Standard Operation Procedure for Trace Element Analysis of Flue Gas Desulfurization Wastewaters Using ICP-MS Collision/Reaction Cell Procedure

1.0 Introduction

1.1 This document describes procedures used to measure elements in Flue Gas Desulfurization (FGD) wastewaters. One of the most widely used technologies for removing pollutants such as sulfur dioxide, from flue gas emissions produced by coal-fired power plants, is a flue gas desulfurization that typically involves spraying a limestone slurry or other sorbent into the flue gas stream to convert gaseous sulfur dioxide to calcium sulfate (gypsum) or calcium sulfite. Many of the contaminants from the coal, limestone and make-up water are concentrated in the circulating water of the scrubbing system. So in order to maintain appropriate plant operating conditions, a purge stream of water containing these contaminants often has to be discharged from the scrubbers. This purge stream can contain high concentrations of gypsum, heavy metals, alkali earth metals, chlorides and dissolved organic compounds.

1.2 The ICP-MS spectrometer with the Universal Cell can operate in reaction, collision and standard modes. The composition of Flue Gas Desulfurization wastewaters can include high levels of dissolved salts. 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 a Perkin Elmer NexION 300D ICP/MS using an Environmental Scientific SC-DX FAST Automated Sample Introduction System.

1.3 The procedure described in this document is applicable to the analysis of acid digested FGD wastewater, and has 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; see Attachment 1. Additional elements may be included provided that the performance criteria presented in Sections 9 and 12 are met.

1.4 Although this procedure is written to address the FGD wastewater matrix, it is also very capable of addressing less complex matrices such as drinking water, non-potable water, and solids. The use of Universal Cell Technology is also effective for the interferences that maybe found in these matrices. Appropriate sample preparation steps and quality assurance practices for these sample types may be different than described herein.

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2.0 Hardware Description

2.1 The NexION 300D with the Universal Cell Technology™ (UCT) allows the analyst to choose the most appropriate collision/reaction cell (CRC) conditions for each analyte in FGD wastewater samples, without any restrictions to the type of gases that can be used. The three modes of interference removal available in the NexION 300 are:

Standard Mode: The cell is actively vented. This enables the instrument to be run in true standard mode, with the cell conditions optimized for maximum ion transition. For FGD

wastewater samples, this mode is ideal for heavy metals like Pb and Tl, where there are very few polyatomic spectral interferences.

Collision Mode: In this mode, the instrument offers conventional collision cell capability with kinetic energy discrimination (KED**).** By using a non-reactive gas, such as helium, the collision mode with KED removes many of the simple solvent- and argon-based polyatomic spectral interferences. This makes it ideal for elements such as Co, Ni, Cu and Zn which are prone to the larger cross-sectional polyatomic interferences to be concerned about. It is also effective for other analytes, such as As and Se.

Reaction Mode: A technique that offers the best available detection capability. This mode, known as DRC (Dynamic Reaction Cell™) technology, removes the majority of interferences with little or no loss of analyte sensitivity by using pure reaction gases like ammonia while not allowing any reaction byproducts to leave the cell which could cause further interferences. DRC technology features a scanning quadrupole with a bandpass that removes by-product reactions created in the Universal Cell. Therefore any reaction gas can be used and in its pure form. And by optimizing the cell's quadrupole conditions, only the element of interest is allowed to pass through to the analyzing quadrupole. It is well recognized that ion-molecule reaction chemistry offers the very best performance for the reduction of polyatomic interferences. This would be the mode of choice for the lowest possible detection limits for elements such as Cr, V and Mn.

The NexION also features a unique **triple cone interface** (TCI), which includes an additional hyper skimmer cone to tightly define and focus the ion beam entering the quadrupole ion deflector. All three cones can be quickly and easily removed, cleaned or replaced, which is particularly relevant for the analysis of FGD wastewaters that contain high levels of matrix components.

The highly focused ion beam then emerges from the TCI and enters a **quadrupole ion deflector** (QID), which is designed around a proprietary, miniaturized quadrupole. This filtering technology bends the ion beam 90 degrees, focusing those of a specified mass into the universal cell and discarding all neutral species into the turbo pump. The path through the quadrupole ion deflector is aligned with the tightly defined beam leaving the triple cone interface, which ensures that ions and neutral species never impact or degrade component surfaces within the cell, virtually eliminating the need for cleaning. By removing the majority of particulates, neutrals and photons, this practical design significantly minimizes drift and delivers exceptional signal stability.

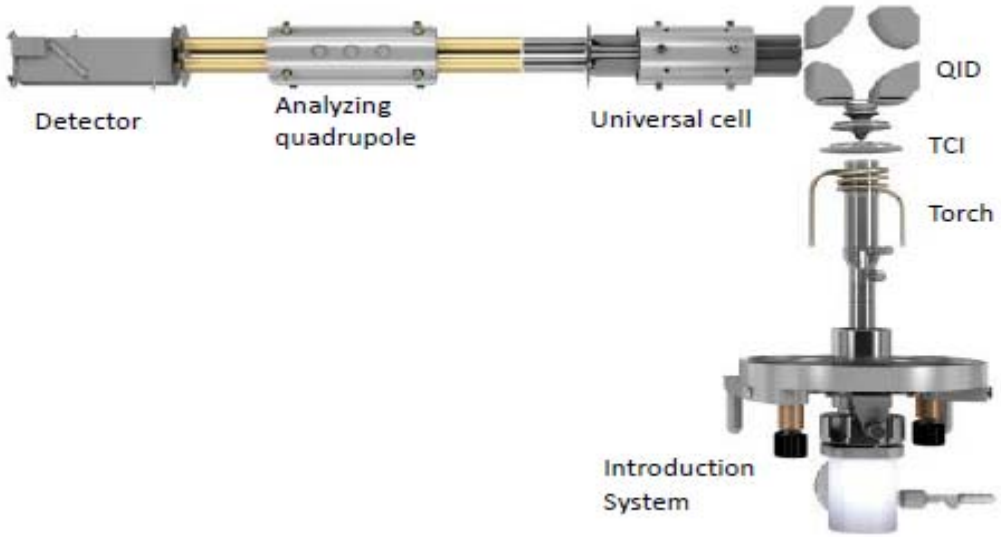

Figure 1. NexION schematic

2.3 The NexION 300 is 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 found in FGD wastewater samples. Any collision/reaction cell instrumentation that meets the specifications, and quality control requirements in this procedure may be used.

2.4 A NexION 300D ICP-MS (Perkin Elmer, Waltham, MA) coupled to an SC DX FAST (ESI, Omaha, NE) automated sample delivery system is used for this procedure. This delivery system is basically a rapid flow injection technique integrated into an autosampler, which significantly reduces the pre- and post-measurement times involved with delivering a new sample to and removing the previous sample from the ICP-MS. By optimizing these times, a significant improvement can be made in the sample throughput. The FAST portion of the delivery system uses a 6-port switching valve containing a Teflon sample loop. The sample loop is rapidly filled and evacuated with a vacuum pump and because the loop sits very close to the spray chamber, the time for the sample to be introduced is dramatically reduced. Equivalent autosamplers with rapid flow injection (aka switching valve) hardware is acceptable.

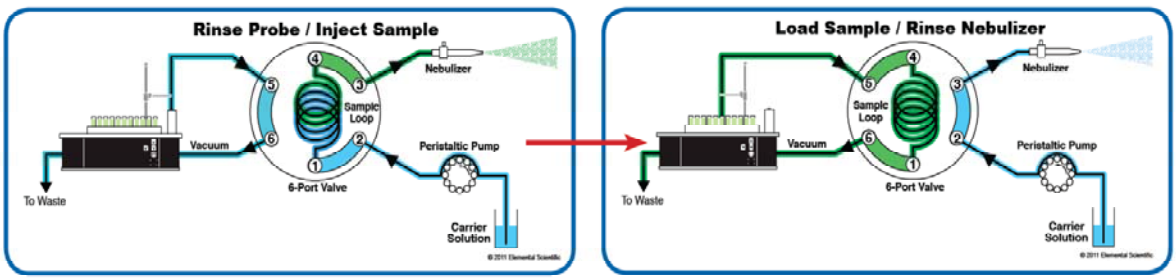

Figure 2. 6-Port valve schematic

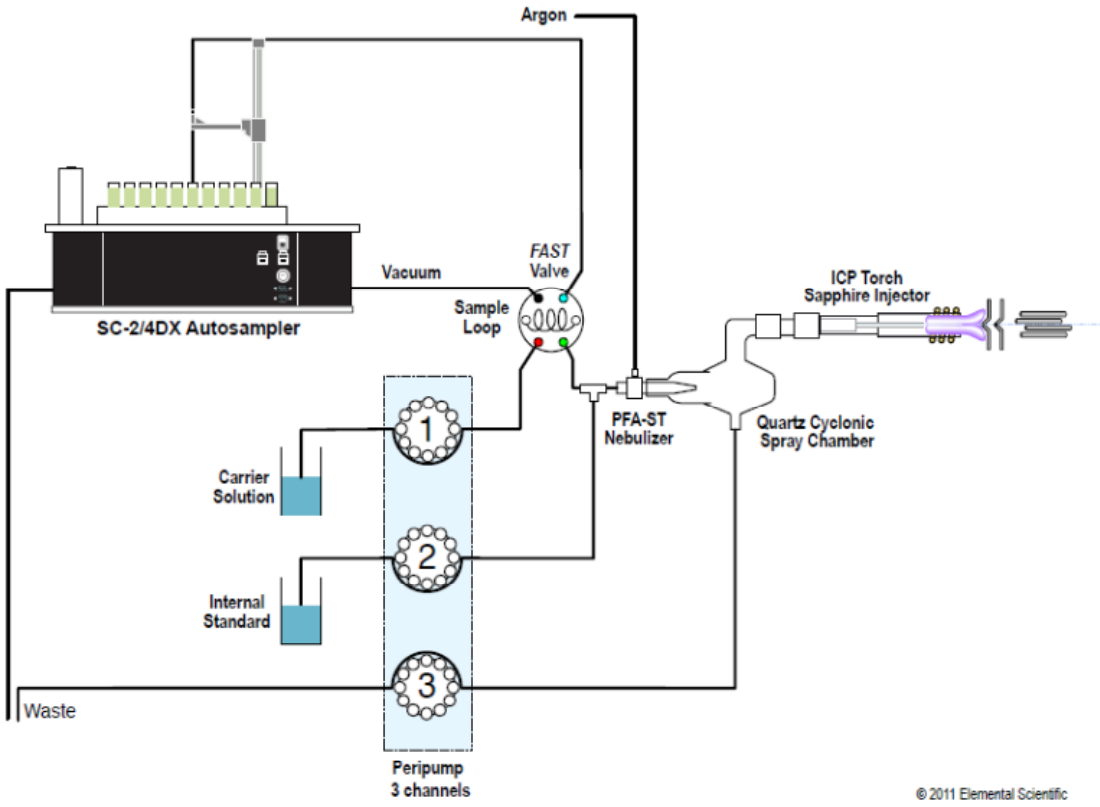

Figure 3. SC DX FAST schematic

2.5 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 desolvated and decomposed. An additional argon stream entering the spray chamber can by utilized for optional sample gas dilution instead of liquid dilution. The baffled, cyclonic spray chamber used in the SC DX FAST introduction system is Peltier-cooled to 2°C to ensure low oxides and greater stability of the instrument. The model PC3 Peltier chiller and spray chamber were used in this SOP but equivalent chilled spray chambers are acceptable.

2.6 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 ion deflector, a reaction/collision cell and 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.

2.7 Universal Cell utilizing helium and/or reactive gases such as NH3 is used to remove molecular interferences. See Attachment 1 for recommended analyte masses and modes of operation.

2.8 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 2. Use of the internal standard technique is required to compensate for suppression and enhancement caused by sample matrices. Recommended internal standards are listed in Attachment 3.

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

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

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

3.6 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.

3.7 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 independently prepared standard at a concentration level near the mid-point of the calibration curve.

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

3.9 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.

3.10 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.

3.11 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 method blank is used to determine the concentrations of trace metals in the reagents used to prepare and analyze the samples as well as the contribution of contamination from the digestion process.

3.12 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).

3.13 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.

3.14 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.

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

3.16 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 small interferences from Sn on In (In used as internal standard) and from Kr on ^{78}Se, which can be avoided by using argon free of Kr, 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 NH3 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 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 usually larger than elemental ions, and so collide with the helium atoms in the collision cell more frequently than the smaller elemental ions. Each collision reduces the energy of the ion, so the molecular ions lose energy more quickly. An energy barrier before the analyzing quadrupole prevents passage of the now low energy molecular ions.

4.2.3 Reaction mode works on the principle that the interfering molecular ion reacts with reactive gas (e.g., NH3) to form new ions of differing mass than the analyte isotope or by effecting charge transfer from the interfering molecular ion to form a neutral molecule.

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. Some double charged interferences may be removed in reaction mode by using NH3.

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 20,000 – 1,500,000 counts of raw signal intensity. The mass of the internal standard should ideally be within 50 amu of the mass of the measured analyte, but this is not mandatory with current instrumentation. 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 intensity in 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 involves hazardous materials, 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 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.

5.3 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.
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.			

6.0 Equipment and Supplies

6.1 Equipment

6.1.1 The discrete sample introduction system enables the use of only the exact amount of sample volume required for data acquisition. In this procedure, a 1.5 ml was adequate to accommodate the necessary analysis time. The loop size can be modified to suit the analysis time as needed.

6.1.2 The sample introduction system also includes a PFA ST concentric nebulizer, 2.0 mm quartz injector, and baffled cyclonic spray chamber with gas addition port (ESI, Omaha, NE), The spray chamber fits into the PC3 chiller described in Section 2.4. Other equivalent accessories and configurations that are designed to accommodate samples with high levels of dissolved solids may be used.

6.1.3 PVC peristaltic pump tubing, orange-white, is used to produce a sample flow rate of 270 uL/min. This flow rate may be adjusted as necessary to optimize method conditions.

6.1.4 A mixing tee is used to blend in the internal standards after the peristaltic pump and before the nebulizer. The mixing tee can be used with or without the discreet sample introduction system. If used with the discreet sample intro system, the mixing tee is inserted after the 6-port valve. The peristaltic pump tubing used for the internal standard solution is orange-white and when used in combination with orange-white pump tubing for the carrier solution or sample, creates a minimum dilution of approximately 8.1%.

6.1.5 Automated sample dilution, liquid or gas, simplifies the dilution process and results in less matrix being deposited on the cones during analysis and minimizes the rinse times normally needed for difficult matrices. However, manual sample dilution is just as effective, albeit more labor intensive.

6.1.6 Autosampler with autosampler tubes.

6.1.7 Block digester with tubes.

6.2 Supplies

6.2.1 Argon gas: High purity grade (99.996%).

6.2.2 Helium gas: Ultra High purity grade (99.999%).

6.2.3 Ammonia gas, anhydrous: Ultra high purity grade (99.999%).

6.2.4 Calibrated automatic 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 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, which are received at ready-to-use concentrations) are prepared fresh daily.

7.2 Standards

7.2.1 Tuning Solution, 1 ppb

7.2.1.1 The tuning solution may be purchased as a custom multi-element mix ready to use as is or prepared according to individual instrument manufacturer directions. The concentrations of the required elements for the NexION 300D ICP-MS are shown in Attachment 4 and the acceptance criteria are shown in Attachment 5.

7.2.2 Dual Detector Calibration Solution

7.2.2.1 The dual detector solution may be commercially purchased as a custom multi-element mix ready to use as is or prepared according to manufacturer's recommendations. See Attachment 6.

7.2.2.2 Alternative elements may be used that are more specific to the analytes being tested. Such solutions should contain elements at 200 ug/L or other concentrations that accommodate the dual detector algorithm.

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% hydrochloric acid matrix, to match the acid strength of the digestates. Suggested concentrations are given in Attachment 7, 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 Mixed Interference Check Solution (Synthetic FGD Wastewater)

7.2.4.1 The concentrations of the interferents below are representative of typical FGD field samples. If the samples are being diluted (liquid or gas) on-line, these concentrations must be used. However, if samples are diluted prior to analysis, the concentrations of the mixed interferent check solution may be reduced by the smallest dilution factor used on the FGD field samples. For example, if the field samples are diluted 1:10, then the Ca concentration would be 200 mg/L.

7.2.4.2 The following solution is prepared in 1.6% HCl

7.2.4.3 Calcium, 2,000 mg/L

7.2.4.4 Magnesium, 1,000 mg/L

7.2.4.5 Sulfate, 2,000 mg/L

7.2.4.6 Sodium, 1,000 mg/L

7.2.4.7 1-Butanol, 2000 mg/L

7.2.5 Initial Calibration Verification (ICV) Standard

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

7.2.5.2 Each day of analysis, the ICV standard is prepared in 2% HNO_3 and 0.5% HCl acid to the concentrations shown in Attachment 7.

7.2.6 Continuing Calibration Verification (CCV) Standard

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

7.2.6.2 The CCV standards are prepared fresh each day of analysis in 2% HNO_3 and 0.5% HCl. The concentrations are shown in Attachment 7.

7.2.7 Internal Standards

7.2.7.1 Internal standards are required, and recommended isotopes are provided in Attachment 3. Inclusion of 10% methanol to the internal standard solution when added via the mixing tee improves the count rate for those elements with high ionization potentials such as arsenic and selenium. A 10% methanol content in the internal standard solution will ultimately blend down to approximately 1% in the sample introduced into the spray chamber.

7.2.8 Spiking Stock Solution

7.2.8.1 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.

7.2.8.2 Spike concentrations are listed in Attachment 7.

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.

7.3.3 Methanol – Semiconductor grade.

8.0 Sample Collection, Preservation, Shipment and Storage

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

8.2 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.

8.3 If dissolved elements are to be determined, the samples are immediately filtered through a 0.45-µm membrane filter on-site by the sampler before adding preservative.

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 8.

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 Synthetic FGD Interference Check Solution

9.3.1 The synthetic FGD matrix solution listed in Section 7.2.4 is analyzed prior to initiating sample analysis. The synthetic FGD matrix solution must be analyzed at least once per day (immediately after calibration) while FGD wastewaters are being analyzed, and after any major changes to instrument operating conditions.

9.3.1.1 Internal standard recovery must meet method criteria (Section 9.7) and concentrations of target elements observed should be less than their reporting limits.

9.3.1.2 In some cases it may not be possible to obtain interference check solutions that are completely free of contamination. In these cases, 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 isotopes 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 and clearly demonstrate that the observed contamination is not a result of polyatomic interferences. 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.

9.3.1.3 If the Synthetic FGD solution has to be diluted in order to analyze it effectively on the ICP-MS (i.e., meet all method criteria), 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 9.

9.3.2 Laboratory Fortified Synthetic FGD solution

9.3.2.1 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 9.3. All target elements must be recovered within 70-130% of the spiked value. For other target elements that are routinely detected at concentrations significantly higher than 100 ug/L, the spike concentrations may be elevated accordingly. Likewise, if zinc and aluminum are routinely detected at concentrations significantly lower than those above, the spike concentrations may be lowered accordingly.

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

9.4 Method Blank (MB)

9.4.1 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.

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

9.4.1.2 **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):

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

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

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

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

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

9.5 Laboratory Control Sample (LCS)

9.5.1 The LCS consists of reagent water that is spiked with the analytes of interest as summarized in Attachment 7. One LCS must be processed (digestion and analysis) for each preparation batch.

9.5.1.1 **Acceptance Criteria**: LCS control limits should be 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.

9.5.1.2 **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 of at least those affected analytes. One possible exception is a recovery for a given element above the upper control limit with no associated detection for the same element in the samples.

9.6 Matrix Spike / Matrix Spike Duplicate (MS/MSD)

9.6.1 The MS is prepared by taking a second aliquot of a selected sample and spiking it with the analytes of interest as summarized in Attachment 7.

9.6.2 The MSD is prepared by taking a third aliquot of the selected sample and spiking it with the analytes of interest as summarized in Attachment 7.

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

9.6.3.1 **Acceptance Criteria**: Control limits should be 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 should be 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 may be reduced and the combined concentration may well exceed the calibration range. 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. The RPD is calculated as follows:

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

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

9.6.3.2 **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. When the concentration of any element in the selected sample is more than 5X the concentration of the spike concentration, then the acceptance criterion does not apply and the spike results should be flagged accordingly.

9.7 Internal Standards Evaluation for Samples

9.7.1 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.

9.7.2 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. Dilution factors should increase as necessary until the IS recovery meets the acceptance criterion.

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

10.0 Procedure

10.1 Procedural variations are allowed only if deemed necessary in the professional judgment of the Laboratory Director to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be thoroughly documented and noted in the laboratory narrative. Any 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 describes Aqueous Sample Preparation.

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

10.2.3 Add 1.0mL of concentrated nitric acid and 0.25mL concentrated hydrochloric acid. (If samples are received unpreserved, add 1% nitric acid and store for at least 16 hours before preparation).

10.2.4 Prepare sample aliquots and spike the LCS and MS/MSD samples per spiking protocols.

10.2.5 Place a ribbed disposable watch glass over the digestion tube.

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

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

10.2.8 Remove the tubes from the block and allow to cool.

10.2.9 Add deionized water to digestates to bring them back to 50.0 ml.

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 5 replicate integrations of the solution.

10.3.2.2 Perform mass calibration and resolution check using the tuning solution at a minimum of every two weeks.

10.3.2.2.1 Mass Calibration Check: The mass calibration results must be within 0.1 amu from the true value.

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.

10.3.3 Dual Detector Calibration

10.3.3.1 The dual detector calibration allows the quantification of results using both the pulse mode and analog mode of the detector. Analysis of a multi-element standard at a concentration sufficient (e.g., 200 ug/L) to allow the detector to function in both modes allows the software to determine conversion factors. These conversion factors are used to quantify elements detected in the analog mode by converting the observed counts to equivalent pulse mode counts.

10.3.3.2 The dual detector calibration is only required for those isotopes that will trigger the analog mode of the detector (e.g., >2 million counts per second). Isotopes or elements that are known to always be present at count rates within pulse mode detection do not need to be included. Note that the dual detector calibration is specific to the isotopes and not necessarily the elements.

10.3.3.3 The dual detector calibration must be performed at least every month. The correlation coefficient for each isotope must be $\geq$0.999. While there is no specific criterion for a minimum number of crossover points, it is recommended to have at least 10. The number of points can generally be increased by modifying the concentration of the affected element. Review of the count rate for the affected element will assist in determining if the element concentration should be increased or decreased from the default 200 ug/L level.

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 replicate integrations.

10.3.4.2 The linearity of the initial calibration is assessed using a linear regression algorithm, based on the intensity counts of both the target elements and the internal standards. Calculate the correlation coefficient (r_2) from the initial calibration. The calibration is sufficiently linear if $r_2 \geq 0.998$. Elements not meeting this criterion are not valid and recalibration is required for at least those affected elements.

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

10.3.5 Second-Source Initial Calibration Verification (ICV)

10.3.5.1 An ICV standard (see Attachment 7) is analyzed immediately after the initial calibration. This is a standard obtained preferably from a different vendor than the standard used for calibration but at a minimum must be a different lot number from the same vendor.

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 in Section 4.4 must be accomplished by analysis of an initial calibration blank (ICB) after the ICV. Continuing calibration blanks (CCBs) are analyzed immediately 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.

10.3.7 Reporting Limit (RL) Verification Standard

10.3.7.1 A standard (such as the low level calibration standard) is analyzed after the ICB to monitor the lab's ability to produce reliable results at the reporting limit 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 7) 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 CCV.

10.4 Sample Analysis

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

10.4.2 Flush the system with a rinse solution between samples and standards during the analytical run. It is recommended that the rinse solution be the same as the matrix (i.e., 2% HNO3 and 0.5% HCl). If using a discreet analyzer or switching valve, the rinsing efficiency can be improved by rinsing the sample loop and valve as well as the sample line itself. Evaluate the effectiveness of this rinse 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.

10.4.4 Where any target element is determined at a concentration exceeding the high calibration standard, those samples must be reanalyzed following dilution for at least those affected elements. The dilution factor must be sufficient to bring the target analyte to within the calibration range.

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

Instrument initialization
Warm-up
Tune instrument
Perform mass calibration, when indicated
Perform resolution check, when indicated
Validate tuning criteria
Calibration blank
Calibration standards
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:

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

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

D = Instrument dilution factor, where applicable

V_1 = Final volume in milliliters after sample preparation

V_2 = Initial volume of sample digested in milliliters

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 per 40CFR Part 136, Appendix B. A summary of this procedure is as follows:

12.1.1.1 Prepare seven replicate samples at three to five times the estimated MDL concentration. The MDL samples are prepared in the Synthetic FGD wastewater matrix. The Synthetic FGD matrix may be diluted if it has previously been determined that the field samples require dilution to meet method criteria; see Section 9.4.

12.1.1.2 Prepare and analyze the MDL standards as described in Section 10, including the digestion procedure.

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-value for the 99th percentile (3.143 for 7 replicates) times the standard deviation of the MDL replicate results, following the procedure at 40CFR Part 136, Appendix B.

12.1.1.5 The calculated MDLs may not exceed the test concentrations used in the 7 samples nor may the test concentrations exceed the MDLs by more than a factor of 10. If either case is encountered, all elements affected must be prepared again at a more appropriate concentration.

12.1.1.6 Some elements may not require spiking if it has previously been determined that the Synthetic FGD matrix is contaminated and meets the criteria in Section 9.4, and the concentrations of the contaminants are within the acceptable range described in Section 12.1.1.5.

12.1.2 Example MDLs are given in Attachment 10.

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.

12.2 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 ICVs from four distinct analytical sequences. Using these four ICVs 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 by PerkinElmer, Inc.

16.0 Attachments

Attachment 1: Suggested Mass Choices
Attachment 2: Recommended Elemental Equations
Attachment 3: Internal Standards and Corresponding Elements
Attachment 4: Tuning Solution
Attachment 5: Suggested Tuning and Response Factor Criteria
Attachment 6: Dual Detector Calibration Solution
Attachment 7: Calibration, Calibration Verification, and Spike Concentrations
Attachment 8: Summary of Quality Control Requirements
Attachment 9: Typical results for synthetic FGD solutions
Attachment 10: Typical Method Detection Limits

Attachment 1: Suggested Mass Choices and Analysis Mode

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.

STD – Standard mode
He – Helium gas used in collision mode
NH3 – Ammonia gas used in reaction mode

Mass	Element of Interest	Analysis Mode
27	Aluminum	STD or He
75	Arsenic	He
111, 114	Cadmium	He
52, 53	Chromium	NH3 or He
63, 65	Copper	He
208, 207, 206	Lead	STD
55	Manganese	NH3 or STD
60, 62	Nickel	He
78, 82	Selenium	NH3 or He
107	Silver	STD or He
205, 203	Thallium	STD or He
51	Vanadium	NH3 or 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.

Na, Mg, K, Ca and Fe are included in the synthetic FGD wastewater but their analytical determination is optional

Attachment 2: 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 3: Internal Standards and Corresponding Elements

Internal Std.	Associated elements[1,2]
Sc	Na, Mg, Al, K, Ca
Ge	Fe, Ni, Cu, Zn, As, Se, Cd
In	V, Cr, Mn, Ag
In or Tb	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 Ir may be considered for use as internal standards.

Attachment 4: 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 range for the NexION 300D. Instrument manufacturer recommendations should be followed for tuning solutions.

Element	Concentration (µg/L)
Be	1
Ce	1
Fe	1
In	1
Li	1
Mg	1
Pb	1
U	1

Attachment 5: Suggested Tuning and Response Factor Criteria

No Gas Mode

Mg24 >20,000cps

In115 >50,000cps

U238 >40,000cps

Background220 ≤1cps

CeO/Ce 156/140 ≤2.5%

Ce++/Ce+ 70/140 ≤3%

Attachment 6: Dual Detector Calibration Solution

A dual detector calibration 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. Other elements can be added as needed. The concentrations used in the solution may be varied as necessary to accommodate the dual detector algorithms and the instrument sensitivity. Instrument manufacturer recommendations should be followed for tuning solutions.

Element	Concentration (µg/L)
Ag	200
Al	200
As	200
Ca	200
Cd	200
Cr	200
Cu	200
Ge	200
In	200
K	200
Mg	200
Mn	200
Na	200
Ni	200
Pb	200
Sc	200
Se	200
Tb	200
Tl	200
V	200
Zn	200

Attachment 7: 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.

NOTE: The concentrations of elements in this table are intended to be the approximate concentrations supplied to the plasma. When the internal standards are added on-line through the use of a mixing tee, these concentrations should not be affected significantly. However, if it is determined that sample dilution is necessary to meet method criteria and this dilution is to be effected through the use of on-line dilutions with a mixing tee, the concentrations of the calibration standards and QC samples must be adjusted accordingly. In such cases, Ag may become unstable at higher dilutions and lower concentrations may be necessary.

Attachment 8: 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.	85 - 115% 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% of intensity in calibration blank	If unacceptable, terminate analysis; correct the problem, recalibrate the instrument, re-verify calibration and rerun all samples since the last acceptable CCB.

Attachment 8: Summary of Quality Control Requirements (continued)

QC Parameter	Frequency	Acceptance Criteria	Corrective Action
Method Blank/Laboratory Reagent Blank	One per batch 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 9.4 for additional requirements.
LCS/LFB	One per preparation batch of 20 samples or fewer	Not to exceed 85-115% recovery	See Section 9.5
Matrix Spike/Laboratory Fortified Matrix	One every ten samples or fewer.	Must be within laboratory control limits.	See Section 9.6 for additional requirements.

Attachment 9: Typical results for the synthetic FGD solution

Analyte	Synthetic FGD solution A (µg/L)	Synthetic FGD solution B (µg/L)	Synthetic FGD solution C (µg/L)	Synthetic FGD solution D (µg/L)	Synthetic FGD solution E (µg/L)	Synthetic FGD solution F (µg/L)	Spike Recovery solution F (µg/L)
27 Al	23.2	36.4	23.5	5.33	7.16	24.4	111%
51 V	0.46	5.11	0.45	4.31	0.19	0.15	114%
52 Cr	106	2.97	1.76	0.76	1.38	2.02	107%
55 Mn	45.2	37.3	21.9	25.4	7.02	21.9	112%
60 Ni	2.83	4.36	4.66	7.44	1.42	4.62	100%
63 Cu	3.45	2.35	3.56	1.78	3.03	1.34	93.0%
66 Zn	7.24	5.84	40.4	27.6	9.26	36.6	94.0%
75 As	4.90	1.11	1.82	2.88	1.09	1.69	110%
78 Se	10.6	3.10	4.00	4.21	3.04	6.48	108%
107 Ag	0.53	0.22	1.36	2.33	0.31	0.02	90.0%
111 Cd	1.00	3.25	2.85	3.92	0.11	1.93	107%
205 Tl	0.31	0.19	1.28	0.94	0.05	0.10	103%
208 Pb	2.05	1.36	5.30	9.23	5.37	4.17	94.2%

Note that these values are examples and not method requirements.

Synthetic FGD solution F was spiked with 40 ug/L of all elements.

Attachment 10: Typical Method Detection Limits

Mass/Element	Int. Time (sec)	Mode	Internal Standard	MDL (µg/L)
27 Al	0.5	STD	Sc	0.54
51 V	0.5	NH3	In	0.02
52 Cr	0.5	NH3	In	0.09
55 Mn	0.5	NH3	In	0.27
60 Ni	0.5	He	Ge	0.28
63 Cu	0.5	He	Ge	0.30
66 Zn	0.5	He	Ge	1.20
75 As	1.5	He	Ge	0.30
78 Se	1.5	He	Ge	1.01
107 Ag	0.5	STD	In	0.03
111 Cd	0.5	He	Ge	0.03
205 Tl	0.5	STD	In	0.01
208 Pb	0.5	STD	In	0.04

MDLs were determined in the synthetic FGD solution. Note that these values are examples, and not method requirements.

It should be noted that contamination present in the synthetic FGD solution may have a significant impact on the determination of MDL values. It may be impractical to spike the synthetic FGD solution for those elements that are already present at concentrations exceeding the 3-5 times estimated MDL value. It may also be problematic to determine an acceptable MDL for any element present in the synthetic FGD at a concentration that exceeds 10 times the calculated MDL.