FGD ICP/MS Standard Operating Procedure: Inductively Coupled Plasma/Mass Spectrometry for Trace Element Analysis in Flue Gas Desulfurization Wastewaters

1.0 Scope and Application

1.1 This document describes procedures used to measure elements in Flue Gas Desulfurization (FGD) wastewaters. Inductively coupled plasma/mass spectrometry (ICP/MS), as described in EPA Methods 200.8 and 1638, was used with a collision/reaction cell to mitigate the effects of interferences in the samples. These procedures are intended for use by analysts experienced with applying ICP/MS to complex wastewater samples.

1.2 These procedures are applicable to the analysis of acid digested FGD wastewater, and have been evaluated for the analysis of 13 elements of interest. These are Al, As, Cd, Cr, Cu, Pb, Mn, Ni, Se, Ag, Tl, V and Zn. Additional elements may be included provided that the performance criteria presented in Sections 9 and 12 are met.

1.3 Flue Gas Desulfurization wastewaters frequently have very high levels of calcium, sodium, magnesium, manganese, chloride, and sulfate (up to thousands of ppm). The use of instrument configurations and/or accessories designed to accommodate samples with high dissolved solids levels is highly recommended. This method was developed on an Agilent 7700 ICP/MS using the High Matrix Interface and discrete sampling with the ISIS system, but other systems designed to allow the analysis of high matrix samples are acceptable.

2.0 Summary

2.1 Digestates are nebulized in a spray chamber where a stream of argon carries the sample aerosol through the quartz torch and injects it into an RF plasma. There the sample is decomposed and desolvated.

2.2 The ions produced are entrained in the plasma gas and by means of a water-cooled, differentially pumped interface, introduced into a high-vacuum chamber that houses a quadrupole mass spectrometer capable of providing a resolution better than or equal to 0.9 amu peak width at 10% of the peak height. The ions are separated according to their mass-to-charge ratio and measured with a detector, such as an electron multiplier.

2.3 A collision/reaction cell utilizing He and (optionally) H_2 gases is used to remove molecular interferences.

2.4 Interferences not eliminated by the collision/reaction cell must be assessed and valid corrections applied, or the data flagged to indicate problems. Interference correction must include compensation for interferences not removed by the collision/reaction cell. Recommended elemental equations are listed in Attachment 1. Use of the internal standard technique is required to compensate for suppressions and enhancements caused by sample matrices.

United States
Environmental Protection
Agency

Office of Water (4303T)
Washington, DC 20460

DRAFT
May 2011

3.0 Definitions

3.1 Batch – A group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

3.2 Dissolved Metals - Those elements which pass through a 0.45-μm membrane filter (sample is acidified after filtration).

3.3 Suspended Metals - Those elements which are retained by a 0.45-μm membrane filter.

3.4 Total Recoverable Metals - The concentration determined on an unfiltered sample following treatment with hot, diluted mineral acids, as described in this procedure.

3.5 Instrument Detection Limit (IDL) - See Section 12.2.

3.6 Sensitivity - The slope of the analytical curve (i.e., the functional relationship between raw instrument signal and the concentration).

3.7 Tuning Solution - This is a multi-element solution containing analytes which are representative of the entire mass range capable of being scanned by the instrument. It is used to optimize the sensitivity of the instrument and to verify the mass resolution meets method criteria.

3.8 Initial Calibration Verification / Quality Control Standard (ICV/QCS) - A multi-element standard of known concentrations prepared to verify instrument calibration. This solution must be an independent standard prepared near the mid-point of the calibration curve, and at a concentration other than that used for instrument calibration.

3.9 Continuing Calibration Verification (CCV) - A multi-element standard of known concentrations prepared to monitor and verify the instrument daily continuing performance.

3.10 Laboratory Control Sample / Laboratory Fortified Blank (LCS/LFB) - A multi-element standard of known concentrations that is carried through the entire sample preparation and analysis procedure. This solution is used to verify method performance in an ideal sample matrix.

3.11 Matrix Spike / Laboratory Fortified Sample (MS/LFS) – A sample to which known concentrations of the elements of interest are added. The fortified sample is taken through all preparation and analytical steps of the procedure. The results are used to determine the effect of the sample matrix on analyte recovery efficiency.

3.12 Laboratory Reagent Blank / Method Blank (LRB/MB) – Reagent water containing the same acid matrix as the calibration standards that is carried through the entire digestion process. The reagent blank is used to determine the concentrations of trace metals in the reagents used to prepare and analyze the samples.

3.13 Calibration Blank – Reagent water acidified with the same acid concentrations present in the standards and samples. Also referred to as the Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB).

3.14 Reporting Limit (RL) – The minimum concentration that can be reported with a specified degree of confidence. The RL can be no lower than the concentration of the lowest initial calibration standard.

3.15 Method Detection Limit (MDL) – Refers to the instructions in Appendix B to 40 CFR Part 136. Also see Section 12.1 of this document. The MDL is determined from analysis of a sample in a given matrix containing the analyte.

3.16 Individual FGD Interference Check Solutions – Single element solutions at concentrations similar to those found in flue gas desulfurization wastewaters.

3.17 Synthetic FGD Wastewater – A mixed solution of elements at typical concentrations found in flue gas desulfurization wastewaters.

4.0 Interferences

4.1 Isobaric Interferences

4.1.1 Isobaric interferences in the ICP/MS are caused by isotopes of different elements forming ions with the same nominal mass-to-charge ratio (m/z).

4.1.2 Except for a very small interference from krypton on ^{78}Se, which can be avoided by using argon free of krypton, the recommended ions used for the elements in this procedure do not have elemental isobaric interferences..

4.2 Isobaric Molecular Interferences

4.2.1 Isobaric molecular interferences are caused by ions consisting of more than one atom. These molecular interferences are minimized by use of the collision/reaction cell utilizing He and/or H_2 gases. Common examples are potential interferences from ^{40}Ar^{35}Cl or ^{40}Ca^{35}Cl on ^{75}As, or ^{35}Cl^{16}O on ^{51}V, or ^{40}Ar^{12}C on ^{52}Cr.

4.2.2 Collision/reaction cell interference removal works both by causing the interfering molecular ion to dissociate and by reducing the kinetic energy of the ion. The latter is termed Kinetic Energy Discrimination (KED), and is the primary mechanism for interference removal. Polyatomic ions are larger than elemental ions and so collide with the helium atoms in the collision/reaction cell more frequently than the smaller elemental ions. Each collision/reaction reduces the energy of the ion, so the molecular ions lose energy more quickly. At the end of the collision cell a positive voltage plate prevents passage of the now low energy molecular ions. Thus, the interference is eliminated because the molecular ions do not reach the detector.

4.3 Doubly Charged Ion Interferences

4.3.1 Doubly charged elemental ion interferences are possible in cases where the second ionization potential of the element is significantly below the first ionization potential for argon (15.7eV). If a doubly charged ion is formed, it will cause a response at half of its elemental mass, potentially causing interference. Fortunately, most elements have high enough second ionization potentials that formation of doubly charged ions is not an issue.

4.3.2 For the target analytes in this procedure, a significant potential for interference is from ^{150}Nd and ^{150}Dy (potential interference on ^{75}As and from ^{156}Gd (potential interference on ^{78}Se). To check for these potential interferences, monitor the

response for mass 150 and 156. If the cps for these masses is > 5 times the cps for the quantitation limit for arsenic (in the case of mass 150) or selenium (in the case of mass 156), interference is possible. In this case, analyze a 100 ppb standard of Nd and Dy (if mass 150 is observed) or Gd (if mass 156 is observed), and measure the response at 150 and 75 (or 156 and 78). This ratio can then be used to create an interference correction equation.

4.3.3 For example, if the response for a 100 ppb Gd standard at mass 156 is 10,000 cps, and the observed response for the same standard at mass 78 is 1,000 counts, then the equation for ^{78}Se would be:

$$^{78}Se = {}^{78}Se - \frac{^{156}Gd}{10}$$

4.4 Physical Interferences

4.4.1 Physical interferences are associated with the transport and nebulization process. Internal standards are used to compensate for these types of interferences.

4.4.2 Internal standards should be added at a level to give approximately 50,000 - 800,000 counts of raw signal intensity. The mass of the internal standard should ideally be within 50 amu of the mass of the measured analyte. Consideration should also be given to matching internal standards to analytes with similar ionization potentials.

4.4.3 Matrix effects are monitored by comparing the internal standard intensity in the sample to the internal standard intensity of the calibration blank. The internal standards must be between 60% and 125% of the calibration blank. If they are outside this window the sample is diluted by a factor of 2 (1:1) and is reanalyzed.

4.4.4 Memory effects are dependent on the relative concentration differences between samples and/or standards which are analyzed sequentially. The rinse period between samples must be long enough to eliminate significant memory interference. See Section 10.3.6

5.0 Safety

5.1 This procedure may involve hazardous material, operations and equipment. This procedure does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are required.

5.2 Specific Safety Concerns or Requirements

5.2.1 Eye protection that satisfies ANSI Z87.1, laboratory coat, and non-powdered nitrile or latex gloves must be worn while handling samples, standards, solvents, and reagents. Disposable gloves that have been contaminated must be removed and discarded; non-disposable gloves must be cleaned immediately.

5.2.2 The ICP plasma emits strong UV light and is harmful to vision. All analysts must avoid looking directly at the plasma. The RF Generator produces strong radio frequency waves, most of which are unshielded. People with pacemakers should not go near the instrument while in operation.

5.3 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in Table 1.

Table 1. Primary Materials with a Serious or Significant Hazard Rating

Material[1]	Hazards	Exposure Limit[2]	Signs and Symptoms of Exposure
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Material[1]	**Hazards**	**Exposure Limit[2]**	**Signs and Symptoms of Exposure**
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

United States
Environmental Protection
Agency

Office of Water (4303T)
Washington, DC 20460

DRAFT
May 2011

6.0 Equipment and Supplies

6.1 Instrumentation

6.1.1 Inductively Coupled Plasma/Mass Spectrometer (ICP/MS) capable of providing resolution, less than or equal to 0.9 amu at 10% peak height from 6-253 amu and 1.0 amu at 5% peak height from 6-253 amu with a data system that allows corrections for isobaric interferences and the application of the internal standard technique. The ICP/MS must be equipped with a collision/reaction cell for the removal of molecular interferences. This procedure was developed using an Agilent 7700 instrument equipped with a high matrix interface (HMI). The interface extends the amounts of total dissolved solids that may be measured into the percent concentration range. Any collision/reaction cell instrumentation that meets the specifications in this procedure may be used.

6.1.2 A discrete sample introduction system enables the use of only the exact amount of sample volume required for data acquisition.

6.1.3 Accessories and configuration that are designed to accommodate samples with high levels of dissolved solids should be used.

6.1.4 The HMI sampling system results in less matrix being deposited in the system during analysis and minimizes the rinse times normally needed for difficult matrices.

6.1.5 Autosampler with autosampler tubes.

6.1.6 Appropriate water cooling device.

6.1.7 Block digester with tubes.

6.2 Supplies

6.2.1 Argon gas: High purity grade (99.99%).

6.2.2 Helium gas: High purity grade (99.99%).

6.2.3 Hydrogen gas: High purity grade (99.99%).

6.2.4 Calibrated automatic pipettes or Class A glass volumetric pipettes.

7.0 Reagents and Standards

7.1 Storage and Shelf-Life

7.1.1 Stock standards are purchased high purity grade solutions obtained from reputable commercial sources. Standard solutions must be traceable to national or international standards measurement, such as NIST. All standards must be stored in glass, FEP fluorocarbon or previously unused polyethylene or polypropylene bottles at room temperature. Standards stored at concentrations as received from the vendor and mid-level dilutions must be replaced prior to the expiration date assigned by the vendor. If no expiration date is provided, the stocks and mid-level standards may be stored for up to one year. They must be replaced sooner if verification from an independent source indicates a problem. See Section 10.3.5 for initial calibration verification acceptance criteria.

7.1.2 Working standards, i.e., all standards at concentrations ready to analyze on the ICP/MS (all except tuning mixes, ICSA and ICSAB mixes, which are received at ready-to-use concentrations), are prepared fresh daily.

7.2 Standards

7.2.1 Tuning Solution, 10 ppb

7.2.1.1 The tuning solution stock is purchased as a custom multi-element mix. The concentrations of the constituents are shown in Attachment 5.

7.2.1.2 Prepare the Tuning Solution as detailed below.

7.2.1.2.1 Obtain a clean 100-mL volumetric flask.

7.2.1.2.2 Place 50 mL of reagent water and 2 mL of conc. HNO_3 and 0.5 mL of conc. HCl in the flask.

7.2.1.2.3 Swirl to mix.

7.2.1.2.4 Pipette 0.1mL of the Tuning Solution Stock into the flask.

7.2.1.2.5 Dilute to volume with reagent water. Stopper and mix.

7.2.2 Tuning Solution

7.2.2.1 The dual detector solution may be commercially purchased as a custom multi-element mix. See Attachment 5.

7.2.2.2 Prepare and use the tuning solution as recommended by the instrument manufacturer.

7.2.3 Calibration Standards

7.2.3.1 Stock calibration standards are purchased as custom multi-element mixes or as single element solutions.

7.2.3.2 Each day of analysis, the standards are diluted to working levels using 2% nitric acid and 0.5% HCl acid matrix, to match the acid strength of the digestates. Suggested concentrations are given in Attachment 8, but the laboratory may adjust calibration standard concentrations as appropriate for the instrument and samples. At a minimum, a 3 point curve must be used.

7.2.4 Individual FGD Interference Check Solutions

7.2.4.1 All individual FGD interference check solutions should be made up in the same acid matrix as the calibration standards.

7.2.4.2 Chloride, 10,000 mg/L

7.2.4.3 Calcium, 5,000 mg/L

7.2.4.4 Sulfate, 4,000 mg/L

7.2.4.5 Magnesium, 3,000 mg/L

7.2.4.6 Sodium, 2,000 mg/L

7.2.4.7 Boron, 500 mg/L

7.2.4.8 Iron, 500 mg/L

7.2.4.9 Nitrate, 250 mg/L

7.2.4.10 Manganese, 200 mg/L

7.2.4.11 Bromide, 100 mg/L

7.2.4.12 Fluoride, 100 mg/L

7.2.4.13 Selenium, 20 mg/L

7.2.4.14 Vanadium, 10 mg/L

7.2.4.15 Zinc, 2 mg/L

7.2.4.16 Chromium, 1 mg/L

7.2.4.17 Copper, 1 mg/L

7.2.5 Mixed Interference Check Solution (Synthetic FGD Wastewater)

7.2.5.1 Chloride, 5,000 mg/L

7.2.5.2 Calcium, 2,000 mg/L

7.2.5.3 Magnesium, 1,000 mg/L

7.2.5.4 Sulfate, 2,000 mg/L

7.2.5.5 Sodium, 1,000 mg/L

7.2.5.6 Butanol, 2000 mg/L

7.2.6 Initial Calibration Verification (ICV) Standard

7.2.6.1 The ICV stock is from a source different than the source for the calibration standards.

7.2.6.2 Each day of analysis, the ICV standard is prepared in 2% HNO_3 and 0.5% HCl acid to the concentrations shown in Attachment 8.

7.2.7 Continuing Calibration Verification (CCV) Standard

7.2.7.1 The CCV standards are prepared from the same source as the calibration standards.

7.2.7.2 The CCV standards are prepared fresh each day of analysis in 2% HNO_3 and 0.5% HCl. The concentrations are shown in Attachment 8.

7.2.7.3 Prepare the CCV standard as detailed below.

7.2.7.3.1 Dilute by 2X a known volume of the CCV standard in the 2% HNO_3 and 0.5% HCl acid matrix.

7.2.8 Internal Standards

7.2.8.1 Internal standards are required, and are specified in Attachment 2.

7.2.9 Spiking Stock Solution

7.2.9.1 The spike stock solution is prepared from the same stocks as the calibration standards using the 2% HNO_3 and 0.5% HCl acid matrix.

United States
Environmental Protection
Agency

Office of Water (4303T)
Washington, DC 20460

DRAFT
May 2011

7.2.9.2 Spike concentrations are listed in Attachment 8.

7.3 Reagents

7.3.1 **Reagent Water** – ASTM Type I or equivalent for the elements of interest, free of the elements of interest at the levels of interest.

7.3.2 **Blank Matrix** 2% HNO_3 and 0.5% HCl.

8.0 Sample Collection, Preservation, Shipment and Storage

8.1 Sample container, preservation techniques, and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests.

8.2 Table 2 lists the holding times and the references that include preservation requirements.

Table 2. Holding Times

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
FGD wastewater	HDPE	50 mL	HNO_3, pH < 2	180 Days	40 CFR Part 136.3

9.0 Quality Control

9.1 Quality control requirements are also summarized in Attachment 7.

9.2 Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. Any QC result that fails to meet control criteria must be documented.

9.3 **Individual Interference Check Solutions**

The individual interference check solutions listed in Section 7.2.4 are analyzed prior to initiating sample analysis, and at least once per quarter while FGD wastewaters are being analyzed, and after any major changes to instrument operating conditions. Concentrations of target elements observed should be less than their reporting limits. In some cases it may not be possible to obtain interference check solutions that are completely free of contamination. In this case, results up to 5X the reporting limit are acceptable if it is confirmed that the elements are actual contaminants. This confirmation can be accomplished by determining that the isotopic ratios correspond to natural abundances. For example, the natural abundances of zinc isotopes are ^{64}Zn 48.6%; ^{66}Zn 27.9%; ^{67}Zn 4.1%; ^{68}Zn 18.8%; ^{70}Zn 0.6%. The measured ratios are not expected to be exact, especially for low abundance isotopes, and some isotope may be masked by other elements in the solution, (for example ^{70}Zn in the above example will be masked by ^{70}Ge) but it must be possible to explain the observed ratios. Because arsenic, manganese and aluminum are monoisotopic, this demonstration is not possible and the level of interference observed must be less than the reporting limit.

9.4 Synthetic FGD Interference Check Solution

9.4.1 The synthetic FGD matrix solution listed in Section 7.2.5 is analyzed prior to initiating sample analysis. The synthetic FGD matrix solution must be ran at least once per day (immediately after calibration) while FGD wastewaters are being analyzed, and after any major changes to instrument operating conditions.

9.4.1.1 Internal standard recovery must meet method criteria (Section 9.9) and concentrations of target elements observed should be less than their reporting limits.

9.4.1.2 In some cases it may not be possible to obtain interference check solutions that are completely free of contamination. In this case, results up to 5X the reporting limit are acceptable if it is possible to demonstrate that the isotopic ratios correspond to natural abundances. For example, the natural abundances of zinc isotopes are ^{64}Zn 48.6%; ^{66}Zn 27.9%; ^{67}Zn 4.1%; ^{68}Zn 18.8%; ^{70}Zn 0.6%. The measured ratios are not expected to be exact, especially for low abundance isotopes, and some isotope may be masked by other elements in the solution, (for example ^{70}Zn in the above example will be masked by ^{70}Ge) but it must be possible to explain the observed ratios. Because arsenic, manganese and aluminum are monoisotopic, this demonstration is not possible, and the level of interference observed must be less than the reporting limit.

9.4.1.3 If the Synthetic FGD solution has to be diluted in order to analyze it effectively on the ICP/MS, then all samples and QC (including the MDL replicates) must be diluted by at least the same factor. Example FGD solution results are given in Attachment 10.

9.4.2 Laboratory Fortified Synthetic FGD solution

9.4.2.1 The synthetic FGD solution is spiked with 40 ug/L of each of the target elements (400 ug/L for zinc and 4000 ug/L for aluminum) and analyzed once per day, immediately after the synthetic FGD check in Section 9.4. All target elements must be recovered within 70-130% of the true value.

9.4.2.2 If the Laboratory Fortified Synthetic FGD solution has to be diluted in order to analyze it effectively on the ICP/MS, then all samples and QC (including the MDL replicates) must be diluted by at least the same factor.

9.5 Linear Range Determination

9.5.1 The linear range for each element is determined prior to initiating sample analysis and at least once per year thereafter. The linear range must also be determined subsequent to changes that will have a major effect on instrument sensitivity, such as changing the detector. The linear range is established using a single element standard at the desired linear range. The result of the analysis must be within 10% of the true value.

United States
Environmental Protection
Agency

Office of Water (4303T)
Washington, DC 20460

DRAFT
May 2011

9.6 Method Blank / Laboratory Reagent Blank (MB/LRB)

9.6.1 The method blank consists of reagent water that has been processed in the same manner as the samples. One method blank must be processed with each preparation batch.

9.6.1.1 **Acceptance Criteria**: Method blank results are acceptable if the concentration for each analyte of interest is less than the reporting limit.

9.6.1.2 **Corrective Action**: If the method blank does not meet the acceptance criteria, the source of contamination should be investigated to determine if the problem can be minimized or eliminated. Samples associated with the contaminated blank shall be reprocessed for analysis, or under the following circumstances, may be reported as qualified (qualifier flags or narrative comments must be included on report):

9.6.1.2.1 The same analyte was not detected in the associated samples;

9.6.1.2.2 The method blank concentration is less than 1/10 of the measured concentration of any sample in the batch;

9.6.1.2.3 The method blank concentration is less than 1/10 the specified regulatory limit; or

9.6.1.2.4 The analyte is a common laboratory contaminant (copper, iron, lead, calcium, magnesium, potassium, sodium, or zinc) less than 2 times the RL.

9.6.1.2.5 If the above criteria are not met and reanalysis is not possible, then the sample data must be qualified. This anomaly must be addressed in the project narrative and the client must be notified.

9.7 Laboratory Control Sample / Laboratory Fortified Blank (LCS/LFB)

9.7.1 The LCS consists of reagent water that is spiked with the analytes of interest as summarized in Attachment 8. One LCS must be processed (digestion and analysis) for each preparation batch.

9.7.1.1 **Acceptance Criteria**: LCS control limits are based on three standard deviations of past laboratory results. These limits are not to exceed 85-115% recovery. The control limits are maintained in a LIMS or other appropriate system.

9.7.1.2 **Corrective Action**: If the LCS % recovery falls outside of the control limits for any analyte, that analyte is judged to be out of control. All associated samples must be reprocessed for analysis. One possible exception is a recovery for a given element above the upper control limit with no detection for the same element in the samples.

9.8   Matrix Spike / Matrix Spike Duplicate / Laboratory Fortified Sample Matrix / Laboratory Fortified Matrix Duplicate (MS/MSD/LFSM/LFMD)

9.8.1   MS is prepared by taking a second aliquot of a selected sample and spiking it with the analytes of interest as summarized in Attachment 8.

9.8.2   An MSD is prepared by taking a third aliquot of a selected sample and spiking it with the analytes of interest as summarized in Attachment 8.

9.8.3   The MS and MSD are processed in the same manner as the samples. One MS/MSD pair must be processed every 10 samples.

9.8.4   Additional Discharge specific MS/MSD requirements should be specified in the sampling and analysis plan and communicated to the laboratory.

9.8.4.1   Acceptance Criteria: Control limits are based on three standard deviations of past laboratory results. These limits are not to exceed 70-130% recovery, and 20% relative percent difference (RPD). The control limits are maintained in the LIMS system. If the sample concentration for a specific analyte in the sample selected for spiking is greater than the concentration added by the spike, then recovery accuracy will be reduced. In this case a dilution test may be performed. A 1:5 dilution should agree within 20% of the original determination. If not, a physical or chemical interference is suspected, and must be discussed in the sample narrative.

$$RPD = \frac{|C(MS) - C(MSD)|}{\frac{1}{2}[C(MS) + C(MSD)]} \times 100\%$$

Where C(MS) is the concentration observed in the MS
C(MSD) is the concentration observed in the MSD

9.8.4.2   Corrective Action: If MS/MSD results and any applicable dilution tests do not meet the acceptance criteria and all other quality control criteria have been met, then a matrix interference is suspected. Failed matrix spikes are flagged, and are discussed in the final report case narrative.

9.9   Internal Standards Evaluation for Samples

9.9.1   The internal standards (IS) in samples and QC (including the synthetic FGD solution) must be between 60 and 125% of the intensity in the calibration blank.

9.9.2   If the sample intensities fall outside this range, the calibration blank is reanalyzed to confirm the instrument has not drifted out of control. If the criteria is met, the sample is diluted by a factor of 2 (1:1) and reanalyzed.

9.9.3   IS limits and corrective actions for standards and blanks are described in Section 10.

10.0 Procedure

10.1 One-time procedural variations are allowed only if deemed necessary in the professional judgment of the supervisor to accommodate variation in sample matrix,

radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

10.2 Sample Preparation

10.2.1 EPA Method 1638 was used as the reference for the digestion of the samples in which section 12.2.8 describes Closed Vessel digestion.

10.2.2 Transfer a 50mL (± 0.5 mL) aliquot from a well mixed acid preserved sample to a 50mL digestion tube.

10.2.3 Add 0.5mL of concentrated nitric acid and 0.25 mL hydrochloric acid. (If samples are received unpreserved, add 1% nitric acid and store for at least 16 hours before preparation).

10.2.4 Spike the LCS and MS/MSD samples per spiking protocols.

10.2.5 The total volume of the solution in the tube is now greater than 50 mLs. The final volume will be 50 ml following the procedure to eliminate the discrepancy in the initial and final volumes.

10.2.6 Tightly cap each digestion vessel.

10.2.7 Place the digestion tube into a block digester adjusted to achieve a temperature of approximately 85°C.

10.2.8 Heat for 2 hours after 85°C is obtained.

10.2.9 Remove from the block and allow to cool.

10.3 Calibration

10.3.1 Instrument Start Up

10.3.1.1 Setup the instrument according to manufacturer's operating instructions.

10.3.1.2 Allow the instrument to become thermally stable for at least 30 minutes before tuning.

10.3.2 Instrument Tuning / Mass Calibration

10.3.2.1 Tune the instrument with a solution containing elements representing all of the mass regions of interest. The relative standard deviations must be less than 5% for a minimum of 4 integrations of the solution.

10.3.2.2 Mass calibration and resolution checks using the tuning solution must be completed at the beginning of every day.

10.3.2.2.1 Mass Calibration Check: The mass calibration results must be within 0.1 amu from the true value. If this criterion is not met, the mass calibration must be adjusted before running samples.

10.3.2.2.2 Mass Resolution Check: The resolution must be verified to be less than 0.9 amu full width at 10% peak height.

United States
Environmental Protection
Agency

Office of Water (4303T)
Washington, DC 20460

DRAFT
May 2011

10.3.3 Mass 75 Interference Check

10.3.3.1 The concentration determined for arsenic (mass 75) must be less than 0.25 x the reporting limit when the blank matrix (2% nitric acid / 0.5% hydrochloric acid) is infused (using the collision/reaction gas mode used for arsenic).

10.3.4 Initial Calibration

10.3.4.1 The ICP/MS is calibrated each day of operation using a blank and at least 3 standards. See Section 7.2.3. Report the average of at least three integrations.

10.3.4.2 The validity of the calibration is determined by the subsequent calibration verifications, which are performed at concentrations as described in the next sections.

10.3.5 Second-Source Initial Calibration Verification (ICV)

10.3.5.1 An ICV standard (see Attachment 8) is analyzed immediately after the initial calibration. This is a standard obtained from a different vendor than the standard used for calibration.

10.3.5.1.1 Acceptance Criteria: The ICV recovery must be within 90-110%. Additionally, the internal standard recoveries must fall between 60-125% of true values. The ICV can be reanalyzed, but must be successful twice in succession or corrective action must be taken.

10.3.5.1.2 Corrective Action: If the ICV results are outside of the acceptance limits, investigate the accuracy of the standards, correct as necessary, and recalibrate.

10.3.6 Calibration Blank

10.3.6.1 Checks for the memory effects described at Section 4.4 may be accomplished by analysis of an initial calibration blank (ICB) after the ICV. Continuing calibration blanks (CCBs) are analyzed after each continuing calibration verification.

10.3.6.1.1 Acceptance Criteria: Results for the calibration blanks must be less than the RL.

10.3.6.1.2 Corrective Action: If the calibration blank exceeds acceptance limits, then the possibility of instrument contamination should be examined, particularly the possibility of carry-over from samples containing high solids. The blank can be reanalyzed, and if successful, analysis can continue. However, samples tested after high-level samples should be retested. If the reanalysis is not successful, then the analysis should be terminated. After the problem is corrected, recalibrate and reanalyze all samples tested since the last acceptable CCB.

EPA United States
Environmental Protection
Agency

Office of Water (4303T)
Washington, DC 20460

DRAFT
May 2011

10.3.7 Reporting Limit (RL) Verification Standard

10.3.7.1 An independent standard is analyzed after the ICV to monitor the lab's ability to produce reliable results at RL-level concentrations. The RL verification standard is analyzed after the daily ICB.

10.3.7.1.1 Acceptance Criteria: For project reporting limits at or above two times the MDL, the results should be within 50% of the expected value. Some programs may require tighter control, in which case the RLs will need to be three or more times the MDL concentration.

10.3.7.1.2 Corrective Action: If the RL verification fails to meet acceptance limits, data for the associated samples must be assessed. For example, if the results are high, consider blank contamination, and if the results are low, consider MDL verifications. At a minimum, sample results must be qualified in the final report.

10.3.8 Continuing Calibration Verification (CCV) Standard

10.3.8.1 A CCV standard (see Attachment 8) is analyzed after every set of ten samples and at the end of the analytical sequence.

10.3.8.1.1 Acceptance Criteria: The CCV recovery must be within 85-115%. In addition, the IS recovery must be within 60-125%. If CCV results are not within these limits, the CCV can be reanalyzed, but it must be successful twice in succession or further corrective action must be taken.

10.3.8.1.2 Corrective Action: If the CCV fails acceptance criteria, then the analysis should be terminated. Recalibrate and reanalyze all samples tested since the last acceptable CCB.

10.4 Sample Analysis

10.4.1 Report the average of at least three integrations for all field and QC samples analyzed.

10.4.2 Flush the system with the rinse blank for at least 30 seconds between samples and standards during the analytical run. Evaluate the effectiveness of this time and increase the flush time, if needed.

10.4.3 It may be valuable to monitor additional isotopes for elements that are potentially susceptible to interferences. In particular, monitoring additional isotopes for selenium may help data analysis.

United States
Environmental Protection
Agency

Office of Water (4303T)
Washington, DC 20460

DRAFT
May 2011

10.4.4 Dilute and reanalyze samples that are more concentrated than the highest calibration standard for an analyte or specific isotope of interest. No analyte may be reported from an analysis of a diluted sample in which the analyte concentration is less than 5 times the RL.

The analytical run sequence should be performed as follows to meet all quality control criteria:

Instrument initialization

Warm-up

Tune instrument

Perform mass calibration

Perform resolution check

Validate tuning criteria

Calibration blank

Calibration standard 1

Calibration standard 2

Calibration standard 3

ICV

ICB

RL verification standard

Synthetic FGD matrix

Spiked synthetic FGD matrix

CCB (carryover check)

CCV

CCB

10 Samples

Ending CCV

Ending CCB

Repeat for all samples with 10% CCV/CCB frequency

11.0 Calculations / Data Reduction

11.1 LCS Percent Recoveries are calculated according to the following equation:

$$\%R = \left(\frac{LCS\ Found\ Value - LRB\ Found\ Value}{LCS\ True\ Value}\right) \times 100\%$$

United States
Environmental Protection
Agency

Office of Water (4303T)
Washington, DC 20460

DRAFT
May 2011

11.2 ICV Percent Recoveries are calculated according to the following equation:

$$\%R = \left(\frac{ICV\ Found\ Value}{ICV\ True\ Value}\right) \times 100\%$$

11.3 CCV Percent Recoveries are calculated according to the following equation:

$$\%R = \left(\frac{CCV\ Found\ Value}{CCV\ True\ Value}\right) \times 100\%$$

11.4 Matrix Spike Recoveries are calculated according to the following equation:

$$\%R = \left(\frac{SSR - SR}{SA}\right) \times 100\%$$

Where:

SSR = Spike Sample Result

SR = Sample Result

SA = Spike Added

NOTE: When the sample concentration is less than the detection limit, use SR = 0 for the purpose of calculating %R.

11.5 The Relative Percent Difference (RPD) between sample duplicates is calculated according to the following equation:

$$RPD = \frac{|DU1 - DU2|}{\frac{1}{2}(DU1 + DU2)} \times 100\%$$

Where:

DU_1 = Sample result

DU_2 = Sample duplicate result

11.6 The final concentration for an aqueous sample is calculated as follows:

$$Result = \frac{C \times V_1 \times D}{V_2}$$

Where:

C = Concentration from instrument readout, ppb

D = Instrument dilution factor

V_1 = Final volume in liters after sample preparation

V_2 = Initial volume of sample digested in liters

United States
Environmental Protection
Agency

Office of Water (4303T)
Washington, DC 20460

DRAFT
May 2011

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

12.1.1 An initial method detection limit study must be performed on each instrument before samples can be analyzed. MDL studies are conducted annually as follows:

> **12.1.1.1** Prepare seven samples at three to five times the estimated MDL concentration. The MDL samples are prepared in the Synthetic FGD wastewater matrix and in reagent water.

> **12.1.1.2** Prepare and analyze the MDL standards as described in Section 10.

> **12.1.1.3** Calculate the average concentration found in µg/L, and the standard deviation of the concentration(s) in µg/L, for each analyte.

> **12.1.1.4** The MDL is calculated as Students t for the 99th percentile times the standard deviation of the MDL replicate results, following the procedure at 40CFR Part 136, Appendix B.

12.1.2 Example MDLs are given in Attachment 9.

> **12.1.2.1** **NOTE 1**: Perform the MDL study in the synthetic FGD wastewater matrix. Spiking this matrix provides detection limits that are better matched to the complex matrix typical of FGD wastewater. These limits can be significantly higher than those obtained in a reagent water matrix. In some cases (zinc in particular), the level of contamination in the synthetic FGD solution may be high enough to result in somewhat elevated MDLs.

> **12.1.2.2** **NOTE 2**: An FGD-MDL may be less than the concentration observed in method blanks. If this occurs frequently, the FGD-MDL should be elevated to the mean of the method blanks plus the Student t factor times the standard deviation of the method blanks.

12.2 Instrument Detection Limit Study

12.2.1 Instrument detection limit (IDL) studies are conducted quarterly for each instrument and each mass used for analysis.

> **12.2.1.1** Prepare ten blanks.

> **12.2.1.2** Analyze the IDL blanks on three non-consecutive days.

> **12.2.1.3** The IDL is equal to three times the standard deviation of the blank results.

12.3 Demonstration of Capabilities

12.3.1 All personnel are required to perform an initial demonstration of capability (IDOC) on the instrument they will be using for analysis prior to testing samples. On-going proficiency must be demonstrated annually. IDOCs and on-going proficiency demonstrations are conducted as follows.

12.3.2 Analyst Instrument Proficiency - Four aliquots of the ICV are analyzed using the same instrumental conditions and procedures used to analyze samples. The analyst must employ ICV's from four distinct analytical sequences. Using these four ICV's demonstrates the analyst's ability to optimize and calibrate the instrument and to prepare analytical solutions. Calculate the average recovery and standard deviation of the recovery for each analyte of interest.

12.3.2.1 If any analyte does not meet the acceptance criteria, (85-115% recovery, unless other criteria are established) the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated.

12.3.2.2 Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

12.3.3 Analyst Preparation Proficiency

12.3.3.1 Each analyst performing the method must complete a demonstration of capability (DOC) by successfully preparing and/or analyzing four consecutive LCSs, or a blind performance evaluation (PE) sample, or other acceptable QC samples.

12.3.3.2 Analysts who continue to perform the method must successfully complete a demonstration of capability annually.

13.0 Pollution Control

13.1 For information about pollution prevention that may be applicable to laboratory operations, consult "Less is Better: Laboratory Chemical Management for Waste Reduction" available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, D.C., 20036, or online at http://www.ups.edu/x7432.xml.

14.0 Waste Management

14.1 All waste must be disposed of in accordance with Federal, State, and local regulations.

15.0 References / Cross-References

15.1 EPA Method 200.8, "Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma - Mass Spectrometry", Revision 5.4, EMMC Version.

15.2 EPA Method 1638, "Determination of Trace Elements in Ambient Waters by Inductively Coupled Plasma – Mass Spectrometry, January 1996.

15.3 This method was developed at TestAmerica Laboratories Inc., Denver laboratory.

16.0 Attachments

Attachment 1: Recommended Elemental Equations
Attachment 2: Internal Standards and Corresponding Metals
Attachment 3: Sample Preservation and Holding Times

Attachment 4: Suggested Mass Choices
Attachment 5: Tuning Solution
Attachment 6: Suggested Tuning and Response Factor Criteria
Attachment 7: Summary of Quality Control Requirements
Attachment 8: Calibration, Calibration Verification, and Spike Concentrations

Attachment 1: Recommended Elemental Equations

Element	Isobaric Correction	Mathematical Equation
Pb	None	$(1.0000)(208M) + (1.0000)(207M) + (1.0000)(206M)$
^{6}Li	Li (natural)	$(1.0000)(6M) - (0.0813)(7M)$
In	Sn	$(1.0000)(115M) - (0.0149)(118M)$

The ^{6}Li correction equation is only needed if ^{6}Li is used as an internal standard for low mass elements.

Attachment 2: Internal Standards and Corresponding Metals

Internal Std.	Associated elements[1,2]
Sc	Na, Mg, Al, K, Ca, V, Cr, Mn
Ge	Fe, Ni, Cu, Zn, As, Se
In	Ag, Cd
Ho	Tl, Pb

Footnotes:

(1) Na, Mg, K, Ca and Fe are included in the synthetic FGD wastewater but their analytical determination is optional – the interferences caused by these elements are more important than the determination of their exact concentration.

(2) Other internal standards may be used. For example, ^{6}Li, Ga, Rh, Bi, Ho and Tb may be considered for use as internal standards.

EPA United States
Environmental Protection
Agency

Office of Water (4303T)
Washington, DC 20460

DRAFT
May 2011

Attachment 3: Sample Preservation and Holding Times

Measurement Parameter	Container[1]	Preservative[2]	Maximum Holding Time[3]
FGD Waters: Metals[4]	P,G	HNO_3 to pH $\leq$ 2	6 months

Footnotes:
(1) Polyethylene (P)

(2) Sample preservation is performed by the sampler immediately upon sample collection or shipped to the laboratory unpreserved for preservation at the laboratory. If preserved at the laboratory, then the sample must be held for at least 16 hours prior to digestion.

(3) Samples must be analyzed as soon as possible after collection. The times listed are the maximum times that sample may be held before analysis and still considered valid. Holding times are calculated from the date when the sample was collected.

(4) Samples are filtered immediately on-site by the sampler before adding preservative for dissolved elements.

United States
Environmental Protection
Agency

Office of Water (4303T)
Washington, DC 20460

DRAFT
May 2011

Attachment 4: Suggested Mass Choices

The isotope in bold is recommended as the most appropriate mass for quantitation. Additional masses listed are recommended for use as confirmation and to monitor for interferences.

Mass	Element of Interest	Analysis mode
27	Aluminum	No gas
75	Arsenic	He
111 114	Cadmium	He
52 53	Chromium	He
63 65	Copper	He
208, 207, 206	Lead	No gas or He
24	Magnesium	No gas
55	Manganese	He
60 62	Nickel	He
39	Potassium	No gas or He
78 82	Selenium	He (H_2)
107	Silver	He
23	Sodium	No gas or He
205 203	Thallium	No gas or He
51	Vanadium	He
66	Zinc	He

NOTE: It is strongly recommended that elements other than those of interest be monitored to indicate other potential molecular interferences which could affect the data quality.

Attachment 5: Tuning Solution

A tuning solution containing elements representing all of the mass regions of interest must be analyzed. Below is a suggested solution covering a typical mass calibration range. Instrument manufacturer recommendations should be followed for tuning solutions.

Element	Concentration (μg/L)
Mg	10
Rh	10
Ba	10
Be	10
U	10
Ce	10
Y	10
Pb	10
Li	10
Co	10
In	10
Tl	10

United States
Environmental Protection
Agency

Office of Water (4303T)
Washington, DC 20460

DRAFT
May 2011

Attachment 6: Suggested Tuning and Response Factor Criteria

No Gas Mode

Li7   >2000cps

Tl205   >3000cps

CeO/Ce 156/140   1%

Ce++/Ce+ 70/140   <3%

He Mode

ArAr 78   2-3 counts/sec

ArCl 75   2-3 counts/sec

United States
Environmental Protection
Agency

Office of Water (4303T)
Washington, DC 20460

DRAFT
May 2011

Attachment 7: Summary of Quality Control Requirements

QC Parameter	Frequency	Acceptance Criteria	Corrective Action
ICV/QCS	Beginning of every analytical run.	90 - 110% recovery IS, 60-125% recovery	Terminate analysis; correct the problem; recalibrate.
ICB/CCB	Immediately after each ICV.	Result is < RL IS, 60-125% recovery	Terminate analysis; correct the problem; recalibrate.
Synthetic FGD interference check	Prior to initiating analysis and at least quarterly.	Result for target elements is < RL, unless actual presence of target element can be demonstrated, in which case result is < 5X RL. IS 60-125% recovery	Correct the problem prior to sample analysis.
Individual element interference checks	Prior to initiating analysis and at least quarterly.	Result for target elements is < RL, unless actual presence of target element can be demonstrated, in which case result is < 5X RL. IS 60-125% recovery	Correct the problem prior to sample analysis.
CCV	Beginning and end of run and every 10 samples OR every 2 hours, whichever is more frequent. Beginning and end of each analytical sequence.	90 - 110% recovery IS, 60-125% recovery	If unacceptable, terminate analysis; correct the problem; recalibrate the instrument, re-verify calibration and rerun all samples since the last acceptable CCV.
CCB	Immediately following each CCV.	The result must be < RL IS, 60-125% recovery	If unacceptable, terminate analysis; correct the problem, recalibrate the instrument, re-verify calibration and rerun all samples since the last acceptable CCB.

Attachment 7: Summary of Quality Control Requirements (continued)

QC Parameter	Frequency	Acceptance Criteria	Corrective Action
Method Blank/Laboratory Reagent Blank	One per lot of 20 field samples or fewer.	The result must be less than the RL. Sample results greater than 10x the blank concentration or samples for which the contaminant is < RL, do not require re-digestion or reanalysis.	Re-run once. If > than the RL, re-digest and reanalyze samples. Note exceptions under criteria section. See Section 9.6 for additional requirements.
LCS/LFB	One per preparation batch of 20 samples or fewer.	Not to exceed 85-115% recovery.	See Section 9.7.
Matrix Spike/Laboratory Fortified Matrix	One every ten samples or fewer.	Must be within laboratory control limits.	See Section 9.8 for additional requirements.

United States
Environmental Protection
Agency

Office of Water (4303T)
Washington, DC 20460

DRAFT
May 2011

Attachment 8: Calibration, Calibration Verification, and Spike Concentrations

Element	Initial Calibration (μg/L)	ICV (μg/L)	CCV (μg/L)	LCS (μg/L)	MS/MSD (μg/L)
Aluminum	100, 1,000, 10,000	4000	5000	4000	4000
Arsenic	1, 10, 100	40	50	40	40
Cadmium	1, 10, 100	40	50	40	40
Chromium	1, 10, 100	40	50	40	40
Copper	1, 10, 100	40	50	40	40
Lead	1, 10, 100	40	50	40	40
Manganese	1, 10, 100	40	50	40	40
Nickel	1, 10, 100	40	50	40	40
Selenium	1, 10, 100	40	50	40	40
Silver	1, 10, 100	40	50	40	40
Thallium	1, 10, 100	40	50	40	40
Vanadium	1, 10, 100	40	50	40	40
Zinc	1, 10, 100	40	50	40	40

Additional elements may be included in the calibration solution at the above levels. Levels may be adjusted to meet specific requirements – in particular, higher spiking levels for selenium and manganese may be needed to be able to reliably determine the spike above the sample concentration.

United States
Environmental Protection
Agency

Office of Water (4303T)
Washington, DC 20460

DRAFT
May 2011

Attachment 9: Typical Method Detection Limits

Mass/Element	Int. Time (sec)	ORS Mode	Internal Standard	MDL (µg/L)
51V	0.05	He	Sc	0.42
52 Cr	0.05	He	Sc	--
55 Mn	0.05	He	Sc	0.68
60 Ni	0.05	He	Sc	0.45
63 Cu	0.05	He	Sc	0.48
66 Zn	0.05	He	Ge	2.04
75 As	0.10	He	Ge	0.61
78 Se	0.05	H_2	Ge	0.31
107 Ag	0.05	He	In	0.29
111 Cd	0.05	He	In	0.59
121Sb	0.05	He	In	0.36
205 Ti	0.05	He	Ho	0.23
208 Pb	0.05	He	Ho	0.36

MDLs were determined using 2 ug/L spikes in the synthetic FGD solution. Note that these values are examples, and not method requirements.

Chromium was not determined due to a high level of contamination in the synthetic FGD solution.

United States
Environmental Protection
Agency

Office of Water (4303T)
Washington, DC 20460

DRAFT
May 2011

Attachment 10: Typical results for the synthetic FGD solution

Analyte	Synthetic FGD solution	Spiked FGD solution	Spike Recovery	50 ug/L CCV	CCB
51 V	-0.187	20.259	102.2%	48.885	0.101
52 Cr	12.699	32.013	96.6%	48.851	0.117
55 Mn	-0.101	18.765	94.3%	48.435	0.100
60 Ni	0.247	17.926	88.4%	48.535	0.154
63 Cu	0.094	18.405	91.6%	47.316	0.115
66 Zn	3.181	20.404	86.1%	49.804	-0.100
75 As	0.107	22.107	110.0%	48.205	0.009
78 Se	0.538	24.586	120.2%	49.605	-0.186
107 Ag	0.145	19.006	94.3%	47.632	0.003
111 Cd	0.039	19.810	98.9%	48.695	-0.017
114 (Cd)	-0.003	19.772	98.9%	50.311	0.014
121 Sb	0.181	19.857	98.4%	50.806	0.031
205 Tl	0.021	18.077	90.3%	48.108	-0.008
208 Pb	0.436	18.848	92.1%	48.381	0.008

Chromium presence in the synthetic FGD solution was verified using the ^{53}Cr isotope.

Note that these values are examples and not method requirements.