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Standard Operating Procedure for EPA Method 6010C: Inductively Coupled Plasma-Optical Emission Spectroscopy

1. SCOPE AND APPLICABILITY

Inductively coupled plasma-optical emission spectroscopy (ICP-OES) is a powerful tool for the analysis of trace elements; however, the sample must be in solution-form for analysis. As a result, all solid and aqueous matrices (except groundwater samples) must be digested using an appropriate acid-digestion method before analysis can occur. Groundwater samples that were pre-filtered and acidified upon sample receipt do not need acid digestion. To the extent possible, standards and samples shall be matrix-matched. Prior to analysis, analysts shall review all preparation methods used to prepare samples for analysis to familiarize themselves with the relevant quality control procedures, development of QC acceptance criteria, calculations, and general guidance.

Table 1 lists the elements for which this method has been validated. Additional elements may be analyzed by this method if appropriate validation at the concentrations of interest is provided.

This SOP is intended as a technical reference to EPA Method 6010C and describes the theory and required quality control for metals analysis by ICP-OES. Use of this method is restricted to use by analysts appropriately experienced and trained in the correction of potential spectral, chemical, and physical interferences. Each analyst must also demonstrate the ability to generate acceptable results with this method.

Detailed information regarding the operation of current instruments can be found in their respective technical SOPs. Further information on the current instrument settings, standard concentrations, and expected concentrations of both instrument and batch quality control samples may be found in Appendix A.

2. PRINCIPLE

Inductively coupled plasma – atomic emission spectroscopy works by exciting the electrons in the analyte to an elevated state using RF-induced argon plasma. The excited electrons then collapse back to their ground state, emitting light at one of a fixed set of wavelengths characteristic to the specific analyte, often referred to as spectral lines. The instrument then measures the intensity of light emitted at specific spectral lines (as designated by the instrument operator), allowing for the simultaneous analysis of a wide range of analytes.

Due to variations in background radiation and scattering, background correction is essential for accurate trace element determination. To do so, background emission is measured adjacent to spectral lines for each analyte during analysis. The positions selected for the background-intensity measurement, which may be on either or both sides of the analytical line, are determined during method development based on the complexity of the spectrum adjacent to the spectral line. Ideally, the positions used should be as free as possible from spectral interference and should undergo the same change in background intensity as at the analyte wavelength measured during sample analysis. There is a possibility of interferences with the background correction (Section 3.2); these can be monitored using method blank and laboratory control spike samples (as described in Section 6.3).

3. INTERFERENCES

3.1. Contamination

Trace-level analysis requires careful and clean preparation and analysis technique along with high-purity standards and solutions. Solvents, reagents, glassware, and other items used during sample preparation may introduce unexpected interferences or contamination to the sample prior to analysis. These materials must be demonstrated to be free from interferences and contamination by analyzing method blanks with every sample batch.

3.2. Spectral Interferences

Spectral interferences can be caused by background emissions, stray light from the emission of high concentration elements, wavelength overlaps between elements, or the unresolved overlap of molecular band spectra.

Any time a new matrix is analyzed or a new instrumental method is developed, analysts must verify the absence of spectral interference by scanning over a range of 0.5 nm centered on the desired analytical wavelength. The determination of spectral interferences must be done using analyte concentrations that produce a significant but relevant level of interference. Typically, the analysis of concentrations ranging from 100 - 500 mg/L in single-element or multi-element interference check solutions is sufficient to find spectral interferences. However, for analytes or common ions that may be found in the sample at high concentration, higher concentrations may be used, up to the limit of the linear dynamic range.

Samples that show an elevated background emission across the range may be background corrected by applying a correction factor equal to the emission adjacent to the line or at two points on either side of the line and interpolating between them. Similarly, uncorrected spectral overlaps can interfere with analysis to produce false positive or positively biased determinations of sample concentration. These overlaps can be avoided by using an alternate wavelength (that does not exhibit a background shift or spectral overlap) or compensated for using equations that correct for inter-element contributions.

The following considerations should be made when dealing with spectral interferences.

3.2.1. Background Correction

It is possible to compensate for background emission and stray light by subtracting the background emission measured at wavelengths adjacent to the analyte wavelength peak. To determine the location for background corrections, the area on either side adjacent to the analytical wavelength must be scanned and the apparent emission intensity from all other method analytes is determined. A background correction factor equal to the emission adjacent to the analytical wavelength or interpolated from between two points on either side of the wavelength can then be applied to the analysis. The background correction point(s) selected must be free of any analyte or interfering signal and represent the baseline around the analyte wavelength. Once selected, these values are stored as part of the instrumental method and are applied by the WinLab software to any spectral measurement made in the designated region around the analytical wavelength.

3.2.2. Inter-Element Correction Models

Analysts may apply inter-element correction (IEC) equations (as determined for that specific instrument) on an element-by-element basis to elements that experience more than a ±20% variation in concentration as a result of the presence of an interfering element. This requires the interfering elements to be analyzed at the same time as the element of interest and a correction equation applied by the software to the calculated results (as shown in Appendix B). Inter-element corrections that constitute the majority of an emission signal may not yield accurate data.

IEC models must be developed for each individual instrument. Measured intensities and the magnitude of interference can vary from instrument to instrument for the same emission line because of differences in resolution (as a function of detector grating and slit widths) and dispersion of the signal. IEC factors can also vary due to changes in background correction points; where practical, analysts should avoid placing a background correction point in the location of an expected interfering emission line. Guidelines and instructions for building and applying an IEC model can be found in Appendix C.

If an IEC model is applied, the accuracy must be verified before each analysis by analyzing an IEC verification sample (see Section 6.2.7). In addition, all IEC factors within the model must be verified and/or updated when any change or maintenance occurs that affects the plasma conditions (such as changing the torch, nebulizer, or injector, or changing gas flows or RF settings).

For all analytes without inter-element correction, verification of the absence of interferences is still required using an interference check solution (which may be the same as the IEC verification solution; Section 6.2.7).

3.3. Physical and Chemical Interferences

3.3.1. Physical Interferences

Physical interferences are associated with the sample introduction system from sample probe, through the nebulizer and out of the injector. Changes in physical

properties such as viscosity and surface tension can cause variation in signal intensities, especially in samples containing high dissolved solids or high acid concentrations. In addition, high salt concentrations can result in significant signal suppression and salt build-up on the nebulizer tip. These physical interferences can be reduced by dilution of the samples or compensated for using an internal standard to monitor signal suppression. Use of appropriate post-digestion spikes and serial dilutions can also monitor for physical interferences (see Sections 6.3.5 and 6.3.6).

3.3.2. Chemical Interferences

Chemical interferences are highly dependent on matrix type and the specific analyte element and can include the formation of molecular compounds, ionization effects, and solute vaporization effects. Normally, these are not significant issues with this method of analysis; however, if observed, they can generally be minimized by proper matrix matching, dilution, and careful selection of operating conditions (including RF power, torch and injector position, and plasma gas flow).

3.3.3. Internal Standardization

The use of internal standards involves adding one or more elements (such as yttrium or scandium) that are both not found in the samples and verified to not cause an inter-element spectral interference to the samples, standards, and blanks. This technique is very useful in overcoming matrix interferences, especially in matrices with high dissolved solids or other interferences resulting in signal suppression. See Section 6.2.2 for a full discussion of the use of internal standards in this analysis.

3.4. Memory Effects

Memory effects occur when analytes in a previous sample contribute to the signal measured in a new sample and are generally a result of sample deposition on the injector and plasma torch. Less commonly, memory effects can also be caused by build-up in the sample probe and tubing, the nebulizer, and inside the spray chamber. The site where this occurs can vary based on the element and is best minimized by sufficient flushing of the system with a rinse solution between samples.

With the advent of loop injection sample introduction, memory effects have been mitigated for most matrices. Rinse times should be appropriate for the matrix. If memory effects are suspected, the sample should be reanalyzed after allowing the system to rinse for a sufficient length of time. If the memory effect remains, analysis should stop and the sample introduction system should be cleaned and/or tubing should be replaced.

4. PRESERVATION AND HOLDING TIMES

All digested or extracted samples must conform to the preservation and holding times specified by the digestion or extraction method. Aqueous samples which do not require digestion shall be filtered, preserved by bringing the sample to a pH < 2 using concentrated HNO_3 (to minimize any dilution) and must be analyzed within 6 months.

5. EQUIPMENT AND REAGENTS

5.1. Key Hardware and Consumables

5.1.1. ICP-OES: Agilent 5100/5110 with SPS4 Autosampler or Perkin-Elmer Optima 7300DV with Elemental Scientific FAST 2DX Autosampler

5.1.2. Sample Tubing (0.76 mm i.d., black/black, or 1.02 mm i.d., white/white)

5.1.3. Waste Tubing (1.14 mm i.d., red/red, 1.30 mm i.d. grey/grey or 1.65 mm i.d., blue/blue)

5.1.4. Internal Standard Tubing (0.19 mm i.d., orange/red)

5.1.5. Rinse Tubing for Autosampler (1.4 mm i.d., red/red/red)

5.1.6. Disposable Plastic Standard Tubes (50 mL capacity)

5.1.7. Disposable Plastic Sample Tubes (15 mL capacity)

5.1.8. Argon Gas Supply, High-purity

5.2. Reagents and Standards

A complete list of all stock solutions and the procedure for the preparation of all solutions and standards can be found in Appendix A. All standard preparation shall be recorded in the "ICP-OES Standards Preparation Log Book".

5.2.1. Reagent Water

All references to water in the method refer to reagent water, unless otherwise specified. Reagent water must be free of interferences.

5.2.2. Concentrated Nitric Acid (68-70% HNO_3) – Ultrapure Trace Metal Grade

5.2.3. 5% (v/v) HNO_3 in Reagent Water for Mixing Standards

5.2.4. 2% (v/v) HNO_3 in Reagent Water as Instrument Rinse Solution

5.2.5. Stock Solutions – *See Appendix A for a list of all stock solutions*

All stock solutions shall be purchased as a certified standard with both lot number and expiration date on the bottle. These solutions shall be labeled with the date they are received by the laboratory and with the date the solution was first opened.

5.2.6. 50 ppm Yttrium Internal Standard

5.2.7. 200 ppm Iron Standard

5.2.8. Inter-Element Correction (IEC) Standard

5.2.9. 100 ppm Calibration Working Standard

5.2.10. Instrument Calibration Standards

A description of the current calibration standards and ranges for the ICP-OES can be found in Appendix A.

5.2.11. Second Source Calibration Verification Standard

The second source calibration verification standard must be prepared using a certified solution obtained from a different supplier than that used for calibration. If there is only one supplier for the desired analyte, the second source may be from a stock with a different lot number than the calibration stock solutions.

5.2.12. X-Y Alignment Solutions – 1 ppm Mn (axial), 10 ppm (radial)

This solution is used for the alignment of the torch on the Perkin Elmer Optima 7300. The source of these solutions may be the same as either the calibration stock or the second source stock or may be from a different source entirely. Because the X-Y alignment looks for the strongest signal as a set point and is not calibrating for a specific value, solutions must be from a certified source but may exceed the expiration date by 1 year before replacement is needed.

5.2.13. ICP-OES Wavelength Calibration Solution

This solution is obtainable through Agilent and is used at 10x to calibrate the detector on the Agilent 5100 ICP-OES. An equivalent solution may be prepared from alternative sources.

6. METHOD PROCEDURE

6.1. Instrument Validation

Before using this procedure to analyze samples, the following data shall be available documenting the initial demonstration of performance. The linear dynamic range, instrumental detection limit, method detection limits and interference corrections need to be established for each individual target analyte on each particular instrument. These data shall be generated using the same instrument, operating conditions, and calibration routine to be used for sample analysis. Any new wavelength or analyte added to the method must be validated before analysis at that wavelength may commence. A summary of the recurring validation analyses can be found in Table 2.

A hardcopy of all of the validation data shall be kept in a binder at the instrument and be available for review. Any modifications shall be updated in the binder at the time of change.

Additionally, past methods, IEC models, and detection limit development data will be stored in digital format on media separate from the computer associated with the instrument, when practicable.

6.1.1. Instrument Method Parameters

The instrument method parameters are defined within the controlling software and may vary slightly over time. This includes (but is not limited to) background correction locations, spectral lines used, lens settings, RF and gas flow settings and pumping rates. Typical spectral lines used for analysis along with the lens setting (axial or radial) are shown in Table 1. Typical plasma conditions and pump settings are show in Table 3.

Any time the instrument method is revised, the revision date must be included in the name of the method file when saved. This is essential to allow the connection of instrumental methods with past data sets, enabling re-examination of sample data if necessary.

6.1.2. Linear Dynamic Range

The linear dynamic range must be established for each analyte at each specific wavelength utilized under the same operating conditions as routine sample analysis by determining the signal responses across a wide range of sample concentrations. To do this, analyze a series of standards with increasing concentrations plot the measured intensity (not measured concentration) as a function of theoretical concentration. The linear dynamic range is the range over which there is a linear relationship between concentration and signal intensity.

This process must be completed as part of the initial demonstration of performance and repeated annually or whenever a modification to the instrument results in a significant change in signal response (such as repair or replacement of detector components).

6.1.3. Calibration Range

Any range of calibration standards used for analysis of samples must be entirely within the determined linear dynamic range for that specific instrument and analyte. A minimum of a calibration blank and three non-zero standards must be used to define the calibration range, with the lowest standard defined as the lower limit of quantitation (LOQ), often referred to as the reporting limit.

Both a simple linear regression and a linear regression forced through zero are acceptable for the calculation of the best fit curve in the calibration as long as the resulting calibration meets all acceptance criteria and can be verified by acceptable QC results. Forcing the regression through zero cannot be used as a rationale for reporting results below the lowest standard in the calibration curve.

Once the calibration range has been established, a standard at the upper limit shall be prepared and analyzed using the normal calibration curve and must have a measured value within ±10% of the expected true value. This upper limit validation shall be repeated every three months.

Note: This represents a deviation from EPA Method 6010C. Because a calibration range with a defined maximum concentration is used, there is no need to confirm the upper limit of the linear dynamic range.

Additionally, the LOQ shall be verified every three months by analyzing a blank spiked at 1 – 2 times the reporting limit and must have a recovery within ±30% of the expected value. If the LOQ cannot be verified, the reporting limit must be increased until the validity of the lower limit can be re-established.

6.1.4. Instrument Detection Limits (IDLs)

Instrument detection limits (IDLs) allow a user to evaluate the background noise inherent to a single instrument and are a function of the change in signal over time in the analyses of reagent blanks at the wavelength for each analyte. They are unrelated to reporting limits and should not be used to establish the reporting limit.

IDLs are determined by calculating the average of the standard deviations of three runs on non-consecutive days, with each run consisting of the analysis of seven consecutive measurements of a reagent blank solution. Each measurement must be performed as though it were a separate analytical sample; each blank must undergo any procedure normally performed between the analyses of samples.

The IDLs shall be determined as a part of the initial demonstration of proficiency and checked every six months by running a single set of seven blank samples and comparing the standard deviation to the established IDLs. If the check is not within the 95% confidence interval (see Appendix B) for the established IDLs, the sample introduction system on the instrument shall be cleaned and a new set of IDLs established.

6.2. Instrument Operation

The following instrument QC shall be included with every analysis. The analysis data for all of the initial and subsequent calibration verification analyses listed below shall be kept on file with the sample analysis data. A summary of the required frequency of instrument verification analyses can be found in Table 4. A list of current concentrations used for instrument quality control for each of the active ICP-OES instruments can be found in Appendix A.

Note: Because the typical ICP-OES analytical method includes many elements, it is acceptable to ignore the failure of QC acceptance criteria for a specific analyte when that analyte is not of concern for the project goals for a given analysis (e.g. the analysis is specifically for lead but selenium does not pass). However, effort shall be made to determine the cause of the QC failure and corrections shall be implemented prior to any future analyses.

6.2.1. Calibration Curve

To be considered acceptable, the calibration curve shall have a correlation coefficient greater than or equal to 0.998 for each target analyte. If the required linear response cannot be attained using three non-zero calibration standards, more standards shall be added, particularly at lower concentrations to better define the

linear range and LOQ. The linear range may be narrowed to improve performance by removing the extreme upper and/or lower calibration points as long as three non-zero points remain and the non-linear upper and/or lower portions are removed.

6.2.2. Internal Standardization

The intensities of an internal standard must be monitored in every analysis. An internal standard is one or more elements that are both not found in the samples and verified to not cause an inter-element spectral interference to the samples, standards, and blanks. The addition of an internal standard to the samples ensures consistency in the analysis by correcting for small deviations in signal strength (as described in Appendix B).

The concentration of internal standard shall fall within the normal calibration range of the instrument and must be added to all blanks, standards, and samples. This may be done by manual addition or using an on-line addition as part of the sample introduction system on the instrument. The online addition method is preferred because the constant pump rate adds exactly the same amount of internal standard to each sample analyses and does not risk the chance of "missing" a sample upon manual addition.

Internal standard recoveries shall fall within 70-130% of the intensity measured in the calibration blank. If the percent recovery of the internal standard in a sample falls below 70%, a significant matrix effect must be suspected. Under these conditions, the LOQ has degraded and the internal standard correction becomes questionable. If the percent recovery is above 130%, the presence of internal standard native to the sample must be suspected. These issues shall be addressed as follows.

- Make sure the poor recovery is not a result of an issue with the instrument (such as drift or sample introduction issues) by checking the internal standard intensities in the nearest standard or blank. If the low internal standard intensities are also seen in the nearest calibration blank, terminate the analysis, find and correct the problem, recalibrate, verify the new calibration, and reanalyze the affected samples.
- If there is no evidence of instrument-related issues, both matrix effects and native quantities of the internal sample need to be removed by dilution of the affected sample until the internal standard falls within the acceptable range (70-130%). Reported results must be corrected for all dilutions and a notation made about the matrix effect or native internal standard in the report.

6.2.3. Initial Calibration Verification

After initial calibration, the calibration curve shall be verified by the analysis of an initial calibration verification (ICV) standard, which shall be prepared from a second source (independent) material at or near the mid-range of the calibration curve. The acceptance criteria for the ICV standard is ±10% of its true value.

If the recovery is outside of the acceptance criteria, the ICV standard shall be rerun once for confirmation and if recoveries are still not acceptable, the ICV standard shall be remade. If the calibration curve cannot be verified within the acceptable limits after remaking the ICV standard, the cause must be determined and the instrument must be recalibrated before analysis of samples may begin. Quantitative sample analyses shall not proceed for those analytes that fail to meet the acceptance criteria unless the results are flagged as estimated values.

6.2.4. Low-Level Calibration Verification

In addition to the ICV standard, an initial low-level calibration verification (LLCV) standard shall be prepared and analyzed prior to any samples. The LLCV standard shall also be analyzed every 10 samples and at the end of each analysis. This frequency is intended to minimize the number of samples for re-analysis should the LLCV fail at the end of the analysis batch.

The LLCV standard shall be prepared at a concentration equal to the reporting limit from the same source as the calibration standards. If practicable, the LLCV standard should be the same solution as the lowest standard used during calibration. The acceptance criteria for the LLCV is ±30% of its true value. If the LLCV standard fails to meet the acceptance criteria, steps shall be taken to correct any problems up to and including recalibration as described in Section 6.2.9. All samples following the last acceptable LLCV must be reanalyzed.

6.2.5. Calibration Blank Verification

During the initial calibration verification, after every ten samples, and at the end of every analysis, a calibration blank (CCB) must be analyzed. When practicable, this blank should be the same blank used as the initial calibration blank. The CCB must have a measured concentration less than one quarter (1/4) of the reporting limit for any desired analyte. If the CCB fails to meet the acceptance criteria, steps shall be taken to correct any problems up to and including recalibration as described in Section 6.2.9. All samples following the last acceptable CCB must be reanalyzed.

6.2.6. Continuing Calibration Verification

After every ten samples and at the end of every analysis, a continuing calibration verification (CCV) standard must be analyzed. The CCV standard shall be prepared from the same stock as the calibration standards at or near the mid-range of the calibration curve. If practicable, the CCV should be the same solution used as a mid-point used during calibration. The acceptance criteria for the CCV standard is ±10% of its true value. If the CCV fails to meet the acceptance criteria, steps shall be taken to correct any problems up to and including recalibration as described in Section 6.2.9. All samples following the last acceptable CCV must be reanalyzed.

6.2.7. Interference Check Solution/Inter-Element Correction (IEC) Verification

Whether or not inter-element corrections are applied to the sample, the absence of uncorrected interferences is necessary. This is monitored by the analysis of an interference check solution (also referred to as the IEC standard) which contains high concentrations of major components typical to most samples (>100 mg/L) on a continuing basis to verify the absence of effects at the selected analytical wavelengths.

If analysis of the IEC standard results in a recovery outside of an acceptable range of ±20% of the true value, the analyte must be determined using an alternate analytical wavelength free of the interference or with the development. It is also acceptable to develop and apply an inter-element correction model for the specific interaction between analyte and interference (see Section 3.2.2 and Appendix C).

This solution can also serve to check any inter-element corrections applied to the analysis, as long as all interfering elements in the IEC model are included as major components in the IEC standard. If the ±20% acceptance criteria cannot be achieved when the IEC model is applied, then the model either must be rebuilt (see Appendix C) or the interference is deemed non-correctable and a different analytical wavelength must be chosen.

6.2.8. Diluent Check

If necessary, samples are diluted with 5% nitric acid. This diluent must be analyzed prior to unknowns to ensure it is free of analytes. Analyte concentration must be less than 50% of the reporting limit.

6.2.9. Instrument QC Failure

If any of the instrument QC samples fail to meet the criteria listed above, the sample shall be rerun. After 2 consecutive QC failures, an attempt to find and correct the cause of the failed QC must be made. The following represents a general order of corrections that do not require recalibration:

- Allow the system to rinse for 5 – 10 minutes and then reanalyze the QC sample.
- Re-prepare the QC sample from the same stock (or working standard) and analyze the new QC sample.
- Re-prepare the QC sample from an alternate stock (or fresh working standard) and analyze the new QC sample.

Reanalysis after a correction allows an additional 2 attempts before another correction must be attempted. If the QC sample still does not pass after the above corrections, a more significant issue is present which will likely require changes to the sample introduction system (and therefore recalibration). If recalibration is needed, the current analytical run must be aborted and all samples since last passing QC must be rerun after the issue causing failed QC is found and resolved.

Each correction made **must** be noted on the print-out of the raw data of the first re-analyzed QC sample for inclusion in the analytical file.

Note: The controlling software includes an automated quality control system which is set up as part of instrument method parameters. When used, it automatically evaluates designated instrument quality control samples against user-set acceptance criteria and flags the QC sample as either "passed" or "failed" in the printed results summary. The "QC failed" notation does not invalidate the analysis of the samples. It only indicates that one or more elements did not meet the method-defined QC criteria and the data must be reviewed by the analyst before continuing with the analysis. If an active back-up spectral line passes the QC acceptance criteria (indicating interference on the primary line) or if the analyte with failed QC is not of concern, then the data can be used and analysis can continue. Otherwise, corrective steps shall be taken as described previously.

6.3. Method-Based Quality Control Samples

Quality control samples included in sample batches will vary based on project-specific requirements but will include some or all of the following. The quality control requirements of the project or specific sample preparation method shall supersede any requirements expressed in this section. A summary of the typical frequency of method-based quality control samples can be found in Table 4. A description of the calculations for percent recovery and relative percent difference (along with other relevant equations) can be found in Appendix B.

Note: As described in Section 6.2, it is acceptable to ignore the failure of QC acceptance criteria for a specific analyte when that analyte is not of concern for the project goals for a given analysis.

6.3.1. Method Blanks

Method blanks are necessary to monitor the sample preparation process for background contamination. At least one method blank must be prepared per batch of 20 samples using a volume (or mass) of reagent water matching the volume (or mass) of the samples which is then carried through the complete extraction, digestion, and/or other sample preparation process.

A method blank is considered acceptable if it does not contain target analytes at a concentration >25% of the reporting limit or >10% of the lowest sample concentration for each analyte in a given batch, whichever concentration is higher. If the method blank cannot be considered acceptable, the method blank shall be re-run once, and if still unacceptable, then the entire sample batch must be reprepared and reanalyzed including all batch QC samples.

If the method blank exceeds the criteria, but the samples are all either below the reporting level or below the applicable action level then a notation of the sample data may be used despite the contamination of the method blank as long as it is accompanied by notation or flagging of the contamination in the report.

6.3.2. Laboratory Control Samples

At least one laboratory control sample (LCS) must be prepared per batch of 20 samples by spiking reagent water with each analyte of interest at a concentration at or near the midpoint of the calibration range. The LCS is then carried through the complete extraction, digestion, and/or other sample preparation process along with the samples. The acceptance criteria for the LCS is ±20% of the spiked value. If the LCS does not meet the acceptance criteria, it shall be re-run once, and if still unacceptable, the entire sample batch must be reprepared and reanalyzed including all batch QC samples.

In cases where matrix spiking is not possible or unsuitable for the sample matrix or when an additional measure of accuracy and precision for the analysis is needed, a laboratory control sample duplicate (LCSD) may be used along with the normal LCS. The acceptance criteria for recovery for the LCSD is the same as for the LCS and the pair must have a relative percent difference (RPD) of ≤20%

The analyses of standard reference materials containing known amounts of analytes in the matrix of interest (if available) may be used as a substitute for the LCS; however, manufacturer-suggested acceptance criteria should be used in place of the standard acceptance criteria.

For California Waste Extraction Test (WET) leachate samples, preparation of LCS/LSCD is described in detail in Appendix D as the extraction requires only a method blank.

6.3.3. Duplicate Samples

The analysis of duplicate samples is an essential measure of analytical precision in samples known to contain analytes of interest. Each sample batch must include at least two subsamples split from a single sample that undergo the same preparation and analysis steps. The acceptance criteria for the sample duplicates is ≤20% RPD. Measured values for analytes that fall below the reporting limit should not be considered as criteria for acceptance or failure of the sample supplicates. If the sample duplicates do not meet the acceptance criteria, the original sample must be examined to determine if the failure is due to issues with the digestion or an unavoidable lack of homogeneity in the sample. Failure to meet acceptance criteria due to an unavoidable lack of homogeneity must be noted in the final report. Otherwise the entire sample batch and all related QC samples must be reprepared and reanalyzed.

Samples may also be split into triplicate or more for a more robust examination of analytical precision. If three or more duplicates are analyzed, they must have a relative standard deviation (RSD) ≤20% (see Appendix B for formula).

6.3.4. Matrix Spikes

It is important to document any potential changes in precision and bias as a result of the method in a given matrix (known as matrix effects) by the analysis of matrix spike (MS) and matrix spike duplicate (MSD) samples. In general, a sample batch

must have at least one MS and one duplicate sample (if the samples are expected to contain the target analytes) or one MS and one MSD (if the samples are not expected to contain the target analytes). This may vary based on project and sample specific requirements, such as matrices where matrix spiking is ineffective due to the required dilution. In these cases, post digestion spiking is essential to monitor precision and bias (see Section 6.3.5).

MS/MSD samples are prepared by splitting a sample and spiking one (or more) portion(s) with a known concentration of each analyte of interest prior to sample preparation and analysis. If both a MS and a MSD sample are prepared, they must be spiked at the same concentration and with the same spiking material as the LCS for the sample batch. The spike concentration shall be at approximately mid-point of the calibration range. The acceptance criteria are ± 25% of the spiked value for accuracy and ≤20% RPD for precision. **If the sample concentration is >4x the spike concentration, the MS/MSD recoveries are not useful and are reported as "Not Calculated" or "NC".**

If the recovery and/or RPD are outside the laboratory control limits, post digestion spikes and serial dilutions shall be used to determine if the failure to meet acceptance criteria is due to matrix effects or other interferences. These tests shall be performed with each batch of samples that does not meet MS/MSD acceptance criteria. If matrix effects are confirmed, they must be documented in the final report along with the additional testing completed.

MS/MSD analysis is not required for WET analysis.

NOTE: Samples prepared by method EPA 3050B mod can be highly heterogenous. Results for such samples often fail MS/MSD recoveries and RPDs for duplicates and/or MS/MSD. Therefore, it is recommended to prepare and analyze duplicate dilutions for each MS, MSD, DUP, and the associated unknown samples, and to prepare one post-spiked sample. Such data helps to confirm QC failures and can potentially prevent QC failures as well.

6.3.5. Post Digestion Spikes

If MS/MSD recoveries are unacceptable, a post digestion spike (PS) sample shall be prepared and analyzed. The PS is prepared by spiking a second portion of prepared sample (or its dilution) that was used to originally prepare the MS/MSD samples. If there is insufficient sample volume remaining from the original sample, another sample from the same preparation batch shall be used as an alternative. The spike concentration must be at or near the center of the calibration range and should fall between 10 times and 100 times the reporting limit. General practice is to add 0.5 mL of the calibration working standard (See Appendix A) to 9.5 mL of a prepared sample or its dilution.

The PS sample has acceptance criteria of ±20% of the spiked value. If this spike fails and the analyte concentrations are sufficiently high, a serial dilution shall be run on the sample to distinguish between matrix effects and interferences. If both the MS/MSD and the post digestion spike fail but the serial dilution passes, matrix effects are confirmed.

Both a PS sample and a PS duplicate sample shall be included in any analytical batch which does not include a MS sample, with a required RPD of ≤10%. Since MS/MSD analysis is not required for WET analysis, PS/PSD samples shall be prepared and analyzed. Preparation of PS/PSD is described in detail in Appendix D.

It is acceptable to prepare and analyze a PS sample at the same time as the original samples to minimize the need for recalibration and secondary analyses.

6.3.6. Serial Dilution

If the questionable analyte concentration is sufficiently high (at least a factor of 10 above the reporting limit after dilution), the analysis of a 1:5 serial dilution should agree within ±10% of the original value. If not, then potential interferences should be investigated. If the interference is the result of spectral overlap, the analyte concentration must either be determined at an alternate wavelength or an IEC model must be applied to the current wavelength and the sample must be reanalyzed.

It is acceptable to prepare and analyze a serial dilution sample at the same time as the original samples to minimize the need for recalibration and secondary analyses.

6.4. Reporting Data

A completed report packet shall include:

- The complete report form (including all relevant batch QC)
- A copy of the authorization request form (ARF)
- A copy of the sample analysis request form (SAR)
- A copy of all related sample receipt and chain-of-custody documentation, including any photographs taken upon receipt
- A copy of the digestion book page for each digestion batch (if relevant)
- A copy of the TCLP or WET extraction preparation book page **and fluid prep log** for each batch (if relevant)
- A copy of the Sample Preparation Report generated by LIMS
- A copy of the Sample Dilution Factor Worksheet generated by LIMS
- For each analytical run used in the report:
    - The hardcopy of the raw data for each analytical run used in the report (including the run sequence and any initialed notations regarding instrument QC failure)
    - A printed copy of the QC Analysis worksheet for each analytical run (including any initialed notations)**, if used**
    - A copy of the ICP-OES Analytical Run Log Book **page or Agilent ICP Run Log showing all dilutions and post-spikes completed**

- A copy of the certification for all standards used and all Standard Preparation Log Book pages associated with the analysis
- Any other notes collected during sample preparation or analysis
- The Inorganic Data Review Checklist

7. MAINTENANCE AND TROUBLE SHOOTING

Maintenance required on an as-needed basis (such as the removal and cleaning of the torch and nebulizer) is described in Appendix C. Common issues and suggested steps for troubleshooting are also described in Appendix C. Each instrument shall have a maintenance log indicating daily, weekly and monthly tasks.

8. REFERENCES

United States Environmental Protection Agency, "Method 6010C – Inductively Coupled Plasma-Atomic Emission Spectroscopy" from "Test Methods for the Evaluation of Waste", SW-846. http://www.epa.gov/waste/hazard/testmethods/sw846/pdfs/6010c.pdf
(Last accessed on 14 September, 2011)

DCN: 07.0012.00 ICP-OES Analytical Run Log Sheet

DCN: 07.0013.00 ICP-OES Standard Preparation Log Sheet

DCN: 07.0107.00 Inorganic Data Review Checklist

DCN: 07.0156.00 ICP-OES Daily Maintenance/Performance Checklist

DCN: 07.0157.00 ICP-OES Monthly Maintenance Log

DCN: 07.0158.00 ICP-OES Weekly Maintenance Log

DCN: 07.0240.00 Agilent ICP Run Log

9. TABLES

Table 1: Analytical Wavelengths

Analyte	Wavelength (nm)	Analyte	Wavelength (nm)
Aluminum[a]	308.22 396.152	Lead	220.35
Antimony	217.582 206.84 206.84 [b c]	Magnesium[a]	279.08 279.553
Arsenic	188.98 193.696	Molybdenum	203.85 202.03[c]
Barium	413.07 493.408	Nickel	231.60
Beryllium	313.11 313.042	Phosphorus	214.9[b]
Cadmium	226.50 228.80 [c]	Selenium	206.279 196.03[bc]
Calcium[a]	317.93	Silver	328.07 338.29[bc]
Chromium	267.72	Thalium	351.92 190.80[c]
Cobalt	228.62 238.892	Vanadium	292.40
Copper	324.75 327.395	Zinc	213.86
Iron[a]	234.35		

a. Analyte is a common interferant with other analytes and is typically monitored for background and correction purposes.
b. This wavelength is measured using the radial detector for increased linear range.
c. Spectral line used as a backup line in case of interferences on the primary analytical line.
d. Internal standard; for comparative purposes only

Table 2: Recurring Validation Analyses (sorted by frequency)

Frequency	Validation	Frequency	Validation
Initial Proficiency *(and as needed)*	Linear Dynamic Range Calibration Range Instrument Detection Limits Method Detection Limits	**Quarterly** *(3 months)*	Upper Calibration Range Verification LOQ Verification LOD Verification
Annually	Updated MDLs Check Linear Dynamic Range	**Every Analysis**	Calibration Range Verification
Bi-annually *(6 months)*	Check IDLs		

Table 3: Typical Plasma Conditions and Pump Settings

Argon Gas	Flow Rate	
Plasma	15	L/min
Auxiliary	0.2	L/min
Nebulizer	0.6 - 0.8	L/min

Pump	Duration	Pump Rate	
Flush	20	2.0	mL/min
Sample		2.0	mL/min
Rinse	60	1.4	mL/min

Plasma		
RF Power	1300	watts
View Distance	15	mm
Aerosol Type	wet	

Spectrometer		
Source Equilibration Delay	15	sec
Read Delay	45	sec
Number of Reads	3	

Table 4: Instrument and Method Quality Control Sample Frequency and Acceptance Criteria

QC Sample	Frequency	Acceptance Criteria
Instrument Quality Control		
Calibration Curve	Before Analysis	$R \geq 0.998$
Internal Standard Recovery	Every Sample	±30% of Internal Standard in Calibration Blank
Initial Calibration Verification (ICV)	Before Analysis	±10%
Calibration Blank Verification (ICB or CCB)	Before Analysis; Every 10 samples; After Analysis	≤ 25% of RL
Low Level Calibration Verification (LLCV)	Before Analysis; Every 10 samples; After Analysis	±30%
Continuing Calibration Verification (CCV)	Every 10 samples; After Analysis	±10%
Interference Check Solution (IEC)	Before Analysis	±20%
Diluent Check Solution	Before Analysis	≤50% of RL
Batch Quality Control		
Method Blank (MB)	One per 20 sample batch	≤ 25% of RL or ≤10% of lowest sample concentration
Laboratory Control Spike (LCS)	One per 20 sample batch	±20% recovery
Matrix Spike/Matrix Spike Duplicate (MS/MSD)	One per 20 sample batch	±25% recovery, ≤ 20% RPD
Sample Duplicate	One per 20 sample batch	≤ 20% RPD
Post Digestion Spike (PS)	If MS/MSD does not pass	±20% recovery
Serial Dilution	If PS does not pass	±10% RPD

10. FIGURES

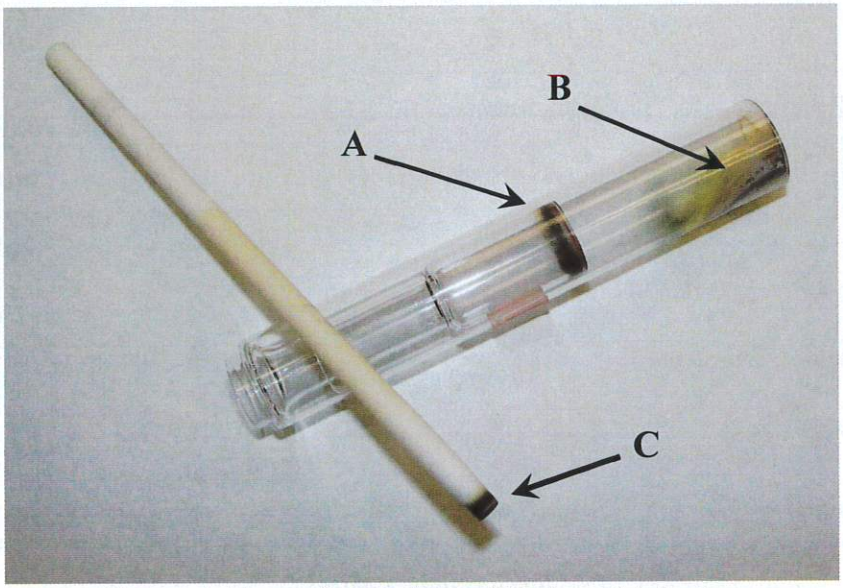

Figure 1: Example of a Dirty Torch and Injector

After prolonged use, the torch will exhibit deposition of metals on the end of the inner tube where the plasma forms (A) and the slow build-up of sample and devitrification of the quartz at the end of the torch (B). Deposition and build-up also occur at the tip of the injector where the sample is released into the plasma (C).

11. APPENDICIES

Appendix A
Current Verification Levels and
Solution Preparation for ICP-OES Analyses

CURRENT VERIFICATION AND SPIKE LEVELS

Calibration Verification Levels

The following levels are currently used to verify the calibration during analysis:

	Optima 7300DV/Agilent 5100/5110
Initial Calibration Verification (ICV)*	5 ppm
Continuing Calibration Verification (CCV)	5 ppm
Low Level Calibration Verification (LLCV)**	0.5 ppm
	0.1 ppm

** Unlike the calibration standards, the ICV sample contains Al, Be, Ag, Ca, and Mg at the same concentration as the other metals.*

*** The Optima 7300DV has two separate LLCV samples due to sporadic Cu spikes and the sensitive nature of very low level analysis. In order for the lower LLCV to be used, all LLCV measurements for a single metal in a given analytical run must pass the QC criteria.*

Current Spiking Levels

The following levels are currently used for method-based QC samples:

	Optima 7300DV/Agilent 5100
Laboratory Control Spike (LCS)	5 ppm (WET) 25 ppm (EPA 3050/3010)
Matrix Spike (MS/MSD) *-in digestate-*	25 ppm
Post Digestion Spike (PS/PSD)	5 ppm
MDL Spike (LLQC)	25 ppb

* *LCS, MS/MSD and LLQC spiking solutions must be validated by analyzing a ~200x dilution prior to use in sample preparation.*

These levels are current as of: **Revision Date**

STOCK SOLUTIONS

The stock solutions currently in use are as follows:

Name	Analytes
Conc. HNO_3	Concentrated Nitric Acid (Ultrapure Trace Metal Grade)
Yttrium Stock	1000 ppm Y or $Y(NO_3)$ salt
Minors Stock	200 ppm Be 1000 ppm As, Ba, Cd, Cr, Co, Cu, Pb, Mo, Ni, Se, Tl, V, Zn
Silver Stock	1000 ppm Ag
Antimony Stock	1000 ppm Sb
Majors Stock (CLP Interferants A Solution)	2000 ppm Fe 5000 ppm Al, Ca, Mg
Second Source Stock (Instrument Calibration Standard 2)	1000 ppm Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sn, Sr, Ti, Tl, V, Zn
X-Y Alignment Stock (Optima Family Multi-element Standard)	1 ppm Ba, Mg 10 ppm La, Li, Mn, Ni 50 ppm As, K
ICP-OES Wavelength Calibration	50 mg/L Al, As, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Se, Sr, Zn 500 mg/L K

Source standards may be purchased from the following suppliers:

Inorganic Ventures, Ultra, Agilent, Ricca, Environmental Express, CPI International, SPEX Certiprep, and Perkin Elmer. See current bottle for supplier and product number information

These levels are current as of: Revision Date

SOLUTIONS FOR RINSING AND DILUTION

Reagent Water

All references to water in the method refer to reagent water, unless otherwise specified. Reagent water must be free of interferences.

~2% (v/v) HNO_3 Instrument Rinse Solution

Dilute 40 mL of concentrated HNO_3 (ultrapure trace metal grade) to a final volume of 2 L with reagent water in a volumetric flask or other volumetric container of sufficient size and mix thoroughly.

5% (v/v) HNO_3 Solution for Standard and Sample Dilutions

Dilute 100 mL of concentrated HNO_3 (ultrapure trace metal grade) to a final volume of 2 L with reagent water in a volumetric flask and mix thoroughly. All subsequent uses of the term "5% HNO_3" refer to this solution.

OPTIMIZATION SOLUTIONS FOR PERKIN-ELMER OPTIMA 7300

Radial X-Y Alignment Solution – 10 ppm Mn

The X-Y Alignment Stock solution is used for the radial X-Y alignment without dilution. Place a minimum of 15 mL of the stock in a 50 mL standard tube for analysis.

Axial X-Y Alignment Solution – 1 ppm Mn

Dilute 5 mL of the X-Y Alignment Stock solution to a final volume of 50 mL using 5% HNO_3 solution in a 50 mL standard tube to create a 10-fold dilution of the stock, resulting in a concentration of 1 ppm Mn.

Wavelength Calibration Solution

Dilute 5 mL of the ICP_OES Wavelength Calibration solution to a final volume of 50 mL using 5% HNO_3 solution in a 50 mL standard tube to create a 10-fold dilution of the stock, resulting in a concentration of 5 ppm.

CALIBRATION STANDARDS

Calibration Blank

The calibration blank shall be an aliquot of the same 5% HNO_3 solution used for the preparation of all standards.

Calibration Working Standard – 100 ppm Minors, Fe, Sb, & 20 ppm Ag & Be

To prepare the calibration working standard, pipette 5 mL of the Majors stock and 10 mL each of the Minors and 1000 ppm Sb, and 2 mL of the 1000 ppm Ag stock solutions into a 100 mL volumetric flask. Bring to volume using 5% and mix thoroughly. This solution is good for a maximum of 1 month.

Note: Because of the difference in analyte concentrations in the various stock solutions, the concentration of Be is always 1/5 of the nominal concentration. Due to solubility issues, the concentration of Ag is always 1/5 of the nominal concentration. Similarly, the concentrations of Al, Mg, and Ca are 2.5x greater than the nominal concentration.

Calibration Standards for the Optima 7300DV and Agilent 5100/5110

ICP-OES uses a series of calibration standards at 0.1, 0.5, 1, 5, 20, and 50 ppm (nominal concentration; represents concentrations of the Minors, Fe, and Sb) which shall be prepared in a volumetric flask the stock solutions as follows:

Calibration Standard *(in ppm)*	Volume of Calibration Working Standard *(in mL)*	Final Volume *(in mL)*
0.1	0.100	100
0.5	0.500	100
1	1.00	100
5	5.00	100
20	20.0	100
50*	5 mL each of Minors and Sb stocks; 1 mL of Ag stock; 2.5 mL of Majors stock	100

Note: In spite of the use of a 50 ppm standard in the calibration, the calibration curve for Pb on the Optima 7300DV has a maximum value of 20 ppm due to linearity issues that arise between 20 and 50 ppm.

Bring the standards to volume using 5% HNO_3 solution. Standards may be made to final concentrations and/or volumes other than those shown above as needed. **These standards are good for no longer than 30 days but are generally prepared fresh as needed for analysis.**

CALIBRATION VERIFICATION SOLUTIONS

50 ppm Yttrium Internal Standard

Dilute 50 mL of the 1000 ppm Y Stock solution to a final volume of 1 L using 5% HNO_3 solution in a volumetric flask. Mix thoroughly and **transfer into plastic storage bottle**. Once prepared, this standard should be entered into the working standard log book along with its

preparation date and the instrument on which it will be used. This working standard is good for up to three months.

Initial Calibration Verification Solution

The ICV solution should be prepared as follows:

- Dilute 5 mL of the 100 ppm second source stock solution to a final volume of 100 mL using 5% HNO_3 solution in a volumetric flask. Mix thoroughly. Once prepared, this standard should be entered into the working standard log book along with its preparation date and the instrument on which it will be used. This working standard is good for up to a month.

Low Level Calibration Verification and Continuing Calibration Verification Solutions

The LLCV and CCV solutions are the same as the calibration standards with corresponding concentrations.

Interference Check/Inter-Element Correction (IEC) Standard

To prepare the IEC standard, pipette 10 mL of the "Majors" stock and 0.1 mL each of the "Minors", 1000 ppm Sb and 1000 ppm Ag stock solutions into a 100 mL volumetric flask. Bring to volume using 5% HNO_3 and mix thoroughly. This solution is good for a maximum of 30 days but generally should be prepared fresh alongside each new set of calibration solutions.

Appendix B

Sample Calculations used in ICP-OES Analyses

BASIC CALCULATIONS

Sample Average

$$\bar{x} = \left(\frac{1}{n}\right)\sum_{i=1}^{n} x_i$$

where $\bar{x}$ is the sample average;
$\{x_1, x_2, x_3 \ldots x_n\}$ are the measured value for each sample;
n is the total number of samples

Sample Standard Deviation

$$s = \sqrt{\left(\frac{1}{n-1}\right)\sum_{i=1}^{n}(x_i - \bar{x})^2}$$

where s is the sample standard deviation;
$\bar{x}$ is the average value;
$\{x_1, x_2, x_3 \ldots x_n\}$ are the measured value for each sample;
n is the total number of samples

Confidence Interval

Given confidence level of 100(1-α)% with (n-1) degrees of freedom, the confidence interval is defined as:

$$\left[\bar{x} - t_{(\alpha,n-1)}\frac{s}{\sqrt{n}},\ \bar{x} + t_{(\alpha,n-1)}\frac{s}{\sqrt{n}}\right]$$

where $\bar{x}$ is the average value;
s is the sample standard deviation;
n is the total number of samples;
$t_{(\alpha,n-1)}$ is the Student's t statistic

Dilution and Dilution Factors

To calculate the volume of a stock solution or digestate needed to produce a desired concentration:

$$M_s V_s = M_d V_d$$

where M_s and V_s represent the concentration and volume of the stock
M_d and V_d represent the concentration of the diluted sample

To determine the dilution factor of a digestion or other sample preparation:

$$DF = \frac{V_{final}}{V_{initial}}$$

where DF is the dilution factor
V_{final} represents the final solution volume after dilution
$V_{initial}$ represents the initial mass or volume of the sample

To calculate the concentration of the original sample from measured values of sample dilutions:

$$\text{Sample Concentration} = \text{Measured Concentration} \times DF_1 \times DF_2 \times \ldots \times DF_n$$

where $\{DF_1, DF_2 \ldots DF_n\}$ are the dilution factors resulting from sample preparation

For example, 1.000 g of sample was digested and brought to a volume of 50 mL. That digestate was then diluted 1:10 and found to contain 2.75 mg/L of the analyte. The sample concentration would be:

$$1{,}375\ \frac{mg}{kg} = 2.75\ \frac{mg}{L} \times \frac{10\,mL}{1\,mL} \times \frac{50\ mL}{1.000\ g}$$

Sample Concentration

Measured Concentration

Dilution of Digestate

Dilution from Digestion

SPIKE RECOVERIES

Laboratory Control Spikes

$$\%\,\text{Recovery} = \frac{measured\ concentration}{spike\ concentration} \times 100$$

Matrix Spikes

$$\%\,\text{Recovery} = \frac{(MS - Sample)}{Spike} \times 100$$

where MS is concentration of the spiked sample
"Sample" is the concentration of the unspiked sample
"Spike" is the expected concentration of the spike

Post-Digestion Spikes

The calculation of post digestion spike recoveries is identical to the calculation of matrix spike recoveries seen in Section 24.2 above.

REPRODUCIBILITY

Relative Percent Difference, RPD (for sample duplicates)

$$RPD = \frac{|D_1 - D_2|}{\left(\frac{|D_1 + D_2|}{2}\right)} \times 100$$

where D_1 is the measured value for the original sample
D_2 is the measured value for the duplicate sample

Relative Standard Deviation, RSD (for three or more identical samples)

$$\%\,RSD = \frac{s}{\bar{x}} \times 100$$

where $\bar{x}$ is the sample average
s is the sample standard deviation

INTERFERENCES

Recovery of Calibration Verification Samples

The calculation of recovery for the calibration verification samples (e.g. ICV, CCV, LLCV, and IEC Check samples) is identical to the calculation of LCS recovery seen above in Section 24.1.

Inter-Element Corrections (IEC)

Inter-element corrections are ***calculated automatically by the WinLab software*** if the option is activated in the method and a valid IEC model has been developed. The following description of the correction method is to ensure the process can be reproduced by hand if necessary.

If an inter-element correction has been applied to an analyte in the analytical method, the following equation is used to correct for spectral interferences:

$$\text{Corrected Concentration} = \text{Measured Concentration} - \left(\text{Interferent Concentration} \times \frac{\text{IEC Factor}}{1000}\right)$$

where the IEC Factor is a value determined during the building of the IEC model by the following equation:

$$\text{IEC Factor} = \frac{\text{Apparent concentration of Analyte due to Interferent at the Analyte wavelength}}{\text{Actual concentration of Interferent measured at its own characteristic wavelength}} \times 1000$$

For example, it is known that Fe creates interference on a particular Pb spectral line. It is found that 200 ppm Fe causes an apparent reading of 0.25 ppm of Pb.

So the IEC factor is:

$$\text{IEC Factor} = \frac{0.250\,\text{ppm Pb (apparent)}}{200\,\text{ppm Fe}} \times 1000 = 1.25$$

If a sample is then analyzed at the wavelength in question and is found to have 2 ppm Pb and 120 ppm Fe, the signal in Pb that is actually due to Fe would be:

$$120\ ppm\ Fe \times \frac{0.00125\ ppm\ Pb}{1\ ppmFe} = 0.15\ ppm$$

And the corrected concentration for Pb would be:

$$2\ ppm\ Pb\ (\text{measured}) - \left(120\ ppm\ Fe \times \frac{1.25}{1000}\right) = 1.85\ ppm\ Pb\ (\text{corrected})$$

Internal Standard Recovery

This calculation is completed automatically by the WinLab software by adjusting the measured sample intensity for an analyte by the ratio of the internal standard signal in the calibration blank to the internal standard signal in the sample as follows:

$$\left(I_{\text{sample}} \times \frac{I_{\text{IS-CalBlank}}}{I_{\text{IS-Sample}}}\right) = f(C)$$

where I_{sample} is signal intensity for an analyte

$I_{IS\text{-}CalBlank}$ is the signal intensity of the IS in the calibration blank

$I_{IS\text{-}Sample}$ is the signal intensity of the IS in the sample

f(C) is the function relating concentration to signal intensity for the analyte (usually in the form of "mx" or "mx + b")

Linear Regression for Calibration Curve Fitting

This calculation is completed automatically by the WinLab software and may be recreated using Microsoft Excel or other spreadsheet software with a linear regression function by inputting the measured intensities of the standards relative to their theoretical concentration.

Appendix C

Routine Maintenance
Non-Routine Maintenance
Troubleshooting and Common Issues

Remove/replace nebulizer (as needed)

The nebulizer should be replaced as needed (e.g. when back pressure rises dramatically, or background/internal standard intensities become suppressed). Examination under 20x-30x magnification will reveal any physical blockages or damage to the nebulizer's tip.

Remove the nebulizer by gently pulling it away from the spray chamber and disconnect the argon supply line (quick-release) and sample capillary tubing.

Concentric nebulizers can be cleaned using aqua regia and gentle heating, if necessary. Do not use sonication or wire to clean, as they may damage the nebulizer.

Remove/replace spray chamber (as needed)

The spray chamber contains o-rings which require periodic replacement. If the o-rings appear flattened, cracked or show signs of deposits, they should be replaced or cleaned using mild soap and water.

Remove/replace injector (as needed)

The injector should be replaced periodically. Examine the injector for signs of deposits and discoloration. Injectors can be cleaned using aqua regia followed by sonication. Be sure to engage the locking tab when removing or installing the injector in the torch housing.

Remove/replace torch (as needed)

The torch can be examined by opening the torch box door, and should be replaced periodically. If calibration blanks or continuing calibration samples show high bias for elements such as copper, lead, silver or zinc, replacing the torch may remedy the problem.

Removal of the torch requires removal of the nebulizer and spray chamber. Once removed, twist the torch housing in a counter-clock-wise rotation and pull gently to remove the housing from the

instrument. Exploded-view schematics are available in the laboratory to assist in torch disassembly/assembly.

To prevent devitrification of glassware, it is necessary to remove all traces of alkali caused by handling with bare hands. To remove, wipe the glassware clean with a cotton swab or kim-wipe and alcohol.

IEC model building

All measurements (of both target analytes and interferants) need to be within the instrument linear range where the correction equations are valid. If a measured interferant that is present above the upper dynamic limit is used to apply an inter-element correction, the correction may not be valid and analytes using this correction may be inaccurately reported. Inter-element corrections will vary for the same emission line among instruments because of differences in resolution, as determined by the grating, the entrance and exit slit widths, and by the order of dispersion. Inter-element corrections will also vary depending upon the choice of background correction points. Selecting a background correction point where an interfering emission line may appear should be avoided when practical. Inter-element corrections that constitute a major portion of an emission signal may not yield accurate data. Users should continuously note that some samples may contain uncommon elements that could contribute spectral interferences.

The interference effects must be evaluated for each individual instrument, whether configured as a sequential or simultaneous instrument. For each instrument, intensities will vary not only with optical resolution but also with operating conditions (such as power, viewing height and argon flow rate). When using the recommended wavelengths, the analyst is required to determine and document for each wavelength the effect from referenced interferences as well as any other suspected interference that may be specific to the instrument or matrix. The analyst is encouraged to utilize a computer routine for automatic correction on all analyses. The correction factors or multivariate correction matrices tested on a daily basis must be within the 20% criteria for five consecutive days. Verifying working corrections/lack of correction needed.

If the correction routine is operating properly, the determined apparent analyte(s) concentration from analysis of each interference solution should fall within a specific concentration range around the calibration blank. The concentration range is calculated by multiplying the concentration of the interfering element by the value of the correction factor being tested and dividing by 10. If after the subtraction of the calibration blank the apparent analyte concentration falls outside of this range, in either a positive or negative direction, a change in the correction factor of more than 10% should be suspected. The cause of the change should be determined and corrected and the correction factor updated. The interference check solutions should be analyzed more than once to confirm a change has occurred. Adequate rinse time between solutions and before analysis of the calibration blank will assist in the confirmation. Refer to the individual instrument manuals for explicit instructions on IEC model development. Whenever a new IEC model is applied, save the method with the date of the IEC model.

Remove/replace windows (when uv performance suffers)

Purge viewing windows require replacing or cleaning when uv performance drops. Windows can be cleaned with de-ionized water or, if necessary, dilute nitric acid or aqua regia.

Clean/replace air filters

The RF Generator air filter on the back of the instrument should be changed as needed. Remove and replace or clean the filter with water, allowing it to dry completely before reinstallation. Make sure the fine screen side of the filter is towards the instrument, with the open mesh facing the outside of the instrument.

The spectrometer air filter on the side of the instrument should be replaced as needed. To change the filter, the spectrometer must be shut down and switched off. TO remove the filter, carefully pull of the snap-on plastic grid holding the filter in place. Replace or clean the filter with water, allowing it to dry completely before replacing. Carefully push the plastic grid onto the ventilator and power up the instrument.

Check shear gas water trap (Optima 7300)

The shear gas water trap contains a colored indicator. Green indicates the filter is operating normally. Red indicates the need for service or replacement. To service the filter, shut off air supply and remove the red housing from the unit. Empty any water in the housing and replace the filter. Replace the housing.

Archive/delete data and pack library (Optima 7300)

The database requires occasional maintenance, based on the accumulation of data. As needed, use the data manager to archive, pack and delete historical data. Under the File menu, select "Utilities" and open the data manager. Select a calendar unit of datasets for archiving, select "Archive" and follow the prompts. Upon completion, delete the selected datasets. Following deletion, pack the library to clean up the disk.

Appendix D

Sample Preparation of California Waste Extraction Test (WET) Leachate Samples

According to US EPA Method 6010C "Inductively Coupled Plasma-Atomic Emission Spectroscopy," all aqueous and solid matrices need acid digestion prior to analysis with the exception of groundwater samples. Groundwater samples that were prefiltered and acidified will not need acid digestion. Samples which are not digested need either an internal standard or should be matrix-matched with the standards. Since WET samples are always filtered and acidified like groundwater samples, WET leachates do not require acid digestion prior to analysis. WET leachates must be analyzed with the yttrium internal standard (See Appendix A) and matrix-matched with the standards.

Detail Sample Preparation of WET Leachate Samples

- WET leachates shall be diluted and spiked on the day of analysis to mitigate matrix interference.
- In general, dilute WET leachates including QC samples to 1:10 to minimize contamination of the instrument.

  Note: Any sample which exceeds the linear calibration range for any reported element or exceeds 300 ppm Fe must be diluted such that the concentration falls within the calibration range or below 300 ppm Fe.

- Prepare LCS/LCSD by spiking 0.5 mL of the calibration working standard (See Appendix A) to 9.5 mL of a method blank of WET leachate or its dilution.

  Note: For example, add 0.5 mL of the calibration working standard and 1 mL of a method blank to 8.5 mL of 5 % HNO_3 to prepare a LCS of 1:10 dilution factor.

- Select one sample from a leachate batch to perform PS/PSD analysis. Prepare PS/PSD by spiking 0.5 mL of the calibration working standard (See Appendix A) to 9.5 mL of the selected sample or its dilution.

  Note: For example, add 0.5 mL of the calibration working standard and 1 mL of a sample leachate to 8.5 mL of 5 % HNO_3 to prepare a PS of 1:10 dilution factor.

- Analyze all samples including QC samples as described in the main sections of this SOP.

12. REVIEW

Signatures	Date