next element. Pressing any key will allow the curve display to remain on the screen longer. If the graph includes several peaks, no peak, or a saturated peak the curve will remain on the screen awaiting input.*

7.9.10 IF any doubt exists about the line selected,
THEN repeat the search using a single element standard.

7.9.11 Evaluate the wavelength-intensity plot for each analyte and ensure that the analytical peak has been properly selected as follows:

7.9.11.1 A plus sign (+) indicates the peak selected by the software. This will always be the closest peak to the window center and may not be the correct peak. Type in an assigned peak number to select a peak and to view a table of possible elements at that wavelength. (Press <Enter> to close this table.)

7.9.11.2 When the (+) appears above the correct peak, press <F10>.

7.9.11.3 If the peak selected is different than the one selected by the computer, respond “Y” to the prompt to verify your selection. The computer will then ask if you want to search the element again. Press <F5> for yes or <F9> for no.

NOTE: *When a peak has been selected and verified for an element, the search routine will be initiated for the next element in the method. When all elements in the method have been searched and selected for all highlighted elements, the program returns to the PREPARATION MENU.*

7.10 Auto Attenuate, Sequential

NOTE: *The "Auto-Attenuate" function adjusts the photomultiplier voltage for each wavelength so that the count rate resulting from the aspirated standard is most favorable for analytical measurement. Auto-Attenuate is applicable to sequential spectrometers only.*

7.10.1 From the PREPARATION menu, select "Auto Attenuate."

7.10.2 Use the arrow keys to highlight "small" and press <F10> or <Enter> to accept.

7.10.3 Aspirate the high calibration standard.

7.10.4 Press <F10> to set gain voltages for all wavelengths in the analytical method program.

7.10.5 IF the auto attenuate is to include only specific elements, THEN press <F5> or <F9> to scroll through the method elements. To select an element press <F5> while the element symbol is blinking. Press <F9> to de-select the element. When only the desired elements are highlighted, press <F10> to initiate the Auto Attenuate routine.

NOTE: *The Auto-attenuation routine is complete when the PREPARATION menu appears on the screen. At this point, the Auto Search routine, Section 7.9, may be repeated.*

7.11 Acquiring Sample Profiles, Sequential

NOTE: *All samples are analyzed using background correction. When analyses of any samples of unknown or uncharacterized matrix type are performed using a sequential spectrometer, wavelength-intensity plots are obtained for a standard, a blank, and a sample from each unknown or uncharacterized matrix type to be analyzed. These plots are compared to verify the adequacy of established background set points and interelement correction studies. These plots are also studied to determine interfering elements to be quantified.*

7.11.1 From the PREPARATION menu, select "**P**rofiles."

7.11.2 Respond to the prompts with specific solution identifiers.

7.11.3 Aspirate a prepared sample of the unknown matrix type and acquire profiles for all target analytes. Acquire blank and standard profiles by aspirating solution and instrument data acquisition or by opening filed scans acquired since the current IDL effective date.

7.11.4 When all necessary profiles have been acquired, press <F3>"Go to graph". The profile choices are displayed. To select the profile choices to be included in the plot, press <F5>"select" or press <Enter>. Include the standard, the blank, and the sample profiles in the graph. As the profile is selected, the color of the profile name is highlighted. Press <F10> "Go to next screen".

NOTE: *Up to four solutions may be included in one graph.*

7.11.5 The option is presented to display the profile graphs on the screen or to send them to the printer. Initially, move the cursor to "screen" and press <F10> "Select" or <Enter>.

7.11.6 The program will prompt "Plot Blinking Element?" Press <F10> to plot the highlighted elements.

7.11.7 Press <F10> "Graph" to display the profiles for each element. Each of the profiles are superimposed on one graph.

NOTE: *Profiles are typically evaluated using the screen display. However, hard copies of the profiles may be obtained by pressing <F9>.*

7.12 Evaluating Sample Profiles for Background Correction, Sequential

7.12.1 Evaluate the background correction set points indicated by a yellow tick mark along the baseline of the sample profiles acquired in Section 7.11. Consult with supervision if unusual interferences are present near the desired peak or the background set point.

7.12.2 Enter background correction set point changes, if needed. Press <F5> to set and <F6> to clear. The graph scale must be expanded to properly evaluate new background correction set points. Expand the scale of the graph by pressing the down arrow and <F3>.

7.12.3 Redetermine interelement correction factors (Section 7.32) whenever a background correction set point is changed.

7.13 Evaluating Sample Profiles to Determine Interferents to be Quantified, Sequential

7.13.1 Compare sample and standard interferent intensities in the sample profiles acquired in Section 7.11 to determine if interfering elements not on the analyte list must be quantified.

NOTE: *The intensity comparison may be omitted for interferents which will be quantified regardless of profile results.*

7.13.2 IF the intensity of an interfering element not on the analyte list indicates that the element is above the interference threshold determined in Section 7.32,
THEN quantify that element for that sample.

NOTE: *The quantitative interferent results will be used to calculate interference corrected results according to Equation 9.9.*

7.14 Calibration, Sequential

NOTE 1: *Instructions for performing simultaneous system calibrations are included in Step 7.16.2, Sample Data Input and Analysis, Simultaneous.*

NOTE 2: *A two-point calibration is typically performed using one multielement high standard and the calibration blank. The high standard analytes may be distributed between multiple solutions aspirated sequentially.*

7.14.1 From the PREPARATION menu, select “Calibration.” The “Calibration Screen” will appear, select “Calibrate.”

7.14.2 IF only certain elements are to be calibrated within a method,
THEN press <F8> (“Help”) and then <F3> “Select Elements to Calibrate.” Press <F5> or <F9> to scroll through the method elements. To select an element press <F5> while the element symbol is blinking. Press <F9> to de-select the element. When only the desired elements are highlighted, press <F10> to initiate the calibration routine.

NOTE: *The order in which calibration standards are measured may be altered. STDLOW need not be the first standard aspirated.*

7.14.3 Perform the solution introduction sequence (see Section 7.8) for the blank calibration standard (STDLOW). When the introduction sequence is complete, move the cursor to “yes” and press <Enter> to begin the measurement process.

7.14.4 When the readings for the STDLOW are complete, follow the screen prompts to select “Next Standard”. Perform the solution introduction sequence for the next standard identified on the screen and press <Enter> to begin the measurement process.

7.14.5 Continue the introduction and measurement process for each calibration standard displayed.

7.14.6 When all calibration standards have been measured save and print calibration coefficients by ONE of the following:

7.14.6.1 Press <Esc> to obtain the 'save coefficients' screen prompt, use the arrow keys to select 'Yes', and press <Enter>.

OR

7.14.6.2 Press <F3> then use the right arrow to cycle through and accept calibration coefficients for each analyte individually. Press <Esc>.

7.14.7 Evaluate the calibration for each analyte against the requirements of Steps 8.5.1 and 8.5.2 before continuing with sample analysis.

7.15 Re-sloping During the Analytical Run

It is sometimes necessary to perform a reslope, a one or two point correction of the calibration curve, during the analytical run. The calibration standards used in the reslope procedure are those identified as "STDLOW" and "STDHIGH".

A 'reslope' must be immediately preceded and followed by analysis of both CCV and CCB. In other words, no analytical sample data generated in the time interval between a CCV/CCB pair and a reslope can be reported. When using the sequential system, 'Autosearch' may be performed between the preceding CCV/CCB and the reslope.

7.15.1 Re-sloping During the Analytical Run, Sequential

7.15.1.1 From the MAIN MENU select "Analysis".

7.15.1.2 On the Analysis Menu, select "Sample File."

7.15.1.3 Press <F2> in response to the prompt "Enter the file name for sample names." Enter the sample name: "STDLOW" in the box beside which the cursor is blinking and press <Enter>. Press <F3> to record.

NOTE: *The reslope may be performed for all elements or a subset of elements from the method. Step 7.16.1.3 provides instructions for selecting element subsets.*

7.15.1.4 Enter the sample name: "STDHIGH" and press <Enter>. Again Press <F3> to record. Press <F10> "Analyze".

7.15.1.5 The current sample name ("STDLOW") and the next sample name ("STDHIGH") are displayed. Complete the solution introduction sequence for the "STDLOW", then respond to the prompt "Measure?" by moving the cursor to "yes" and pressing <Enter>. When the analysis is completed, press <F10> "Next Sample" and the net intensities and statistics are printed. Press any key to continue.

7.15.1.6 Complete the solution introduction sequence for the next calibration standard, then select "yes" and press <Enter>. When the readings are complete, press <F10>. The net intensities and statistics are printed for each element. Press any key to continue.

7.15.1.7 Check the validity of your reslope by performing a CCV (Section 7.27) analysis followed by a CCB analysis (Section 7.18).

7.15.2 **Re-sloping During the Analytical Run, Simultaneous**

7.15.2.1 Edit the Sample Information File (SIF) to begin with CCV/CCB pair and continuing with all analytical samples to be run (including those to be rerun). See Section 7.16, Sample Data Input and Analysis, for SIF entry instructions.

7.15.2.2 Open the analysis page within the automatic analysis window and click the 'rebuild' button.

7.15.2.3 Click the 'analyze all' button to reslope the calibration and continue to analysis of the solutions in the SIF.

<u>OR</u>

7.15.2.4 Click the calibrate button and when the calibration is complete, click the analyze samples button to continue to analysis of all solutions in the SIF.

7.16 Sample Data Input and Analysis

7.16.1 **Sample Data Input and Analysis, Sequential**

7.16.1.1 Entering Sample Identifiers

In the first box of the sample identifier section, type in the lab sample ID and press <Enter>.

NOTE: *The sample identification entry field is displayed as three boxes. The sample identifier is entered in the first box. The second and third boxes are used to enter sample dilution data.*

7.16.1.2 Entering Dilution Information

When applicable, enter data for dilutions performed during preparation and analysis steps in the second and third boxes of the sample identification section. Enter initial and final volumes separated by the forward slash (/) symbol. For example, if 0.5 g of sample was diluted to 100 mL and then a 0.25-mL aliquot of that dilution was taken to 50 mL, the entry in this field would be 0.5/100/0.25/50. Continue entry into the third box if additional characters are needed for dilution entry. Press <Enter> to complete dilution entry.

7.16.1.3 Element Selection

After entering the sample identification the analyst has the option of selecting for analysis all elements or a subset of elements from the method for analysis.

7.16.1.3.1 Press <F3> to select all of the elements in the method.

OR

7.16.1.3.2 Press <F6> to select individual elements to analyze. As the display of each element of the method blinks, press <F5> to select that element or <F9> to deselect that element from the current analysis routine. Press <F10> or <Esc> when finished selecting elements, and press <F3>to record.

NOTE: *A sample may be skipped or a previous sample rerun by responding "no" and pressing <F10> or <Enter> when the computer prompts "measure?." Alternately, the cursor may be moved to "Jump" and the identifier for the sample to be measured may be entered.*

7.16.1.4 Initiate Analysis

7.16.1.4.1 Press <F10> "Analyze". The sample name is displayed and the prompt *measure?* will appear.

7.16.1.4.2 Initiate or continue the *Solution Introduction Sequence* (see Section 7.8). When this sequence is complete, move the cursor to "yes" and press <Enter> to begin acquisition of sample intensity readings.

7.16.1.4.3 When the screen prompt indicates that the readings are completed, press <F10> *next sample.* Measurement results are printed. Press any key to continue.

7.16.2 **Sample Data Input and Analysis, Simultaneous**

7.16.2.1 Open the WIPP analysis workspace.

7.16.2.2 Open the WIPP analysis software method.

7.16.2.3 Perform the sample analysis using the instrument control software. Alternate/equivalent software commands may be used to complete these tasks.

7.16.2.3.1 Open an existing SIF or create a new SIF.

7.16.2.3.2 Enter sample identifiers in the sample ID field.

7.16.2.3.3 Edit the SIF to schedule QC samples according to Appendix C, by manual entry of QC samples in the SIF or use automatic QC scheduling.

7.16.2.3.4 Enter sample dilution information as applicable in the remarks or text field in the SIF. When applicable, enter data for dilutions performed. Enter one or more pairs of initial and final volumes with each value separated by the forward slash (/) symbol.

7.16.2.3.5 IF the autosampler is used for the analysis, THEN enter autosampler locations for all solutions in the autosampler location field.

7.16.2.3.6 Save the SIF.

7.16.2.3.7 Open the automatic analysis window.

7.16.2.3.8 Select or enter the correct SIF in the appropriate location in the analysis window.

7.16.2.3.9 Select or enter a results storage location in the appropriate location in the analysis window.

7.16.2.3.10 Open the analysis page within the automatic analysis window and click the ‘rebuild’ button.

7.16.2.3.11 Check that the resulting run sequence meets the requirements of Appendix C.

7.16.2.3.12 Check sample identifiers and dilution factors for accuracy.

7.16.2.3.13 IF the autosampler is used,
THEN place sample and QC solutions in the indicated autosampler locations.

7.16.2.3.14 Click the 'analyze all' button to perform the calibration followed by analysis of all solutions in the SIF.

OR

7.16.2.3.15 Click the calibrate button and when the calibration is complete, click the 'analyze samples' button to continue to analysis of all solutions in the SIF.

7.17 ICV Analysis

7.17.1 Analyze the ICV solution according to the instructions in Section 7.16.

7.17.2 IF the ICV result obtained is within ±10% of the ICV 'true' value,
THEN continue with the next analysis in the analytical run sequence.

7.17.3 IF the ICV result obtained is NOT within ±10% of the ICV 'true' value,
THEN correct the problem, recalibrate, and re-analyze the ICV.

7.18 ICB and CCB Analysis

7.18.1 Analyze the calibration blank solution according to the instructions in Section 7.16.

7.18.2 IF the absolute value of result obtained is ≤ PRDL for each analyte determined,
THEN continue with the next solution in the analytical run sequence.

7.18.3 IF the absolute value of result obtained is > PRDL for one or more analytes,
THEN mark all analytical sample results for the non-conforming analyte(s) generated since the last compliant ICB or CCB to indicate that the data are rejected due to a failed CCB,
AND terminate the analysis and correct the problem. If necessary to correct the problem, recalibrate or reslope for the failed element(s).

NOTE: *Analyses must be repeated for those results marked as not reported.*

7.18.4 Continue with the analytical run sequence.

NOTE: *Data marking must be completed before data are submitted for review.*

7.19 Low Level Concentration (LLC) Check

7.19.1 Analyze the Low Level Concentration check solution (LLC) according to the instructions in Section 7.16, assigning this analysis the sample name "LLC."

7.19.2 IF the LLC result obtained is within ±20% of the LLC 'true' value, THEN continue with the next analysis in the analytical run sequence.

7.19.3 IF the LLC result obtained is NOT within ±20% of the LLC 'true' value, THEN correct the problem, and re-analyze the LLC. Do not continue with the analytical run sequence until LLC results meet acceptance criteria.

7.20 ICSA Analysis

7.20.1 Analyze the ICSA solution according to the instructions in Section 7.16, assigning this analysis the sample name "ICSA."

7.21 ICSAB Analysis

7.21.1 Analyze the ICSAB according to the instructions in Section 7.16, assigning this analysis the sample name "ICSAB."

7.21.2 IF the result obtained is within ±20% of the ICSAB 'true' value for target analytes,
THEN continue with the next analysis in the analytical run sequence.

7.21.3 IF the ICSAB result obtained is NOT within ±20% of the ICSAB 'true' value for target analytes,
THEN reanalyze the ICSAB.

7.21.4 IF the ICSAB passes the second time,
THEN continue with the analytical run sequence.

7.21.5 IF the ICSAB fails again,
THEN mark affected element results obtained since the last passing ICSAB sample (if any) for which the 'as run' solution concentration of one or more interferents is above the concentration in the ICSA solution as not reported due to failed ICSAB.

NOTE: *Acceptance criteria and corrective action for ICSAB apply only if interferents are found in samples at levels greater than in the ICSA solution.*

7.21.6 Correct the problem, recalibrate, verify the recalibration, reanalyze the ICSA and ICSAB for the non-conforming analyte. Continue with the analytical run sequence,

NOTE: *Analyses must be repeated for those results marked as not reported.*

7.22 Laboratory Blank (LB) Analysis

7.22.1 Analyze the LB according to the instructions in Section 7.16.

7.22.2 IF the result obtained is ≤3 × PRDL for each analyte determined,
THEN continue with the next solution in the analytical run sequence.

7.22.3 IF the result obtained is >3 × PRDL for one or more analytes,
THEN flush the system with rinse solution water and reanalyze the LB.

7.22.4 IF this result is within limits,
THEN continue with the next solution in the analytical run sequence.

7.22.5 IF the LB once again fails,
THEN continue with the next solution in the analytical run sequence. Evaluate sample results when the analysis run is complete. Redigest and reanalyze all samples with measured analyte concentrations ≤10 times the LB concentration AND ≥0.5 × PRQL for the failed analytes.

7.23 LCS Analysis

7.23.1 Analyze the LCS according to the instructions in Section 7.16.

7.23.2 IF the result obtained for the LCS is within the limits set by the manufacturer's Certificate of Analysis or within established statistical control limits,
THEN continue with the next solution in the analytical run sequence.

7.23.3 IF the LCS result obtained is not within these limits,
THEN flush the system with rinse solution and reanalyze the LCS.

7.23.4 IF this result is within limits,
THEN continue with the next solution in the analytical run sequence.

7.23.5 IF the LCS once again fails,
THEN terminate the analysis, check instrument operation and correct the problem, recalibrate the instrument for the element(s) failed.
OR continue with the determination of all other analytes, followed by problem correction, recalibration or re-slope, and reanalysis for the failed analyte(s).

7.23.6 IF the repeated result for the failed analyte is within limits,
THEN continue with the next solution in the analytical run sequence.

7.23.7 IF the LCS fails again,
THEN terminate the analysis for the failed analyte. The samples associated with the batch must be redigested and reanalyzed for the failed analyte. Consult with supervision for direction prior to proceeding.

7.24 MS and MSD Analysis

7.24.1 Analyze the MS and MSD according to the instructions in Section 7.16.

7.24.2 Estimate spike recoveries for both MS and MSD using Equation 9.2.

NOTE: *Analyte results will be flagged for poor spike recovery if % R is not between 80 and 120%.*

7.25 Serial Dilution

7.25.1 For each analytical batch, select one sample for serial dilution. If possible, choose a sample in which the concentration of most analytes is greater than 50 times the IDL.

7.25.2 Prepare and analyze a 5-fold dilution of the sample by combining 1 part of sample with 4 parts of calibration blank.

7.25.3 Estimate percent difference using equation 9.5 for samples with analyte concentrations greater than 50 times the IDL.

7.25.4 IF the serial dilution result (corrected for the fivefold dilution) agrees within 10% difference of the original dilution for each analyte,
OR the analyte concentration in the sample selected is LESS than 50 times the IDL,
THEN continue with the next solution in the analytical run sequence.

7.25.5 IF the serial dilution result (corrected for the fivefold dilution) does not agree within 10% difference of the original dilution,
AND the analyte concentration in the sample selected is greater than 50 times the IDL,
THEN the five-fold dilution of the sample may be re-prepared and re-analyzed.

NOTE: *Repetition of a failed serial dilution is suggested but not required. Analyte results that do not meet acceptance criteria will be flagged for poor serial dilution agreement.*

7.26 Post Digestion Spike

7.26.1 IF serial dilution, matrix spike, and matrix spike duplicate results for a batch meet acceptance criteria based on estimates performed in Steps 7.24.2 and 7.25.3,
THEN post-digestion spike analysis may be omitted.

7.26.2 IF serial dilution, matrix spike, or matrix spike duplicate results fail to meet acceptance criteria,
THEN prepare at least one Post Digestion Spike (PDS) sample per batch for the failed analyte(s).

7.26.3 PDS Preparation

7.26.3.1 Whenever possible, use the unspiked prepared sample which was used for MS and MSD analysis to prepare the PDS.

7.26.3.2 Pipette the following into a vial:

- 20 mL of prepared sample (may be diluted)
- 0.200 mL of ICVSt

NOTE: *Alternate spiking levels may be used for PDS. The volume of spike solution added should be less than 10% of the volume of sample plus diluent added. If the spike solution volume is greater than 2% of the spike sample volume, dilution due to spike addition must be included in spike recovery calculations.*

7.26.4 Analyze the PDS and estimate the spike recovery (Equation 9.2).

7.26.5 IF the PDS recovery is 100 ± 25%,
THEN continue with the next solution in the analytical run sequence.

7.26.6 IF the PDS recovery is NOT 100 ± 25%,
THEN the post digestion spike may be re-prepared and re-analyzed.

NOTE: *Repetition of a failed PDS is suggested but not required. If the repeated spike recovery is not 100 ± 25%, then a matrix effect may be suspected.*

7.26.7 Continue with the next solution in the analytical run sequence.

7.27 CCV analysis

7.27.1 Analyze the CCV according to the instructions in Section 7.16.

7.27.2 IF the result obtained is within ± 10% of the true value,
THEN continue immediately to CCB analysis.

7.27.3 IF the result obtained is NOT within ± 10% of the true value,
THEN stop the analysis.

7.27.4 For the non-conforming analyte, mark all results obtained since the last passing CCV as not reported due to failed CCV.

NOTE: *Analyses must be repeated for those results marked as "not reported."*

7.27.5 Re-slope or recalibrate the instrument for the non-conforming analyte using the calibration blank (STDLOW) and/or the high calibration standard (STDHIGH).

7.27.6 Reanalyze the CCV.

7.27.7 IF the result obtained is now within ± 10% of the true value, THEN continue with the CCB analysis and the next solution in the analytical run sequence.

7.27.8 IF the second CCV analysis is not within ±10% of the true value, THEN terminate the analysis for failed analytes, correct the problem, recalibrate the instrument for the element(s) failed, and verify the recalibration. Continue with the next solution in the analytical run sequence.

7.28 End of Run

End the run with analysis of ICSA (Section 7.20), ICSAB, (Section 7.21), CCV (Section 7.27), and CCB (Section 7.18). Analyze these solutions after the last reported sample or QC solution (other than CCV and CCB) has been analyzed. No results may be reported from analytical samples analyzed after the last CCV/CCB pair.

7.29 Instrument Shutdown

7.29.1 Instrument Shutdown, Sequential

7.29.1.1 When the analyses have been completed, press <ESC> several times to return to the Windows Desktop©.

7.29.1.2 Aspirate water for a minimum of five minutes.

7.29.1.3 Press *STOP* on the plasma control screen.

NOTE: *The remaining steps in Section 7.29 may be completed in any order.*

7.29.1.4 Loosen the peristaltic pump clamp.

7.29.1.5 Turn the cooling water off.

7.29.1.6 IF the argon gas use is not expected for the remainder of the shift,
THEN turn the argon gas off.

7.29.1.7 IF the nitrogen gas use at 30 psi is NOT expected for the remainder of the shift,
THEN reduce nitrogen pressure to 20 psi.

NOTE: *The monitor and the printer may be turned off or left on.*

7.29.1.8 Verify that the Instrument Performance Check was recorded.

7.29.2 Instrument Shutdown, Simultaneous

7.29.2.1 Aspirate water for a minimum of five minutes.

7.29.2.2 Open the plasma control window and click the plasma off icon.

7.29.2.3 Loosen the peristaltic pump clamps.

NOTE: *The monitor and the printer may be turned off or left on.*

7.29.2.4 Verify that the Instrument Performance Check was recorded.

7.30 Reporting

7.30.1 Number the pages of the instrument raw data printouts and record the instrument identifier on the first page.

7.30.2 Add the date and sign or initial the print out.

7.30.3 Record information as directed in CCP-TP-188.

7.30.4 IF QC sample results associated with the reported samples do NOT meet Appendix C acceptance criteria,
AND the QC failure is not due to sample matrix,
THEN ensure that a nonconformance report (NCR) is initiated per CCP-QP-005, *CCP TRU Nonconforming Item Reporting and Control*.

7.30.5 Calculate and enter sample results in the laboratory information management system or on forms per CCP-TP-188, as follows:

A. Report sample results in mg/kg to two significant figures

B. Report sample concentrations measured as less than the IDL as the IDL adjusted for dilution factor followed by a ‘U’ qualifier, which indicates that the analyte was not detected

C. Report quality control summary data using formats specified in CCP-TP-188

D. Use data qualifying flags defined in CCP-TP-188.

7.30.6 Assemble and submit the following to the independent technical reviewer for evaluation and review:

A. photocopies of sample and standard preparation logbook pages

B. originals of any other paperwork used to record data about sample preparation and analysis

C. the instrument printouts.

7.31 IDL Determination

NOTE: *Section 8.1 provides requirements for the frequency for determining IDLs.*

7.31.1 Prepare or obtain a solution of calibration blank matrix containing analytes at a concentration of approximately 2 to 5 times the estimated IDL.

7.31.2 Perform at least seven analyses of this standard solution. Perform each measurement as though it were a separate analytical sample (that is, follow each measurement with a rinse and/or any other tasks normally performed between the analysis of separate samples).

NOTE: *Analyses performed for IDL determinations must meet all calibration verification requirements for the analysis of samples. Acceptable ICV and ICB or CCV and CCB readings must bracket all data used to determine IDLs.*

7.31.3 Calculate the IDL using Equation 9.6.

7.31.4 Round the calculated IDL value UP (away from zero) to the nearest 0.001 mg/L.

NOTE: *For example, if an IDL calculated according to Equation 9.6 is 0.0012 mg/L the IDL will be reported as 0.002 mg/L.*

7.31.5 Compare the reported IDLs to the Appendix B PRDL values.

7.31.5.1 IF a reported IDL is greater than the PRDL for that analyte, THEN correct the problem and redetermine the IDLs before analyzing samples.

7.32 Determination of Interelement Correction Factors (IECs), Sequential

NOTE: *Section 8.2 provides requirements for the frequency for performing interference studies and determining IECs.*

7.32.1 Perform instrument calibration and initial calibration verification (ICV and ICB) as directed in Section 7.

NOTE: *ICB or CCB results will be subtracted from interferent results for determining the correction factors to be applied.*

7.32.2 Analyze appropriate high-concentration standards for each interfering element. At a minimum, analyze standards for Al, Ca, Fe, Mg, and U.

NOTE: *Interference study solutions typically contain 100 to 1000 mg/L of the interfering element.*

7.32.3 Calculate interelement correction factors (k) using Equation 9.7.

7.32.4 Calculate interelement correction thresholds using Equation 9.8 using the k values determined and the current applicable IDLs.

7.32.5 IF the interferent concentration in the sample is greater than the interferent concentration threshold for the element,
THEN apply the IEC prior to calculating the result. If the interferent concentration is less than the threshold for the element, no IEC need be applied.

7.33 Determination of Interelement Correction Factors (IECs), Simultaneous

NOTE: *Section 8.2 provides requirements for the frequency for performing interference studies and determining IECs.*

7.33.1 Perform instrument calibration and initial calibration verification (ICV and ICB) as directed in Section 7.

7.33.2 Analyze appropriate high-concentration standards for each interfering element. At a minimum, analyze standards for Al, Ca, Fe, Mg, and U.

NOTE: *Interference study solutions typically contain 100 to 1000 mg/L of the interfering element.*

7.33.3 Confirm that the reading is due to signal from the interfering element by examining the spectral plot of the analyte and consulting with reference wavelength tables and books.

7.33.4 Calculate IECFs using the instrument software,
OR
Calculate interelement correction factors (k) using Equation 9.10.

7.33.5 Enter calculated IECFs into the instrument software.

7.33.6 IF interferent concentrations cannot be measured simultaneously with analyte concentrations,
THEN perform the following steps.

7.33.6.1 Calculate interelement correction factors (k) using Equation 9.10.

7.33.6.2 Calculate interelement correction thresholds using Equation 9.11 using the k values determined and the current applicable IDLs.

7.33.6.3 IF the interferent concentration in the sample is greater than the interferent concentration threshold for the element,
THEN apply the IEC using Equation 9.12 prior to calculating the result.

NOTE: *No IEC is needed if the interferent concentration is less than the threshold for the element.*

7.34 Verification of Interelement Correction Factors (IECFs)

7.34.1 Perform instrument calibration and initial calibration verification (ICV/ICB).

7.34.2 Analyze appropriate high-concentration standards for each interfering element.

NOTE 1: *Solutions typically contain 50 to 1000 mg/L of the interfering element.*

NOTE 2: *The IECF has been verified if the absolute value of the IECF-corrected result is less than or equal to the greater of the following:*

A. 5× the IDL,

B. 0.10 × the absolute value of the correction amount.

7.34.3 IF the IECF is NOT verified,
THEN examine the spectral plot of the analyte to determine if an actual shift in the correction factor has occurred.

NOTE 1: *Memory effect or contamination of the high concentration standard may cause a positive reading that is actually due to analyte and not interferent. The interference check solutions may be analyzed more than once to confirm a change has occurred.*

NOTE 2: *Corrective actions may include:*

A. Calculating IECFs using multiple analyses of interferent solutions,

B. Using longer rinse times between high concentration interferent analyses,

C. Examining wavelength vs. intensity plots to confirm that apparent interference readings are not due to spectral interference,

D. Checking interferent solutions for analyte concentrations and correcting readings for analyte concentrations.

7.34.4 IF a shift in the correction factor has occurred,
THEN calculate IECFs by Equation 9.10 and enter the updated IECF into the instrument software.

7.35 Determining the Documented Linear Range (DLR)

The upper linear measurement range is limited to the concentration of the high calibration standard unless a higher DLR has been demonstrated and documented according to the following instructions.

NOTE: DLR*s are applicable only for a specific analyte, instrument, and set of operating conditions. A* DLR *may be used for up to six months after its determination date.*

7.35.1 Prepare one or more single element solutions with known analyte concentrations. These concentrations should include values near the desired DLR.

7.35.2 Calibrate the instrument as directed in Section 7.14.

7.35.3 Perform initial, continuing, and end-of-run calibration verifications as directed in Steps 7.17, 7.18, 7.27, and 7.28.

7.35.4 Analyze the single element solutions as samples.

7.35.5 Assign the DLR as the concentration of the highest concentration solution with an observed signal within 10% of its 'true' value.

8. QUALITY CONTROL REQUIREMENTS

8.1 IDL Determinations

8.1.1 Determine Instrument Detection Limits (IDLs) every six months.

8.1.2 Determine IDLs for each instrument used to obtain reported data and for each specific set of operating conditions.

8.1.3 If instrument conditions are adjusted in any way that may affect the IDL, re-determine the IDLs for that instrument and use the results as the established IDLs for all subsequent reporting.

NOTE: *Parameters which could affect instrument conditions include, but are not limited to, nebulizer type, spray chamber type, intake tubing diameter, forward power setting, and plasma source gas flow settings.*

8.2 IEC Determinations

8.2.1 Examine each analytical wavelength for potential interferences due to aluminum, calcium, chromium, copper, iron, magnesium, manganese, nickel, titanium, uranium, and vanadium.

8.2.2 At a minimum, determine IECs for spectral interferences due to aluminum, calcium, iron, magnesium, and uranium at all wavelengths used for each analyte reported by ICP-AES.

8.2.3 Perform interference studies for any additional elements which may be present in samples at potentially interfering levels.

8.2.4 Determine IECs for any additional spectral interferences identified.

8.2.5 Determine these IECs before any samples are analyzed and verify or re-determine IECs at least once every six months thereafter.

8.2.6 Verify or re-determine IECs if the instrument is adjusted in any way which may affect the ICP IECs (for example, change of background correction offset or a change in forward power). Apply the new IECs to all data generated under the new operating conditions.

8.3 Method Performance Demonstration (Precision and Accuracy)

8.3.1 Demonstrate method performance initially before analyzing any samples.

8.3.2 Demonstrate initial method performance by preparing 7 replicate aliquots of a control standard having all target analytes at quantifiable concentration.

8.3.2.1 Digest solid method performance samples (the solid LCS may be used for this purpose) by CCP-TP-183.

8.3.3 Analyze digested method performance samples.

8.3.4 Calculate average percent recovery and the percent relative standard deviation of the results. Initial and continuing method performance demonstrations are acceptable if the average percent recovery meets the acceptance criteria for LCSs and the percent relative standard deviation is ≤30.

8.3.5 If the method performance demonstration is NOT acceptable, terminate sample analysis until acceptable method performance has been demonstrated. Repeat the demonstration until acceptance criteria are met.

8.3.6 Demonstrate continuing method performance semiannually using a minimum of four (4) method performance samples.

8.4 Analytical Batch QC Requirements

The QC parameters covered in Section 8.4 are analytical-batch specific, their frequency and use are determined on the basis of an analytical batch or matrix type. Detailed instructions for meeting these requirements are included in Sections 7 and 9 of this procedure. See Appendix B and Appendix C for acceptance criteria and required corrective actions.

8.4.1 Laboratory Blank (LB) Requirements

The laboratory blank, LB, an aliquot of water digested and analyzed with each analytical batch of samples, is prepared to determine the extent of sample contamination caused by the digestion process. *Laboratory blanks* are equivalent to *method blanks* in SW-846.

Laboratory blank results are calculated and reported in the same units as the associated samples. LB results for solid samples are reported in mg/kg.

8.4.2 Laboratory Control Sample (LCS) Requirements

The LCS is a sample matrix containing known, measurable amounts of all target analytes. At least one LCS is digested and analyzed with each analytical batch to monitor the accuracy of the analytical process. The LCS matrix should be similar to that of the samples in the analytical batch. LCS statistical control limits are established using a 2-tailed t test at the 99% confidence interval, using a minimum of seven data points.

8.4.3 Matrix Spike (MS) QC Requirements

The MS is an aliquot of sample to which known amounts of analytes have been added prior to the sample preparation and analysis steps. At least one MS sample is prepared and analyzed with each analytical batch. MS recoveries are used to identify concentration biases for the sample matrix occurring due to the digestion process. Matrix spike results are evaluated as percent recovery (%R) of the added analyte concentration.

8.4.4 Matrix Spike Duplicate (MSD) Requirements

A MSD is a replicate MS sample prepared and analyzed in lieu of a matrix duplicate. At least one MSD sample is prepared and analyzed with each analytical batch. The variability between MS and MSD results are used to assess the precision of the measurement process.

MS results are evaluated as %R of the added analyte concentration and as the relative percent difference (RPD) between results for the MS and MSD.

8.4.5 Post-Digestion Spike (PDS) Requirements

The PDS is an aliquot of digested sample spiked with analytes of interest. PDS results, together with matrix spike recoveries, are used to determine if poor recoveries are due to the sample preparation or analysis process.

8.4.6 Serial Dilution (L) Requirements

The serial dilution is a five-fold dilution of a digested field sample analyzed to assess matrix effects on the sample results. The overall dilution factor for the serial dilution is determined by the dilution of the digestate used for sample result quantitation. For example, if an analyte was quantified from neat digestate for the original sample, the serial dilution is analyzed on a five-fold dilution (1:5) of the sample. If an analyte was quantified from a ten-fold dilution of the digestate for the original sample, the serial dilution is analyzed on a fifty-fold dilution (1:50).

8.5 Analysis Run QC Requirements

The QC parameters covered in Section 8.5 are specific to the analytical run. Detailed instructions for meeting these requirements are included in Sections 7 and 9 of this procedure. See Appendix B and Appendix C for acceptance criteria and required corrective actions.

8.5.1 Initial Calibration and Initial Calibration Verification (ICV) Requirements

The ICP-AES is calibrated for all analytes daily prior to analysis of samples, using standards which contain the same acid matrix as the samples to be analyzed.

The ICV is a solution with known analyte values prepared from a source(s) independent from those used for the calibration standards. The ICV is analyzed immediately after each initial calibration to verify the accuracy of the calibration standards and the resulting calibration curve.

ICV results are evaluated as %R of the known or "true" concentration standard.

8.5.2 Initial Blank Verification (ICB) Requirements

The ICB is a solution identical to the calibration blank which is analyzed immediately after the ICV. The ICB is used to verify the accuracy of the low end of the calibration curve.

8.5.3 Low Level Concentration (LLC) Check

The LLC is a solution analyzed to meet the WIPP-WAP requirement to set the concentration of at least one QC or calibration standard at or below the solution concentration equivalent of the PRQL. The LLC is used to assess the accuracy of the calibration curve at or below the level of interest.

8.5.4 Interference Check Samples (ICS) Requirements

Interference check samples consist of two standard solutions, ICSA and ICSAB. The ICSA contains Al, Ca, Fe, Mg, and U at levels sufficient to test the ICP-AES interelement corrections. The ICSAB solution contains interfering analytes at concentrations similar to ICSA plus a quantifiable concentration of all target analytes. ICSA and ICSAB results are used to verify interelement and background correction factors for target analytes.

ICSA and ICSAB are analyzed at the beginning and end of each analytical run. In addition the ICSA and ICSAB solutions must be analyzed periodically so that no more than 8 hours elapses between analyses of ICSA and ICSAB pairs. In other words, if the analysis run is longer than 8 hours, an intermediate ICSA and ICSAB must be inserted into the run.

8.5.5 Continuing Calibration Verification (CCV) Requirements

The CCV is a solution with known analyte values analyzed periodically to verify instrument calibration stability through the analytical run. The CCV is analyzed at the beginning of the run (the ICV), after each set of ten analytical samples (as defined in Appendix D), and once again at the end of the run after all analytical samples have been analyzed.

8.5.6 Continuing Calibration Blank Verification (CCB) Requirements

The CCB is a solution identical to the calibration blank, which is analyzed immediately after the each CCV. The CCB is used to monitor instrument baseline stability throughout the analytical run.

9. CALCULATIONS

Use internally consistent units wherever units are not specified in the following calculations. For example, in the Matrix spike recovery calculation SSR, SR, SA must all be in the same units.

9.1 Sample Results

$$C_S = \frac{X_C \times V}{W} \times \frac{(a+d)}{a}$$

where:

C_s	=	Sample concentration in mg/kg
X_c	=	Interelement-corrected sample concentration from the instrument readout in mg/L
V	=	Final preparation volume in mL
W	=	Initial weight of sample in g
a	=	Post-preparation sample aliquot taken
d	=	Volume of diluent added to the post-preparation aliquot

9.2 Matrix Spike and Post Digestion Spike Recovery

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

where:

%R	=	% Recovery
SSR	=	Measured concentration in the spike sample
SR	=	Measured concentration in the unspiked sample (SR=0 if the analyte was not detected in the unspiked sample)
SA	=	Known concentration of the spike added

NOTE: *For post digestion spikes SR may be adjusted to compensate for dilution due to spike addition.*

9.3 Matrix Spike Duplicate Agreement

$$RPD = \left| \frac{S - D}{\frac{(S + D)}{2}} \right| \times 100 = \left| \frac{S - D}{(S + D)} \right| \times 200$$

where:

RPD = Relative Percent Difference

S = Concentration of first spike sample in report units

D = Concentration of second spike sample in report units

9.4 Percent Recovery for ICV, CCV, LCS, LLC

$$\%R = \frac{C_m}{C_t} \times 100$$

where:

%R = % Recovery

C_m = Measured concentration in the solution

C_t = Known, or 'True', concentration of the solution

9.5 Percent Difference (%D) for Serial Dilutions

$$\%D = \left| \frac{SR - SDR}{SR} \right| \times 100$$

where:

%D = Percent Difference

SR = Undiluted sample result

SDR = Serial Dilution sample result, corrected for the five-fold dilution

9.6 Instrument Detection Limit (IDL) Calculation

$$IDL = t_{(n-1,1-\alpha=.99)} \times s$$

where:

IDL	=	Instrument Detection Limit.
s	=	The standard deviation of the replicate measurements
$t_{(n-1,1-\alpha=.99)}$	=	The T-distribution value appropriate to a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom
n	=	The number of replicate measurements obtained

t Distribution Values for n=7 to n=11

n	n-1	$t_{(n-1,1-\alpha=.99)}$
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821
11	10	2.764

9.7 Interelement Correction Factor, k, Sequential Measurements

IF $|C_a - B| \leq IDL$

THEN $k = 0$

IF $|C_a - B| > IDL$

THEN $k = \dfrac{C_a - B}{C_i}$

where:

k	=	Interelement Correction Factor
C_a	=	Measured concentration (positive or negative) for the analyte in the presence of the interferent solution, mg/L.
C_i	=	Known concentration of the interferent, mg/L.
B	=	Analyte reading for an ICB or CCB analyzed during the interferent analysis run, mg/L.

9.8 Interelement Correction Threshold Concentration, Sequential Measurements

$$C_t = \frac{5 \times IDL}{|k|}$$

where:

C_t = Interferent threshold concentration, mg/L.

IDL = Current analyte IDL, mg/L

k = Interelement correction factor calculated per Equation 9.7

9.9 Interelement Correction of Sample Results, Sequential Measurements

<u>IF</u> $C_i > C_t$ <u>THEN</u> $SR_{corr} = SR - k \times C_i$

<u>IF</u> $C_i \leq C_t$ <u>THEN</u> $SR_{corr} = SR$

where:

SR_{corr} = Interelement corrected value, mg/L.

SR = Uncorrected analyte reading in the sample solution, mg/L.

k = Interelement correction factor calculated per Equation 9.7

C_i = Interferent concentration in the sample solution, mg/L.

C_t = Interferent threshold concentration, mg/L

9.10 Interelement Correction Factor, k, Simultaneous Measurements

<u>IF</u> $|C_a| \leq IDL$

<u>THEN</u> $k = 0$

<u>IF</u> $|C_a| > IDL$

<u>THEN</u> $k = 1000 \times \left(\frac{C_a}{C_i} \right)$

where:

k = Interelement Correction Factor

C_a = Measured or blank-corrected measured concentration for the analyte in the presence of the interferent solution, mg/L.

C_i = Known concentration of the interferent, mg/L.

9.11 Interelement Correction Threshold Concentration, Simultaneous Measurements

NOTE: *For simultaneous measurements threshold concentrations are used only when interferent concentrations cannot be measured simultaneously with analyte concentrations (See Step 7.33.6).*

$$C_t = \frac{5 \times IDL}{|0.001 \times k|}$$

where:

C_t = Interferent threshold concentration, mg/L.

IDL = Current analyte IDL, mg/L

k = Interelement correction factor calculated per Equation 9.10

9.12 Interelement Correction of Sample Results, Simultaneous Measurements

NOTE: *For simultaneous measurements this calculation is performed by the instrument software prior to raw data output.*

$$SR_{corr} = SR - k \times 0.001 \times C_i$$

where:

SR_{corr} = Interelement corrected value, mg/L.

SR = Uncorrected analyte reading in the sample solution, mg/L.

k = Interelement correction factor calculated per Equation 9.10

C_i = Interferent concentration in the sample solution, mg/L.

10. RECORDS

Records generated during the performance of this procedure are maintained as QA records in accordance with CCP-QP-008, *CCP Records Management*. The records are the following:

QA/Nonpermanent

- Instrument Detection Limit (IDL) Determination File
- Precision and Accuracy (P&A) Demonstration File
- Interelement Interference Correction Factor (IECF) Determination File
- Documented Linear Range (DLR) Determination File

The following records generated during the performance of this procedure will be compiled into the Supporting Data Package, in accordance with CCP-TP-188, *CCP Analytical Data Recording, Review and Reporting.*

QA/Nonpermanent

- Copies of applicable pages of the Sample Preparation Logbook
- Copies of applicable pages of the Instrument Run Logbook
- Instrument Print Outs/Raw Data
- Copies of applicable pages of the Standard Preparation Logbook

11. REFERENCES

11.1 ACLP-0.21, “Work Control Procedure for the Analysis of Nonroutine Samples”

11.2 ACLP-0.24, “Laboratory Spill Cleanup”

11.3 ACLP-0.25, “Labware Cleaning For Environmental Analyses”

11.4 ACLP-0.255, “Mechanical Pipetor Calibration Verification”

11.5 ACLP-0.27, “Routine Handling of Corrosives”

11.6 ACLP-0.40, “Analytical Laboratories Waste Management”

11.7 ACLP-1.01, “Preparation of Reagents and Standards”

11.8 ACLP-2.05, “Control, Distribution and Use of Spectrochemical Standards”

11.9 CCP-QP-002, *CCP Training and Qualification Plan*

11.10 CCP-QP-005, *CCP TRU Nonconforming Item Reporting and Control*

11.11 CCP-QP-008, *CCP Records Management*

11.12 CCP-TP-183, *CCP Microwave Assisted Digestion of Homogeneous Solids and Soil/Gravel*

11.13 EPA. 1996. *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods.* SW-846, Fourth Edition, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response.

11.14 CCP-TP-188, *CCP Analytical Data Recording, Review, and Reporting*

11.15 MCP-3635, “Chemical Hygiene Plan”

11.16 MCP-7, “Radiological Work Permit”

11.17 New Mexico Environment Department, 1999. *Hazardous Waste Facility Permit Issued to Waste Isolation Pilot Plant*, EPA No. NM4890139088, New Mexico Environment Department

Appendix A – Analyte and Interferent Parameters

Appendix A, Table 1: Analyte and Interferent Parameters, Sequential

Element	Interferent or Target Analyte	Nominal Analytical Wavelength, nm	Typical IDL, JY-138, mg/L	Target ICSAB Concentration, mg/L
Aluminum	Interferent	237.312	0.007	500
Antimony	Target Analyte	206.833	0.005	1
Arsenic	Target Analyte	189.042	0.005	1
Barium	Target Analyte	233.527	0.001	0.5
Beryllium	Target Analyte	234.861	0.001	0.5
Cadmium	Target Analyte	226.502	0.001	1
Calcium	Interferent	317.933	0.004	500
Chromium	Target Analyte	205.552	0.001	0.5
Iron	Interferent	238.204	0.004	200
Lead	Target Analyte	182.150	0.006	1
Magnesium	Interferent	279.079	0.007	500
Nickel	Target Analyte	231.604	0.002	1
Selenium	Target Analyte	196.090	0.006	1
Silver	Target Analyte	338.289	0.001	1
Thallium	Target Analyte	190.864	0.004	1
Uranium	Interferent	263.553	0.017	200
Vanadium	Target Analyte	292.402	0.002	0.5
Zinc	Target Analyte	213.856	0.001	1

Appendix A Table 2: Analyte and Interferent Parameters, Simultaneous

Element	Interferent or Target Analyte	Nominal Analytical Wavelength, nm	Typical IDL, Optima 4300, mg/L	Target ICSAB Concentration, mg/L
Aluminum	Interferent	308.215	0.020	500
Antimony	Target Analyte	206.833	0.005	1
Arsenic	Target Analyte	188.979	0.004	1
Barium	Target Analyte	233.527	0.003	0.5
Beryllium	Target Analyte	313.107	0.001	0.5
Cadmium	Target Analyte	214.440	0.001	1
Calcium	Interferent	317.933	0.029	500
Chromium	Target Analyte	205.560 or 267.716	0.001	0.5
Copper	Interferent	324.754	0.002	N/A
Iron	Interferent	273.955	0.004	200
Lead	Target Analyte	220.353	0.003	1
Magnesium	Interferent	279.079	0.004	500
Manganese	Interferent	257.610	0.001	N/A
Nickel	Target Analyte	231.604	0.001	1
Selenium	Target Analyte	196.026	0.013	1
Silver	Target Analyte	328.068	0.002	1
Thallium	Target Analyte	190.801	0.005	1
Titanium	Interferent	334.940	0.001	N/A
Uranium	Interferent	409.014	0.028	200
Vanadium	Target Analyte	292.402	0.002	0.5
Zinc	Target Analyte	213.857 or 206.200	0.001	1

Appendix B – Metals Target Analyte List and Quality Assurance Objectives

Analyte	CAS Number	Precision (%RSD or RPD)[a]	Accuracy (%R)[b]	PRDL (µg/L)	PRQL (mg/kg)	Completeness (%)
Antimony	7440-36-0	≤30	80-120	100	100	90
Arsenic	7440-38-2	≤30	80-120	100	100	90
Barium	7440-39-3	≤30	80-120	2000	2000	90
Beryllium	7440-41-7	≤30	80-120	100	100	90
Cadmium	7440-43-9	≤30	80-120	20	20	90
Chromium	7440-47-3	≤30	80-120	100	100	90
Lead	7439-92-1	≤30	80-120	100	100	90
Nickel	7440-02-0	≤30	80-120	100	100	90
Selenium	7782-49-2	≤30	80-120	20	20	90
Silver	7440-22-4	≤30	80-120	100	100	90
Thallium	7440-28-0	≤30	80-120	100	100	90
Vanadium	7440-62-2	≤30	80-120	100	100	90
Zinc	7440-66-6	≤30	80-120	100	100	90

[a] ≤ 30 percent control limits apply when sample and duplicate concentrations are ≥ 10 × IDL for ICP-AES. If less than these limits, the absolute difference between the two values shall be less than or equal to the PRQL.

[b] Applies to laboratory control samples and laboratory matrix spikes. If a solid laboratory control sample material which has established statistical control limits is used, then the established control limits for that material should be used for accuracy requirements.

Appendix C – Summary of Laboratory Quality Control Samples and Frequencies for Metals

QC Sample	Minimum Frequency	Acceptance Criteria	Corrective Action [a]
Method performance samples	Seven (7) samples initially and four (4) semiannually	Meet Appendix B QAOs	Repeat until acceptable
Laboratory blanks	One (1) per analytical batch	≤ 3 × PRDL	Redigest and reanalyze any samples with analyte concentrations which are ≤10 × blank value and ≥ 0.5 × PRQL
Matrix spikes	One (1) per analytical batch	Meet Appendix B accuracy QAOs	NCR if %R outside the range specified in Appendix B.
Matrix spike duplicates	One (1) per analytical batch	Meet Appendix B accuracy and precision QAOs	Nonconformance if RPDs > values and %Rs outside range specified in Appendix B.
Initial Calibration 1 blank, 1 standard	Daily	90-110 %R for ICV	Correct problem and recalibrate; repeat initial calibration
Continuing Calibration	Every 10 samples and beginning and end of run	90-110% for CCV	Correct problem and recalibrate; rerun last 10 samples
Serial Dilution	One (1) per analytical Batch	5 × dilution must be ≤ 10% D of initial value for sample > 50×IDL	Flag Data if >10% and >50 × IDL
Interference Correction Verification	Beginning and end of run or every 8 hours whichever is more frequent	80-120% recovery for analytes. [b]	Correct problem and recalibrate, nonconformance if not corrected
Laboratory Control Samples	One (1) per analytical Batch	Appendix B accuracy QAOs	Redigest and reanalyze for affected analytes; non conformance if not reanalyzed

a Corrective action when final reported QC samples do not meet the acceptance criteria. Nonconformances do not apply to matrix related exceedances.

b Acceptance Criteria and Corrective Action apply only if interferents found in samples at levels greater than ICSA solution.

Appendix D – Typical Analytical Run Sequence

Task	Step	Notes	See Also
Auto-Search, Sequential	7.9	Applicable to sequential instruments only.	
Auto-Attenuate, Sequential	7.10	Applicable to sequential instruments only. A second AutoSearch may follow AutoAttenuate	
Auto-Search, Sequential	7.9	Optional step applicable to sequential instruments only.	
Profile, Sequential	7.11	Applicable to sequential instruments only.	
Wavelength alignment, Simultaneous	7.5.3.2	Applicable to simultaneous instruments only.	
Calibration	7.14, 7.16.2	Calibration standard values are entered in mg/L.	8.5.1
ICV analysis	7.17	The ICV must be analyzed immediately after each initial calibration.	8.5.1
ICB analysis	7.18	The ICB must be analyzed immediately after the ICV.	8.5.2
LLC analysis[c]	7.19		8.5.3
Initial ICSA analysis[c]	7.20		8.5.4
Initial ICSAB analysis[c]	7.21		8.5.4
CCV	7.27	Analysis of CCV and CCB is required prior to sample analysis only if ICV and CCV are different solutions.	8.5.5
CCB	7.18		8.5.6
LB analysis [b]	7.22		8.4.1
LCS analysis [b]	7.23		8.4.2
Sample 1 [b]	7.16		
Sample 1 MS [b]	7.24		8.4.3
Sample 1 MSD [b]	7.24		8.4.4
Analysis of up to 2 additional analytical samples. [b]		If analysis of a CCV/CCB pair follows the ICSAB analysis, then up to 5 additional analytical samples can be analyzed before proceeding to the CCV/CCB No more than 10 analytical samples [a] can be analyzed between the calibration verifications.	
CCV	7.27		8.5.5
CCB	7.18		8.5.6
Analysis of up to 8 analytical samples [b]			
Serial Dilution [b]	7.25		8.4.6

Task	Step	Notes	See Also
Post Digestion Spike [b]	7.26	The post-digestion spike analysis may be omitted if serial dilution, matrix spike, and matrix spike duplicate results meet acceptance criteria.	8.4.5
CCV	7.27		8.5.5
CCB	7.18		8.5.6
**Analysis of up to 10 analytical samples [a]		If the time from the most recent ICS is nearing 8 hours, include analysis of ICSA and ICSAB as the last 2 analytical samples analyzed prior to the CCV CCB pair.	
**CCV	7.27		8.5.5
**CCB	7.18		8.5.6
At this point, the 3 steps preceded by ** are repeated in order until most samples are analyzed.			
Analysis of up to 8 analytical samples [a]			
Final ICSA analysis[c]	7.20		8.5.4
Final ICSAB analysis[c]	7.21		8.5.4
CCV	7.27		8.5.5
CCB	7.18		8.5.6
End of Run	7.28		
Instrument Shutdown	7.29		
Laboratory Blank Evaluation [d]	7.22	See Note d.	8.4.1

[a] The term 'Analytical Samples' in the above table is as defined in Section 7.6, Analytical Run Sequence. No more than ten analytical samples can be analyzed between calibration verifications. Re-analysis of any analytical sample must be counted as an additional analytical sample.

[b.] Indicates a suggested sequence. Another solution may be substituted (one-for-one) for solutions marked with [b].

[c] Initial ICSA, Initial ICSAB, LLC, Final ICSA, and Final ICSAB analyses are not required for analytical runs which do not include measurement of target analytes.

[d] Laboratory blank evaluation can be performed at any time between the analysis of the LB and completion of Section 7.

Appendix E – Acronyms and Abbreviations

%R	Percent recovery
CalSt	Calibration Stock Solution(s) (Item 5.2.6)
CCB	Continuing calibration blank
CCV	Continuing calibration verification
DLR	Documented linear range
HDPE	High density polyethylene
ICB	Initial calibration blank
ICV	Initial calibration verification
ICVSt	Initial Verification Stock Solution(s) (Item 5.2.7)
IDL	Instrument detection limit
ISSt	Internal Standard Stock Solution
LB	Laboratory blank
LCS	Laboratory control sample
MS	Matrix spike sample
MSD	Matrix spike duplicate sample
NIST	National Institute for Standards and Technology
PDS	Post-digestion spike
PRDL	Program-required detection limit
PRQL	Program-required quantitation limit
PVC	Polyvinyl chloride
QC	Quality control
RPD	Relative percent difference
RWP	Radiological work permit
SIF	Sample Information File
SW-846	*Test Methods for Evaluating Solid Waste*, Third Edition
TRU	Transuranic
VTSR	Validated time of sample receipt
WIPP-WAP	Waste Analysis Plan from the Hazardous Waste Facility Permit Issued to Waste Isolation Pilot Plant