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Trace Metals Determination in Flue Gas Desulfurization Water

Optimization of Dynamic Reaction Cell (DRC) Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

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Technical Update, December 2009

EPRI Project Manager

N. Goodman

ELECTRIC POWER RESEARCH INSTITUTE
3420 Hillview Avenue, Palo Alto, California 94304-1338 ▪ PO Box 10412, Palo Alto, California 94303-0813 ▪ USA
800.313.3774 ▪ 650.855.2121 ▪ askepri@epri.com ▪ www.epri.com

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Brooks Rand Labs, LLC
3958 6th Ave NW
Seattle, WA 98107 USA

Principal Investigator
M. Briscoe

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PRODUCT DESCRIPTION

Flue gas desulfurization (FGD) scrubbers are used on coal-fired power plants to reduce sulfur dioxide emissions to air. While effective for this purpose, wet FGD scrubbers produce an aqueous blowdown stream that contains trace levels of metals adsorbed from flue gas. Power plant owners need to measure concentrations of these metals for purposes of process control, discharge monitoring, or design and operation of wastewater treatment systems. FGD water has proven to be a very difficult matrix to analyze accurately for trace metals because it contains elevated concentrations of solids and dissolved salts that interfere with most commercially available analytical methods. This report describes an EPRI project to develop improved analytical methods for the determination of trace elements in FGD water samples using inductively coupled plasma–mass spectrometry (ICP-MS) equipped with Dynamic Reaction Cell (DRC) technology.

Results and Findings

DRC technology, an addition to standard ICP-MS, is used to reduce interferences through gas phase reactions. In specific, gases such as oxygen, ammonia, or methane are reacted with the ionized sample inside a reaction cell in order to change the mass of either the target element or the interfering species so that one can be distinguished from the other. Research conducted for this project determined that the use of an ICP-MS with DRC improves accuracy over standard ICP-MS for seven elements: arsenic, antimony, chromium, copper, selenium, vanadium, and zinc. An optimized method for application of this technique to the analysis of FGD water is presented in the form of a Standard Operating Procedure (SOP). Future EPRI research will attempt to identify a technique to overcome high matrix spike recoveries for arsenic, evaluate additional reaction gases, and verify performance of the SOP in additional laboratories.

Challenges and Objective(s)

Environmental staff at coal-fired power plants encounter challenges in identifying appropriate analytical techniques for the complex and difficult FGD water matrix. The overarching goal of this research is to produce an SOP for analysis of target trace metals in FGD water by ICP-DRC-MS that 1) can be implemented in a commercial or utility laboratory without the need for extensive method development or optimization and 2) can ultimately achieve acceptance as an approved method for compliance monitoring. The specific objective of this report is to assist in the selection of ICP-DRC-MS methods for analyzing water discharges at coal-fired power plants equipped with wet scrubbers. The report will be of particular benefit to analytical laboratory chemists, who can use the SOP to improve the accuracy of their ICP-MS results.

Applications, Values, and Use

This report will help environmental staff at coal-fired power plants better characterize FGD water and avoid reporting inaccurate data to treatment system design engineers and permitting authorities. Without use of the DRC modification (or similar techniques such as collision/reaction cell ICP-MS, not tested as part of this project), standard ICP-MS may greatly over-report trace elements such as arsenic and selenium. By requesting that laboratories implement the procedures reported here, power plant owners can avoid overestimating trace metal content of their water discharges. This in turn avoids costs resulting from over-engineering treatment systems and from regulatory penalties for exceeding discharge limits.

EPRI Perspective

EPRI is engaged in research to understand the behavior of trace elements in coal-fired power plant FGD scrubbers and wastewater treatment systems. It is important for EPRI research to provide improved methods for obtaining accurate measurements of trace metals in FGD water in order to enhance industry understanding of the fundamental chemistry of FGD water. For the power industry, broader availability of accurate methods for measuring trace metals in FGD waters will be critical in the future if more restrictive discharge limits are implemented.

Approach

The technical approach used in this project included the following: 1) development and/or optimization of an ICP-DRC-MS method using actual FGD water samples, 2) validation of the method by analysis of split samples using high-resolution ICP-MS, 3) performance of method detection limit studies for each of the target elements, 4) development of a draft SOP, and 5) verification by having a second laboratory implement the SOP.

Keywords

Flue Gas Desulfurization
Water Discharges
Trace Metals
FGD Analytical Methods
Standard Operating Procedure (SOP)
ICP-DRC-MS Method
Dynamic Reaction Cell (DRC) Technology

ACRONYMS AND ABBREVIATIONS

AFT	Axial field technology
BRL	Brooks Rand Laboratories
CCV	Continuing calibration verification
CRM	Certified reference material
DRC	Dynamic Reaction Cell
EPA	U.S. Environmental Protection Agency
EPRI	Electric Power Research Institute
FGD	Flue gas desulfurization
HR-ICP-MS	High resolution ICP-MS
ICP-MS	Inductively coupled plasma mass spectrometry
IDL	Instrument detection limit
L	Liter
MDL	Method detection limit
mg	Milligram
MRL	Method reporting limit
MS/MSD	Matrix spike/matrix spike duplicate
NIST	National Institute of Standards and Technology
NPDES	National Pollutant Discharge Elimination System
QA	Quality assurance
QC	Quality control
RPq	Rejection parameter q
S/N	Signal to noise ratio
SOP	Standard Operating Procedure
SRM	Certified standard reference material
TOC	Total organic carbon
TDS	Total dissolved solids

TSS	Total suspended solids
UA	University of Arizona
V	Voltage
WWTP	Wastewater treatment plant

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EXECUTIVE SUMMARY

This report describes a research project to develop improved analytical methods for the determination of trace elements in flue gas desulfurization (FGD) water samples using inductively coupled plasma mass spectrometry (ICP-MS) equipped with Dynamic Reaction Cell (DRC) technology. The trace metals included in this study are aluminum, antimony, arsenic, chromium, cobalt, copper, nickel, selenium, silver, vanadium, and zinc.

ICP-MS is an analytical technique that is commonly used for measuring low concentrations of multiple metals in water. The method is generally more sensitive than other methods such as ICP-atomic emission spectroscopy or atomic absorption spectroscopy. Several ICP-MS methods have been developed by the U.S Environmental Protection Agency for use for drinking water and wastewater discharge compliance monitoring, including EPA Method 200.8 and Draft EPA Method 1638.

FGD waters are very difficult to analyze accurately for trace metals by most commercially available analytical methods, because they contain elevated concentrations of solids and dissolved matrix constituents (sulfides, chlorides and other salts). In ICP-MS, these components of the FGD water matrix can combine with each other to form polyatomic interferences that mimic the presence of the target element, leading to a bias or overestimate of the true sample concentration. Other polyatomic interferences can be formed by reactions between the instrument carrier gas (typically argon) and the sample components. The positive bias from these interferences can be very large, for some elements comprising 99 percent of the total amount measured in a FGD water sample.

DRC is an addition to standard ICP-MS that is used to reduce polyatomic interferences through gas phase reactions. Gases such as oxygen, ammonia, or methane are reacted with the ionized sample inside a reaction cell in order to change the mass of either the target element or the interfering species so that one can be distinguished from the other. The DRC technique is highly powerful and adaptable but historically has required the analyst to tailor the technique to each element and matrix, and sometimes even to optimize the approach to an individual sample. This level of effort and resulting high cost has typically limited the application of DRC to a few elements (primarily arsenic and selenium), where it has been shown to produce a major improvement in accuracy over standard ICP-MS.

Other approaches are available to reduce polyatomic interferences, such as the collision/reaction cell used in some ICP-MS instruments. EPRI did not test alternative techniques in this project because they require different instrumentation and procedures, but may investigate them in future research.

The primary objective of this research project was to develop and optimize ICP-DRC-MS methods for FGD water for the eleven elements listed above. In addition, the project included efforts to improve the performance of an existing ICP-DRC-MS method for arsenic, and to evaluate methods to improve the stability of silver in FGD water samples. The product of this research will be a Standard Operating Procedure (SOP) for analysis of the target trace metals in FGD water by ICP-DRC-MS that can be implemented in a commercial or utility laboratory without the need for extensive method development or optimization.

The technical approach used in this project included development and/or optimization of an ICP-DRC-MS method for the target elements using actual FGD water samples, validation of the method by analysis of split samples using high-resolution ICP-MS, performance of Method Detection Limit (MDL) studies for each of the target elements, development of a draft SOP, and verification of the SOP by having a second laboratory implement the procedures. The draft SOP was revised based on the verification laboratory results and peer review by ICP-MS experts. The resulting SOP, which is included as an appendix to this report, is expected to be further modified in the future based on additional research and as more laboratories implement the procedures.

The research conducted for this project determined that ICP-DRC-MS has a significant benefit of reducing bias due to polyatomic interferences for seven of the elements studied: arsenic, antimony, chromium, copper, selenium, vanadium, and zinc.

For arsenic, FGD water samples from certain power plants consistently exhibit recoveries on matrix spike analyses that are above the upper limit of the acceptance criteria. An attempt was made to resolve this issue by adding carbon (in the form of organic solvent) to the samples and standards. This approach was not completely successful, and more research is needed to resolve this problem. High-resolution (HR) ICP-MS was found to not be an appropriate method to validate the ICP-DRC-MS measurements for arsenic, as it was determined that interferences impact the HR result for this element. Nevertheless, ICP-DRC-MS appears to largely eliminate the bias in arsenic measurement due to polyatomic interferences, and is a significant improvement in accuracy over standard mode ICP-MS.

Two elements were not found to benefit from the use of DRC with the instrument settings tested during this project: nickel and silver. These elements were not found to exhibit significant bias from interferences. They may still be included in a multi-element analysis using DRC with no loss of accuracy, or analysis by standard mode ICP-MS may also be acceptable.

Cobalt and aluminum were evaluated but were not included in the SOP, as no DRC settings were identified that improved accuracy in all of the study samples as measured against the HR results.

The goal of this research is to produce a SOP that provides accurate results for FGD waters, can be performed by a non-specialty commercial or utility laboratory, and can ultimately achieve acceptance as an approved method for compliance monitoring. The current report demonstrates significant progress toward this goal; however, additional effort will be required. Future EPRI research will identify a technique to overcome high matrix spike recoveries for arsenic, evaluate additional reaction gases, and verify the performance of the SOP in additional laboratories.

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INTRODUCTION AND BACKGROUND

Introduction

Flue gas desulfurization (FGD) systems are being installed throughout the U.S. electrical power industry in response to federal and state air pollution regulations. FGD systems are used to remove sulfur dioxide (SO_2) from the flue gas from coal- and oil-fired power plants. Wet FGD systems (also known as wet scrubbers) pass flue gas through a slurry of lime or limestone to remove acidic SO_2 vapors. FGD systems produce an aqueous waste stream or blowdown that contains high concentrations of sulfur compounds as well as trace levels of metals absorbed from flue gas. FGD waters undergo solids removal processes before they are discharged to a wastewater treatment plant or holding pond, but the treated water still contains elevated dissolved salts as well as trace levels of metals. Accurate measurement of these metals at low concentrations is important for power plants that need to monitor for compliance with water discharge permits.

The objective of this project is to develop improved methods for measuring trace elements in FGD waters. The scope of this effort is limited to the following elements: aluminum (Al), antimony (Sb), arsenic (As), chromium (Cr), cobalt (Co), copper (Cu), nickel (Ni), selenium (Se), silver (Ag), vanadium (V), and zinc (Zn). The approaches developed may be useful for other trace metals; however, due to resource constraints, the scope was narrowed to the above elements. The ultimate goal of this research is to develop a Standard Operating Procedure (SOP) that can be implemented in a commercial or utility analytical laboratory using widely available equipment. The availability of such a SOP will assist the electrical power industry to obtain more consistent and accurate results from FGD water analyses.

This report presents the interim results of method development research and a SOP that will serve as the basis for further method improvements and interlaboratory comparison studies. The method development research for this project was conducted by Brooks Rand Laboratories, LLC (BRL) with support from the Electric Power Research Institute (EPRI).

Background

FGD waters are difficult to analyze for trace metals due to high concentrations of solids, salts, chloride, sulfate, and other matrix constituents that can produce physical and chemical interferences. The trace and major element composition of FGD waters is impacted by the type of FGD system, as well as the coal burned and the operation of the FGD system and the type of wastewater treatment processes employed [1].

One instrumental technique that is commonly used to measure metals in FGD waters is inductively coupled plasma – mass spectrometry (ICP-MS). Several U.S. Environmental Protection Agency (EPA) test methods make use of this technique, including Method 200.8 and Draft Method 1638. ICP-MS has the advantage that it can be used to measure multiple elements in a single test run, reducing the cost of analysis compared to single-element analyses. However, the standard ICP-MS method is known to produce inaccurate results for some elements in FGD waters. In particular, arsenic and selenium have been shown to suffer from a positive bias due to interferences from constituents of the FGD water matrix [1]. Other elements are also suspected to be inaccurate when measured by ICP-MS. As there is no certified reference material available to provide a benchmark for analysis of FGD waters, the evidence of bias has relied on comparisons with other analytical methods such as hydride generation atomic absorption spectroscopy (for arsenic and selenium) or ICP optical emission spectroscopy (OES) - (for other elements). These methods are also affected by interferences and in the case of ICP-OES, may not be sensitive enough to quantify some of the trace elements at levels of interest.

In an ICP-MS instrument, samples are introduced into an argon gas plasma that forms ionized species. Some of the atomized/ionized ions are drawn into a mass spectrometer/mass filter in which charged particles are separated by a quadrupole magnetic field based on their mass-to-charge (m:z) ratios. By careful adjustment of electrical fields, target analyte m:z ratios are selected. Ions that pass through the mass filter are directed to a detector that counts particle arrival. One source of interference in ICP-MS is that many ions can have the same unit m:z ratio. An example is shown below for arsenic:

$^{75}As^+$ = m:z 74.922
$^{40}Ar^{35}Cl^+$ = m:z 74.931
$^{40}Ca^{35}Cl^+$ = m:z 74.931

The species ArCl is formed by reaction between the argon carrier gas and chloride, if present in the sample. CaCl is another common interferent in FGD waters, due to high levels of calcium originating in the lime or limestone. A low–resolution ICP-MS, which is the type of instrument used in all but a few research labs, will measure all of these species as m:z 75, resulting in a positive bias for arsenic. These polyatomic or molecular ion interferences are highly variable from sample to sample and difficult or impossible to correct for by usual analytical techniques.

One modification to ICP-MS that has been used to reduce polyatomic interferences is to employ a chemical reaction to shift the mass of either the target ion or the interfering ions by collision based gas phase reactions. One such method modification is the dynamic reaction cell (DRC) technology developed by the PerkinElmer Corporation. Similar approaches developed by other manufacturers are known generically as collision/reaction cell ICP-MS.

A DRC is a second quadrupole magnet placed between the ion optics and the quadrupole mass filter. Figure 4-1 shows a schematic of a PerkinElmer Elan II DRC instrument configuration. The DRC can be used with a variety of reaction gases, such as oxygen, methane, and ammonia. These gases react with the introduced sample ion stream and reduce levels of polyatomic interferences that can cause false results for the isotope(s) of interest. Examples for mass shifts of either the target ion or the interfering ions by collision are shown below.

Removing the undesired overlap ion: ArO presents an interference for determination of iron at mass 54 (^{54}Fe). Using ammonia reaction gas reduces this interference.

$$^{38}Ar^{16}O^+ + NH_3 \longrightarrow NH_3^+ + ArO$$

Generating a new analyte-containing molecular ion: ArCl forms an interference for the determination of arsenic at mass 75 (^{75}As). Using oxygen reaction gas allows the formation of $^{75}As^{16}O$, which can be quantified at mass 91.

$$^{75}As^{+} + O_2 \longrightarrow {}^{75}As^{16}O^{+}$$

It is necessary to optimize the analytical method for analysis by ICP-DRC-MS for each element, and the optimization is specific to a particular matrix. This report details the development of a method to determine low-level trace metals concentrations in FGD waters using an ICP-DRC-MS.

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EXPERIMENTAL APPROACH

The project consisted of the following sequence of tasks:

1. Determine the required method modification and approach
2. Collect, prepare, and characterize FGD water samples
3. Develop and optimize ICP-DRC-MS method
4. Prepare a draft Standard Operating Procedure(SOP)
5. Validate method with high-resolution ICP-MS
6. Verify SOP in a second laboratory
7. Conduct peer review and revise SOP

The project was conducted in two phases. In Phase I, method development was conducted for aluminum (Al), arsenic (As), chromium (Cr), copper (Cu), nickel (Ni), selenium (Se), silver (Ag), vanadium (V), and zinc (Zn). In Phase II, antimony (Sb) and cobalt (Co) were added.

Determine the Method Modification and Approach

At the outset of this project, EPRI made the decision to evaluate the DRC technology as a modification to standard ICP-MS. As discussed above, DRC can use several reaction gases to eliminate polyatomic interferences. An alternative approach, collision/reaction cell technology, uses hydrogen or helium as a collision/reaction gas. In collision mode, larger size polyatomic ions undergo more collisions with the gas than the smaller target ion, are slowed by the collisions, and can therefore be separated by their energy level. Collision/reaction cell technology differs sufficiently from DRC that it is not possible to develop a detailed SOP to apply to both, and most laboratories own either one or the other. As several of the trace metal specialty labs previously used by EPRI use DRC instruments, EPRI decided to evaluate the DRC approach. EPRI has not evaluated the accuracy of collision/reaction cell methods for use with FGD waters, but will look for opportunities to do so in the future.

The ICP-MS used in this project was a PerkinElmer ELAN® DRC™ II. This model provides capability for more reaction gases than other models by this vendor. Due to the decision to use this instrument, the SOP presented in this report is only applicable to the Elan DRC II instrument. A high-efficiency sample injection system (ESI® SC-FAST™ or equivalent) was found to improve method sensitivity and instrument stability. This system is included in the SOP as optional but recommended equipment.

The method used as the basis for the modifications tested in this project is Draft Method 1638. This EPA Office of Water method is intended for analysis of low-level metals in aqueous matrices. Draft Method 1638 contains enhanced quality control requirements that are not included in Method 200.8, the method approved in 40 CFR Part 136, Appendix B for use for National Pollution Discharge Elimination System (NPDES) compliance testing.

The intent of EPRI's research is to develop procedures that can be implemented by a commercial or utility laboratory that has access to the proper equipment and trained chemists, but is not a research or specialty laboratory. Due to the fact that many of the target elements have multiple isotopes that can be used for quantification, and the complex and variable nature of the FGD matrix, EPRI's experience has been that each FGD water sample is treated as a research project. Laboratories often monitor multiple isotopes, use several reaction gases, and reanalyze the sample several times at different dilutions to detect and overcome interferences. DRC gives a high degree of flexibility to tailor the reaction gas and instrument settings to a particular interferent; however, few laboratories have sufficient expertise to successfully apply the technique in that manner. Therefore, the approach adopted for this project was to develop a SOP that provides recommended instrument settings, reaction gases, and isotopes for each target element. EPRI recognizes that this simplified approach will not be successful for every FGD water sample, but the expectation is that it will reduce interferences for the majority of samples. Additional guidance to laboratories may be needed, and the SOP may be revised after sufficient samples are analyzed to determine the success of this approach.

Collect, Prepare and Characterize FGD Water Samples

To ensure that the procedures developed in this project would be successful with a wide range of FGD waters, EPRI requested and obtained samples of FGD treatment system effluent from a number of power plants. The plants were selected based on the results of past sampling efforts, to include both relatively "easy" samples (those with lower levels of interfering substances) and more difficult samples. The samples were digested using an in-bottle digestion procedure and the digestate was split into portions for use by BRL and subcontract laboratories. This approach was used to minimize variability due to sample digestion procedure, a major factor influencing between-laboratory variability [1]. The digestates were analyzed for total recoverable trace and major elements, as well as for parameters that could potentially contribute to analytical bias such as total suspended solids (TSS) and total organic carbon (TOC).

Develop and Optimize ICP-DRC-MS Method

Using the collected FGD water samples, BRL identified instrument conditions, reaction gases, and other operating procedures for analysis of the target metals by ICP-DRC-MS. For some of the target elements, BRL had a previously developed method which was optimized for FGD waters and included in the draft SOP. For other elements, a new method was developed and optimized for this matrix.

Prepare a Draft Standard Operating Procedure (SOP)

An SOP was drafted that included the instrument conditions, reaction gases, and other procedures for conducting the analysis. The SOP assumes a basic understanding of analytical chemistry and some experience in operation of the ICP-MS in DRC mode.

Validate Method with High-Resolution ICP-MS

High resolution ICP-MS was selected as the validation technique for this project. This type of instrument can measure fractional masses, in theory allowing for differentiation between the target ions and interfering polyatomic ions with slightly different masses. Portions of each sample were shipped to a subcontractor laboratory for analysis of the target species. Results of the BRL analyses using the initial SOP were compared to the high-resolution ICP-MS results, and the BRL methods were modified if necessary to improve accuracy.

Verify SOP Usability

The draft SOP was provided to a subcontractor laboratory along with portions of the digested FGD water samples. The purpose of this task was to verify that a laboratory with the appropriate equipment would be able to follow the SOP procedures. Since the intent was for the SOP to be usable in a general analytical laboratory, the subcontractor selected was one that had the appropriate equipment and some experience using DRC, but that had never applied the technique to FGD water samples. Based on the results from the verification analysis, the draft SOP was revised to provide additional guidance.

Conduct Peer Review and Revise the Draft SOP

The draft SOP was sent to peer reviewers, including experts from commercial, utility, and university laboratories, as well as from the instrument manufacturer. Comments that could be addressed without additional method development were incorporated into a revised SOP that is included as appendix to this report. Other comments and suggestions, that would require a modified approach or test procedures, were reviewed and used as the basis for recommendations for possible future research.

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CHARACTERIZATION OF FGD WATER SAMPLES

Sample Collection

For Phase I of this research, BRL shipped precleaned sample containers to four power plants selected by EPRI. Power plant personnel were requested to fill the sample bottles (adding up to about 3 liters) with unfiltered FGD water from the requested sampling location. The samples were shipped overnight on ice to BRL. The four samples collected for use in Phase I of the study are described in Table 3-1.

Table 3-1
Description of Phase I Wastewater Treatment System Effluent Samples

BRL Sample ID	Sample Description
0842036-01	Effluent from a FGD wastewater treatment plant – secondary clarifier effluent
0842036-02	Effluent from a FGD wastewater treatment plant
0842036-03	FGD system effluent – overflow from vacuum drum filtration
0842036-04	FGD system primary clarifier effluent

Samples were received by BRL on October 14-27, 2008. Sample temperatures upon receipt were 1.5-3.2 ºC. On the day of sample receipt, samples for characterization analyses with short holding times were immediately transported to the subcontract laboratory responsible for those analyses.[1]

Due to the in-bottle digestion procedure used by BRL, the portions of Phase I samples provided to subcontractor labs were not true splits, but were field replicates. The sampling personnel were instructed to fill the bottles in as short a time as possible to minimize inter-bottle variability.

For Phase II, BRL shipped sample containers to five power plants selected by EPRI. Due to resource constraints, only four of the samples were used for method development. A 10-L carboy was provided to each plant, and the samples were homogenized and subdivided into individual bottles on receipt at BRL. For Phase II, samples were shipped without cooling to BRL, and were received on July 10-27, 2009. The samples for Phase II are described in Table 3-2.

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[1] Fremont Analytical, Inc., Seattle WA

Table 3-2
Description of Phase II Wastewater Treatment System Effluent Samples

BRL Sample ID	Sample Description
0930032-01	FGD system secondary clarifier effluent
0930032-02	Effluent from a FGD wastewater treatment plant
0930032-03	Effluent from a FGD wastewater treatment plant
0930032-04	Effluent from a FGD system (settling pond influent)
0930032-05	Effluent from a FGD wastewater treatment plant

Sample Characterization Analyses

To facilitate method development, analyses were performed to characterize the FGD water samples. Table 3-3 lists the characterization analyses.

Table 3-3
Sample Characterization Analyses

Parameter	Method	Laboratory
Major Elements: Aluminum (Al) [Phase I only], Boron (B), Calcium (Ca), Iron (Fe), Magnesium (Mg), Manganese (Mn), Potassium (K), and Sodium (Na)	Draft EPA Method 1638, Modified	Brooks Rand Labs (BRL)
Chloride (Cl) and Sulfate (SO_4)	EPA Method 300.0	Fremont Analytical
Total Dissolved Solids (TDS)	Method SM2540C	Fremont Analytical
Total Organic Carbon (TOC)	EPA Method 415.1 (Phase I); Method SM 5310C (Phase II)	Subcontracted by Fremont Analytical to Am Test[2] for Phase I; Fremont Analytical for Phase II
Total Suspended Solids (TSS)	Method SM2540D	Fremont Analytical

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[2] Am Test, Inc., Kirkland WA

Table 3-4 summarizes the results from all sample characterization analyses for the Phase I samples, and Table 3-5 summarizes the results for the Phase II samples. After reviewing the sample characterization data, EPRI selected four of the five Phase II samples to use in the method development effort; sample 0930032-02 was not used for method development. Sample selection was based on the results of prescreening ICP-MS analysis (to ensure that target analytes were at detectable concentrations and to include samples with a wide range of concentrations of interfering substances.

Table 3-4
Phase I Sample Characterization Results

Analyte	0842036-01	0842036-02	0842036-03	0842036-04
Al	0.126	0.0727	0.187	0.201
B	47.4	467	921	21.9
Ca	731	4900	737	765
Cl	1900	13,000	10,000	3700
Fe	< 1.5	< 3.7	< 1.5	< 1.5
K	9.19	177	218	111
Mg	391	3590	7640	4940
Mn	3.02	0.398	81.4	7.39
Na	22.1	2020	1460	792
SO_4	450	2000	19,000	17,000
TDS	3900	37,000	48,000	68,000
TOC	5.2	1100	320	73
TSS	45	60	120	58

Results are in mg/L.

Table 3-5
Phase II Sample Characterization Results

Analyte	0930032-01	0930032-02	0930032-03	0930032-04	0930032-05
B	16.8	62.0	199	242	1010
Ca	705	1090	1440	5640	693
Cl	4300	2500	18,000	6500	11,000
Fe	0.100	0.0100	1.10	0.300	0.0100
K	112	10.6	18.5	52.7	218
Mg	5750	468	1610	1920	6500
Mn	37.6	4.79	8.34	6.58	85.0
Na	860	23.3	311	112	1780
SO_4	22,000	595	1600	3000	21,000
TDS	26,000	5900	14,000	26,000	44,500
TOC	14	1.6	3.9	2.8	230
TSS	12	< 10	17	29	24

Results are in mg/L.

Sample Preparation and Splitting

All samples were preserved and prepared with a closed-vessel digestion. Each sample was preserved with 5% HNO_3 and digested at 85°C overnight. The same preservation and digestion procedure was applied to four method blanks. Each digested method blank and sample was split into four fractions in a manner to ensure homogeneity between splits. The four splits were used as follows:

1. Retained at BRL for analysis following method development
2. Retained at BRL for possible future analyses or method development
3. Shipped to a subcontract laboratory for validation analyses by HR-ICP-MS[3]
4. Shipped to a subcontract laboratory for verification analyses by ICP-DRC-MS[4]

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[3] Trace Elements Research Laboratory (TERL) at The Ohio State University, Columbus OH.

[4] Arizona Laboratory for Emerging Contaminants, University of Arizona, Tucson AZ

4

METHOD DEVELOPMENT

Introduction

Prior to beginning method development work, BRL submitted four archived FGD water samples to Elemental Scientific, Inc. (Omaha, NE) for pre-screening by high-resolution ICP-MS. The samples included FGD influent, treatment system mid-point, and effluent samples from two power plants. The samples were analyzed on a Thermo Element2 instrument.

Based on the screening comparison of standard and high-resolution ICP-MS results, a subset of metals was identified for method development in Phase I. Table 4-1 summarizes the findings from this comparison and whether BRL had already developed a DRC method for the element. Target metals for the EPRI project were selected based on two factors: environmental hazard (as indicated by water quality criteria for each element) and the likelihood that matrix constituents were causing positive polyatomic interferences resulting in a high bias to the results reported by standard mode ICP-MS. Several metals, including antimony, beryllium, lead, manganese, molybdenum, thallium, and tin, showed little or no potential to be influenced by the polyatomic interferences formed during analysis of FGD water samples in standard mode ICP-MS; therefore these metals were not selected for Phase I; however, antimony and cobalt were investigated in Phase II. Titanium showed a strong indication of bias, but is considered relatively non-toxic and so was not included in the EPRI study.

Silver did not show evidence of a significant bias due to polyatomic interferences; however, analysis of silver is highly matrix-dependent and is prone to low bias due to precipitation of insoluble silver compounds. Therefore, the initial research objective for this metal was to identify techniques for keeping silver in solution in FGD water samples. Although it was originally thought that an improved method for silver analysis would be developed using the ICP-MS in the standard (non-DRC) mode, BRL found that the DRC method also produced good results for silver; therefore, a DRC method for silver was added to the SOP to support multi-element analysis.

The metals selected for development and/or optimization were as follows:

Phase I: Al, As, Cr, Cu, Ni, Se, Ag, V, and Zn
Phase II: Co, and Sb

Table 4-1
Results from ICP-HR-MS Prescreening of FGD Water Samples

Element	Approximate Fraction of ICP-MS Value from Interferences	Interfering elements (Polyatomic ions)	Existing BRL Method Available?
Aluminum	0%	CN, BO	In process
Antimony	0%	ArBr	No
Arsenic	With DRC • 0% Without DRC • 100%	Cl (ArCl, ArClO)	Yes[5]
Barium	0%	Zn (ZnZn)	No
Beryllium	0%	-	No
Cadmium	0%	Mo (MoO)	No
Chromium	86-100% (without correction factors)	C (ArC, ArCH), Cl (ClO)	Yes[5]
Cobalt	98-100%	Ca (CaO, CaOH)	No
Copper	Without DRC • 90 %	P (POO), S (SOO), Na (ArNa)	In process
Lead	0%	-	No
Manganese	0%	-	No
Molybdenum	0%	-	No
Nickel	different isotopes used for HR	Ca (CaO), NaCl	Yes[5]
Selenium	With DRC • 0% Without DRC • 85%	Kr, Ar (ArAr, ArCl, ArCa)	Yes
Silver	0%	-	In process
Thallium	0%	-	No
Tin	0%	-	No
Titanium	92-98%	P (PO)	No
Vanadium	70-99%	Cl (ClO), C (ArC)	Yes[5]
Zinc	100% (without correction factors)	Cr (CrO), Si (ArSi), Mg (ArMg)	In process

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[5] A BRL DRC method had been developed for another matrix, but required optimization for FGD wastewater

All FGD water samples were analyzed by BRL for total recoverable metals using a PerkinElmer Elan II DRC. The instrument was equipped with an ESI® SC-FAST™ sample introduction system with a Peltier-cooled spray chamber. Schematics of the ICP-DRC-MS instrument and sample introduction system are shown in Figure 4-1 and Figure 4-2, respectively.

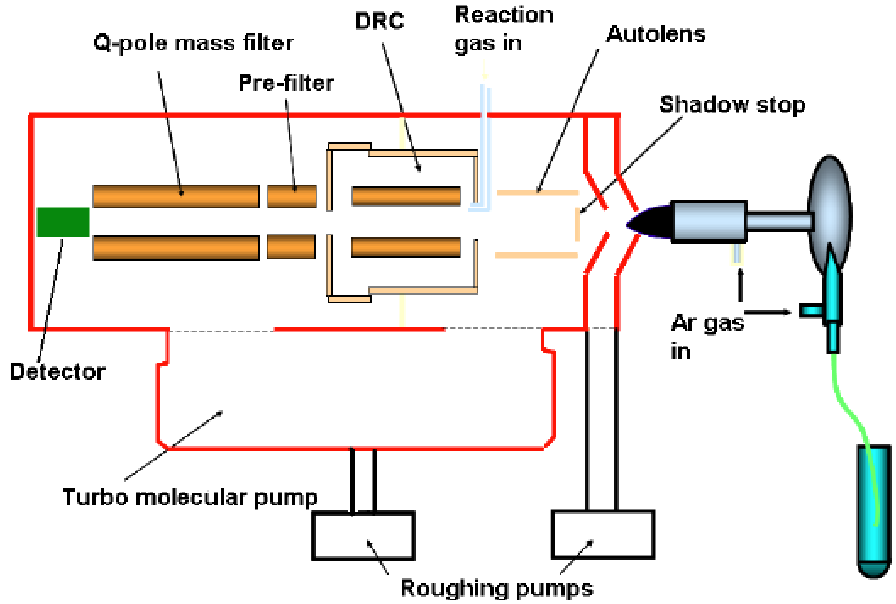

Figure 4-1
Schematic of PerkinElmer SCIEX™ ELAN® DRC™ ICP-MS

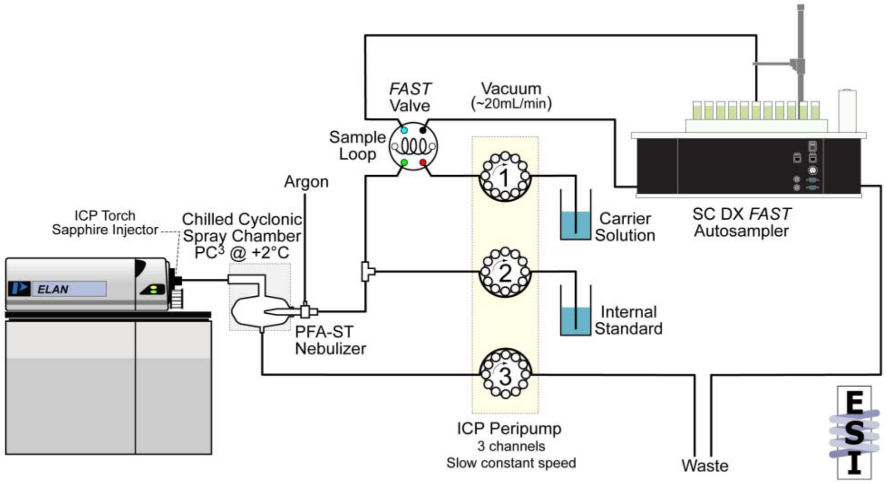

Figure 4-2
Schematic of ESI® SC-FAST™ Sample Introduction System

ESI FAST™ is an automated flow-injection sample introduction system. BRL found that use of this system improves method performance in several ways. The MDLs are lowered due to decreased matrix loadings and quicker washouts. By reducing the sample uptake (both in time and volume), the quantity of sample matrix reaching the torch injector and MS-interface cones (mostly the sampler cone) is significantly decreased and the sample load on the plasma is almost halved. This results in significantly improved long term stability, decreased drift effect and therefore better CCV and MS/MSD recoveries due to the less variable instrument sensitivity.

A summary of the reaction gases, internal standards, and instrumental parameters selected for each element included in the SOP is presented in Table 4-2. Detailed descriptions of the method development efforts for each element are provided in Appendix A for the benefit of analytical chemists that need to understand the complexities involved in optimization of a DRC method for the FGD water matrix.

Table 4-2
Summary of ICP-DRC-MS Instrument Conditions

Analyte	Isotope*	Internal Standard	DRC Gas	RPq	Cell Gas Flow Setting	Dwell Time (ms)
As (as AsO)	91	Rh	O_2	0.70	0.6	50
Se	78	Rh	O_2	0.80	0.6	200
V	51	Rh	NH_3	0.80	0.6	50
Cr	52	Rh	NH_3	0.75	0.6	50
Cr	53	Rh	NH_3	0.75	0.6	50
Ni	62	Rh	NH_3	0.80	0.6	50
Ni	62-1	Rh	NH_3	0.75	0.6	50
Cu	63	Rh	NH_3	0.75	0.6	50
Zn	66	Rh	NH_3	0.85	0.6	50
Zn	66-1	Rh	NH_3	0.80	0.6	50
Ag	109	In	NH_3	0.80	0.6	50
Ag	107	In	NH_3	0.80	0.6	50
Sb	121	In	NH_3	0.75	0.6	50
Sb	121-1	In	NH_3	0.80	0.6	50

* "-1" refers to a different RPq setting for the same isotope.

Summary

Following the completion of the all of the experiments related to the method development for each analyte of interest, the optimized methods were documented in a draft SOP. Even with the use of the ESI FAST sample introduction system and DRC, dilution was still required for most samples. A list of the typical dilution ranges for each target analyte is presented in Table 4-3. Samples were analyzed at the greatest dilution possible while still maintaining high enough signal for successful analyte quantitation. The MDLs achieved by BRL (reported in Section 5) were sufficiently low that most target elements were quantifiable in all of the FGD samples after the specified dilutions (Table 4-3).

Table 4-3
Typical Dilution Factors for FGD Effluent Samples Analyzed by ICP-DRC-MS

Element	Typical Dilution Factor
Aluminum	10 –100
Antimony	1–5
Arsenic	10–200
Chromium	2–50
Cobalt	10–100
Copper	1–10
Nickel	1–50
Selenium	10–200
Silver	1–10
Vanadium	10–100
Zinc	1–50

5

METHOD DETECTION LIMIT STUDIES

Method detection limit (MDL) studies for the FGD water matrix were performed for all target metals following procedures specified in Draft EPA Method 1638 (modified) and 40 CFR 136, part B. It was important to use a matrix as similar as possible to the FGD water matrix, because there is a presence of interferences that increase the typical method detection limits, compared to the MDLs found with aqueous standards. The MDL study samples consisted of four method blanks, eight replicates of simulated FGD water matrix spiked at approximately 2-5 times the expected MDL, five initial precision and recovery (IPR) samples spiked with analytes at concentrations roughly fifty times the expected MDL, and two MDL validation samples spiked at approximately 2-4 times the expected MDL. The simulated FGD water matrix was composed of 10 mg/L Ca, 1 mg/L Mg, 5% (v/v) concentrated HNO_3, and 0.5 % (v/v) HCl. This matrix was sufficiently "analyte free" (as required by referenced EPA MDL guidance), yet would produce many of the types of interferences that would be expected from FGD water samples.

As specified in 40 CFR 136 part B, a MDL is calculated from the standard deviation (σ) of a minimum of seven replicate spiked samples which is then multiplied by the Student's t-coefficient at appropriate statistical confidence level. For eight samples, the MDL is calculated as:

$$MDL = 2.998 * \sigma.$$

To calculate the method reporting limit (MRL), it is first set equal to the lowest calibration standard. If the resulted MRL is then outside the range 2-10 times MDL the following corrections are applied:

- In case MDL is less than 1/10th of the MRL (upper limit stated above), than MRL value is kept and MDL is artificially increased to 1/10th of MRL value;
- In case MRL is less than 2 times the MDL, MRL is increased to 3 times MDL value.

The MDLs and MRLs for undiluted samples, those achieved in this study, are listed in Table 5-1. The full MDL Study report for each metal can be found in Appendix C. Sample-specific MDLs and MRLs would be calculated as the achieved MDL multiplied by the dilution factor of the FGD water sample. Table 4-3 lists the typical dilution factor ranges that can be expected for FGD waters.

When setting MDLs, it is also important to consider the signal-to-noise ratios, as unrealistically low MDLs may be achieved following the EPA guidance. The National Environmental Laboratory Accreditation Conference (NELAC) standard for signal-to-noise ratio is that a standard analyzed at ~2x the MDL should produce a signal that is at least 3 times the noise level.

Working in the range of the MDLs determined by these studies requires extremely strict adherence to ultra-clean sample collection and handling techniques, such as those described in EPA Methods 1669 and 1638. Without very careful attention to contamination control and ultra-clean techniques, the MDLs described here will not be achievable.

Table 5-1
Achieved MDLs and MRLs for FGD Waters by ICP-DRC-MS

Element	MDL (µg/L)	MRL (µg/L)
Aluminum*	0.25	1.00
Antimony	0.006	0.020
Arsenic	0.010	0.025
Chromium	0.015	0.150
Cobalt*	0.010	0.100
Copper	0.020	0.200
Nickel	0.062	0.200
Selenium	0.019	0.050
Silver	0.004	0.020
Vanadium	0.015	0.150
Zinc	0.028	0.200

* Not included in the SOP

6

FINAL ANALYSES USING THE SOP

After completion of method development, a Draft SOP was prepared that outlined the instrument settings, cell flow gases, and other conditions required for analysis of each of the target metals. As discussed previously, aluminum and cobalt were not included due to negative outcomes in the method development studies. Phase I and II FGD water samples were analyzed at BRL using the Draft SOP procedures. A summary of the results for the Phase I and II samples are presented in Table 6-1 and Table 6-2, respectively. Results that are less than or equal to the sample-specific MDL are reported as "<" the MDL and results greater than the MDL but less than or equal to the sample-specific MRL are flagged with a "B". All sample concentrations were blank corrected before reporting. This approach is not in accordance with EPA Method 200.8 or Method 1638; however, it has been allowed in some metals methods used for regulatory purposes (such as EPA Method 1631). Considering the blank levels were usually negligible, blank correction may not be necessary; however it may account for minor reagent contamination.

Table 6-1
Trace Metals Results for Phase I

Parameter	0842036-01	0842036-02	0842036-03	0842036-04
Al	102	< 58	210	352
As	2.00	17.2	11.2	21.3
Cr	< 0.23	2.73 B	< 1.2	3.37 B
Cu	1.89	6.49	48.2	21.6
Ni	62.9	135	2230	22.6
Se	102	5460	504	6220
Ag	< 0.008	0.070 B	0.290	0.061 B
V	0.546 B	53.4	0.864 B	5.67 B
Zn	11.4	3.04 B	4640	5.45 B

B = result ≤ MRL. Results are in µg/L.

Table 6-2
Trace Metals Results for Phase II

Parameter	0930032-01	0930032-03	0930032-04	0930032-05
Sb	2.95	1.33	11.6	12.8
Co	1.98	6.76	31.5	330

B = result ≤ MRL. Results are in µg/L.

Comparison of Standard Mode ICP-MS and ICP-DRC-MS Analyses

In order to better demonstrate the effectiveness of the DRC technology in removing suspected polyatomic interferences for FGD water samples, the study samples were also analyzed by ICP-MS in standard mode on the same instrument. All other method parameters were the same as those used in the ICP-DRC-MS SOP. Table 6-3 and Table 6-4 compare results of standard mode ICP-MS and ICP-DRC-MS for the Phase I and II samples, respectively. Ag is not included, as the standard mode ICP-MS analyses were not supported by sufficient quality control data. Al and Co are shown in these tables, although they were not included in the draft SOP.

Table 6-3
Comparison of Standard Mode ICP-MS and ICP-DRC-MS Results for Phase I

	0842036-01		0842036-02		0842036-03		0842036-04	
	STD	DRC	STD	DRC	STD	DRC	STD	DRC
Al	118	102	45.1	< 58	167	210	172	352
As	25.9	2.00	512	17.2	105	11.2	3,210	21.3
Cr	30.6	< 0.23	267	2.73 B	222	< 1.2	96.8	3.37 B
Cu	1.31	1.89	28.9	6.49	89.0	48.2	56.4	21.6
Ni	66.6	62.9	175	135	2,070	2,230	25.3	22.6
Se	151	102	6,740	5,460	750	504	14,100	6,220
V	10.6	0.546 B	131	53.4	73.8	0.864 B	33.8	5.67 B
Zn	6.82	11.4	24.9	3.04 B	4,840	4,640	54.8	5.45 B

B = result ≤ MRL. Results are in µg/L.

Table 6-4
Comparison of Standard Mode ICP-MS and ICP-DRC-MS Results for Phase II

	0930032-01		0930032-03		0930032-04		0930032-05	
	STD	DRC	STD	DRC	STD	DRC	STD	DRC
Sb	3.24	2.95	1.72	1.33	12.7	11.6	14.8	12.8
Co	2.29	1.98	5.98	6.76	26.9	31.5	322	330

B = result ≤ MRL. Results are in µg/L

For most metals, a significant to moderate decrease in measured concentration was reported, indicating that DRC appeared to be reducing positive biases due to polyatomic interferences. A list of the major polyatomic interferences that are expected to be important for FGD water samples was presented in Table 4-1. The exceptions to this pattern were Al and Co, as discussed previously.

7

VALIDATION BY HIGH-RESOLUTION ICP-MS

Splits of the Phase I samples were analyzed for validation purposes by sector-field high-resolution ICP-MS (HR-ICP-MS) at two subcontract laboratories. Due to instrumentation and procedural problems in the initial subcontract laboratory, the samples were redirected to Trace Elements Research Laboratory (TERL) at The Ohio State University for analysis. Data from the initial analyses are not included in this report. Phase II samples were sent to TERL only. A comparison of the ICP-DRC-MS and HR-ICP-MS results for the Phase I and II samples are presented in Table 7-1 and Table 7-2, respectively. All method blank results reported by TERL were below the associated TERL MDL: the results for the method blanks were reported as <MDL. Therefore, TERL results were not blank-corrected, in contrast to BRL's results.

Table 7-1
Comparison of ICP-DRC-MS and TERL HR-ICP-MS Results

	0842036-01		0842036-02		0842036-03		0842036-04	
	DRC	HR	DRC	HR	DRC	HR	DRC	HR
Al	102	89	< 58	< 30	210	96	352	227
As	2.00	5	17.2	42	11.2	23	21.3	11
Cr	< 0.23	0.5	2.73 B	3.2	< 1.2	0.6	3.37 B	3.2
Cu	1.89	< 2	6.49	5.4	48.2	44	21.6	18
Ni	62.9	59	135	130	2230	2100	22.6	16
Se	102	115	5460	5580	504	550	6220	6270
Ag	< 0.008	< 0.1	0.069 B	< 0.2	0.288	< 0.2	0.059 B	< 0.2
V	0.546 B	0.8	53.4	50	0.864 B	1.3	5.67 B	5.5
Zn	11.4	< 14	3.04 B	< 28	4640	4600	5.45 B	< 28

B = result ≤ MRL. Results are in µg/L.

Table 7-2
Comparison of ICP-DRC-MS and TERL HR-ICP-MS Results for Phase II

	0930032-01		0930032-03		0930032-04		0930032-05	
	DRC	HR	DRC	HR	DRC	HR	DRC	HR
Sb	2.95	2.5	1.33	1.4	11.6	13	12.8	13
Co	1.98	0.70	6.76	4.1	31.5	20	330	289

B = result ≤ MRL. Results are in µg/L.

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VERIFICATION AND STABILITY TESTING

Splits of the Phase I and Phase II samples were analyzed by ICP-DRC-MS at the Arizona Laboratory for Emerging Contaminants (University of Arizona, Tucson AZ). The purpose of this exercise was to determine whether the draft SOP could be followed with acceptable results, by a laboratory with appropriate equipment and expertise. This laboratory had no previous experience analyzing FGD water samples.

Initial results from the verification laboratory were not acceptable due to inappropriate sample dilutions. Additional guidance was provided that sample dilutions should be made greater than that required to achieve the maximum TDS level. The verification laboratory continued to have problems with internal standard and matrix spike recoveries even with increased sample dilution, using a standard sample introduction system. After UA purchased an ESI-SC FAST sample introduction system, results met the required quality control limits. However, the matrix spike recoveries were still unacceptable due to inappropriate spiking level. Guidance was added to the SOP detailing the spike level calculation approach. After the sample introduction system was installed, the sample dilutions increased, and appropriate spiking levels chosen, the verification laboratory reported satisfactory results for the samples.

A comparison of the ICP-DRC-MS results generated by BRL and the final ICP-DRC-MS results produced by the University of Arizona (UA) for the Phase I and Phase II samples is presented in Table 8-1 and

Table 8-2, respectively. For the Phase II samples, only Sb was analyzed by UA, as BRL was unable to develop a successful DRC method for cobalt.

Table 8-1
Comparison of BRL and Verification Lab ICP-DRC-MS Results for Phase I

	0842036-01		**0842036-02**		**0842036-03**		**0842036-04**	
	BRL	**UA**	**BRL**	**UA**	**BRL**	**UA**	**BRL**	**UA**
Al	102	104	< 58	72.0	210	230	352	418
As	2.00	1.61	17.2	6.20	11.2	9.60	21.3	9.55
Cr	< 0.23	0.63 B	2.73 B	5.35 B	< 1.2	1.97 B	3.37 B	4.03 B
Cu	1.89	1.48	6.49	5.85	48.2	40.4	21.6	19.0
Ni	62.9	57.6	135	127	2230	2140	22.6	21.2
Se	102	99.7	5,460	4,665	504	419	6,220	5,350
Ag	< 0.008	0.68	0.069 B	3.65	0.288	< 1.0	0.059 B	1.20 B
V	0.546 B	0.47 B	53.4	71.5	0.864 B	0.76 B	5.67 B	4.68 B
Zn	11.4	14.6	3.04 B	28.0	4,640	4,940	5.45 B	55.5

B = result ≤ MRL. Results are in µg/L.

Table 8-2
Comparison of BRL and Verification Lab ICP-DRC-MS Results for Phase II

	0930032-01		**0930032-03**		**0930032-04**		**0930032-05**	
	BRL	UA	BRL	UA	BRL	UA	BRL	UA
Sb	2.95	2.88	1.33	1.4 B	11.6	12.2	12.8	13.1

B = result ≤ MRL. Results are in µg/L

Sample Stability Investigation

About 10 months elapsed between the initial Phase I ICP-DRC-MS analyses performed at BRL and the analysis of these samples at the UA. Visible changes in the samples were seen over that time period. To evaluate the stability of the analytes, BRL reanalyzed the Phase I samples during the same month that the analyses were performed at UA. For most analytes, there was no significant change in concentration and relative percent differences were low. However, aluminum and arsenic showed instability over time, as shown in Table 8-3. The high resolution ICP-MS (HR) result is also shown for comparison. BRL-1 indicates the initial analysis, conducted in November, 2008, and BRL-2 the second analysis conducted in August, 2009.

Table 8-3
Selected Stability Study Results

0842036-01				
	BRL-1	BRL-2	UA	HR
Al	102	148	104	89
As	2.00	1.61	1.61	5
0842036-02				
	BRL-1	BRL-2	UA	HR
Al	< 58	72.2	72.0	< 30
As	17.2	7.46	6.20	42
0842036-03				
	BRL-1	BRL-2	UA	HR
Al	210	234	96	230
As	11.2	10.5	23	9.60
	BRL-1	BRL-2	UA	HR
0842036-04				
	BRL-1	BRL-2	UA	HR
Al	352	446	227	418
As	21.3	13.3	11	9.55

Results are in µg/L.

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QUALITY ASSURANCE/QUALITY CONTROL

For all analyses (standard mode ICP-MS analyses at BRL, ICP-DRC-MS analyses at BRL, HR-ICP-MS analyses at TERL, and ICP-DRC-MS analyses at UA), quality control (QC) samples were prepared and analyzed as required by Draft EPA Method 1638. All calibrations contained a more than 5 non-zero points and the achieved weighted linear correlation coefficients were at least 0.995. Initial calibration verification (ICV) standards were prepared from a second, independent source, and analyzed following each calibration. Continuing calibration verification (CCV) standards were prepared and analyzed after every ten analytical runs and at the end of an analytical sequence. All ICV and CCV standard recoveries met the quality control criteria listed in the SOP (Appendix B). In addition, each analytical batch included the following batch QC samples: method blanks, certified reference material, matrix spike (MS) samples, and matrix spike duplicate (MSD) samples.

Method Blanks

All sample preparation was performed at BRL. With each digestion batch, four method blanks were prepared. These blanks were acidified and digested in exactly the same manner as the samples. When split samples were provided to the validation and verification laboratories, the associated method blanks were also provided.

All ICP-DRC-MS data were corrected for the mean of the method blanks. All sample signals were blank corrected before reporting. We should note that this approach is not in accordance with Method 1638, which states that results should be reported without blank correction.. However, this method remains in draft form and has not been promulgated for regulatory purposes. EPA Method 1631, one of the few 1600-series methods that has been promulgated for regulatory work, does allow for method blank correction. Considering the blank level was usually negligible, blank correction may not be always necessary; however, it may account for minor reagent contamination; therefore, blank correction is included as an option in the SOP. Method blanks for HR-ICP-MS analyses were less than the associated MDLs.

Standard Reference Materials

All analyses performed by ICP-MS, ICP-DRC-MS, and HR-ICP-MS were associated with the analysis of the SRM NIST 1643e. While the analysis of a matrix-matched FGD water SRM would be preferable, such a material is not available at this time. NIST 1643e - Trace Elements in Water, is an acceptable alternative, as it is relatively high in the major cations (e.g., calcium, magnesium, sodium, etc.) and relatively low in the target elements. The data from all labs produced results for this SRM that agreed well (within 10%) of the certified values.

Matrix Spike/Matrix Spike Duplicate Samples

FGD waters frequently exhibit matrix effects due to the high levels of dissolved solids. Therefore, analyzing MS/MSD samples is required to check for such effect and correct the sample dilution factor, if required. The results from these sample analyses can also reveal the presence of uncorrected drift and chemical interferences (causing precipitation, for example). Each sample, analyzed in this study, was prepared and analyzed together with set of MS/MSD samples, in which the spike concentrations for each analyte was 1-10 times higher than the concentration of the same analyte in the native sample. To determine the appropriate spiking levels, all samples were pre-screened using standard mode ICP-MS and custom spiking standards were prepared for each sample. All MS/MSD recoveries were within the acceptance range of 75-125%, unless otherwise noted (see Quality Control Issues, below).

Quality Control Issues

The MS/MSD for arsenic (As) by ICP-DRC-MS performed by BRL on samples 0842036-02 and 0842036-04 produced high recoveries. For sample 0842036-02, the MS recovery was 147% and the MSD recovery was 143%. Sample 0942036-04 produced recoveries of 145% for both MS and MSD. Addition of carbon in the form of acetic acid was not sufficient to mitigate the positive matrix effects.

The MS/MSD for vanadium (V) by ICP-DRC-MS performed by BRL on sample 0842036-04 produced recoveries of 126% and 127%, respectively. The spiking levels were appropriate, at approximately 7 times the native sample concentration. The HR-ICP-MS result for vanadium in this sample is very close to BRL's (5.5 μg/L and 5.67 μg/L, respectively). At this concentration, vanadium is detectable but not reportable by BRL (flag B). The respective MS/MSD recoveries obtained with HR-ICP-MS were 96% and 113%. The ICP-DRC-MS verification data obtained by UA showed similar values – 4.68 μg/L for V, but matrix spike and spike duplicate recoveries were acceptable (reported 98% and 108%). The sample was reanalyzed at BRL for the Sample Stability Study about 10 months later, and the reanalysis produced a result of 5.84 μg/L (above the MRL of 2.11μg/L), with acceptable MS/MSD recoveries at 111% and 116%, respectively.

The MS/MSD for selenium (Se) by HR-ICP-MS performed by TERL on sample 0842036-03 produced recoveries of 134% and 118%, respectively. The spiking levels were appropriate, at approximately 1.1 times the native sample concentrations. The HR-ICP-MS result for Se on sample 0842036-03 is only about 10% higher than the ICP-DRC-MS result produced at BRL (which was associated with MS/MSD recoveries of 104% and 100%, respectively). The same positive bias in HR-ICP-MS spike results was monitored for one more sample. The concentration difference between the results obtained by BRL and TERL for the native sample 0842036-04, was less than 1% and the analysis of a Se MS/MSD by HR-ICP-MS for the same sample produced recoveries of 129% and 121%, respectively. However, such a high bias was missing in the BRL's results. The reason for these biases is not clear.

The SOP (Appendix B) lists many of the recommended QC samples to be prepared and analyzed in association with FGD water samples, and lists the acceptance criteria for each type of QC sample.

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DISCUSSION AND CONCLUSIONS

A detailed review was performed of data from the laboratories that participated in this study. For most elements, the results obtained by BRL following the SOP were confirmed by the HR-ICP-MS results from the TERL and verified by the ICP-DRC-MS results from the UA. As discussed earlier, a satisfactory method was not identified for aluminum and cobalt, and these elements were not included in the SOP. Silver was not detected by HR-ICP-MS, a less sensitive technique than either standard mode or DRC mode ICP-MS. The findings of the between-lab comparisons are discussed below.

Comparison of Standard Mode and DRC Mode ICP-MS

Of the eleven metals included in this study, seven (As, Cr, Cu, Sb, Se, V, Zn) demonstrated lower results when analyzed by ICP-DRC-MS, compared to standard mode ICP-MS. As shown in Figure 10-1, for four of the elements (As, Cr, Cu, and V), the percent reduction of bias using the DRC methods was large and consistent for analyte concentrations above the MRL. For Se, the effects were more moderate. Figures 10-1 through 10-4 show the percentage change in concentration for all elements included in this study when DRC is used, as compared to the standard mode ICP-MS concentrations.

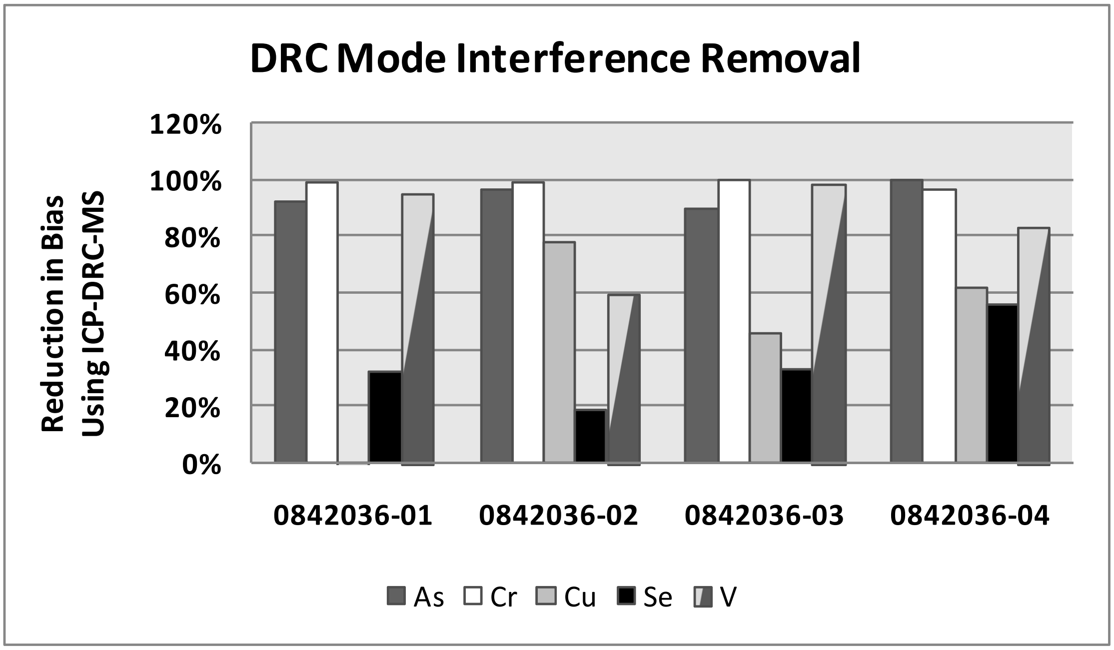

Figure 10-1
DRC Mode Interference Removal as a Percentage of the Standard Mode ICP-MS Value

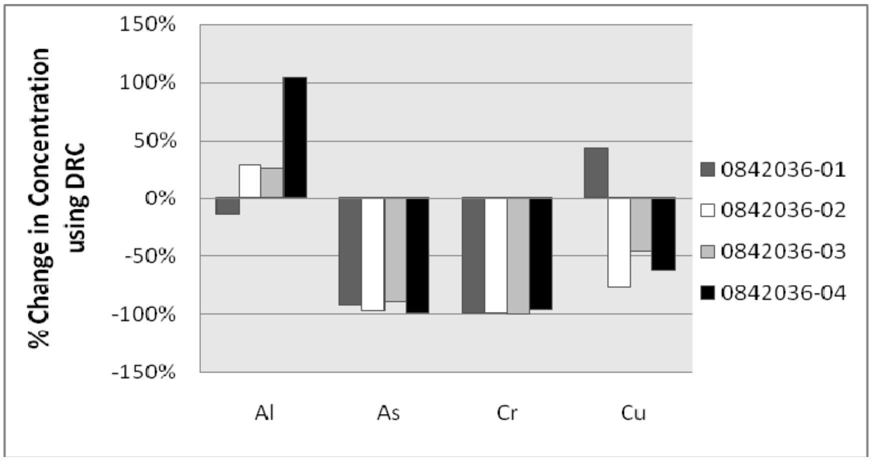

Figure 10-2
Percent Change in Concentration with DRC Usage (Al, As, Cr, and Cu)

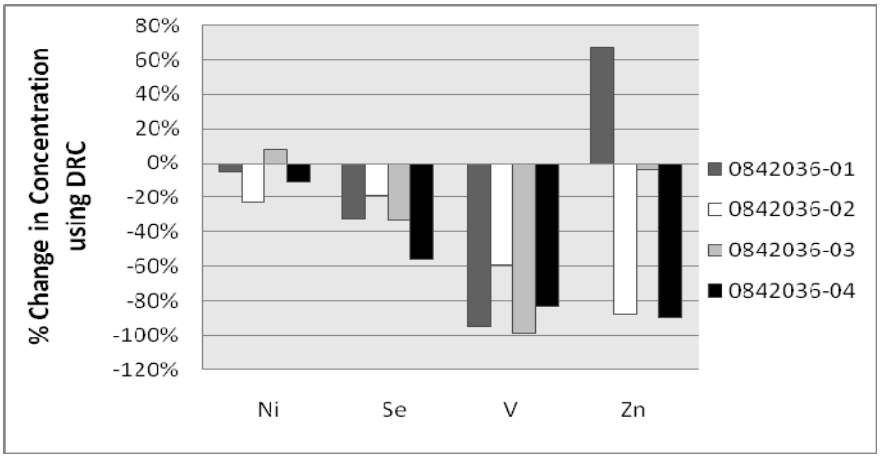

Figure 10-3
Percent Change in Concentration with DRC Usage (Ni, Se, V, and Zn)

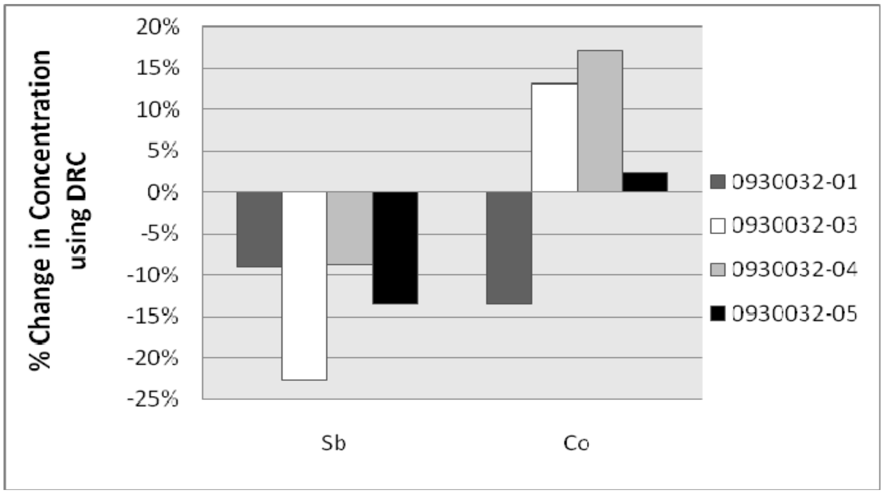

Figure 10-4
Percent Change in Concentration with DRC Usage (Sb and Co)

For the metals with a significant DRC benefit, only one element in one study sample showed an increase with DRC: Cu in sample 0842036-01. However, most of the remaining elements in the same sample showed a substantial decrease in their apparent concentration with DRC mode. Using standard ICP-MS for these five metals can produce results that are biased high by up to two orders of magnitude.

Results for Zn, Ni, and Sb showed some reduction of bias using DRC, but the extent of the reduction varied among samples. As shown in Table 10-1, two samples had significant reductions in Zn concentrations using DRC (88-90%), while the other two samples showed little or no reduction. In fact, sample 0842036-01 produced higher results for Zn by ICP-DRC-MS (11.4 μg/L) than by standard mode ICP-MS (6.82 μg/L). The ion $^{26}Mg^{40}Ar$ is a major interference for ^{66}Zn, and this sample was ~10 to 20 times lower in magnesium (Mg) than the other samples, suggesting that this sample has less of a high bias in standard mode. The TERL HR result was < 14 μg/L; thus, there is no value available to validate the result in this sample.

Table 10-1
Comparison of Zinc Results by ICP-DRC-MS and Standard Mode ICP-MS

	0842036-01	**0842036-02**	**0842036-03**	**0842036-04**
Standard Mode ICP-MS, μg/L	6.82	24.9	4,840	54.8
ICP-DRC-MS, μg/L	11.4	3.04	4,640	5.45
% Reduction by DRC	-67%	88%	4%	90%

Ni results were about the same in standard and DRC mode, which was surprising because interferences are expected when Ca, Na, and Cl are present at high concentrations as in FGD waters (possible interferences from $^{46}Ca^{16}O^+$, $^{23}Na^{39}K^+$, $^{43}Ca^{16}O^1H^+$ on $^{62}Ni^+$ or $^{23}Na^{37}Cl^+$ on ^{60}Ni). Sb results averaged 13 percent higher by standard mode ICP-MS than by DRC.

No comparison could be made for Ag because concentrations were very close to the limit of detection. Additionally, without a HCl addition to the sample diluents, Ag precipitation occurred.

A reduction in polyatomic interferences was not evident for Al in any of the samples; in fact, as shown in Figure 10-2, the concentration appeared to increase when DRC was used.

The results for Co were generally equivalent by standard mode ICP-MS and ICP-DRC-MS; however, these results were consistently and significantly higher than the results by HR-ICP-MS. This discrepancy is discussed below.

Comparison of ICP-DRC-MS and HR-ICP-MS Results

Figure 10-5 through Figure 10-14 show a comparison of the HR results reported by TERL and the corresponding BRL ICP-DRC-MS results for all study elements. The verification analyses from UA are also included in the plots. Concentrations are shown normalized to the highest concentration reported by any of the three laboratories (highest value = 100%).

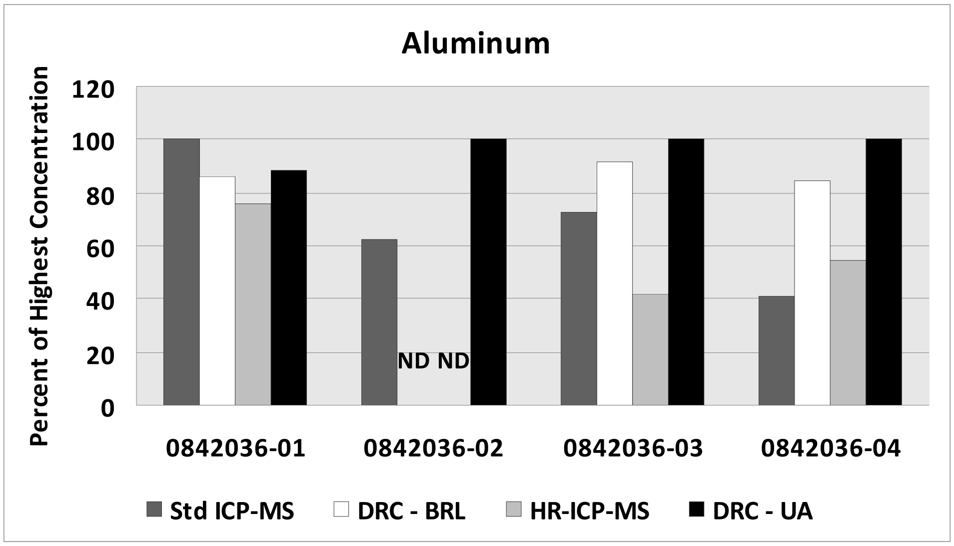

Figure 10-5
Comparison of Aluminum Concentrations by ICP-DRC-MS and HR-ICP-MS

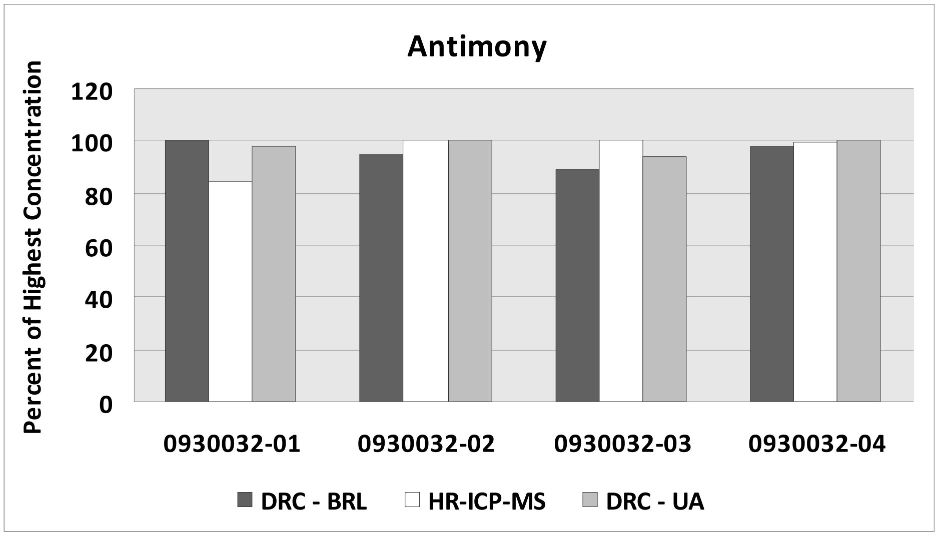

Figure 10-6
Comparison of Antimony Concentrations by ICP-DRC-MS and HR-ICP-MS

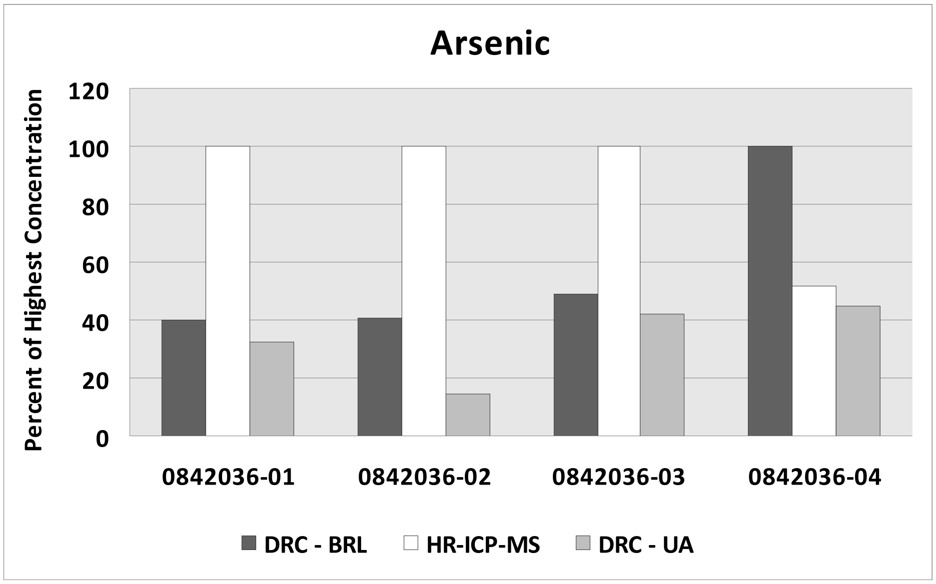

Figure 10-7
Comparison of Arsenic Concentrations by ICP-DRC-MS and HR-ICP-MS

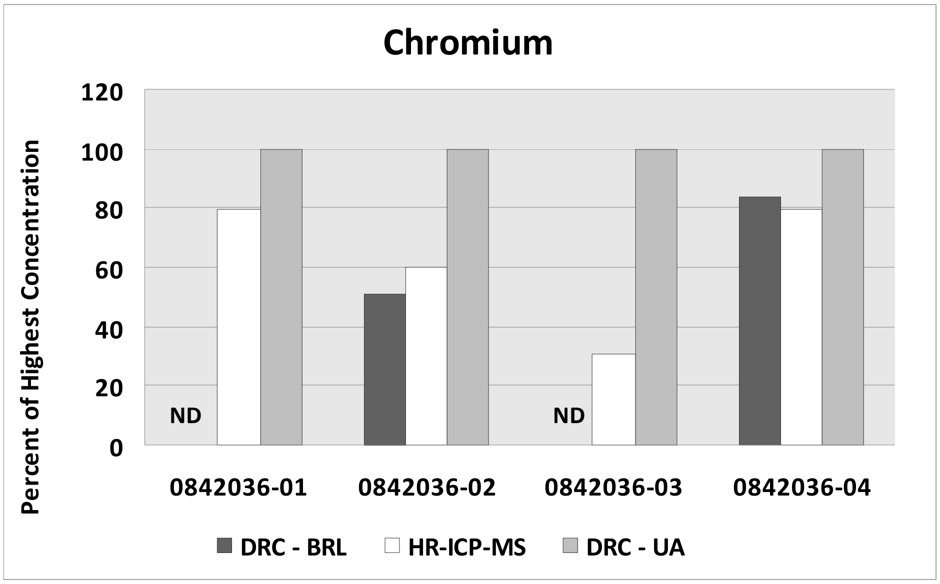

Figure 10-8
Comparison of Chromium Concentrations by ICP-DRC-MS and HR-ICP-MS

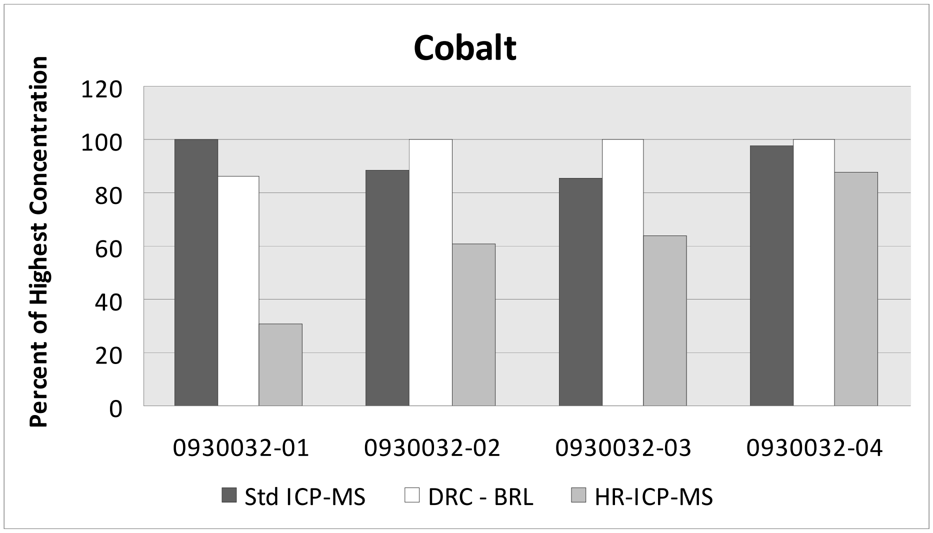

Figure 10-9
Comparison of Cobalt Concentrations by ICP-DRC-MS and HR-ICP-MS

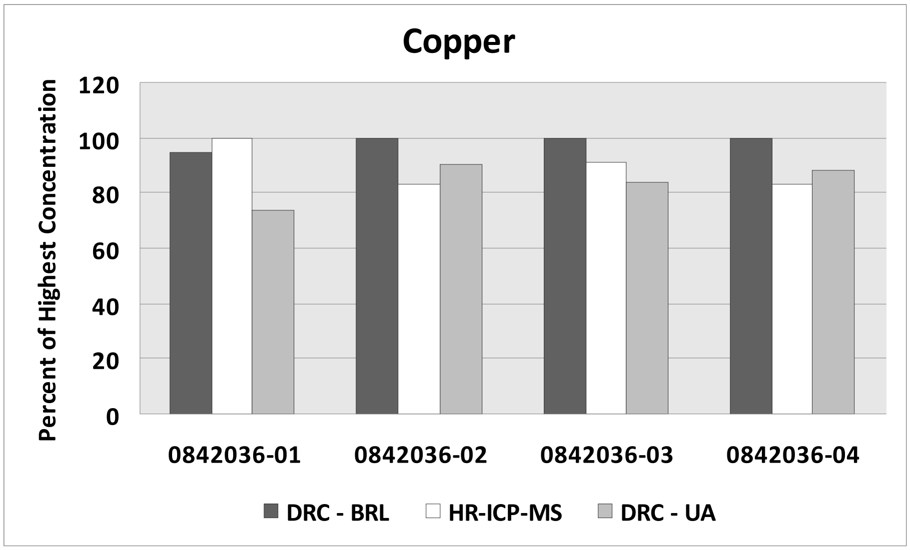

Figure 10-10
Comparison of Copper Concentrations by ICP-DRC-MS and HR-ICP-MS

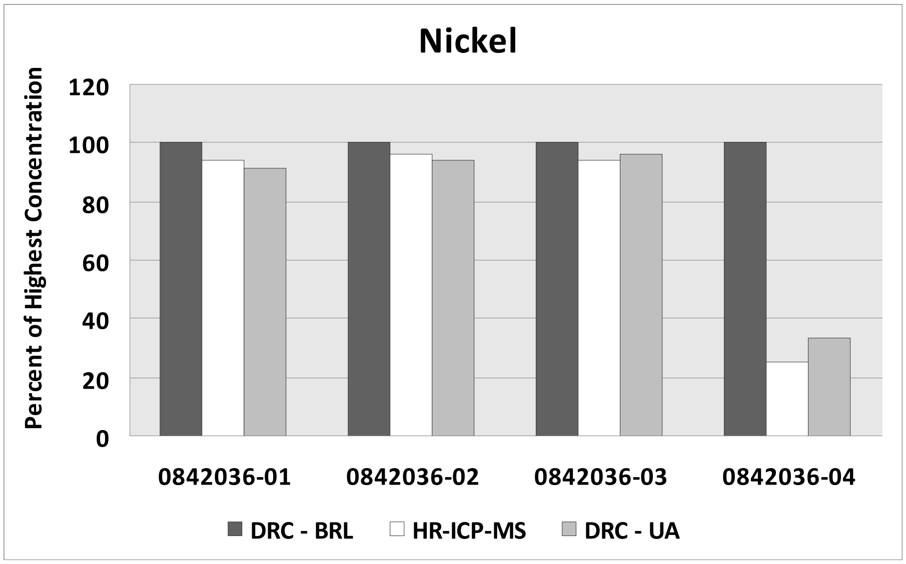

Figure 10-11
Comparison of Nickel Concentrations by ICP-DRC-MS and HR-ICP-MS

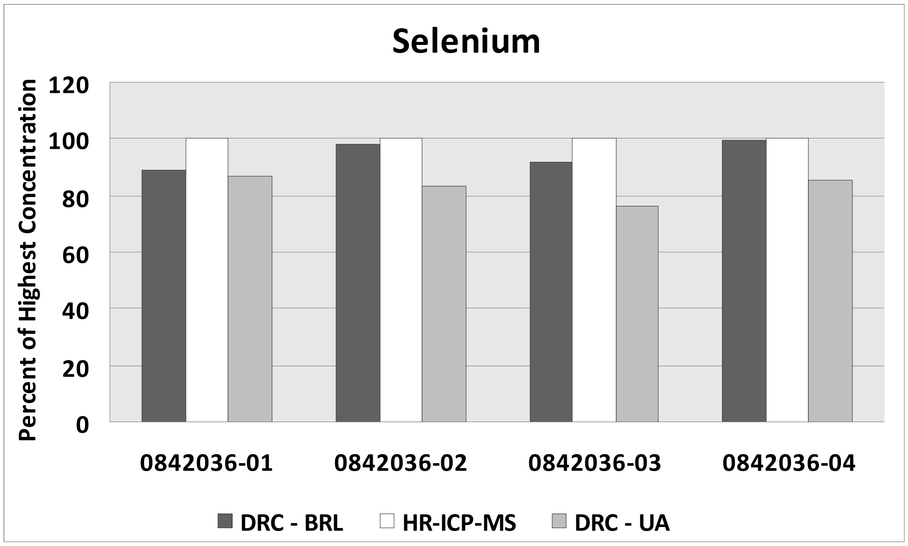

Figure 10-12
Comparison of Selenium Concentrations by ICP-DRC-MS and HR-ICP-MS

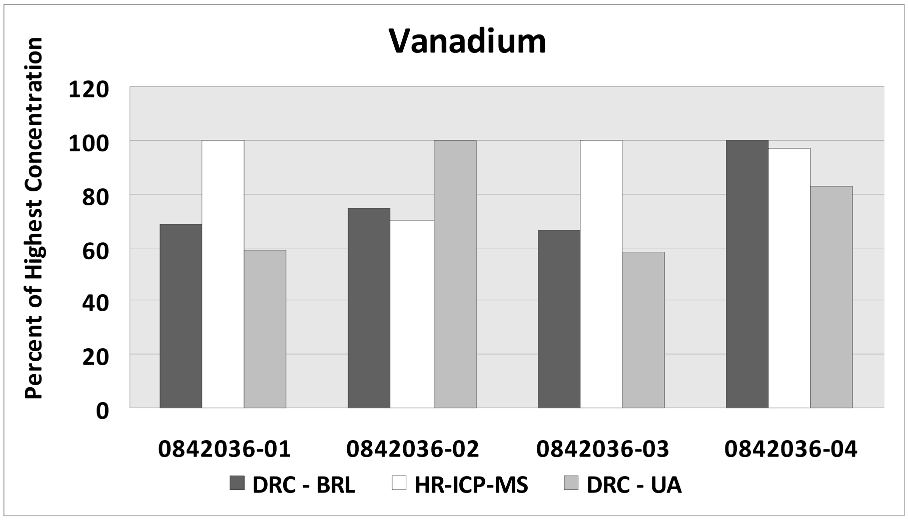

Figure 10-13
Comparison of Vanadium Concentrations by ICP-DRC-MS and HR-ICP-MS

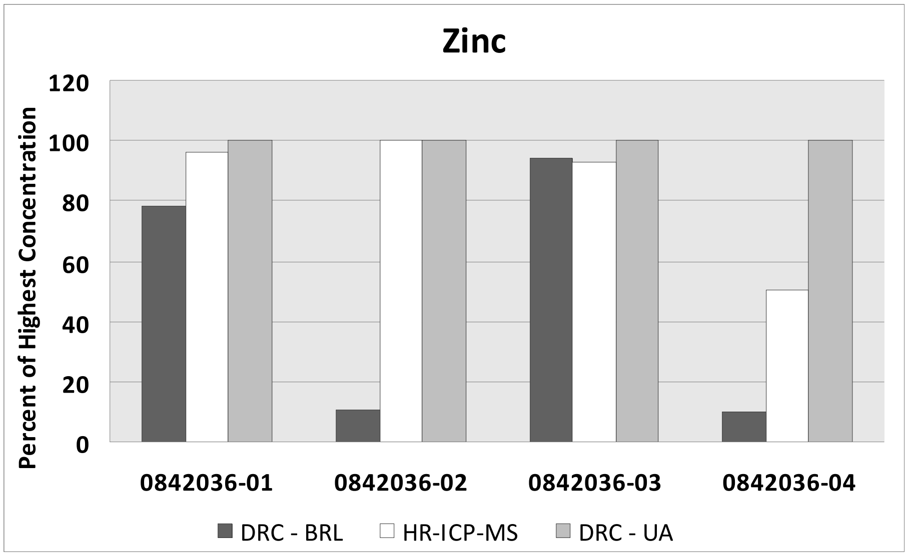

Figure 10-14
Comparison of Zinc Concentrations by ICP-DRC-MS and HR-ICP-MS

For element concentrations above the respective MRLs for the ICP-DRC-MS and HR-ICP-MS instruments, the elements Sb, Cr, Cu, Ni, Se, V, and Zn showed a good correlation between the BRL ICP-DRC-MS results and the TERL HR-ICP-MS results. Ag could not be compared because HR results were below detection limits in all samples.

HR-ICP-MS is often considered the "gold standard" for metals analysis as it has the ability to differentiate between a target metal signal and the signal of a nearby polyatomic interference, leading to a more definitive result. While this is true for many of the elements, there are still elements in some matrices which cannot be accurately quantified. Some the biggest errors in non-HR-ICP-MS analyses are caused by polyatomic interferences. While HR-ICP-MS can be employed for successfully resolving the polyatomic interferences, it does so at the expense of higher detection limits (and cost of analyses). However, for some elements, such as As, even at a very high resolution setting, there is not sufficient resolution for accurate metal quantification, especially in a complex matrices such as FGD water.

Comparing the As results from standard mode ICP-MS analysis to ICP-DRC-MS results obtained by both BRL and UA, it is obvious that DRC mode is effective in reducing the significant polyatomic interferences observed in standard mode ICP-MS. However, as shown in Table 10-2, the HR-ICP-MS results in three of the four samples are intermediate between the standard and DRC mode ICP-MS, indicating that the high resolution instrument cannot completely resolve the polyatomic interferences for As. The HR-ICP-MS results are biased high. TERL researchers concurred with this interpretation, which was corroborated by visual inspection of the mass spectra peaks. We have not identified an appropriate validation method for As, but that DRC is strongly preferred to standard mode ICP-MS because it is clearly reducing bias due to polyatomic interferences.

Table 10-2
Comparison of Arsenic Results by Standard Mode ICP-MS, ICP-DRC-MS and HR-ICP-MS

Sample ID	Std Mode ICP-MS	ICP-DRC-MS (BRL)	ICP-DRC-MS (UA)	HR-ICP-MS
0842036-01	25.9	1.61	1.61	5
0842036-02	512	7.46	6.20	42
0842036-03	105	10.5	9.60	23
0842036-04	3210	13.3	9.55	11

In evaluating the results for Al by ICP-DRC-MS and HR-ICP-MS, no clear understanding was gained as to which analytical technique produced more accurate data. This is primarily due to the relatively high detection limit for Al by both techniques and the high risk of contamination for this ubiquitous element. As the ICP-DRC-MS results are higher than the standard mode ICP-MS results, there is no indication that DRC is an appropriate technique for this element. Al is not included in the SOP.

For the analysis of Co, the polyatomic interferences from CaO affecting the standard mode ICP-MS results were not reduced by any of the DRC settings investigated for this study. The HR-ICP-MS results for Co were generally lower than the standard mode ICP-MS and ICP-DRC-MS results, though within the range of acceptable analytical variability. This finding indicates that Co is likely biased high in standard mode ICP-MS but that DRC conditions to address the interferences have not yet been identified. Due to the lack of an adequate DRC method, Co is not included in the SOP.

ICP-DRC-MS Verification Analyses

The purpose of these verification analyses was to determine if a laboratory with less experience in ICP-DRC-MS analyses could perform the procedure as written. A Draft SOP was provided to the UA along with splits of the Phase I and Phase II samples. The verification laboratory was not told the sample concentrations, and did not receive any initial assistance in carrying out the procedures. Following initial analyses that did not meet QC requirements for matrix spike recoveries due to incorrect spiking levels, a revised Draft SOP was provided to UA for repeat analyses The feedback received from UA resulted in the clarification of many sections of the Draft SOP, most significantly the areas addressing proper quality control samples, calculations for appropriate spiking levels for MS/MSD samples, and the importance of using a high-performance sample introduction system.

In general, the final verification laboratory results compared well with the ICP-DRC-MS data produced at BRL. Noted exceptions were As and Zn in some samples.

In comparing the initial As values for Samples 2 and 4 from BRL with the data from UA (Table 10-2), the UA results are significantly lower; however, as demonstrated in the sample stability study discussed above, when BRL reanalyzed the samples near the same date as the UA analyses, the results were comparable.

The Zn data produced by UA was consistently higher than the ICP-DRC-MS results generated by BRL. The HR-ICP-MS results were not helpful in validating the ICP-DRC-MS results, as most sample concentrations for Zn were below the HR-ICP-MS detection limits. For the one sample with a high enough concentration to be detectable by HR-ICP-MS (0842036-03), there was good correlation between BRL's ICP-DRC-MS result and the HR-ICP-MS results. The UA ICP-DRC-MS result was higher than both BRL's reported value and the result by HR-ICP-MS. There is no evident reason for the discrepancy between the ICP-DRC-MS results from BRL and UA; however, polyatomic interferences are always additive, suggesting that the BRL and HR-ICP-MS data are accurate.

Conclusions

The ICP-DRC-MS SOP developed during this project was validated using HR-ICP-MS and its usability was verified with ICP-DRC-MS in a second laboratory that had no experience in analyzing FGD waters. Based on this research, the procedures detailed in the SOP were found to be useful for reducing or eliminating polyatomic interferences that impact standard mode ICP-MS for the following elements: arsenic, antimony, chromium, copper, selenium, vanadium, and zinc.

For arsenic, some FGD water samples from certain power plants consistently exhibit excessively high recoveries on matrix spike analyses. An attempt was made to resolve this issue by adding carbon (in the form of organic solvent) to the samples and standards. This approach was not completely successful, and more research was needed to resolve this problem. High-resolution ICP-MS was found to not be an appropriate method to validate the ICP-DRC-MS measurements, as it was determined that interferences impact the HR result for this element. Nevertheless, ICP-DRC-MS appears to largely eliminate positive bias due to polyatomic interferences, and is showing a significant improvement in accuracy over standard mode ICP-MS.

Copper and zinc exhibited more variability than the other elements in their response to DRC interferences removal. One of four samples showed an increase in concentration of these two elements with DRC use (see Table 6-3). The reason for this discrepancy is unknown; but the ICP-DRC-MS results were in the same range as the HR results.

Two elements were not found to benefit from the use of DRC: nickel and silver. However, these elements can be included in a multi-element analysis using DRC with no loss of accuracy.

Cobalt and aluminum were evaluated but were not included in the SOP, as no DRC settings were identified that improved accuracy in all of the study samples (as compared to the HR results).

Suggestions for Further Research

Concentrations of aluminum and arsenic in FGD water samples were found to change over time. Improved sample preservation techniques should be evaluated in future research. It is likely that some samples are prone to the formation of precipitates following sample acidification, and therefore target analytes may co-precipitate, thus creating a low bias to the sample results.

The cell gases used in the EPRI SOP were selected to provide a balance between accuracy and simplicity (fewest number of analytical runs). Therefore, only oxygen and ammonia were evaluated in this study. However, future research should also evaluate methane (CH_4) as a DRC gas for the analysis of Ni and Se in environmental samples. The use of CH_4 as a DRC gas will break the $Ar\text{-}Ar^+$ dimer more effectively than the use of O_2, thus allowing for increased sensitivity in the analysis of Se and the use of additional isotopes for quantitation. CH_4 will also be able to mitigate the $Ca\text{-}O^+$ polyatomic interference much more effectively than NH_3, allowing for the use of the ^{60}Ni isotope, which is a much more prevalent isotope than ^{62}Ni. The use of CH_4 as the DRC reaction gas may also allow the use of Sc as an internal standard. This element cannot be used with NH_3 gas, which reacts with Si in the samples to form a polyatomic interference. The use of Sc as an internal standard may be more appropriate for the determination of Al and other low mass analytes.

Future method development for the determination of As in FGD water samples should focus on sample introduction by hydride generation, which may produce better instrument sensitivity, allowing for lower detection limits and reduced sample loading. The analysis of As is often effected by sample constituents that interfere with accurate quantification. This can result in the need to extensively dilute samples, raising the uncertainty in the analysis. Hydride generation could be used as a sample introduction mechanism that would be capable of separating the amenable target analytes, such as As and Se, from the matrix of the samples. The much higher efficiency of analyte transport by hydride generation (compared to nebulization) could also result in lower detection limits, allowing for quantification of samples with lower As concentrations.

Future method development for the determination of Cu in FGD water samples should include sourcing a cleaner supply of HCl and the evaluation of the use of methane (CH_4) as a cell reaction gas. The use of CH_4 as the DRC gas may allow for the quantification of both Cu isotopes.

While many different elements were investigated for internal standards in this study, there are other elements that were not evaluated, but may demonstrate improved performance. For example, the use of tellurium (Te) as an internal standard for the determination of As and Se may be more appropriate due to its similar ionization potential and electron affinity.

11

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[1] *Guidelines for FGD Water Sampling and Analysis: Trace Metals.* EPRI, Palo Alto, CA: 2009. 1018223.

[2] National Institute of Standards and Technology Standard Reference Material® NIST 1643e: Trace Elements in Water.

[3] Certificate of Analysis for Magnesium 10.00 mg/mL Standard, Lot Number 0825220, High Purity Standards, Charleston, SC, 29423.

[4] *Isotopic Compositions of the Elements 1989*, Pure Appl. Chem., Vol. 63, No. 7, pp. 991-1002, 1991. © 1991 IUPAC.

A
METHOD DEVELOPMENT SUMMARIES

Aluminum

Aluminum (Al) is monoisotopic at mass 27. The HR-ICP-MS prescreening suggested that less than 1% of the apparent Al concentration measured by standard ICP-MS was the result of an interference; however, due to the high levels of this element occasionally observed in FGD water (up to several hundred mg/L in unfiltered, treated effluent), Al was included in the EPRI study.

Initial optimization of the cell gas flow was performed using both oxygen (O_2) and ammonia (NH_3) as DRC gasses to evaluate the relative potential for the removal of possible polyatomic interferences such as $^{10}B^{16}O^+$ and $^{13}C^{14}N$. There was no apparent improvement in background levels at any of the cell gas flow rates evaluated, suggesting that Al determination would not show significant benefit from analysis in DRC mode with the proposed gases. Further, no DRC optimization settings that were initially evaluated produced a method that gave an acceptable recovery for the certified reference material NIST 1643e [2].

Instrument calibration curves for Al were evaluated with different DRC settings in order to determine if any would allow simultaneous quantification of Al with the other elements included in this study. Using NH_3 as a DRC gas, various DRC optimization settings produced acceptable weighted-linear calibration curves (correlation coefficient of ≥ 0.995, individual calibration standard recoveries between 80-120%); however, none of the optimization settings evaluated produced a measured concentration for SRM NIST 1643e within 10% of the certified value. Interestingly, analysis without the use of internal standardization produced a better SRM recovery. Following consultation with engineers at PerkinElmer, the axial field technology (AFT) voltage was raised to 400 V. Subsequent analyses of the SRM showed a dramatic improvement in the recoveries, to within 5% of the certified value.

These experiments showed that adjusting the AFT voltage could improve the accuracy of results; however, setting the AFT voltage to 400 V greatly lowered instrumental sensitivity. Due to the need to dilute FGD water samples by many times to reduce levels of dissolved solids entering the ICP-MS, very low detection limits are needed for this matrix. Therefore, running the instrument at 400 V was not an option. AFT voltage was lowered to 325 V, which produced a slightly lower SRM recovery than the SRM recovery at 400 V, but maintained sufficient instrument sensitivity.

With the AFT voltage set to 325-350 V, the SRM recoveries for Al were acceptable when internal standardization was not utilized. It was suspected that extended instrument conditioning (exposing the instrument to the FGD water matrix or a similar high-matrix sample, such as a solution of sodium acetate, for a lengthy period of time) could improve the SRM recovery, while at the same time, a lower than 400V AFT potential would produce improved instrument sensitivity.

A number of internal standards were evaluated at various AFT voltage settings, with most efforts focusing on the use of scandium (Sc) as an internal standard. Sc is typically used as an internal standard for Al during analysis by ICP-MS in standard (non-DRC) mode, but gallium (Ga) is the internal standard recommended by PerkinElmer for DRC analysis for Al. However, analysis of

FGD water samples showed that both Sc and Ga were not appropriate internal standards for Al in DRC mode. Sc was prone to silicon-based polyatomic interferences, and Ga exhibited erratic results at low sample dilutions (high levels of FGD water sample matrix constituents). Experiments showed that the inaccuracy of the Ga internal standard correction was not due to potentially different sensitivity regimes for the lower concentration target analytes and the higher-concentration internal standard elements. Sc and Ga were both removed from consideration as possible internal standards for Al.

Experiments were performed evaluating the use of germanium (Ge) and rhodium (Rh) as potential internal standards for Al. Matrix spikes (MS) were prepared on FGD water samples that were spiked with Al, and the results showed poor spike recoveries. Samples with low Al concentrations produced MS recoveries below 70%, while samples with higher Al concentrations produced MS recoveries around 120%. Upon further review of those results, it was later suspected that the variable MS recoveries were due more to the low dilution factors at which these samples were analyzed.

Following the issues encountered when evaluating the use of Ge and Rh as internal standards for Al, the DRC gas flow rate optimization was repeated at a wider range of rejection parameter q (RPq) settings. The RPq setting determines the alternating current voltage on the DRC quadrupole and is used to decrease the stability of lower mass ions as they travel through the DRC quadrupole. The goal of this experiment was to determine if DRC gas flow rates might have an effect on background levels, and to confirm that very low levels of polyatomic interferences were, in fact, being mitigated by the use of the DRC. The DRC cell gas flow rate settings seemed to have a minor effect on the spiked sample to background ratio, compared to RPq settings. While the spiked sample to background ratio remained constant at each cell gas flow rate, the ratio was lower when the RPq was set to higher values. A cell gas flow rate optimization was performed using NH_3 to determine the setting that would give the optimum sensitivity for the widest range of target elements, and a value of 0.6 mL/minute was determined to be ideal.

Al was subsequently analyzed at a range of RPq values in order to understand why method development had been relatively unsuccessful up to that point. After an extended instrument conditioning period, including the analysis of a sodium acetate solution and quite a few FGD water samples, the instrument was calibrated for Al and the analysis of the SRM NIST 1643e produced acceptable recoveries of 90-110%. During these experiments, the RPq value for Al was set to a very high value of 0.85. A lengthy analytical run was processed to evaluate the stability of the instrument and the QC sample results at these settings, and while the sensitivity was somewhat limited at this RPq value, the instrument calibration curves and the QC sample results were acceptable. In addition, equivalent results were obtained with the RPq value set to 0.80 or 0.85.

Some of the Al results for samples analyzed by ICP-DRC-MS produced higher results than those from the analyses by ICP-MS in standard mode. While this could be caused by the formation of CN, this would seem unlikely due to the presence of acetic acid in the internal standard solution and the use of NH_3 as a cell reaction gas. The higher results produced by the DRC method could be the result of differences in internal standard corrections using Sc as an internal standard in standard (non-DRC) mode ICP-MS and Rh as an internal standard in DRC mode. Bias due to internal standards failure was assessed through MS sample recoveries.

While attempting to determine instrument detection limits (IDL) with a sample introduction rate of 200 µL/minute, it was found that an extended analytical run of FGD water samples produced acceptable MS recoveries and a calculated IDL in the range of 0.2 µg/L. However, Al recoveries for spiked samples drifted above acceptable limits over time. Upon further review of the data, it was suspected that the drift was the result of inadequate sample dilution. Another extended analytical run of FGD water samples was analyzed to evaluate method stability. Instrument drift was acceptably low; however the relative standard deviation (RSD) for n = 8 samples was over 5%, potentially due to the still low dilution factor at which the samples were analyzed. All MS recoveries for samples that were spiked at appropriate levels were within acceptance criteria.

In the final stages of method development, it was determined that instrument drift and analytical precision could be improved by analyzing samples at higher dilution factors. However, this may result in some sample results falling below the dilution-adjusted MDL.

It was concluded that the DRC method for Al analysis was unsuccessful due to higher apparent Al concentration obtained for many of the samples, analyzed by ICP-DRC-MS mode, compared to both HR-ICP-MS and standard mode ICP-MS results.

Antimony

Antimony (Sb) presents analytical challenges similar to silver. It precipitates in some matrices, but also shows carryover effects that were not experienced in Ag determinations. Antimony has two isotopes at mass 121 and 123. Samples high in Br may be biased high if quantified by ^{121}Sb due to the formation of the polyatomic interferent $^{40}Ar^{81}Br^{+}$. Bromine may be elevated in FGD water samples if brominated activated carbon or bromine is used in the power plant for mercury removal. This interference was successfully removed in DRC mode with NH_3. Responses were monitored at both Sb masses throughout the method development study and both isotopes showed agreeable results, but only ^{121}Sb is included in the final SOP due to occasional difficulty experienced by BRL in achieving a linear calibration with mass 123.

After sufficient instrument conditioning (at least one hour of repeated analyses of an FGD water sample diluted to approximately 0.5% TDS), DRC cell gas flow rate and RPq value optimizations were performed. It was determined that acceptable sample-to-noise ratios (S/N) for Sb could be obtained using NH_3 as a reaction gas with a sample uptake rate of 200 µL/minute.

The NH_3 cell gas flow rate was investigated over the range of 0.2 - 2.0 mL/minute. The flow rate was optimized for the highest S/N at 0.5 mL/minute. The analysis of all Phase I analytes gave comparable or better results at 0.6 mL/minute; therefore, a DRC cell gas flow rate of 0.6 mL/minute was selected with very little compromise to the Sb S/N. RPq values were investigated from 0.4 to 0.9, and optimal settings were found to be in the range of 0.75 to 0.8. At RPq values above 0.85, the S/N was greatly reduced.

Rh and In were evaluated as possible internal standards. Based on the recoveries of the SRM NIST 1643e and the matrix spikes, In was found to be the better internal standard. It should be noted that there was not a significant reduction in the calculated method detection limit for Sb by ICP-DRC-MS when compared to standard mode ICP-MS.

For all samples, DRC results yielded concentration results that were less than the standard mode results. This may be due to a reduction of polyatomic interferences, or it may be a result of calculating the DRC concentrations with a different internal standard than that used for the standard mode analyses.

Arsenic

Analytical runs for the determination of As and selenium (Se) are often performed concurrently. This report presents a new method that uses the same cell reaction gas (oxygen) for the both analytes. Arsenic is a mono-isotopic element and have mass-number equal to 75. This mass suffers from a substantial interference in presence of chloride ($^{40}Ar^{35}Cl^{+}$). The developed method involves use of oxygen (O_2) as a cell reaction gas to form AsO, and therefore allows successful quantification of this element as a molecule at mass 91 ($^{75}As^{16}O^{+}$). Probability of $^{40}Ar^{35}Cl^{16}O^{+}$ formation in the reaction cell is negligible and arsenic is quantified free of chloride interferences.

Historically, analyses of FGD water samples at BRL for arsenic (As) produced MS recoveries for some samples that were well above the acceptable limits. This affect appeared to be power plant specific, and was not mitigated by increased dilution of the samples. The addition of the carbon source methanol (MeOH) to the internal standard solution, which has the effect of increasing the ionization of As in the plasma, initially seemed to improve the MS recoveries.

The HPLC-grade MeOH that was available in the BRL lab was too high in Se to use for this purpose; therefore, we switched our carbon source to trace metals-grade acetic acid. When FGD water samples were analyzed with the acetic acid addition, the MS recoveries were still above the acceptance limits, despite the addition of a carbon source, which was indication of presence of a positive matrix effect. However, the sensitivity of the method for As can be so much improved by using optimized DRC settings and a high-performance sample introduction system, that it is possible to dilute the samples further, resulting in acceptable MS recoveries for FGD water samples with a sample flow rate of 400 μg/L.

There are still some FGD water samples for which the current As method is not adequate. EPRI is continuing to work with BRL on resolving these issues. Future method development will focus on sample introduction to the ICP-DRC-MS by hydride generation, which may result in higher and unified ICP-MS sensitivity. This could result in lower detection limits and reduced matrix loading.

Chromium

Chromium (Cr) has two isotopes at masses 52 and 53. BRL had previously developed a method for the determination of Cr in urine by ICP-DRC-MS, which was used as the basis for this research. However, the existing DRC optimum settings proved inadequate to remove the polyatomic interferences created by the higher levels of chloride (usually present at high concentrations in FGD water samples) and carbon (present, if acetic acid is added to the internal standard). The formed interferences are $^{35}Cl^{16}O^{1}H^{+}$ and $^{40}Ar^{12}C^{+}$ (at mass 52), and $^{37}Cl^{16}O^{+}$ and $^{40}Ar^{13}C^{+}$(at mass 53). Furthermore, when Sc (the internal standard most appropriate for use in urine analyses) was used as an internal standard, a significant positive bias was observed for Cr results in FGD water samples. This bias was determined to be due to the creation of silicon-based polyatomic interferences when NH_3 is used as a cell reaction gas.

Multiple RPq settings were evaluated during analyses of FGD water samples, associated MS samples, and spikes of polyatomic parent products, containing C and Cl. A variety of internal standards were evaluated, as were the effects of methanol addition and increased RF power settings (“hot plasma”). The effects of sample flow rate, DRC gas flow rate, and different RPq value settings were evaluated with the aim of minimizing the equivalent concentrations of polyatomic interferences. It was determined that polyatomic interferences were relatively more pronounced at lower sample flow rates. The NH_3 cell gas flow rate was optimized for highest interferences removal for a variety of elements, and it initially appeared that setting the cell gas flow at 0.5 mL/minute would give the best accuracy; however, earlier analyses showed that slightly higher cell gas flow rates reduced the formation of polyatomic interferences more efficiently in difficult matrices, rich in TDS. Thus, a DRC cell gas flow rate of 0.6 mL/minute of NH_3 was selected.

It was initially suspected that a long period of instrument conditioning was required in order to provide suitable instrument stability; therefore, after an extended instrument conditioning period during which sodium acetate was aspirated to the instrument, two extended analytical runs were analyzed to evaluate instrument stability. In the first run it appeared that with the RPq value set to 0.80, both isotopes ^{52}Cr and ^{53}Cr would give adequate sensitivity, while with the RPq value set to 0.85, only the isotope ^{52}Cr gave an adequate S/N ratio. For ^{53}Cr, an RPq value of 0.75 seems adequate to overcome most polyatomic interferences. Both isotopes were measured during all experiments and results for both isotopes were very similar. After an instrument conditioning period, an extended analytical run of FGD water samples was performed. The Cr results for multiple replicates were consistent, and the resulting RSDs for n = 8 replicates of each of the FGD water research samples were well below 10%. MS samples were prepared with a variety of Cr spiking levels, and all recoveries for appropriately spiked samples were within the acceptance criteria. Analyses were attempted without pre-conditioning the instrument; however, this resulted in significant drift for other target elements. Only ^{52}Cr results (isotope, which has a > 8-fold higher relative natural abundance), measured at an RPq of 0.75, are reported in this report.

Instrument detection limit (IDL) studies for Cr were analyzed at a variety of sample flow rates. While lower sample flow rates produce better instrument stability, it was determined that a minimum sample flow rate of 200 µL/minute is necessary to achieve acceptable detection limits. A mixed-acid diluent consisting of 1.0% concentrated HNO_3 and 0.5% concentrated HCl (v/v) was also utilized, in order to allow for the simultaneous determination of Ag. The calculated IDL with ^{52}Cr was equivalent to that obtained in standard mode ICP-MS(0.04 µg/L). Method stability was additionally confirmed by the repeated analysis of a FGD water sample, diluted to approximately 1% TDS. Rhodium internal standard recoveries and continuing calibration verification (CCV) standard recoveries showed minimal drift after repeated analysis of diluted of FGD waters.

Another IDL study was performed, again after a lengthy instrument conditioning period. This IDL study demonstrated excellent precision; however, the instrument showed drift over time. It was suspected that AFT voltage could be adjusted to provide better instrument stability; therefore, an AFT voltage optimization was performed using vanadium (V) as the target analyte and a diluted FGD water sample as matrix. Despite the best sensitivity was achieved at an AFT voltage of 350 V, the AFT voltage was raised to 375 V, as the difference in sensitivity from 350 V to 375 V was minimal, and a higher AFT voltage setting produces better internal standard correspondence between blank samples and FGD water samples. Optimization of the AFT value was done with V but all the elements investigated in this report did benefit from the increased AFT voltage.

As a side note, early efforts to determine the optimized DRC settings that would overcome polyatomic interferences for Cr determination were hindered by apparent contamination of our stock standards. This made it appear that higher levels of polyatomic interferences were present than were actually being created. Since BRL does not receive certificates of analysis for elements other than the principal analyte, it was impossible to conclusively determine the source of the contamination. However, it was suspected that at least some of the contamination was present in the standards when they were purchased, as the levels of contamination as the "typical" background levels described by the manufacturer would have been sufficient to produce the levels observed in our samples.

Cobalt

Cobalt (Co) is monoisotopic at mass 59 and is affected by a major interference from calcium (as $^{43}Ca^{16}O^+$) in FGD waters. Levels of Ca in the Phase II samples ranged from 700-5,700 mg/L, suggesting that the risk of a high bias to Co data by standard mode ICP-MS from polyatomic interferences is high (this was confirmed by high resolution ICP-MS).

DRC method development was first performed using NH_3 as a cell gas with a sample introduction flow rate of 200 µL/minute. Initial experiments using the DRC optimization settings, developed for the Phase I elements determined that NH_3 was not adequate to remove the polyatomic interferences. An aqueous Cr standard solution, spiked with 10 mg/L of Ca was used for this interferences removal test. At a cell gas flow rate of 0.6 mL/minute with RPq values ranging from 0.7 - 0.9, the Ca interference was not efficiently removed. There was a significant reduction in the formation of CaO when the levels of Ca in a spiked standard were below 5 mg/L; however, FGD waters have Ca levels much higher than this, so the finding did not have a significant impact on this study.

Cell gas flow rates were next evaluated in the range of 0.2 - 2.0 mL/minute. No improvement in interference reduction was observed at either higher or lower cell gas flow rates. RPq values from 0.4 - 0.85 were also evaluated. Although we would expect higher RPq values to eliminate more interferences, this effect was not seen for this analyte.

The effect of raising the applied radio-frequency power to the RF-coil in an attempt to decrease the formation of the polyatomic interferences was investigated next. An RF-power setting of 1500 W had been utilized for all of the DRC method development to date. Raising the RF-power to 1600 W did not mitigate the CaO formation.

The effect of changing the sample introduction flow rate was investigated at two levels – 100 µL/minute and 400 µL/minute. Lowering the sample introduction flow rate did not decrease the interferences observed on mass 59, and raising the sample introduction flow rate caused an increase in the amount of polyatomic interference seen at this mass.

Methane (CH_4) was evaluated as a reaction gas using the same cell gas flow rates and RPq values. The results were equivalent to NH_3 gas, with no decrease in the observed polyatomic interferences.

The best background equivalent concentration achieved for Co was 1.4 µg/L, indicating that CaO could not be removed at levels necessary for the accurate quantification of low-level Co in FGD waters. In fact, all samples yielded higher results in DRC mode than in standard mode. This may be due to the use of a different internal standard, or a result of the creation of new polyatomic interferences in the DRC cell that are not properly attenuated by the DRC settings.

The reported results for all study samples were obtained using Rh as the internal standard, an NH_3 cell gas flow of 0.6 mL/minute, and an RPq value of 0.75. These settings resulted in the best quality control sample recoveries. Recoveries of NIST 1643e and matrix spikes using these settings were 95-105%.

Due to the negative outcome of the method development studies described above, cobalt was not included in the SOP and was not analyzed by the verification laboratory. More investigation should be performed to assess the applicability of ICP-MS technique for cobalt analysis. Preconcentration and calcium matrix separation by reductive precipitation may be beneficial for the quantitation of Co in FGD waters.

Copper

Copper (Cu) has two isotopes, at masses 63 and 65, that are suitable for quantitation analysis. DRC method development began with an NH_3 cell gas flow rate optimization using FGD water sample 0842036-02 at a 50x dilution. Both the sample and associated MS sample exhibited acceptable sensitivity at a cell gas flow rate of 0.55 mL/minute. Increasing the RPq value up to 0.7 did not show severe sensitivity drop and S/N ratios were consistent for all RPq values. At RPq values above 0.70, the sensitivity sharply decreased, making it difficult to discern the MS signal from the background noise.

Isotope ^{63}Cu produced much lower signal than isotope ^{65}Cu, which is unusual as the relative natural abundance ratio between ^{63}Cu and ^{65}Cu is roughly 70:30. This finding suggests that a polyatomic interference was probably not being sufficiently mitigated for isotope ^{65}Cu.

Oxygen was also investigated as a cell gas and it was found that at a variety of DRC settings (RPq settings and flow rates) the obtained isotopic ratios were more closely matching the published values [4]. However, the possibility of creating titanium oxide interference (TiO) precludes the use of O_2 as an acceptable cell reaction gas as the RPq setting required to overcome the TiO interference would greatly decrease instrument sensitivity.

At the optimum NH_3 DRC settings, polyatomic interferences removal was examined. The targeted interferences were $^{31}P^{16}O_2^+$ and $^{40}Ar^{23}Na^+$ and phosphorus (P) and sodium (Na) were spiked into 0842036-02 sample splits such that the native concentration of these elements was doubled in the resulting experimental sample. For the Na spiked sample, an increase of 0.03 µg/L of ^{63}Cu (at the instrument) was noted when the RPq value was set to 0.80. However, there was also an apparent Na-based polyatomic interference on ^{65}Cu that produced an equivalent concentration. If this interference was $^{23}Na^{40}Ca$, then the equivalent concentration on ^{63}Cu should be much higher than the equivalent concentration on ^{65}Cu. As this was not the case, it is likely that Cu contamination is present in the Na stock solution and that these DRC optimization settings are adequate for the removal of the Na-based interferences found in FGD water samples.

The FGD water sample spiked with P (from phosphoric acid) demonstrated that the RPq settings were not adequate to mitigate the interference caused by PO_2. Increasing RPq values produced lower Cu equivalent concentrations. It is suspected that there is a significant amount of Cu contamination in BRL's supply of phosphoric acid.

Further experiments were conducted to attempt to determine the optimized DRC settings for the analysis of FGD water samples for Cu. Over 20 different DRC optimization settings for both Cu isotopes were evaluated for instrument calibration, SRM NIST 1643e and MS recoveries, interference check standard A and AB recoveries, and polyatomic ion removal. Review of this significant amount of data suggested that an RPq value of 0.70-0.80 would be adequate to remove polyatomic interferences, with higher RPq values needed at lower cell gas flow rates. At a RPq value of 0.75, a cell gas flow rate optimization showed a maximum sensitivity at approximately 0.5 mL/minute for NH_3. When the results for other target elements were considered, it was determined that a cell gas flow rate of 0.6 mL/minute for NH_3 was the best compromise between maximum sensitivity and polyatomic interference minimization.

After an extended instrument conditioning period using sodium acetate, which was believed would contribute to higher instrument stability, Cu calibration curve was analyzed, using Rh as the internal standard. Unfortunately, the internal standard response had not yet stabilized after more than an hour of instrument conditioning with a sodium acetate solution. After allowing the conditioning solution to rinse out of the sample introduction system and the instrument, an extended analytical run (including an instrument calibration, analysis of the SRM NIST 1643e, and multiple FGD water sample replicates) was analyzed to evaluate method stability. It appeared that the S/N would be adequately high at a variety of RPq value settings. The instrument was calibrated and several replicates of SRM NIST 1643e were analyzed. The ^{65}Cu isotope did not give consistent values for sample analysis at any RPq setting, while the results for the ^{63}Cu isotope produced consistent values at RPq values ≥ 0.75, indicating that near-complete reduction of the polyatomic interferences for ^{63}Cu was possible with this method. Based on that finding, only ^{63}Cu results are included in this report.

IDL studies were performed at a variety of sample flow rates to determine the value that would allow adequate sensitivity while minimizing instrument exposure to the FGD water matrix. A sample flow rate of 200 µL/minute was determined to be the lowest rate that would maintain the required sensitivity and precision. With this sample flow rate, the instrument was tested for stability by repeated analysis of samples diluted to ~0.8% total dissolved solids (TDS). These analyses were bracketed by CCV standards, and stability for both internal standard response and CCV standard recoveries was demonstrated. Subsequently, the instrument was conditioned for an extended amount of time (1 hour) by the aspiration of FGD water samples diluted to approximately 1% TDS. An additional IDL study was performed, confirming that the required detection limits could likely be achieved with a 200 µL/minute sample flow rate.

For later experiments, the AFT voltage was raised to 375 V (for the reasons detailed above). The ICP-DRC-MS was run without pre-conditioning and the level of acetic acid in the internal standard solution was lowered to from 5.0% (v/v) to 2.5% (v/v), bringing the final concentration of acetic acid in each sample to 0.5% (v/v). The calibration curve, SRM NIST 1643e recovery, various FGD water samples and associated MS samples repeatability, and CCV standards were examined, demonstrating acceptable stability, accuracy, and replicate precision. The measured RSDs for several replicates of each FGD water sample were all below 5%, and MS recoveries for all appropriately spiked samples met acceptance criteria of 75-125%.

This method produces excellent sensitivity for Cu determination, with the lowest calibration standard (0.2 µg/L) giving signal of more than 10 times the background. It appears that most of the copper background originates from Cu impurities in Trace Metals-Grade HCl. It was determined that the 0.5% HCl contained approximately 2 µg/L Cu, which is above the certified limit stated by the vendor of < 1 μg/L Cu. Future research should include sourcing a cleaner supply of HCl. Further method development should also evaluate the use of methane (CH_4) as a cell reaction gas. The use of CH4 as the DRC gas may allow for the quantification of both Cu isotopes.

Nickel

Nickel has five isotopes at masses 58, 60, 61, 62, and 64 that can be used for quantitation. ^{60}Ni and ^{62}Ni are recommended due to highest isotope abundance. BRL had previously developed a method for the determination of nickel (Ni) in urine samples by ICP-DRC-MS, which served as the basis for initial development of a method for the analysis of Ni in FGD water samples.

A variety of DRC optimization settings were evaluated, with the aim of minimizing the polyatomic interferences signal contribution. Spiked blank samples and FGD water samples with a variety of possible polyatomic interferents were used to test the removal efficiency. High levels of calcium ($^{44}Ca^{16}O^+$) resulted in a polyatomic interference for ^{60}Ni. A slightly elevated background level was also found for ^{62}Ni; however, this was suspected of being the result of contamination, due to its consistency across multiple DRC settings. Blank samples spiked with sodium ($^{23}Na^{37}Cl^+$ on $^{60}Ni^+$) also demonstrated high background equivalent concentrations; however, the consistency of the measured values across both isotopes and multiple DRC settings suggested that this elevated concentration was caused by contamination, not by polyatomic interference.

Further experiments were performed with the same spiked samples to evaluate the effects of sample flow rate, DRC gas flow rate, and DRC RPq settings effect. As stated above, the contamination of the Ca stock standard solutions with low levels of Ni was confirmed by analysis at a variety of DRC settings and multiple dilutions. Once the level of Ni contamination in the standard was quantified, it was determined that the effect of Ca-based polyatomic interference on ^{62}Ni was mitigated at RPq settings ≥ 0.75.

The NH_3 cell gas flow optimized for ^{62}Ni maximum sensitivity, and the maximum response was found to be in line with the other DRC elements (V, Cr, and Cu optimized at ~0.55-0.60 mL/minute); therefore, the NH_3 gas flow rate was set to 0.60 mL/minute.

It was initially believed that an extended instrument conditioning period was required to maintain instrument stability; therefore, prior to initial experiments, a sodium acetate conditioning solution was analyzed for a lengthy period of time, followed by an instrument calibration curve and FGD water samples punctuated with CCV standards. The recoveries for the CCV standards remained fairly consistent between replicates. The low-end sensitivity of the instrument calibration curve was limited by background noise, possible caused by contaminated blanks. With the RPq value set at 0.75 to 0.80, the isotope ^{62}Ni produced consistent sample and MS spike results.

When FGD water samples 0842036-02 and -04 were acidified to 1% (v/v) with HCl, there appeared to be a polyatomic interference formed, amounting to ~0.1 μg/L. Due to the stability of this response, it is suspected to be due to contamination.

Possible polyatomic interferences were investigated by spiking blanks and FGD samples with polyatomic interference parent material. The addition of H_2SO_4 as a possible source of S-based polyatomic interferences resulted in a low-level response increase on isotope ^{62}Ni ($^{34}S^{12}C^{16}O^+$)

when the RPq value was set below 0.85. Nonetheless, with the RPq value set at 0.80, acidifying samples to 1% (v/v) H_2SO_4 contributed only 0.004 µg/L to the sample response, which was determined to be an acceptable level (the target MDL for this analysis is 0.02 µg/L). FGD water samples, at dilutions required for analysis, will present much less S than the spiked research samples used for these experiments, and the resulting positive bias will amount to less than 20% of the calculated MDL.

The presence of Na in the FGD water sample matrix also produced an insignificant polyatomic interference. Samples spiked with 100 mg/L Na, with the RPq value set at 0.80, resulted in a 0.03 µg/L increase in instrument response for ^{62}Ni.

The RPq value for Ni can be set to 0.85 and still allow enough sensitivity to calibrate the instrument down to 0.2 µg/L; however, an RPq setting of 0.80 adequately removes most polyatomic interferences and results in greater analyte sensitivity. Further experiments with the ^{62}Ni isotope produced a calibration curve calibration coefficient ≥ 0.9999 with the RPq value set at 0.80. Long term stability for analysis of FGD water samples was demonstrated, with CCV standard recoveries remaining consistently in the 93-107% range. Only results from the ^{62}Ni isotope are included in this report.

IDL studies were performed at a variety of sample flow rates, and it was determined that 200 µL/minute was the lowest flow rate that would allow for the necessary sensitivity and low-end precision. The instrument was pre-conditioned by aspirating a dilution of a FGD water sample. The samples were initially prepared with the addition of HCl (with the intent of simultaneously analyzing for Ag). Later experiments were performed omitting the HCl addition. Improved internal standard recoveries were observed when the AFT voltage was raised to 375 V.

Future method development efforts may include evaluation of CH_4 as a possible DRC reaction gas for use in Ni determination, to determine whether this will allow analysis on the ^{60}Ni isotope and the removal of the S-based polyatomic interference on ^{62}Ni isotope.

Selenium

Selenium has six isotopes at masses 74, 76, 77, 78, 80, and 82. The isotopes that are most useful for FGD water determinations are 77 and 82 for standard mode and 78 for DRC mode. A method for the determination of selenium (Se) in FGD water samples was previously developed at BRL using oxygen as a reaction gas, and no further DRC method development was included in the scope of work for this project.

When high MS recoveries were noted in the matrix for As, the Se method was modified to incorporate the addition of methanol (a carbon source that would improve the ionization efficiency in the plasma) to the internal standard solution. However, this method change produced elevated blank levels for Se; therefore, acetic acid was substituted as the carbon source.

A new MDL study was prepared and analyzed, the results of which are incorporated in this report. Future method development efforts will focus on the potential use of methane gas to overcome the possible interference from the formation of argon dimer ($^{40}Ar^{40}Ar^+$) on $^{80}Se^+$ (the most abundant selenium isotope).

Silver

The initial project objective for Ag was to develop a method that would give acceptable recoveries for Ag using standard mode ICP-MS. Ag is difficult to keep in solution due to formation of insoluble salts. Pre-screening indicated that Ag was unlikely to be affected by polyatomic interferences in FGD waters since they are not rich in Zr ($^{91}Zr^{16}O^+$ on $^{107}Ag^+$); therefore, the project work plan did not include development of a DRC method for this metal.

Evaluation Ag signals was not possible due to low native concentrations in the FGD samples; thus, all conclusions are based on results from spiked FGD water samples. Initial attempts to determine silver (Ag) spike recovery resulted in MS sample recoveries far below the acceptance criteria. To prevent the precipitation of Ag during storage, digestion or analysis, a diluent composed of a mix of 5% HNO_3 and 0.5% HCl was investigated. The MS recoveries improved greatly and it was decided to adopt this approach for all future Ag analyses. To rule out the possibility of the low MS recoveries being due to bottle wall loss, we prepared sample splits and analyzed a batch of identical FGD water samples by four different sample preparation/analysis method combinations:

- Digestion with 5% HNO_3 + 0.5% HCl and digestate dilution with 5% HNO_3 + 0.5% HCl
- Digestion with 5% HNO_3 + 0.5% HCl and digestate dilution with 5% HNO_3 only
- Digestion with 5% HNO_3 only and digestate dilution with 5% HNO_3 + 0.5% HCl
- Digestion with 5% HNO_3 only and digestate dilution with 5% HNO_3 only

The HNO_3 + HCl diluent was required to obtain adequate MS recovery, while the comparison of digestion methods was inconclusive due to the low sample Ag concentrations.
To minimize the number of separate analyses in a multi-element determination, a DRC method for Ag was developed. DRC cell gas flow rate and RPq value optimizations were performed. It was determined that the values used for more typical “DRC elements” could produce acceptable S/N for the determination of Ag.

After an extended period of instrument pre-conditioning, experiments were performed to optimize the RPq value for Ag. It was determined that a RPq of 0.85 provided still adequate sensitivity. Ag analysis using the ^{109}Ag isotope produced results higher than results for the ^{107}Ag isotope. The reason for that is still not completely revealed.

An extended analytical run was analyzed to evaluate instrument stability. The analysis with the RPq value set to 0.80 and 0.85 gave comparable results for Ag at mass 107. At RPq set to 0.85, Rh performed well as an internal standard for ^{107}Ag quantitation.

Vanadium

Vanadium (V) has two isotopes at masses 50 and 51 but ^{51}V has much greater abundance. BRL had previously developed a method for the determination of V in urine samples by ICP-DRC-MS that was used as the basis for initial development of a method for FGD water.

Various DRC optimization settings were evaluated, with the aim of minimizing the equivalent concentration of polyatomic interferences. Spiking blank samples and FGD water samples with HCl was used to evaluate the potential interference of $^{35}Cl^{16}O^+$ on ^{51}V. This polyatomic interference was sufficiently reduced by the use of NH_3 cell gas, a cell gas flow rate of 0.8 mL/minute, and an RPq value of 0.70. Rh was found to be suitable internal standard for V.

Further experiments were conducted to evaluate the effects of varying sample introduction flow rates, DRC cell gas flow rates, and RPq settings. A DRC cell gas flow rate optimization was performed, and an acceptable analytical sensitivity was observed at 0.55-0.60 mL/minute. An NH_3 cell gas flow rate of 0.6 mL/minute was selected in order to provide consistency for all elements analyzed with this cell gas.

The instrument was pre-conditioned with a sodium acetate solution, a process which was thought to contribute to instrument stability. As analyses progressed, MS sample and CCV standard recoveries drifted above acceptable limits. It appeared that the addition of HCl (to 0.5% final concentration) to all samples and standards did not contribute significantly to the background response, but alleviated this negative drift effect.

Addition of Na, Ca, and Mg produced a low-level positive bias. This effect is not understood but it is not plausible to be due to formation of polyatomic interferences.

IDL studies were performed at a variety of sample flow rates, and it was determined that 200 µL/minute was the lowest flow rate that would allow for the necessary instrument sensitivity. This setting was tested for stability by the repeated analysis of FGD water samples diluted to ~0.8% TDS, bracketed by CCV standards. Significant instrument drift was observed over the length of the analytical run. After extensively pre-conditioning of the instrument by aspiration of a dilution of an FGD water sample, the instrument was re-calibrated and a new IDL study was performed. Significant instrument drift was still noted. The IDL was immediately re-analyzed following a repeated instrument calibration. After the final IDL study very little instrument drift was found. While the best internal standard signal stability was achieved at 350 V AFT, the difference in sensitivities between 350 V and 375 V was minimal. A higher AFT voltage might provide more accurate results.

In subsequent experiments, the instrument was calibrated without extensive pre-conditioning, and the acetic acid concentration in the internal standard solution was lowered from 5.0% (v/v) to 2.5% (v/v). A new IDL study was conducted, resulting in a sufficiently low IDL; however, some instrumental drift was still observed. The drift was most noticeable in the evaluation of the results from the associated CCV standards and MS samples. After an extended instrument conditioning process, the V concentrations seemed to stabilize and produced acceptable and consistent MS sample recoveries.

An extended analytical run was performed to evaluate instrument stability and MS sample recovery. Seven of the eight appropriately-spiked MS samples produced recoveries within the acceptance criteria (75-125%) with one outlier producing a recovery of 74%. Minimal instrument drift was noted and the final CCV standard recovery was103%. Unfortunately, for analyses performed with the same method on later dates, the instrument calibration was quickly lost, and MS sample and CCV standard recoveries again drifted upwards. Additional experiments and optimizations were performed, and it was eventually determined that a combination of a short period of instrument pre-conditioning and an increased dilution factor for the FGD water samples was the most appropriate method for overcoming the instrument drift.

Zinc

Zinc (Zn) has five isotopes at masses 64, 66, 67, 68, and 70. ^{66}Zn is the most beneficial isotope for analysis and ^{70}Zn was not evaluated due to its low abundance (0.62%). Initial experiments for the determination of Zn in FGD water samples focused on determining the most appropriate DRC cell gas. Cell gas flow rate optimizations were performed for NH_3 and O_2. Both gasses appeared efficient in the removal of polyatomic interferences; however, O_2 produced a lower S/N; therefore, method development continued using NH_3.

Although O_2 initially seemed promising for use as the DRC gas for Zn analysis, it was found that this gas actually produce polyatomic interference in presence of sulfur ($^{34}S^{16}O_2^+$ on $^{66}Zn^+$). This negative effect was observed while analyzing interference check samples (A and AB), containing sulfur. The DRC cell gas was switched to NH_3, and after various optimizations, the applicability of this gas for Zn analyses was confirmed.

The next step was to determine an appropriate internal standard to use for the analysis of Zn in FGD water samples. Initially, experiments with multiple internal standard candidates showed a consistent, significant (compared to the aqueous solutions) increase in their sensitivity when samples with high level of TDS were analyzed. The increased sensitivity caused the sample results for Zn to be greatly underestimated while using the Elan DRC internal standard calibration equations. It was suspected that an adjustment of the AFT voltage could correct this issue. An AFT voltage optimization was performed, measuring the response of a1.0 µg/L manganese (Mn) solution in 1% (v/v) HNO_3 and 100 µg/L indium (In) solution in 1% HNO_3. It was determined that an AFT voltage of 325 V would give a consistent internal standard response during low- and high-matrix samples analyses. Acetic acid was added to the internal standard solution and a high RF power was used to limit the carbon deposition on the ICP-MS cones and other instrument components (e.g., on the lens, the shadow stop, etc.). Acetic acid had been added in earlier experiments as a carbon source for As determination, and the side benefit of decreased deposition had been noted.

With the NH_3 cell gas flow rate set to 0.75 mL/minute, instrument calibration curves were analyzed with a wide range of RPq values. Higher RPq values produced 85% recoveries for SRM NIST 1643e with internal standardization. Analyses of the SRM fortified with Zn spikes produced similar recoveries, demonstrating that the low recovery of 85% could be improved by better internal standardization and possibly by method of standard addition (MSA) calibration. Analysis of interference check standards A and AB suggested that an RPq $\geq$0.75 would produce Zn results free of polyatomic interferences. Replicate analyses of FGD water samples produced results with good precision across various RPq values, and the MS sample recoveries were very good (82-107%) with RPq value set at 0.75.

Due to the instrument drift, observed for other analytes (e.g. vanadium) when quantified by internal standardization, the AFT voltage was adjusted to 375 V and the recoveries for Zn in SRM NIST obtained by internal standardization 1643e improved from 85% to 95-105%. MS prepared from FGD water samples produced good recoveries, too.

A cell gas flow rate optimization was performed. As with several other elements of similar mass, an acceptable sensitivity was found at a DRC gas flow rate of 0.55-0.60 mL/minute. The cell gas flow rate was set to 0.6 mL/minute for subsequent analyses.

The instrument was pre-conditioned with a sodium acetate solution to improve instrument stability and then calibrated for Zn. FGD water samples with associated MS samples were analyzed, along with CCV standards. The MS spikes and Caves were both recovered within control limits (75-125%) and the measurement precision was acceptable.

An extended analytical run was performed, consisting of two independent instrument calibrations, multiple analyses of FGD water samples with associated MS samples, a second source check standard, and SRM NIST 1643e sample analyses. SRM recoveries were variable (the lowest was 80%), which imposed research for improvement of the instrument stability. The concentration of acetic acid in the internal standard solution was lowered from 5.0 % (v/v) to 2.5% (v/v), and the diluent was changed from 1% HNO_3 only to a solution of 0.5% HCl + 1% HNO_3. An IDL study was performed with the sample flow rate set at 100 µL/minute, but this did not achieve adequate sensitivity and SRM recoveries. The IDL study was performed at a sample introduction flow rate of 200 µL/minute, and this produced acceptable sensitivity to achieve a sufficiently low detection limit. The optimal concentration of acetic acid in the internal standard solutions was found to be 5.0 % (v/v). Diluents acid concentrations were changed from 0.5% HCl + 1% HNO_3 to 0.5% HCl + 5.0 % HNO_3 for consistent matrix matching of all standards and samples. Internal standardization and instrument optimizations resolved the issues with the low SRM recovery and it was brought to nearly 100%.

Further AFT voltage optimization experiments showed that the optimum AFT potential is 375 V. This value resulted in improved internal standard recoveries for the FGD water samples. The overall instrument response stability was adequate, and the average RSD for multiple replicates of FGD water sample was 4%. With an appropriate sample dilution, acceptable MS sample and CCV standard recoveries were achieved. Most CCV recoveries remained in the 97-103% range even over extended analytical runs.

B

DRAFT STANDARD OPERATING PROCEDURE (SOP)

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Determination of Antimony, Arsenic, Chromium, Copper, Nickel, Selenium, Silver, Vanadium, and Zinc in Flue Gas Desulfurization Water Samples by Inductively Coupled Plasma – Dynamic Reaction Cell – Mass Spectrometry using a PerkinElmer ELAN® DRC™ II

Prepared by:
Brooks Rand Labs
3958 6th Avenue NW
Seattle, Washington 98107 USA
(206) 632-6206
www.brooksrand.com

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Determination of Antimony, Arsenic, Chromium, Copper, Nickel, Selenium, Silver, Vanadium, and Zinc in Flue Gas Desulfurization Water Samples by Inductively Coupled Plasma – Dynamic Reaction Cell – Mass Spectrometry using a PerkinElmer ELAN® DRC™ II

1. DESCRIPTION AND SCOPE

1.1. This standard operating procedure (SOP) describes methods of analysis for the determination of total recoverable and dissolved trace elements in flue gas desulfurization (FGD) waters using inductively coupled plasma – dynamic reaction cell – mass spectrometry (ICP-DRC-MS).

1.2. This procedure is written specifically for use with a PerkinElmer ELAN® DRC™ II ICP-MS, and was developed using an ESI® SC-FAST™ sample introduction system with a Peltier-cooled spray chamber. The use of this specific equipment has been shown to improve method sensitivity and instrument stability; however, acceptable data may be produced using alternative sample introduction systems. The software used with the DRC II is ELAN Version 3.4 for use on Windows XP®.

1.3. This procedure or modifications of this SOP potentially can be utilized to determine a large list of analytes. However, at this time this SOP has been fully validated only for antimony (Sb), arsenic (As), chromium (Cr), copper (Cu), nickel (Ni), selenium (Se), silver (Ag), vanadium (V), and zinc (Zn). It has been determined that Ag and Sb may be analyzed by either standard mode ICP-MS or ICP-DRC-MS with acceptable accuracy for the tested sample matrices.

1.4. Aluminum (Al) and cobalt (Co) by ICP-DRC-MS were also evaluated as part of this study; however, acceptable results were not been obtained for these two elements using the reaction gases and other conditions evaluated; therefore, Al and Co are not included in this SOP.

1.5. This procedure must only be used by chemists experienced in the operation of the PerkinElmer ELAN® DRC™ II ICP-MS instrument and in the interpretation of ICP-MS spectra. This procedure must be followed in conjunction with the standard operation procedure used for normal ICP-MS analyses by a laboratory. Only the procedures which are unique to analyzing FGD water samples by ICP-DRC-MS are included in the scope of this procedure.

1.6. This procedure must be followed to assure accuracy and reproducibility of the sample results generated by all of the operating chemists. An analyst must first be fully trained in the use of ICP-MS, including the interpretation of spectral and matrix interferences and procedures for their correction, as well as ultra-clean sample handling.

1.7. This SOP does not purport to address all potential safety concerns associated with its use. It is the responsibility of the user of this SOP to establish appropriate safety and health practices prior to use.

2. SUMMARY OF METHODS

2.1. An aliquot of homogenous sample is prepared for analysis. The determination of dissolved elements requires the sample be filtered through a 0.45-µm pre-cleaned filter unit and then preserved with nitric acid (HNO_3). The determination of total recoverable elements in water samples requires the samples to be acid digested at elevated temperature. A closed-vessel digestion is recommended to prevent the loss of volatile elements such as As and Se, and to minimize the risk of sample contamination. The sample preparation procedure described in this SOP is a closed-vessel, oven heating digestion (similar to the alternative procedure described in Draft EPA Method 1638). When applied for FGD water sample analyses, it includes acidification to 5% (v/v) with concentrated HNO_3 prior to digestion.

2.2. A digested or filtered, aqueous sample is pumped through a nebulizer, where the liquid forms aerosol droplets as it enters a spray chamber. The aerosol separates into a fine aerosol mist and larger droplets. The larger droplets collide with the walls of the spray chamber and drain out of the bottom of the spray chamber. The finer droplets are transported out of the spray chamber and enter the ICP torch through an injector.

2.3. Inside the ICP torch, the aerosol droplets are transported into a high-temperature plasma, where they become desolvated, atomized, and ionized. The ions are transported from the plasma through a differentially-pumped interface. The ion stream is then focused through a cylindrical variable-voltage ion lens with a controlled electrical field. The ion stream is directed into the quadrupole where, when operating in DRC mode, the DRC cell is pressurized by the appropriate reaction gas. In the DRC the ion beam undergoes chemical modifications (due to collisions and gas-phase reactions) to reduce polyatomic interferences. When not operating in DRC mode, the ion stream will be further focused and pass through the cell intact.

2.4. The ion stream is then transported to the quadrupole mass filter, which allows only ions having a specific mass-to-charge ratio (m/z) to pass through. The ions exiting the quadrupole are detected by a solid-state detector and processed by the data handling system.

3.0 EQUIPMENT

3.1. Facility: An ultra-clean laboratory environment is critical for the successful production of quality data at ultra-low concentrations. Although FGD water samples can contain high concentration of some elements, they can be very low in others, down to trace levels. The presence of former could impose high sample dilutions, lowering the concentration of the trace elements to extremely low values. In order to achieve the method detection limits (MDL) required for these ultra-trace concentrations, ultra-clean protocols must be followed. All sample preparation must take place in a Class-100 clean hood. Metallic surfaces should be kept to a minimum in the lab and coated with an acrylic polymer gel. Adhesive floor mats should be used at entrances to the lab and changed regularly to prevent the tracking of dust and dirt from the outside environment. Clean room booties should be worn over shoes by all laboratory personnel. Clean-room gloves must be worn and changed whenever contact is made with anything not ultra-clean. The lab floor should be wiped regularly to remove any particles without stirring up dust.

3.2. Instrument: ICP-MS (PerkinElmer ELAN® DRC™ II) with a free-running 40 MHz RF generator and controllers for nebulizer gas flow, plasma gas flow, auxiliary gas flow, DRC gas A flow, and DRC gas B flow. Ammonia gas is required for some of the metals determined by this SOP; therefore, an oxygen getter must be installed on-line between the ammonia gas cylinder and the mass flow controller (standard on the DRC™ II instrument). The quadrupole mass spectrometer has operational mass range of 5 to 270 atomic mass units (amu). The turbo molecular vacuum system should achieve 10^{-6} torr or better.

3.3. All standard laboratory equipment and supplies that would be needed for routine ICP-MS analysis will also be needed to follow this procedure.

3.4. Elemental Scientific, Inc. (ESI) SC-8 auto-sampler with the ESI FAST valve (with high-flow fittings), or equivalent.

3.4.1. More traditional auto-samplers may be used; however, the method development research that supports this SOP has shown a significant increase in the quality of the data produced when this autosampler is used. Use of a traditional auto-sampler may increase instrument loading and lead to drift in the instrument quality control results such as internal standard and continuing calibration verification (CCV) standard recoveries. Instrument drift may also cause a decrease in analytical precision, especially at the low end of the calibration curve.

3.4.2. If a traditional auto-sampler is used, an increased rinse time may be required to avoid carryover effects.

3.5. Platinum skimmer and sampler cones are recommended to be used, as they are more resistant to high concentration matrices (like FGD waters), compared to the commonly used Ni cones. The use of Ni cones may lead to inaccurate results for Ni determination;

therefore, they are not recommended. However, acceptable data quality may be achieved for metals other than Ni using the Ni cones.

3.6. An ESI PC^3 Peltier-cooled quartz cyclonic spray chamber (or equivalent).

3.7. Quartz or sapphire injectors with a 2-mm i.d. aperture.

3.8. Copper RF coil.

3.9. ESI PFA-ST microflow nebulizer, or equivalent.

3.10. Teflon tubing (¼" o.d., ⅛" i.d.) for nebulizer gas.

3.11. Peristaltic pump tubing:

3.11.1. Waste Line: Phar-med or Santoprene, grey-grey, 1.855-mm i.d.

3.11.2. Sample Line: PVC, orange-yellow, 0.51-mm i.d.

3.11.3. Internal Standard Line: PVC, blue-orange, 0.27-mm i.d.

3.11.4. Flared tubing will ease set up and can be obtained from ESI.

3.12. ESI autosampler probe (0.8-mm i.d.) with lines to connect to SC-FAST switching valve.

3.13. Sample loop of desired volume for analysis, typically 500 μL.

3.14. Connection tubing from SC-FAST switching valve to nebulizer, equipped with ST fitting.

3.15. Connectors for sample and internal standard lines.

3.16. Gases:

3.16.1. Argon, high-purity grade, > 99.996%

3.16.2. Oxygen, Ultra-X grade, 99.9999% minimum purity

3.16.3. Ammonia, electronic grade, 99.999% minimum purity

3.16.4. The gases are stored in a ventilated gas storage safety cabinet.

3.17. Variable-speed peristaltic pump for solution delivery to the nebulizer.

3.18. Clean-room vinyl gloves (tested low in trace-metals).

3.19. Sample and reagent bottles constructed of fluoropolymer (FEP, PTFE, or FLPE), polyethylene (HDPE or LDPE), polycarbonate (PC), polypropylene (PP), or glass. HDPE bottles are preferred. LDPE, PC, and PP bottles are not recommended for use during the sample digestion process. All bottles must be pre-cleaned using acid solutions made of trace metals-grade concentrated acid and water which have been pre-tested and found to be sufficiently low in trace metals. Every new lot of vials must be cleaned, tested and must be found to be sufficiently low in trace metals prior to use.

3.20. Auto-sampler vials (15-mL and 50-mL) which have been pre-cleaned by rinsing with water, soaking in 2% (v/v) HNO_3 for at least 24 hours, rinsing three more times with reagent water, and drying in a Class-100 clean hood. Graduated vials (class A) must be used volumetric measurements and should be checked for accuracy and precision. Class B vials, like the autosampler ones, should be used just as a reference.

3.21. Assorted calibrated pipettes for volumes from 0.005 - 10 mL, and assorted plastic pipette tips appropriate for each pipette size. Pipettes must be calibrated weekly by gravimetrically measuring a volume of reagent water dispensed from the pipette. The volumes at which each pipette is calibrated must bracket the range of volumes that the pipette is used to dispense and be temperature-density corrected.

4. INTERFERENCES

4.1. Contamination

4.1.1. Contamination of the samples during sample collection is a great risk and extreme care should be taken to avoid this. Potential sources of contamination during sampling include metallic or metal-containing lab ware, containers, and sampling equipment. Therefore, non-metallic alternatives should be used whenever practical.

4.1.2. Sample collection equipment such as tubing, pumps, filters, and homogenization equipment should be non-metallic (whenever possible) and tested for metals through the analysis of equipment blanks.

4.1.3. Contamination of samples by airborne particulate matter is a major concern. Sample containers should remain closed as much as possible. Container lids should only be removed briefly and in a clean environment during sample preservation and processing, so that exposure to an uncontrolled environment is minimized.

4.1.4. In general, the sample collection and handling procedures that are described in EPA Method 1669 should be followed. As EPA Method 1669 is a performance-based method, the procedures may be modified to be more specific to FGD water collection, as long as the field-QC frequencies and concentration criteria are met.

4.1.5. Laboratory

4.1.5.1. All labware (ICP-MS autosampler vials, sample and digestion bottles, extraction apparatus, reagent bottles, etc.) should be acid-cleaned and tested for the presence of low-level trace-metals prior to use. Any equipment blanks with metals concentrations above the method reporting limits (MRL) listed in this SOP (Table 12.2) should result in the associated equipment not being used.

4.1.5.2. Pipette tips must be triple-rinsed with 5% (v/v) HNO_3 and then rinsed once with the solution to be dispensed by pipette prior to use.

4.1.5.3. The Equipment section of this SOP describes other steps that should be taken to ensure no contamination occurs from the use of equipment that is too high in the trace metals of concern.

4.1.5.4. All reagents and gases used for analysis and sample preparation must be tested for the presence of trace metals prior to use in the lab. Due to the ultra-low detection limits of this method, it is imperative that all the reagents and gases be as low in metals as possible. It is often required to test several different sources of reagents until an acceptable source has been found. Metals contamination can vary greatly between different lot numbers of a given reagent. Once an acceptable reagent lot has been identified, several cases of the lot number should be sequestered from the supplier. Records, either in the form of a logbook or in an electronic spreadsheet, must be maintained to track the acids.

4.1.5.5. Metals concentrations in both the water and the HNO_3 must be monitored and recorded each day the instrument is used, and the results should be compared to the control limits. In general, all instrument blanks should have metals concentrations at least as low as the method detection limits (MDL) listed in Table 12.2.

4.1.5.6. Great care should be taken to keep the laboratory facility free from all sources of metals contamination. Class-100 clean hood HEPA filters should be replaced with new filters on a regular basis (at least annually) to reduce the risk of airborne contaminants. Metal corrosion in any part of the laboratory facility should be addressed by replacing or sealing. Every piece of apparatus that is directly or indirectly used in the collection, preservation, or processing of samples should be tested to be sufficiently low in trace metals.

4.2. Elemental interferences

4.2.1. Interference sources that may inhibit the accurate collection of ICP-MS data for trace elements are addressed below.

4.2.2. Isobaric elemental interferences are isotopes of different elements that form singly or doubly charged ions of the same mass-to-charge ratio (m/z) and cannot be resolved by the mass spectrometer.

4.2.2.1. Data obtained by the measurement of isotopes with isobaric overlaps must be corrected for. The procedure described in this SOP currently utilizes the default internal isobaric elemental interference correction equations incorporated into the Perkin Elmer ELAN 3.4 software. Correction equations for the analysis of samples by ICP-MS in the standard (non-DRC) mode are not directly transferable to DRC mode analyses.

4.2.3. Polyatomic interferences are interferences caused by ions, composed of multiple atoms, which have the same m/z as the isotope of interest, and which cannot be resolved by the mass spectrometer. These ions are commonly formed in the plasma or the interface system from the support gases or sample components. The objective of DRC analysis is to remove or reduce these interferences, and as a result, correction factors for polyatomic interferences should not be necessary. If these types of interferences are determined to still be present, then they can be corrected by the following procedure.

4.2.3.1. Spike a sample with varying amounts of a polyatomic parent (e.g. Cl for the production of ClO, which can be detected at mass 51, thus interfering with the determination of V) and calculate a correction factor based on the change in counts-per-second (cps) at the parent mass and the change in cps at the analyte mass. Once a correction factor has been determined, it can be added to the Corrections tab in the Method file in the ELAN 3.4 software.

4.2.3.2. Many polyatomic interferences specific to the analysis of FGD waters were investigated as part of the method development that supports this SOP. Some of these polyatomic interferences affect only a single isotope and do not prevent accurate quantification of a given metal by this SOP, provided an alternative isotope is available. For a more detailed explanation, refer to section 8.9.2.

4.2.4. Abundance sensitivity overlaps occur when part of an elemental peak overlaps an adjacent peak. This often occurs when measuring a low abundance m/z peak next to a high abundance m/z peak. The abundance sensitivity is affected by ion energy and quadrupole operating pressure. Proper optimization of the resolution during tuning will minimize the potential for abundance sensitivity interferences.

4.2.5. Physical interferences occur when there are differences in the physical properties of the calibration standards and the sample solutions (viscosity, surface tension, ion concentration etc.). They are associated with the physical processes that govern the transport of sample into the plasma, sample conversion processes in the plasma, and the transmission of ions through the plasma-mass spectrometer interface. ICP-MS analysis is especially susceptible to physical interferences. The presence of physical interferences should be monitored through the matrix spike recoveries.

4.2.5.1. Proper internal standardization can compensate for many of these types of physical interferences. The internal standards should have chemical properties, such as ionization potential, electron affinity, and mass (in that order of importance) similar to the associated elements.

4.3. Memory effects can be caused by carryover of elements from a previous sample in the sample tubing, cones, torch, spray chamber, connections, and autosampler probe.

4.3.1. Bias due to carry-over is monitored for and minimized by the analysis of an instrument blank after each FGD water sample. Depending on sample characteristics and target analytes, a second instrument blank may be analyzed to confirm absence of carry-over. If carry-over is detected, rinse times between samples should be extended.

4.3.2. Use an ESI SC-FAST autosampler (or equivalent) is optional but has been shown to greatly reduce the risk of carryover interferences.

4.4. Potential Interferences Specific to FGD Waters

4.4.1. In the analysis of FGD waters certain interferences are characteristic. This SOP specifically addresses many of them.

4.4.1.1.Ionization Enhancement – Certain analytes such as As, Se, and Zn are not completely ionized in an ICP-MS plasma operating under standard conditions and using standard procedures. For these elements, the addition of a high level of certain elements such as carbon to the ICP-MS plasma can increase the effective ionization of the plasma and cause a higher response factor, defined as analytical sensitivity. This effect often results in excessively high matrix spike (MS) recoveries. This SOP reduces the negative effects of ionization enhancement through the on-line addition of acetic acid to the internal standard solution, which increases the effective ionization of the analytes with high ionization potential. In addition, less apparent instrument drift is noted with the use of acetic acid.

4.4.1.2.Physical Interferences – Due to the very high levels of dissolved solids in most FGD waters, especially the presence of high levels of dissolved refractory oxides, certain physical interferences are especially common during the analysis of FGD waters.

4.4.1.2.1. Due to the deposition of various salts and oxides on the interface region of the ICP-MS, sensitivity drift may occur. This SOP reduces these negative effects by the use of increased sample dilutions and a lower nebulizer sample flow rate.

4.4.1.2.2. Due to the high levels of easily ionized elements in FGD samples, there will be very high levels of ions entering the ion lens during the analysis of samples. High levels of ions may affect the analytes of interest by varying the efficiency with which the analytes are transported through the lens region. This SOP attempts to address these issues through a lower sample flow rate (in DRC mode with NH_3 DRC gas), though extensive dilution is often required to obtain accurate values for lower mass analytes (refer to Table 12.1). Analytes with masses over 100 amu can be analyzed with total dissolved solids (TDS) levels approaching 1%; however, lower mass analytes will require additional dilution.

5.0 SAFETY

5.1 Hydrochloric acid (HCl) and HNO_3 are very caustic; adequate protective gear must be worn when working with these acids. At a minimum, eye protection, gloves with the appropriate resistance, and a lab coat must be worn when working with acids in the laboratory. An adequate fume hood (ideally constructed of all non-metallic materials) should be used for all acids.

5.2 Many of the reagents used in this SOP have toxicities that are not well established and should be handled with care. For all known chemicals used, the material safety data sheet (MSDS) should be consulted in advance.

5.3 State occupational safety and health administration (OSHA) regulations should be followed. Local sewer limits for pH range and metals content should be posted near waste disposal areas and no materials outside of the limits should be disposed of to the municipal sewer.

5.4 The instrument generates high levels of radio frequency (RF) energy and its torch box region is very hot when the plasma is on.

5.5 DRC gases should be stored safely in a vented safety cabinet. Adequate caution must always be used with pressurized gases. Prior training or experience is necessary to change any gas cylinders. Oxygen gas can be explosive with certain materials. Ammonia has a very low odor threshold and is corrosive to tissue.

6.0 REAGENTS AND STANDARDS

6.1 Reagents may contain elemental impurities that could negatively affect data quality. High-purity reagents should always be used. Each reagent lot must be tested and proven to be low in the elements of interest before being used in the laboratory. The concentration of each metal should be below the MDL for that element (refer to Table 12.2).

6.2 Water, passed through the ASTM Type I purifier, demonstrated to be free from or sufficiently low in the metals of interest and potentially interfering substances.

6.3 HCl, tested to meet the requirements specified in section 6.1 prior to use in the laboratory.

6.3.1 0.5% (v/v) HCl – Analytical diluent.

6.4 Acetic acid (CH_3COOH), concentrated, tested to meet the requirements specified in section 6.1 prior to use in the laboratory.

6.4.1 The internal standard solution (section 6.7) is prepared in 20% (v/v) CH_3COOH.

6.5 HNO_3, concentrated, tested to meet the requirements specified above prior to use in the laboratory.

6.5.1 5% (v/v) HNO_3 – Stock standard preparation diluent, analytical diluent, pipette cleaning solution, and auto-sampler rinse station solution.

6.5.2 2% (v/v) HNO_3 – Auto-sampler vial soaking solution.

6.6 Stock Standard Solutions – obtained from a reputable and professional commercial source.

6.6.1 Single element standards are obtained for each target metal as well as for any metals used as internal standards and interference checks.

6.6.2 A second source is obtained for each determined metal. QCS-26, available from High Purity Standards, can be used as a second source stock solution; it contains 100 mg/L of all elements listed in this SOP, and can be diluted appropriately to check each calibration at different concentrations.

6.6.3 Multi-element stock standard solutions can be prepared from the single element standards. All elements that are included in a multi-element standard must be compatible and stable in solutions together.

6.6.4 Dilute single element stock standards appropriately in order to prepare multi-element standards in 1% (v/v) HNO_3. At concentrations of 1 mg/L or more, these standards will be stable for six months from date of preparation. The composition (selection of elements) in the multi-element stock standard solution may change as the needs for different calibrations change.

6.6.5 Stock solutions for Ag and Sb should be prepared daily and stored in the dark, separately from other stock solutions, due to their photo-reactivity (Ag) and tendency to form precipitates from solution.

6.6.6 Additional elements can be added to these standard mixes in 1% HNO_3 (v/v). Attention should be given to the compatibility of the elements added.

6.7 Internal Standard Solution – Dilute stock standard solutions of indium (In) and rhodium (Rh) to give approximately 500,000 cps when added on-line using a mixing tee. The internal standard solution should consist of 50 µg/L In and Rh in 1% (v/v) HNO_3 and 20% (v/v) $C_2H_4O_2$.

6.7.1 The solution is stable for six months after the date of preparation.

6.7.2 Different internal standards can be chosen based on sample matrix, on-going research, and specific analytical requests.

6.7.3 The internal standard solution is added to all standards and samples by passing through a mixing tee prior to passing through the nebulizer. The sample flow rate and internal standard flow rate should be adjusted such that the internal standard composes approximately 33% of the flow entering the nebulizer. The sum of these two flows should be optimal for the current nebulizer in use. If internal standard is not added through a mixing chamber, all calibration standards, samples, and interference check standards should be matrix matched to contain approximately 7% (v/v) CH_3COOH.

6.7.4 The use of only In and Rh as internal standard was found to be acceptable for this SOP; however, other internal standards can also be added. It is worth noting that internal standards should not necessarily be chosen solely based on their mass, as prescribed by some methodology. Both the ionization potential and the electron affinity are more important characteristics in defining an optimal internal standard for a given element than the mass.

6.8 Calibration Standards – Fresh calibration standards should be prepared daily, or as needed. Calibration standards must be prepared in a 5% (v/v) HNO_3 + 0.5% (v/v) HCl diluent.

6.9 Diluent Solution – All calibration standards and samples must be prepared or diluted in a solution of 5% (v/v) HNO_3 + 0.5% (v/v) HCl. This solution should be remade each analytical day and tested to be contamination free by repeated analysis before use for the instrument calibration or analysis of samples. The additional of HCl to all samples and standards ensure the stability of Ag and Sb in the samples.

6.10 Initial Calibration Verification (ICV) Standard – The ICV standard solution is prepared from secondary source standards in order to verify the validity of the calibration curve.

6.10.1 The ICV standard can be prepared by diluting QCS-26 (described above) with the diluent of 5% (v/v) HNO_3 + 0.5% (v/v) HCl, such that the concentration values of the analytes of interest are within the calibration curve.

6.11 Daily Optimization and Tuning Solution (aka the "Daily solution") – To prepare the Daily solution, dilute stock standard solutions of cerium (Ce), In, Rh, lead (Pb), magnesium (Mg), barium (Ba), and uranium (U) to 1 µg/L in 1% (v/v) HNO_3. The

Daily solution is used to confirm various instrument performance metrics, including sensitivity, background, and the formation of polyatomic and double-charged ions.

6.12 Standard Reference Material – A commercially-available standard reference material (SRM) for waters (such as NIST 1643e or equivalent) should be analyzed with every analytical sequence. NIST 1643e is similar in composition to standard interference check solutions for ICP-MS analyses and it offers a check of the validity of the interference correction equations and DRC optimization parameters.

6.13 Additional reagents (e.g., a dual detector calibration optimization solution) are required for instrument performance optimization, as described in the standard ICP-MS procedures that must accompany this SOP.

7.0 SAMPLE COLLECTION, FILTRATION, PRESERVATION, AND STORAGE

7.1 Samples for dissolved metals determination must be filtered (if not field-filtered) through a 0.45-µm pre-cleaned disposable filter unit upon receipt. Field-filtration is recommended, as some FGD water samples are unstable. Note**:** For regulatory monitoring purposes, the holding time prior to filtration may be as short as 15 minutes, depending on the analytical method referenced in the regulatory permit.

7.2 Samples must be preserved to a pH less than or equal to 2. Sample preservation should take place within 14 days of collection (Ref. 11.5 and Ref. 11.6). For this SOP, the acids for sample digestion are added directly to the original sample container, thus preserving the sample below pH 2.

7.2.1 Preserve FGD waters to a minimum of 5% (v/v) with HNO_3 prior to digestion. Associated method blanks must also be kept in 5% (v/v) with HNO_3. If field blanks are to be batched with the FGD water samples for analysis, then they should also be preserved to 5% (v/v) with HNO_3.

7.3 Preserved samples can be stored at room temperature in a secure area of the laboratory until analysis.

8.0 PROCEDURE

8.1 Sample Preparation and Digestion

8.1.1 For the determination of ***dissolved analytes*** in FGD waters, samples should be preserved with HNO_3 to 5% (v/v) after filtration. Store the preserved samples for a minimum of 48 hours prior to analysis to completely desorb the metals from the container walls. The acidified samples can be heated in an oven along with their total recoverable counterparts, but the oven heating step is not necessary. Rinse pipette tip three times with a 5% HNO_3 pipette rinsing solution and once with the sample, then add the filtered, preserved sample to a pre-cleaned 15-mL auto-sampler vial. If the sample is suspected to be high in metals or total dissolved solids (TDS), then dilute the sample with 5% (v/v) HNO_3 + 0.5% (v/v) HCl. In the case of a high concentration of metals, dilute the sample until the concentration of the metals at the dilution fall within the calibration range of the instrument. More extensive dilution may be required depending on the analyte of interest.

8.1.1.1 Formation of precipitates in the FGD water samples has been noted for multiple sample types. Any change in the visual appearance of the sample must be well documented. Users of this SOP are strongly encouraged to remain up to date regarding on-going research into the stability of acidified FGD water samples.

8.1.1.2 Normally, it can be assumed that a 5% HNO_3 matrix would prevent absorption of metals to the sample container walls for ambient water samples; however, for FGD water samples absorption may still be a risk.

8.1.1.3 TDS can be estimated by evaporating a sample to dryness in an oven or microwave, or by calculation based on conductivity measurements.

8.1.2 For the determination of ***total recoverable analytes*** in FGD waters, samples should be preserved to 5% (v/v) with HNO_3. Store the preserved samples for a minimum of 48 hours prior to analysis (this can include the digestion time) to completely desorb the metals from the container walls. The acidified samples are tightly capped, heated to 85 ºC in a laboratory oven, and held at that temperature for a minimum of 3 hours (minimum total digestion time varies by bottle size); however, it is recommended that samples are maintained at 85 ºC overnight. Samples consisting of total suspended solids (TSS) levels > 1% (m/v) may require biphasic separation, additional HNO_3 addition, or dilution prior to digestion.

8.1.3 Following acidification and digestion, samples should sit for a minimum of three hours or until all of the suspended solids have settled to the bottom of the bottle. Sample aliquots should be taken from the top of the bottle, avoiding disruption of the solids layer settled on the bottom of the bottle, if applicable.

8.1.4 When the metals concentration of a sample is unknown, the samples should be diluted and screened, or diluted and analyzed using a semi-quantitative method, prior to being analyzed undiluted (refer to Table 12.1). This protects the instrument and the sample introduction system from potential contamination and damage.

8.2 Instrument Startup

8.2.1 Follow the standard ICP-MS method or applicable laboratory documentation for instrumentation startup procedures.

8.3 X-Y Adjustment

8.3.1 Perform an X-Y adjustment on the instrument following the standardized procedures.

8.4 Tuning

8.4.1 Tuning must be performed whenever there are changes to the instrument's electronics, whenever there is a need to modify the resolution for elements, daily if required by the referenced method, or monthly (at a minimum). Refer to the applicable ICP-MS analytical procedure for tuning procedures.

8.5 Nebulizer Gas Flow Optimization

8.5.1 The nebulizer gas flow optimization should be performed daily or whenever sample introduction flow rates are changed. Refer to the applicable document(s) for nebulizer gas flow optimization procedures.

8.6 Optimizing the Autolens Voltage

8.6.1 The Autolens optimization should be performed daily or whenever sample introduction flow rates are changed. Refer to the applicable document(s) for instructions for optimizing the Autolens voltage. The use of Autolens is recommended over manual lens voltage optimization.

8.7 Additional instrument performance optimizations (e.g., dual detector calibration, dead time correction, etc.) may be required as per the standard ICP-MS analysis SOP that must accompany this SOP.

8.8 Instrument Performance Check: “Daily”

8.8.1 The instrument performance check is done before the start of each analytical run to ensure proper functioning and sensitivity of the instrument. It is often educational to run a daily performance check before and after optimization in order to observe how performing optimizations change the instrument response. Refer to the applicable document(s) for the daily instrument performance check.

8.8.2 Review the results of the “Daily” to check background cps, sensitivity, double-charged element levels, and oxide levels. Minimum performance specifications can be found in the instrument manual (reference 11.2).

8.8.3 If the performance check is satisfactory, the instrument is ready to begin sample analysis. Place the autosampler probe in the rinse position to begin flushing the system.

8.8.4 If the performance check is not satisfactory, refer to the instrument manual (reference 11.2) for troubleshooting guidelines.

8.8.5 DRC Interference Check Samples

8.8.5.1 Before starting analysis of FGD waters, the DRC optimization must be validated to verify the adequate removal of polyatomic interferences. A test solution containing 1.0 µg/L of the analyte of interest and 1% of the potentially interfering analyte(s) should be analyzed and evaluated against a solution without the addition of the potentially interfering analyte(s). Please refer to Table 12.4 for a list of likely polyatomic interferences encountered when analyzing FGD water samples.

8.8.5.1.1 For the target analytes determined using ammonia as the DRC gas, a test solution containing 1% (v/v) methanol, 1.5% (v/v) concentrated HCl, 1% (v/v) concentrated ammonium hydroxide, 1% (v/v) concentrated sulfuric acid, and 1000 µg/L calcium would be appropriate for most FGD water samples. The cell gas flow and the RPq settings should match those listed below.

8.8.5.1.2 For As and Se using oxygen as the DRC gas, a test solution containing 1% (v/v) methanol, 1.5% (v/v) HCl, and 1000 µg/L calcium would be appropriate for most FGD water samples, assuming the dilution ranges listed in Table 12.1. The cell gas flow and the RPq settings should match those listed below.

8.8.5.2 After analysis, compare the results (in cps) for the interference check samples to each other. If the relative percent difference (RPD) between the signals (in cps) for the two samples is more than 15%, then analysis must be halted. The issue causing the poor method performance must be identified or further DRC method development and optimization must be performed.

8.8.5.3 The analysis of an interference check sample may also be performed after instrument calibration. In that case, compare the calculated result for the interference check sample to the true value of the target analyte. The recovery must be 85-115%. If the recovery is outside of the control limits, then analysis must be halted. The issue causing the poor method performance must be identified or further DRC method development and optimization must be performed.

8.8.6 When the DRC is pressurized with a reaction gas, the polyatomic interferents are converted to a different mass where they no longer interfere with the measurement of a desired element. In the case of As (75 amu), the analyte of interest itself reacts with the oxygen reaction gas to form AsO^+, which is then measured as mass 91 amu, removing it from the interference of $ArCl^+$ (75 amu). Chemical processes occur in the DRC, including charge transfer, proton transfer, and condensation and association reactions. The following procedure describes the process involved with analyzing samples while utilizing the DRC to modify the ion stream chemistry.

Below are some simplified examples of DRC gases removing polyatomic interferences;

Removal of ${}^{40}Ar^{35}Cl^+$ on ${}^{75}As^+$: ${}^{75}As^+ + O_2 \longrightarrow {}^{91}AsO^+$

Removal of ${}^{40}Ar^{38}Ar^+$ on ${}^{78}Se^+$: ${}^{40}Ar^{38}Ar^+ + O_2 \longrightarrow {}^{40}Ar + {}^{38}Ar + O_2^+$

Removal of ${}^{35}Cl^{16}O^+$ on ${}^{51}V^+$: ${}^{35}Cl^{16}O^+ + NH_3 \longrightarrow {}^{35}Cl^{16}O + NH_3^+$

8.8.7 Before beginning analysis, especially for “high-matrix” samples, it is extremely important to condition the instrument to prevent a significant drop in sensitivity. Condition the instrument by diluting a sample such that the final TDS concentration is ~0.5%, and then analyzing this sample repeatedly for at least 1 hour in DRC mode.

8.9 Sample Analysis

8.9.1 General Method Development Considerations

8.9.1.1 During the method development that supports this SOP, each metal was evaluated separately and the instrumental and DRC parameters were optimized specifically for each metal. In the end, it was determined that there were groups of parameter settings that were optimal or near optimal for several metals with little compromise to the individual analyte sensitivity and method performance.

8.9.1.2 While each metal could be optimized individually, it was the goal of this SOP to be able to analyze as many elements as possible together under the same set of conditions. This leads to an increase in throughput and a decrease in costs that, for most laboratories, will outweigh the marginal performance improvements that may be possible if each element is optimized and analyzed separately.

8.9.1.3 For all target analytes, the RF voltage should be set to 1500 W and the axial field technology (AFT) voltage should be set to 350 V. These settings were determined to be optimal during method development.

8.9.2 Constructing a Method

8.9.2.1 The analytical method should be set up in the instrument software as follows:

Analyte	**Isotope**	**Internal Standard**	**DRC Gas**	**RPq**	**Cell Gas Flow**	**Dwell Time (ms)**
As **(as AsO)**	91	Rh	O_2	0.7	0.6	50
Se	78	Rh	O_2	0.8	0.6	200
V	51	Rh	NH_3	0.8	0.6	50
Cr	52	Rh	NH_3	0.75	0.6	50
Cr	53	Rh	NH_3	0.75	0.6	50
Ni	62	Rh	NH_3	0.8	0.6	50
Ni	62-1	Rh	NH_3	0.75	0.6	50
Cu	63	Rh	NH_3	0.75	0.6	50
Zn	66	Rh	NH_3	0.85	0.6	50
Zn	66-1	Rh	NH_3	0.8	0.6	50
Ag	109	In	NH_3	0.8	0.6	50
Ag	107	In	NH_3	0.8	0.6	50
Sb	121	In	NH_3	0.75	0.6	50
Sb	121-1	In	NH_3	0.8	0.6	50

8.9.2.2 Where there are two different lines listed for one element in the above table, the second ones listed (^{53}Cr, ^{62}Ni-1, ^{66}Zn-1, ^{107}Ag, and ^{121}Sb-1) are for confirmation at a different RPq setting or isotope, and these are primarily used only for verification of interference removal.

As part of the method development that supported this SOP, several other isotopes, such as ^{60}Ni, ^{65}Cu, ^{77}Se, ^{82}Se, and ^{123}Sb, were investigated. These isotopes were excluded from the SOP, primarily due to an inability to overcome the polyatomic interferences under the conditions used in this SOP.

8.9.2.3 The As and Se analysis should be performed separately from the analysis for the other metals. It has been shown that switching back-and-forth between DRC gases in a given analytical run can lead to undesirable instrument instability.

8.9.2.4 The cell gas flow settings listed above are values that have been found to give the best overall performance for a wide range of analytes. If better instrument sensitivity is required, gas flow optimizations for individual analytes can be performed. Typically, analytes with lower atomic masses (< 100 amu) may show better interferences removal at lower DRC gas flows, while analytes with higher atomic masses may perform better at higher gas flows.

8.9.2.5 For analysis using NH_3 as the DRC gas, the peristaltic pump rate should be adjusted so that the sample introduction rate is 200 µL/min. This has been found to correspond with 8 revolutions-per-minute (rpm) using the orange-yellow PVC pump tubing described above. For analysis using O_2 as the DRC gas, the pump rate should be adjusted so that the sample introduction rate is 400 µL/min. This has been found to correspond with 16 rpm using orange-yellow PVC pump tubing. The higher flow rate using O_2 as the DRC gas has consistently shown an improved signal to noise ratio. For this reason, it is suggested that FGD samples be analyzed for the metals described in this SOP as two separate analytical runs.

8.9.2.6 The timing delays should be adjusted and optimized such that there is adequate time for the sample flow to reach the instrument and to stabilize.

8.9.2.7 The instrument should be set to perform at least 20 sweeps per reading, 1 reading per replicate, and 3 replicates per sample.

8.9.2.8 An example of the calibration standards that could be used for the instrument calibration are as follows (in µg/L):

Metal	Std 1	Std 2	Std 3	Std 4	Std 5	Std 6	Std 7	Std 8
As	0.025	0.05	0.25	1	5	25	125	500
Se	0.05	0.1	0.25	1	5	25	125	500
V	0.15	0.3	1.5	5	10	20	50	100
Ni	0.2	0.4	2.0	5	10	50	100	200
Cu	0.2	0.4	2.0	5	10	50	100	200
Cr	0.15	0.3	1.5	12.5	25	125	250	500
Zn	0.2	0.4	2.0	5	50	250	500	1000
Ag	0.02	0.04	0.2	1	2	10	20	40
Sb	0.02	0.04	0.2	1	2	4	10	20

The calibration standards for a given set of samples should be selected based on prior information on the likely range of analyte concentrations in the samples, and the dilutions that will be used on those samples.

8.9.3 Instrument Conditioning

8.9.3.1 Prior to the Daily Performance and Daily DRC Performance checks, it is extremely important to condition the instrument to limit drift.

8.9.3.2 Place the internal standard probe in the DRC internal standard, and the carrier solution probe in a 1% HNO_3 solution.

8.9.3.3 Select an FGD water sample for which the TDS levels are known, and dilute so that the final TDS is ~0.5%. Analyze this sample repeatedly for 1 hour in DRC mode, and then begin analysis of the Daily Performance Sample immediately thereafter.

8.9.3.4 In addition to instrument conditioning with a high-TDS sample, it's important to allow the DRC cell at least 1 minute to refill with reaction gas after switching from standard mode to DRC mode. To avoid drift, a cell purge time of 30 minutes is optimal.

8.9.4 Analysis

8.9.4.1 For general ICP-MS analysis procedures, the lab's standard ICP-MS SOP must be followed.

8.9.4.2 Prior to calibration, an initial instrument calibration blank must be analyzed. All subsequent sample analyses should be corrected for the signal (cps) of this blank.

8.9.4.3 Only a weighted-linear calibration should be used, as this will provide the best accuracy at the low end of the calibration curve. Standard linear regression calibrations are not appropriate for low-level work.

8.9.4.4 Sample Dilutions

8.9.4.4.1 As acid-matching between the samples and the standards is critical to the optimal performance of this SOP, all undiluted samples (e.g., method blanks or low-TDS samples) should be acidified to 0.5% (v/v) with concentrated (12 M) HCl.

8.9.4.4.2 Samples must be diluted to achieve a maximum TDS concentration of 1% (10,000 mg/L) in order to avoid major physical interferences and to protect the instrument.

8.9.4.4.3 Additional dilution of a sample may be required to achieve acceptable results for quality control samples (i.e., internal standard recoveries, MS/MSD recoveries, etc.).

8.9.4.4.4 Refer to Table 12.1 for a list of the typical range of dilution factors required for FGD water samples.

9.0 QUALITY CONTROL

9.1 MDLs were determined for each element included in this SOP according to 40 CFR Part 136 B. MRLs are determined as approximately 3-5x the MDL and must be less than or equal to the lowest calibration standard and no more than 10x the MDL. A table listing the MDLs and MRLs achieved by this SOP are listed in Table 12.2.

9.2 All standard quality control samples required and their associated criteria are summarized in Table 12.3.

9.3 Preventative maintenance – Refer to the ICP-MS hardware guide for details on daily, weekly, and monthly preventative maintenance. Instrument optimization is an integral part of quality control. Sometimes optimizing the instrument can take many hours before minimum criteria for proceeding with analysis are met.

9.4 Pipettes must be calibrated weekly, or whenever the status of a pipette is unknown. See Section 3.21 above for instruction on the calibration of pipettes.

9.5 The correlation coefficients of the weighted-linear calibration curves for each element must be ≥ 0.995 to proceed with sample analysis. If the correlation coefficient for any element is < 0.995, the results for that element may not be reported from that run. Standards may be removed starting with either the lowest or highest calibration points, until a linear calibration is found. Results will then only be reported within the range of the linear calibration, thus affecting the achieved MRL. Non-contiguous calibration standards (e.g. only standards 2 and 4) may not be removed. A minimum of 5 non-zero calibration standards must be used for instrument calibration.

9.6 The percent recovery of the ICV standard must be 90-110% for each element being determined. If the percent recovery is not within the control limits of 90-110%, for any element, the results for that element may not be reported from that run.

9.7 Instrument blanks must be analyzed after each FGD water sample. Carry-over effect should be monitoring for closely and minimized by sample dilution or other approaches (acid rinses, sample rinses, etc.).

9.8 Each preservation/digestion batch must have at least 3 preparation (or method) blanks associated with it (it is recommended that at least 4 method blanks are prepared and analyzed). The blanks are treated the same as the samples, and must go through all of the preparative steps. Sample results may optionally be corrected for the mean concentrations of these blanks. Blank correction is not always acceptable to regulators; thus, it may be necessary to report uncorrected data or to report both the corrected and uncorrected values. The criteria for the method blanks are that the mean must be ≤ the method reporting limit (MRL) and the standard deviation must be ≤ the method detection limit (MDL). If these criteria are exceeded, then alternative reporting limits may be calculated (such as estimated MDL = 3x the standard deviation of the method blanks, and estimated MRL = 3x the estimated MDL) and/or method blank correction may not be appropriate. When reporting data, always note whether the data are method blank corrected or not. If data is reported non-method blank corrected, any results within 10x of the highest method blank value should be qualified as an estimate.

9.9 For every 10 field samples (at a minimum), a sample duplicate (DUP) must be prepared and analyzed. In addition, each different matrix type (e.g., absorber liquid, treatment system influent, treatment system effluent) from each different source should be validated by analyzing at least one DUP. As this SOP describes a closed-vessel sample digestion that takes place in the original sample bottles, DUP samples are prepared post-digestion, at the time of sample analysis. The relative percent different (RPD) between the native sample and the DUP sample is calculated as follows:

$$\mathrm{RPD} = |\mathrm{N} - \mathrm{D}| / x \times 100\%$$

where N is the native sample result, D is the duplicate result, and x is the average of the native and duplicate results. The RPD should be ≤ 20% for samples with concentrations ≥ 5x the sample-specific MRL. For every 10 field samples (at a minimum), a matrix spike (MS) and a matrix spike duplicate (MSD) must be prepared and analyzed. In addition, each different matrix type (e.g., absorber liquid, treatment system influent, treatment system effluent) from each different source should be validated by analyzing at least one MS for all applicable analytes. This is critical for good results, as the levels of interfering elements can vary greatly from one FGD system to the next. As this SOP describes a closed-vessel sample digestion that takes place in the original sample bottles, MS/MSD samples are prepared post-digestion, at the time of sample analysis. The percent recovery of the matrix spike is calculated as follows:

$$\% \text{ Recovery} = (\text{MS} - \text{N}) / \text{SL} \times 100\%$$

where MS is the matrix spike result (μg/L), N is the native sample result (μg/L), and SL is the spiking level (μg/L) that was added to the MS sample. The relative percent difference (RPD) between the values of the MS and MSD samples is also calculated as follows.

$$\text{RPD} = |\text{N} - \text{D}| / \text{x} \times 100\%$$

where N is the MS sample result, D is the MSD result, and x is the average of the MS and MSD results.

The percent recovery of the MS and MSD must be 75-125%, with an RPD between the MS and MSD ≤ 20%. MS/MSD sets must be prepared at the same dilution factor as the native sample is analyzed at to achieve the reported result. Spiking levels should be 1-10 times the native sample concentration; sample pre-screening is often necessary to achieve the proper spiking level. Spiking levels must be no lower than 5x the sample-specific MRL regardless of the native sample concentration.

9.9.1 Example calculations of the volumes and concentrations needed for performing sample spiking with more than one element at 5x the native concentration of each metal are as follows:

If a FGD water is pre-screened and estimated to contain ~120 μg/L of Zn and 25 μg/L of Ni, follow the process below.

- To have 5x the native concentration of each element we need to have spikes with concentration:

  5 * 120 μg/L of Zn = 600 μg/L Zn

  5 * 25 μg/L of Ni = 125 μg/L Ni

- After estimating the TDS of the sample, is it decided that the optimal dilution for the FGD water sample used for this example is 50x (more precisely 1+49). In that case, the solution that will be introduced to the ICP-MS instrument will have a 50x lower analyte concentration:

  120 μg/L of Zn / 50 = 2.4 μg/L Zn

  25 μg/L Ni / 50 = 0.5 μg/L Ni

- The same dilution factor should be calculated for the required spikes:

  600 μg/L Zn / 50 = 12 μg/L Zn

125 μg/L Ni / 50 = 2.5 μg/L Ni

- Assuming 15-mL vials are used for the sample and MS/MSD dilutions, 10 mL is a typical final volume.

10 mL / 50x = 0.2 mL of the original sample (add this amount to an empty 15-mL vial)

- For the volume of MS/MSD spiking solution to be added, 0.1 mL is suitable (other volumes may be used). To provide the required 12 μg/L Zn and 2.5 μg/L Ni in a final volume of 10 mL with a 0.1 mL volume of spiking standard, the MS/MSD spiking solution should contain:

(10 mL / 0.1 mL) * 12 μg/L = 1,200 μg/L Zn

(10 mL / 0.1 mL) * 2.5 μg/L = 250 μg/L Ni

- If the mathematical substitutions from the beginning of this section are used, the required spike concentrations for Zn (X μg/L) and Ni (Y μg/L) in the mixed standard spiking solution is calculated as follows:

600 μg/L = (X μg/L * 0.1 mL / 10 mL) * 50x; therefore, X = 1,200 μg/L

125 μg/L = (Y μg/L * 0.1 mL / 10 mL) * 50x; therefore, Y = 250 μg/L

- Prepare a mixed element spike standard that contains 1200 μg/L of Zn and 250 μg/L of Ni from the Zn and Ni single-element stock standards.

- Finally, prepare the MS/MSD samples by adding 0.100 mL of the mixed element spike standard to the 0.200 mL of sample in the 15-mL vial, and add 9.7 mL of diluent to achieve a final volume of 10-mL.

The above example demonstrates the preparation of a spiking standard solution containing only 2 elements. Mixed element spiking solutions should be made to contain as many of the analytes of interest as appropriate.

9.10 A minimum of 1 water standard reference material (SRM) must be analyzed with each analytical sequence (defined as a group of batches analyzed on the same calibration on the same day). The percent recovery of the SRM is calculated as follows:

% Recovery = M / T × 100%

where M is the measured value (typically following method blank correction) and T is the true or expected value.

The percent recoveries of the SRM must be 75-125%. If the results are not within control limits for each analyte, the sample results may not be reportable.

9.11 Continuing calibration verification (CCV) standards are standard that are mid-range in the calibration curve and that are analyzed after every 10 samples and at the end of the analysis. The CCV standard percent recoveries should be within 75-125% (or 85-115% if Method 200.8 is required). If the CCV recoveries are not within the control limits for any analyte, the sample results may not be reportable for that element or CCV-correction may be performed.

9.12 Continuing calibration blanks (CCB) should be monitored for the effects of carry-over and for possible system contamination. If carry-over of the analyte at levels greater than 10 times the MDL (refer to Table 12.2) and more than 10% the level at the instrument of any affected samples is observed, the sample results may not be reportable.

9.13 The absolute response of any one internal standard should not vary from the original response in the calibration blank by more than 60-125%. Some analytical samples, such as those containing high TDS or TSS concentrations, can have a serious effect on the internal standard intensities, but this does not necessarily mean the analytical system is out of control. Careful evaluation of the data and notification to the project manager should be given. If the recovery of an internal standard drifts outside of the recommended range, careful evaluation of the QC samples should be performed. If all QC samples fall within acceptance criteria, the data may be reportable with narration regarding the internal standard recoveries.

10.0 METHOD OBSERVATIONS

10.1 This SOP was researched and developed as part of a larger method development project. This project included analysis of FGD water sample splits by sector field, high-resolution ICP-MS. The use of HR-ICP-MS for confirmation analyses was integral to many of the insights listed in section 10.2.

10.2 Isotope Selection

10.2.1 Arsenic is monoisotopic at mass 75. There are no additional isotopes that can be used for direct quantification of As. Using oxygen as the reaction gas, arsenic may be quantified as $^{75}As^{16}O$ at mass 91. This mass is free from the substantial polyatomic interference of $^{40}Ar^{35}Cl$ at mass 75.

10.2.2 Selenium analysis at mass 78 was the only isotope recommended for use in this SOP. Based on in-house research and method development, ^{78}Se is the only isotope that displayed a sufficient amount of interference reduction and has been found to be the most reliable isotope for the determination of Se in FGD water using oxygen as the reaction gas. Future method development may include the use of different reaction gases for the quantitation of multiple isotopes of Se.

10.2.3 Vanadium is nearly 100% abundant at mass 51; therefore, no other isotopes were evaluated in the development of this SOP.

10.2.4 Chromium method development was performed on mass 52 and mass 53. Both isotopes were relieved from polyatomic interferences in DRC mode; however, mass 52 is typically reported due to its high relative abundance.

10.2.5 Nickel has been developed in this SOP using mass 62. The method conditions evaluated here are not adequate to remove the $^{44}Ca^{16}O+$ interference for ^{60}Ni.

10.2.6 Copper quantification is recommended only at mass 63. During the optimization experiments, it was noted that m/z 63 (measured as ^{63}Cu) produced much lower cps than m/z 65 (measured as ^{65}Cu). As the relative natural abundance ratio between ^{63}Cu and ^{65}Cu is roughly 70:30, this suggests that a polyatomic interference was probably not being sufficiently removed for isotope ^{65}Cu when using ammonia as a reaction gas. Therefore, this method is more suitable for quantitation using ^{63}Cu.

10.2.7 Zinc analysis is recommended to be performed at mass 66. For zinc determination, no combination of optimization settings was successful for mitigating the polyatomic interferences for all Zn isotopes using ammonia as a reaction gas; however, the validation results for ^{66}Zn suggested that most interferences affecting this isotope could be effectively removed.

10.2.8 For silver determination using ammonia as the DRC gas, results for the ^{109}Ag isotope were generally higher than results for the ^{107}Ag isotope. Concentrations of Ag in the test samples were too low to clearly distinguish between these alternatives. Mass 109 was selected as the primary isotope used for this SOP after evaluation of all quality control samples (SRM NIST 1643e and MS/MSD samples). However, it should be noted that polyatomic interferences usually have additive effects (unless there is over-correction by an internal correction equation); therefore, the isotope showing the lowest concentration is usually the best choice.

10.2.9 For antimony, ^{121}Sb is the recommended isotope due to its higher relative abundance. ^{123}Sb could be used as a reference isotope.

10.3 Stability Issues for Filtered, Preserved FGD Water Samples

10.3.1 Arsenic, when analyzed nine months after the initial analysis, exhibited a loss of up to 40% in concentration. On-going research is being performed to attempt to gain some insight as to why this was observed.

10.3.2 All other metals included in this SOP produced equivalent results when analyzed nine to ten months after the initial analysis, demonstrating good sample stability for that time period.

10.3.3 The EPA holding time for trace metals in water samples (as per EPA Method 1638 or EPA Method 200.8) is 6 months from the date of collection. Samples that are analyzed for regulatory purposes should not be analyzed outside of that holding time window.

10.4 Trends to Note

10.4.1 Vanadium has a tendency to experience a high level of upwards drift during analysis. Out of all of the elements included in this SOP, vanadium experiences the greatest amount of instrument drift even with instrument conditioning. The best analytical results have come after three hours of instrument conditioning. For this reason, we recommend use CCV-correction as an adjustment for biased sample results when drift is observed (i.e., CCV standard recoveries exceed the acceptance criteria).

11.0 REFERENCES

11.1 Software Guide-ELAN Version 3.4, PerkinElmer part number 1026615, 2007, Edition PerkinElmer/MDS SCIEX instruments, 71 Four Valley Drive, Concord, ON L4K 4V8.

11.2 Hardware Guide-ELAN DRC II, PerkinElmer part number 1014467, 2005, PerkinElmer Instruments LLC, 710 Bridgeport Avenue, Shelton, Connecticut, 06840.

11.3 “Safety and Health Core Rules” OSHA regulation for Washington State, Chapter 296-800 WAC.

11.4 “ELAN DRC Accessory Training Manual”. PerkinElmer 2008.

11.5 EPA Method 200.8, Revision 5.5. “Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma – Mass Spectrometry.” 1995.

11.6 EPA Method 1638. “Determination of Trace Elements in Ambient Waters by Inductively Coupled Plasma – Mass Spectrometry.” January 1996.

11.7 EPA Method 1669. “Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels.” July 1996.

12.0 TABLES

Table 12.1. Typical Dilution Ranges for FGD Waters Analyzed by ICP-DRC-MS

Element	Typical Dilution Factor Required
Aluminum	10x-100x
Antimony	1x-50x
Arsenic	10x-200x
Chromium	2x-50x
Cobalt	10x-100x
Copper	1x-10x
Nickel	1x-50x
Selenium	10x-200x
Silver	1x-10x
Vanadium	10-100x
Zinc	1x-50x

Table 12.2. Achieved MDLs and MRLs for FGD Water Analysis by ICP-DRC-MS

Element	MDL (µg/L)	MRL (µg/L)
Aluminum	0.25	1.00
Antimony	0.006	0.020
Arsenic	0.010	0.025
Chromium	0.015	0.150
Cobalt	0.010	0.100
Copper	0.020	0.200
Nickel	0.062	0.200
Selenium	0.019	0.050
Silver	0.004	0.020
Vanadium	0.015	0.150
Zinc	0.028	0.200

Table 12.3. Recommended QA Criteria for FGD Water Samples

	Measure	Minimum Frequency	Criteria	Corrective Action
Calibration Standards	Linearity of the calibration curve	Analyzed once per analytical day; Minimum of 5 calibration points	Correlation coefficient ≥ 0.995, 1st standard ≤ MRL, low standard recovery = 75-125%, all other standard recoveries = 80-120%	Reanalyze suspect calibration standard. High calibration standard(s) may be omitted as long as all samples results are still below the highest calibration standard use. If criteria still not met, then re-prepare standards and recalibrate the instrument.
Internal Standards	Variation in sample properties between samples and standards	Each standard, blank, and sample is spiked with internal standard	60-125% recovery compared to calibration blank	If the responses of the internal standards in the following CCB are within the limit, rerun the sample at an additional 2x dilution. If not, then samples must be re-analyzed on a new calibration.
Standard Reference Material (NIST 1643e)	Check the validity of the interference correction and method accuracy	At the beginning of each analytical run	All non-certified analytes < RL; other analytes within ± 25% or ± RL if < 5x RL	If SRM true value is ≥ 5x the MRL and if the recovery is outside of the control limits, then halt analysis, identify and correct problem, recalibrate if necessary, and reanalyze affected samples.
Independent Calibration Verification (ICV)	Independent check of system performance	1 following instrument calibration	Recovery = 90-110%	Correct problem prior to continuing analysis, recalibrate if necessary
Check Calibration Verification (CCV)	Accuracy	1 per 10 sample preparations and at the end of the analytical run	Recovery = 75-125% (85-115% if Method 200.8 is required)	Halt analysis, correct problem, recalibrate, and reanalyze affected samples. CCV-correction may be allowed. Note: If internal standards are not run, then CCV standards must be analyzed at various concentrations.
Method Blanks (MB)	Contamination from reagents, lab ware, etc.	Minimum of 3 per batch	Mean ≤ MRL; SD ≤ MDL or MBs <1/10th sample result	Reanalyze to confirm results. MBs may be omitted if they meet the Grubb's Outlier test and if a minimum of 3 MB remain. If MBs are still high following rejection of any Grubb's outlier, then a batch specific MDL is estimated (EMDL) by multiplying the standard deviation of the remaining MBs by 3x. The batch specific MRL is estimated (EMRL) by multiplying the EMDL by 3x. All results are evaluated against the EMDL and EMRL, and data is qualified if necessary.

Method Duplicates (DUP)	Method precision within a given matrix	Minimum of 1 per 10 client samples (prepared at instrument)	RPD ≤ 20% or ±MRL if results ≤ 5x MRL	If **RPD** criteria not met, then sample may be reanalyzed, but this is not required. Sample matrix may be inhomogeneous, in which case the results would be qualified. RPD is defined as the absolute value of the difference divided by the average of the two measurements.
Matrix Spike/ Matrix Spike Duplicate (MS/MSD)	Method accuracy and precision within a given matrix	Minimum of 1 per 10 client samples (prepared at instrument)	Recovery = 75-125% and RPD ≤ 20%	If **MS/MSD** criteria not met, samples must be qualified. Samples may be reanalyzed at a greater dilution, but this is not required. Matrix effects may be present, in which case the results would be qualified. If **RPD** criteria not met, then sample may be reanalyzed, but this is not required. Sample matrix may be inhomogeneous, in which case results would be qualified. RPD is defined as the absolute value of the difference divided by the average of the two measurements.

Table 12.4. Table of Polyatomic Interferences

^{107}Ag	51.84	$^{91}Zr^{16}O^{+}$
^{27}Al	100	$^{12}C^{15}N^{+}$, $^{13}C^{14}N^{+}$, $^{1}H^{12}C^{14}N^{+}$
^{75}As	100	$^{40}Ar^{35}Cl^{+}$,$^{38}Ar^{37}Cl^{+}$, $^{43}Ca^{16}O_{2}$, $^{23}Na^{12}C^{40}Ar$, $^{12}C^{31}P^{16}O_{2}^{+}$
^{110}Cd	12.5	$^{39}K_{2}^{16}O^{+}$
^{111}Cd	12.8	$^{39}K_{2}^{16}O_{2}^{1}H^{+}$
^{112}Cd	24.1	$^{40}Ca_{2}^{16}O_{2}$
^{113}Cd	12.22	$^{40}Ca_{2}^{16}O_{2}^{1}H^{+}$
^{59}Co	100	$^{43}Ca^{16}O^{+}$, $^{42}Ca^{16}O^{1}H^{+}$, $^{24}Mg^{35}Cl^{+}$, $^{36}Ar^{23}Na^{+}$
^{50}Cr	4.35	$^{34}S^{16}O^{+}$, $^{35}Cl^{15}N^{+}{}^{36}S^{14}N^{+}$, $^{32}S^{18}O^{+}$, $^{33}S^{17}O^{+}$
^{52}Cr	83.76	$^{35}Cl^{16}O^{1}H^{+}$, $^{40}Ar^{12}C^{+}$, $^{37}Cl^{15}N^{+}$, $^{34}S^{18}O^{+}$, $^{36}S^{16}O^{+}$, $^{35}Cl^{17}O^{+}$
^{53}Cr	9.51	$^{37}Cl^{16}O^{+}$, $^{35}Cl^{17}O^{1}H^{+}$, $^{35}Cl^{18}O^{+}$, $^{36}S^{17}O^{+}$, $^{40}Ar^{13}C^{+}$
^{54}Cr	2.38	$^{37}Cl^{16}O^{1}H^{+}$, $^{37}Cl^{17}O^{+}$
^{63}Cu	69.1	$^{40}Ar^{23}Na^{+}$, $^{23}Na^{40}Ca^{+}$, $^{46}Ca^{16}O^{1}H^{+}$, $^{36}Ar^{12}C^{14}N^{1}H^{+}$, $^{14}N^{12}C^{37}Cl^{+}$, $^{16}O^{12}C^{35}Cl^{+}$, $^{31}P^{16}O_{2}^{+}$
^{65}Cu	30.9	$^{32}C^{16}O_{2}^{1}H^{+}$, $^{40}Ca^{16}O^{1}H^{+}$, $^{32}S^{33}S^{+}$, $^{32}S^{16}O^{17}O^{+}$, $^{33}S^{16}O_{2}^{+}$, $^{12}C^{16}O^{37}Cl^{+}$, $^{12}C^{18}O^{35}Cl^{+}$
^{58}Ni	67.77	$^{23}Na^{35}Cl^{+}$, $^{40}Ca^{18}O^{+}$, $^{40}Ca^{17}O^{1}H^{+}$, $^{42}Ca^{16}O^{+}$, $^{23}Na^{35}Cl^{+}$
^{60}Ni	26.16	$^{44}Ca^{16}O^{+}$, $^{23}Na^{37}Cl^{+}$, $^{43}Ca^{16}O^{1}H^{+}$
^{61}Ni	1.25	$^{44}Ca^{16}O^{1}H^{+}$
^{62}Ni	3.66	$^{23}Na^{39}K^{+}$, $^{46}Ca^{16}O^{+}$, $^{34}S^{12}C^{16}O^{+}$
^{64}Ni	1.16	$^{32}S^{16}O_{2}^{+}$
^{121}Sb	57.36	$^{40}Ar^{81}Br^{+}$
^{74}Se	0.87	$^{37}Cl^{37}Cl^{+}$, $^{38}Ar^{36}S^{+}$
^{77}Se	7.58	$^{40}Ar^{37}Cl^{+}$, $^{12}C^{19}F^{14}N^{16}O_{2}^{+}$
^{78}Se	23.52	$^{38}Ar^{40}Ca^{+}$
^{80}Se	49.82	$^{40}Ar^{40}Ar^{+}$, $^{32}S^{16}O_{3}^{+}$
^{82}Se	9.19	$^{12}C^{35}Cl_{2}^{+}$, $^{34}S^{16}O_{3}^{+}$
^{50}V	0.24	$^{34}S^{16}O^{+}$, $^{35}Cl^{15}N^{+}$, $^{36}S^{14}N^{+}$, $^{32}S^{18}O^{+}$, $^{33}S^{17}O^{+}$
^{51}V	99.76	$^{34}S^{16}O^{1}H^{+}$, $^{35}Cl^{16}O^{+}$, $^{38}Ar^{13}C^{+}$, $^{37}Cl^{14}N^{+}$, $^{36}S^{15}N^{+}$, $^{33}S^{18}O^{+}$, $^{34}S^{17}O^{+}$
^{64}Zn	48.89	$^{32}S^{16}O_{2}^{+}$, $^{48}Ca^{16}O^{+}$, $^{32}S_{2}^{+}$, $^{34}S^{16}O_{2}^{+}$
^{66}Zn	27.81	$^{34}S^{16}O_{2}^{+}$, $^{33}S^{16}O_{2}^{1}H^{+}$, $^{32}S^{16}O^{18}O^{+}$, $^{32}S^{17}O_{2}^{+}$, $^{33}S^{16}O^{17}O^{+}$, $^{32}S^{34}S^{+}$, $^{33}S_{2}$
^{67}Zn	4.11	$^{35}Cl^{16}O_{2}^{+}$, $^{33}S^{34}S^{+}$, $^{34}S^{16}O_{2}^{1}H^{+}$, $^{32}S^{16}O^{18}O^{1}H^{+}$, $^{33}S^{34}S^{+}$, $^{34}S^{16}O^{17}O^{+}$, $^{33}S^{16}O^{18}O^{+}$, $^{32}S^{17}O^{18}O^{+}$, $^{22}S^{17}O_{2}^{+}$, $^{35}Cl^{16}O_{2}^{+}$
^{68}Zn	18.57	$^{36}S^{16}O2^{+}$, $^{34}S^{16}O^{18}O^{+}$, $^{35}Cl^{16}O^{17}O^{+}$, $^{34}S_{2}^{+}$, $^{36}Ar^{32}S^{+}$, $^{34}S^{17}O_{2}^{+}$, $^{33}S^{17}O^{18}O^{+}$, $^{32}S^{18}O_{2}^{+}$, $^{32}S^{36}S^{+}$

C

METHOD DETECTION LIMIT STUDIES

Matrix Specific MDL Study:
Aluminum in Flue Gas Desulphurization Wastewaters by Draft Method EPA 1638 (Modified) with Dynamic Reaction Cell (DRC) ICP-MS

August 16th, 2009

Brooks Rand Labs
3958 6th Avenue NW
Seattle, WA 98107

Objective. Determine the method detection limit (MDL) for aluminum (Al) in flue gas desulphurization (FGD) wastewaters prepared with a 5% (v/v) nitric acid (HNO_3) closed-vessel oven digestion, using Draft EPA Method 1638 (modified) and 40 CFR 136 part B. The samples were analyzed using ICP-DRC-MS. As detailed below, the Al MDL reported for this matrix is **0.25 µg/L**.

Analytical Method. A calibration was performed using EPA Draft Method 1638 (modified). Briefly, this method incorporates ionization of the sample in an inductively-coupled RF plasma, with detection of the resulting ions by mass spectrometer on the basis of their mass-to-charge ratio. In this method, all calibration standards and sample dilutions are prepared with 1% HNO_3: 0.5% HCl diluent. Ammonia (NH_4) gas is added to the DRC, which facilitates increased chemical resolution of the signal. Isotope 27 was used for this analysis. Prior to analyses, the samples were acidified to 5% (v/v) with concentrated HNO_3 and prepared with a closed-vessel digestion, heating for a minimum of 6 hours in an oven at 85 °C.

The MDL study consisted of the analysis of four method blanks, eight MDL samples spiked with 1.00 µg/L Al, five initial precision and recovery (IPR) samples spiked with 10.00 µg/L Al, and two MDL validation samples spiked at 0.36 and 0.53 µg/L. There were no statistical outliers. The samples were analyzed using NH_4 as the DRC gas with a flow rate of 0.6 mL/min and an RPq value of 0.80. The results of these measurements are found in the table on the next page, as well as in the raw data sheets archived in BRL's LIMS with sequence 0801229. This MDL study was prepared and analyzed by Andrew Maizel. The MDL and IPR results are reported ***corrected*** for the method blanks.

MDL Calculation. Using 40 CFR 136 part B, the MDL was calculated using the standard deviation of the spiked samples, with n = 8 replicates (7 degrees of freedom). In this case, the t value of 2.998 was used in the following equation, where σ is the standard deviation of the results obtained on samples spiked at a level near the MDL.

$$\mathbf{MDL = t^*\sigma}$$

The MDL calculated from these data is (2.998)*(0.06302) = 0.20 µg/L Al. The MDL is elevated to 0.25 µg/L to meet NELAC signal to noise ratio requirements. The MDL spiking level was 4 times the achieved MDL. The method reporting limit (MRL) is set at 1.00 µg/L. BRL reports all sample concentrations down to the MDL.

Brooks Rand Labs MDL Report

Analyte: Al	**Prepared By: MFP**	**Analyzed By: MFP**
Matrix: FGD Wastewater	**Preparation Date: 08/16/2009**	**Analysis Date: 08/16/2009**
Method: EPA 1638 mod. with DRC HNO3 Oven Digestion	**Batch: B091075**	**Sequence: 0900650**

MDL Spike Recoveries

Sample ID	Result	Units	Spiking Level	Recovery
B091075-BS1	1.22	µg/L	1.050	116
B091075-BS2	1.18	µg/L	1.050	112
B091075-BS3	1.25	µg/L	1.050	119
B091075-BS4	1.28	µg/L	1.050	122
B091075-BS5	1.13	µg/L	1.050	108
B091075-BS6	1.18	µg/L	1.050	112
B091075-BS7	1.09	µg/L	1.050	104
B091075-BS8	1.15	µg/L	1.050	110

Average Recovery: 113% (Criteria = 50 - 150%)
Standard Deviation: 0.06302 µg/L
Achieved MDL: 0.1889 µg/L

Method Blank Results

SampleID	Result	Units
B091075-BLK1	0.09	µg/L
B091075-BLK2	0.06	µg/L
B091075-BLK3	0.04	µg/L
B091075-BLK4	0.04	µg/L

Average: 0.0575 µg/L
Standard Deviation: 0.0236 µg/L

IPR Spike Recoveries

SampleID	Result	Units	Spiking Level	Recovery
B091075-BS9	11.45	µg/L	10.53	109
B091075-BSA	11.34	µg/L	10.53	108
B091075-BSB	11.34	µg/L	10.53	108
B091075-BSC	11.60	µg/L	10.53	110
B091075-BSD	11.40	µg/L	10.53	108

Average Recovery: 109%
Standard Deviation: 1%

MDL Validation Spike Recoveries

SampleID	Result	Units	Spiking Level	Recovery
B091075-BSF	0.44	µg/L	0.3600	122
B091075-BSE	0.61	µg/L	0.5300	115

Brooks Rand Labs MDL Report

Analyte: Al	**Prepared By: MFP**	**Analyzed By: MFP**
Matrix: FGD Wastewater	**Preparation Date: 08/16/2009**	**Analysis Date: 08/16/2009**
Method: EPA 1638 mod. with DRC HNO3 Oven Digestion	**Batch: B091075**	**Sequence: 0900650**

Certified Reference Material Recoveries

Sample ID	SRM Name	Result	Units	Certified Level	Recovery
B091075-SRM1	NIST 1643e	151.4	µg/L	143.2	106

Calibration Standards and Verification

SampleID	Result	Units	True Value	Recovery
0900650-CAL1	0.99	µg/L	1.000	99
0900650-CAL2	2.04	µg/L	2.000	102
0900650-CAL3	10.00	µg/L	10.000	100
0900650-CAL4	48.80	µg/L	50.000	98
0900650-CAL5	490.0	µg/L	500.000	98
0900650-CAL6	2480	µg/L	2500.000	99
0900650-CAL7	5040	µg/L	5000.000	101
0900650-CAL8	10300	µg/L	10000.000	103
0900650-CCV1	55.20	µg/L	50.000	110
0900650-CCV2	55.90	µg/L	50.000	112
0900650-CCV3	54.70	µg/L	50.000	109
0900650-CCV4	54.60	µg/L	50.000	109
0900650-CCV5	53.70	µg/L	50.000	107
0900650-CCV6	53.80	µg/L	50.000	108
0900650-CCV7	54.80	µg/L	50.000	110
0900650-CCV8	53.60	µg/L	50.000	107
0900650-ICV1	57.30	µg/L	50.000	115
0900650-SCV1	150.0	µg/L	141.800	106

Matrix Specific MDL Study: Antimony in Flue Gas Desulphurization Wastewaters by Draft Method EPA 1638 (Modified) with Dynamic Reaction Cell (DRC) ICP-MS

August 16th, 2009

Brooks Rand Labs
3958 6th Avenue NW
Seattle, WA 98107

Objective. Determine the method detection limit (MDL) for Antimony (Sb) in flue gas desulphurization (FGD) wastewaters prepared with a 5% (v/v) nitric acid (HNO_3) closed-vessel oven digestion, using Draft EPA Method 1638 (modified) and 40 CFR 136 part B. The samples were analyzed using ICP-DRC-MS. As detailed below, the Sb MDL reported for this matrix is **0.006 µg/L**.

Analytical Method. A calibration was performed using EPA Draft Method 1638 (modified). Briefly, this method incorporates ionization of the sample in an inductively-coupled RF plasma, with detection of the resulting ions by mass spectrometer on the basis of their mass-to-charge ratio. In this method, all calibration standards and sample dilutions are prepared with 1% HNO_3: 0.5% HCl diluent. Ammonia (NH_4) gas is added to the DRC, which facilitates increased chemical resolution of the signal. Isotope 121 was used for this analysis. Prior to analyses, the samples were acidified to 5% (v/v) with concentrated HNO_3 and prepared with a closed-vessel digestion, heating for a minimum of 6 hours in an oven at 85 °C.

The MDL study consisted of the analysis of four method blanks, eight MDL samples spiked with 0.105 µg/L Sb, five initial precision and recovery (IPR) samples spiked with 1.053 µg/L Sb, and two MDL validation samples spiked at 0.036 and 0.053 µg/L. There were no statistical outliers. The samples were analyzed using NH_4 as the DRC gas with a flow rate of 0.6 mL/min and an RPq value of both 0.75 and 0.80. The results of these measurements are found in the table on the next page, as well as in the raw data sheets archived in BRL's LIMS with sequence 0900650. This MDL study was prepared and analyzed by Michela Powell. The MDL and IPR results are reported ***corrected*** for the method blanks.

MDL Calculation. Using 40 CFR 136 part B, the MDL was calculated using the standard deviation of the spiked samples, with n = 8 replicates (7 degrees of freedom). In this case, the t value of 2.998 was used in the following equation, where σ is the standard deviation of the results obtained on samples spiked at a level near the MDL.

$$\mathbf{MDL = t^*\sigma}$$

The MDL calculated from these data is (2.998)*(0.00177) = 0.006 µg/L Sb for RPQ 0.75 and (2.998)*(0.00146) = 0.005 µg/L Sb for RPQ 0.80. The MDL for both RPQ values is set at **0.006 µg/L Sb.** The MDL spiking level is 3.3 times the achieved MDL. The method reporting limit (MRL) is set at 0.020 µg/L. BRL reports all sample concentrations down to the MDL.

This MDL study meets NELAC signal to noise ratio requirements.

Brooks Rand Labs MDL Report

Analyte: Sb-1	**Prepared By: MFP**	**Analyzed By: MFP**
Matrix: FGD Wastewater	**Preparation Date: 08/16/2009**	**Analysis Date: 08/16/2009**
Method: EPA 1638 mod. with DRC HNO3 Oven Digestion	**Batch: B091075**	**Sequence: 0900650**

MDL Spike Recoveries

Sample ID	Result	Units	Spiking Level	Recovery
B091075-BS1	0.022	µg/L	0.02100	105
B091075-BS2	0.022	µg/L	0.02100	105
B091075-BS3	0.019	µg/L	0.02100	90
B091075-BS4	0.023	µg/L	0.02100	110
B091075-BS5	0.021	µg/L	0.02100	100
B091075-BS6	0.019	µg/L	0.02100	90
B091075-BS7	0.021	µg/L	0.02100	100
B091075-BS8	0.018	µg/L	0.02100	86

Average Recovery: 98% (Criteria = 50 - 150%)
Standard Deviation: 0.00177 µg/L
Achieved MDL: 0.0053 µg/L

Method Blank Results

SampleID	Result	Units
B091075-BLK1	0.0004	µg/L
B091075-BLK2	0.00005	µg/L
B091075-BLK3	0.0006	µg/L
B091075-BLK4	-0.00008	µg/L

Average: 0.0002 µg/L
Standard Deviation: 0.0003 µg/L

IPR Spike Recoveries

SampleID	Result	Units	Spiking Level	Recovery
B091075-BS9	0.192	µg/L	0.2110	91
B091075-BSA	0.200	µg/L	0.2110	95
B091075-BSB	0.204	µg/L	0.2110	97
B091075-BSC	0.197	µg/L	0.2110	93
B091075-BSD	0.203	µg/L	0.2110	96

Average Recovery: 94%
Standard Deviation: 2%

MDL Validation Spike Recoveries

SampleID	Result	Units	Spiking Level	Recovery
B091075-BSF	0.008	µg/L	0.007000	114
B091075-BSE	0.012	µg/L	0.01100	109

Brooks Rand Labs MDL Report

Analyte: Sb-1	**Prepared By: MFP**	**Analyzed By: MFP**
Matrix: FGD Wastewater	**Preparation Date: 08/16/2009**	**Analysis Date: 08/16/2009**
Method: EPA 1638 mod. with DRC HNO3 Oven Digestion	**Batch: B091075**	**Sequence: 0900650**

Calibration Standards and Verification

SampleID	Result	Units	True Value	Recovery
0900650-CAL1	0.020	µg/L	0.020	100
0900650-CAL2	0.042	µg/L	0.040	105
0900650-CAL3	0.199	µg/L	0.200	100
0900650-CAL4	0.975	µg/L	1.000	98
0900650-CAL5	1.960	µg/L	2.000	98
0900650-CAL6	3.920	µg/L	4.000	98
0900650-CAL7	10.10	µg/L	10.000	101
0900650-CAL8	20.80	µg/L	20.000	104
0900650-CCV1	0.926	µg/L	1.000	93
0900650-CCV2	0.926	µg/L	1.000	93
0900650-CCV3	0.907	µg/L	1.000	91
0900650-CCV4	0.878	µg/L	1.000	88
0900650-CCV5	0.923	µg/L	1.000	92
0900650-CCV6	0.904	µg/L	1.000	90
0900650-CCV7	1.000	µg/L	1.000	100
0900650-CCV8	0.854	µg/L	1.000	85
0900650-ICV1	1.030	µg/L	1.000	103
0900650-SCV1	56.00	µg/L	58.300	96

Matrix Specific MDL Study: Arsenic in Flue Gas Desulphurization Wastewaters by Draft Method EPA 1638 (Modified) with Dynamic Reaction Cell (DRC) ICP-MS

December 25th, 2008

Brooks Rand Labs
3958 6th Avenue NW
Seattle, WA 98107

<u>Objective.</u> Determine the method detection limit (MDL) for arsenic (As) in flue gas desulphurization (FGD) wastewaters prepared with a 5% (v/v) nitric acid (HNO_3) closed-vessel oven digestion, using Draft EPA Method 1638 (modified) and 40 CFR 136 part B. The samples were analyzed using ICP-DRC-MS. As detailed below, the As MDL reported for this matrix is **<u>0.010 µg/L</u>**.

<u>Analytical Method.</u> A calibration was performed using EPA Draft Method 1638 (modified). Briefly, this method incorporates ionization of the sample in an inductively-coupled RF plasma, with detection of the resulting ions by mass spectrometer on the basis of their mass-to-charge ratio. In this method, all calibration standards and sample dilutions are prepared with 1% HNO_3: 0.5% HCl diluent. Oxygen (O_2) gas is added to the DRC, which facilitates increased chemical resolution of the signal. Isotope 91 was used for this analysis. Prior to analyses, the samples were acidified to 5% (v/v) with concentrated HNO_3 and prepared with a closed-vessel digestion, heating for a minimum of 6 hours in an oven at 85 °C.

The MDL study consisted of the analysis of four method blanks, eight MDL samples spiked with 0.025 µg/L As, five initial precision and recovery (IPR) samples spiked with 0.125 µg/L As, and two MDL validation samples spiked at 0.010 and 0.015 µg/L. There were no statistical outliers. The samples were analyzed using O_2 as the DRC gas with a flow rate of 0.6 mL/min and an RPq value of 0.70. The results of these measurements are found in the table on the next page, as well as in the raw data sheets archived in BRL's LIMS with sequence 0801230. This MDL study was prepared and analyzed by Andrew Maizel. The MDL and IPR results are reported ***<u>corrected</u>*** for the method blanks.

<u>MDL Calculation.</u> Using 40 CFR 136 part B, the MDL was calculated using the standard deviation of the spiked samples, with n = 8 replicates (7 degrees of freedom). In this case, the t value of 2.998 was used in the following equation, where σ is the standard deviation of the results obtained on samples spiked at a level near the MDL.

$$\mathbf{MDL = t^{*}\sigma}$$

The MDL calculated from these data is (2.998)*(0.003) = **<u>0.010 µg/L</u>** As. The MDL spiking level was 2.5 times the measured MDL. The method reporting limit (MRL) is set at 0.025 µg/L. BRL reports all sample concentrations down to the MDL.

Brooks Rand Labs MDL Report

Analyte: As 91	**Prepared By: ACM**	**Analyzed By: ACM**
Matrix: FGD Wastewater	**Preparation Date: 12/24/2008**	**Analysis Date: 12/25/2008**
Method: EPA 1638 mod. with DRC HNO3 Oven Digestion	**Batch: B082297**	**Sequence: 0801230**

MDL Spike Recoveries

Sample ID	Result	Units	Spiking Level	Recovery
B082297-BS1	0.027	µg/L	0.02500	108
B082297-BS2	0.021	µg/L	0.02500	84
B082297-BS3	0.029	µg/L	0.02500	116
B082297-BS4	0.021	µg/L	0.02500	84
B082297-BS5	0.026	µg/L	0.02500	104
B082297-BS6	0.027	µg/L	0.02500	108
B082297-BS7	0.029	µg/L	0.02500	116
B082297-BS8	0.027	µg/L	0.02500	108

Average Recovery: 104% (Criteria = 50 - 150%)
Standard Deviation: 0.00318 µg/L
Achieved MDL: 0.0095 µg/L

Method Blank Results

SampleID	Result	Units
B082297-BLK1	-0.008	µg/L
B082297-BLK2	-0.005	µg/L
B082297-BLK3	-0.006	µg/L
B082297-BLK4	-0.007	µg/L

Average: -0.0065 µg/L
Standard Deviation: 0.0013 µg/L

IPR Spike Recoveries

SampleID	Result	Units	Spiking Level	Recovery
B082297-BS9	0.126	µg/L	0.1250	101
B082297-BSA	0.116	µg/L	0.1250	93
B082297-BSB	0.130	µg/L	0.1250	104
B082297-BSC	0.121	µg/L	0.1250	97
B082297-BSD	0.127	µg/L	0.1250	102

Average Recovery: 99%
Standard Deviation: 4%

MDL Validation Spike Recoveries

SampleID	Result	Units	Spiking Level	Recovery
B082297-BSF	0.014	µg/L	0.01500	93
B082297-BSE	0.012	µg/L	0.01000	120

Brooks Rand Labs MDL Report

Analyte: As 91	**Prepared By: ACM**	**Analyzed By: ACM**
Matrix: FGD Wastewater	**Preparation Date: 12/24/2008**	**Analysis Date: 12/25/2008**
Method: EPA 1638 mod. with DRC HNO3 Oven Digestion	**Batch: B082297**	**Sequence: 0801230**

Certified Reference Material Recoveries

Sample ID	SRM Name	Result	Units	Certified Level	Recovery
B082297-SRM1	NIST 1643e	56.20	µg/L	60.45	93

Calibration Standards and Verification

SampleID	Result	Units	True Value	Recovery
0801230-CAL1	0.025	µg/L	0.025	100
0801230-CAL2	0.049	µg/L	0.050	98
0801230-CAL3	0.243	µg/L	0.250	97
0801230-CAL4	1.090	µg/L	1.000	109
0801230-CAL5	5.060	µg/L	5.000	101
0801230-CAL6	24.60	µg/L	25.000	98
0801230-CAL7	123.0	µg/L	125.000	98
0801230-CAL8	487.0	µg/L	500.000	97
0801230-CCV1	1.060	µg/L	1.000	106
0801230-CCV2	1.040	µg/L	1.000	104
0801230-CCV3	1.100	µg/L	1.000	110
0801230-CCV4	1.080	µg/L	1.000	108
0801230-CCV5	1.130	µg/L	1.000	113
0801230-ICV1	4.880	µg/L	5.000	98
0801230-SCV1	56.20	µg/L	60.450	93

Matrix Specific MDL Study: Chromium in Flue Gas Desulphurization Wastewaters by Draft Method EPA 1638 (Modified) with Dynamic Reaction Cell (DRC) ICP-MS

August 16th, 2009

Brooks Rand Labs
3958 6th Avenue NW
Seattle, WA 98107

Objective. Determine the method detection limit (MDL) for chromium (Cr) in flue gas desulphurization (FGD) wastewaters prepared with a 5% (v/v) nitric acid (HNO_3) closed-vessel oven digestion, using Draft EPA Method 1638 (modified) and 40 CFR 136 part B. The samples were analyzed using ICP-DRC-MS. As detailed below, the Cr MDL reported for this matrix is **0.015 µg/L**.

Analytical Method. A calibration was performed using EPA Draft Method 1638 (modified). Briefly, this method incorporates ionization of the sample in an inductively-coupled RF plasma, with detection of the resulting ions by mass spectrometer on the basis of their mass-to-charge ratio. In this method, all calibration standards and sample dilutions are prepared with 1% HNO_3: 0.5% HCl diluent. Ammonia (NH_4) gas is added to the DRC, which facilitates increased chemical resolution of the signal. Isotope 52 was used for this analysis. Prior to analyses, the samples were acidified to 5% (v/v) with concentrated HNO_3 and prepared with a closed-vessel digestion, heating for a minimum of 6 hours in an oven at 85 °C.

The MDL study consisted of the analysis of four method blanks, eight MDL samples spiked with 0.150 µg/L Cr, five initial precision and recovery (IPR) samples spiked with 1.500 µg/L Cr, and two MDL validation samples spiked at 0.054 and 0.079 µg/L. The samples were analyzed using NH_4 as the DRC gas with a flow rate of 0.6 mL/min and an RPq value of 0.75. The results of these measurements are found in the table on the next page, as well as in the raw data sheets archived in BRL's LIMS with sequence 0900650. This MDL study was prepared and analyzed by Michela Powell. The MDL and IPR results are reported ***corrected*** for the method blanks.

MDL Calculation. Using 40 CFR 136 part B, the MDL was calculated using the standard deviation of the spiked samples, with n = 8 replicates (7 degrees of freedom). In this case, the t value of 2.998 was used in the following equation, where σ is the standard deviation of the results obtained on samples spiked at a level near the MDL.

$$\mathbf{MDL = t^*\sigma}$$

The MDL calculated from these data is (2.998)*(0.00337) = 0.011 µg/L Cr. The MDL has been elevated to **0.015 µg/L** such that the low standard is 10x the MDL. The MDL spiking level was 10 times the measured

MDL. The method reporting limit (MRL) is set at 0.150 µg/L. BRL reports all sample concentrations down to the MDL.

This MDL study meets NELAC signal to noise ratio requirements.

Brooks Rand Labs MDL Report

Analyte: Cr 52	**Prepared By: MFP**	**Analyzed By: MFP**
Matrix: FGD Wastewater	**Preparation Date: 08/16/2009**	**Analysis Date: 08/16/2009**
Method: EPA 1638 mod. with DRC HNO3 Oven Digestion	**Batch: B091075**	**Sequence: 0900650**

MDL Spike Recoveries

Sample ID	Result	Units	Spiking Level	Recovery
B091075-BS1	0.161	µg/L	0.1580	102
B091075-BS2	0.161	µg/L	0.1580	102
B091075-BS3	0.157	µg/L	0.1580	99
B091075-BS4	0.168	µg/L	0.1580	106
B091075-BS5	0.163	µg/L	0.1580	103
B091075-BS6	0.162	µg/L	0.1580	103
B091075-BS7	0.164	µg/L	0.1580	104
B091075-BS8	0.166	µg/L	0.1580	105

Average Recovery: 103% (Criteria = 50 - 150%)
Standard Deviation: 0.00337 µg/L
Achieved MDL: 0.0101 µg/L

Method Blank Results

SampleID	Result	Units
B091075-BLK1	0.011	µg/L
B091075-BLK2	0.012	µg/L
B091075-BLK3	0.010	µg/L
B091075-BLK4	0.011	µg/L

Average: 0.0110 µg/L
Standard Deviation: 0.0008 µg/L

IPR Spike Recoveries

SampleID	Result	Units	Spiking Level	Recovery
B091075-BS9	1.617	µg/L	1.579	102
B091075-BSA	1.638	µg/L	1.579	104
B091075-BSB	1.642	µg/L	1.579	104
B091075-BSC	1.645	µg/L	1.579	104
B091075-BSD	1.645	µg/L	1.579	104

Average Recovery: 104%
Standard Deviation: 1%

MDL Validation Spike Recoveries

SampleID	Result	Units	Spiking Level	Recovery
B091075-BSF	0.056	µg/L	0.05400	104
B091075-BSE	0.083	µg/L	0.07900	105

Brooks Rand Labs MDL Report

Analyte: Cr 52	**Prepared By: MFP**	**Analyzed By: MFP**
Matrix: FGD Wastewater	**Preparation Date: 08/16/2009**	**Analysis Date: 08/16/2009**
Method: EPA 1638 mod. with DRC HNO3 Oven Digestion	**Batch: B091075**	**Sequence: 0900650**

Certified Reference Material Recoveries

Sample ID	SRM Name	Result	Units	Certified Level	Recovery
B091075-SRM1	NIST 1643e	20.97	µg/L	20.61	102

Calibration Standards and Verification

SampleID	Result	Units	True Value	Recovery
0900650-CAL1	0.151	µg/L	0.150	101
0900650-CAL2	0.296	µg/L	0.300	99
0900650-CAL3	1.480	µg/L	1.500	99
0900650-CAL4	12.30	µg/L	12.500	98
0900650-CAL5	24.50	µg/L	25.000	98
0900650-CAL6	125.0	µg/L	125.000	100
0900650-CAL7	253.0	µg/L	250.000	101
0900650-CAL8	519.0	µg/L	500.000	104
0900650-CCV1	13.10	µg/L	12.500	105
0900650-CCV2	13.10	µg/L	12.500	105
0900650-CCV3	12.70	µg/L	12.500	102
0900650-CCV4	12.90	µg/L	12.500	103
0900650-CCV5	12.70	µg/L	12.500	102
0900650-CCV6	12.60	µg/L	12.500	101
0900650-CCV7	12.80	µg/L	12.500	102
0900650-CCV8	12.50	µg/L	12.500	100
0900650-ICV1	13.50	µg/L	12.500	108
0900650-SCV1	20.80	µg/L	20.400	102

Matrix Specific MDL Study: Cobalt in Flue Gas Desulphurization Wastewaters by Draft Method EPA 1638 (Modified) with Dynamic Reaction Cell (DRC) ICP-MS

August 16th, 2009

Brooks Rand Labs
3958 6th Avenue NW
Seattle, WA 98107

Objective. Determine the method detection limit (MDL) for Cobalt (Co) in flue gas desulphurization (FGD) wastewaters prepared with a 5% (v/v) nitric acid (HNO_3) closed-vessel oven digestion, using Draft EPA Method 1638 (modified) and 40 CFR 136 part B. The samples were analyzed using ICP-DRC-MS. As detailed below, the Co MDL reported for this matrix is **0.010 µg/L**.

Analytical Method. A calibration was performed using EPA Draft Method 1638 (modified). Briefly, this method incorporates ionization of the sample in an inductively-coupled RF plasma, with detection of the resulting ions by mass spectrometer on the basis of their mass-to-charge ratio. In this method, all calibration standards and sample dilutions are prepared with 1% HNO_3: 0.5% HCl diluent. Ammonia (NH_4) gas is added to the DRC, which facilitates increased chemical resolution of the signal. Isotope 59 was used for this analysis. Prior to analyses, the samples were acidified to 5% (v/v) with concentrated HNO_3 and prepared with a closed-vessel digestion, heating for a minimum of 6 hours in an oven at 85 °C.

The MDL study consisted of the analysis of four method blanks, eight MDL samples spiked with 0.105 µg/L Co, five initial precision and recovery (IPR) samples spiked with 1.053 µg/L Co, and two MDL validation samples spiked at 0.036 and 0.053 µg/L. There were no statistical outliers. The samples were analyzed using NH_4 as the DRC gas with a flow rate of 0.6 mL/min and an RPq value of 0.75. The results of these measurements are found in the table on the next page, as well as in the raw data sheets archived in BRL's LIMS with sequence 0900650. This MDL study was prepared and analyzed by Michela Powell. The MDL and IPR results are reported ***corrected*** for the method blanks.

MDL Calculation. Using 40 CFR 136 part B, the MDL was calculated using the standard deviation of the spiked samples, with n = 8 replicates (7 degrees of freedom). In this case, the t value of 2.998 was used in the following equation, where σ is the standard deviation of the results obtained on samples spiked at a level near the MDL.

$$\mathbf{MDL = t^*\sigma}$$

The MDL calculated from these data is (2.998)*(0.00141) = **0.010 µg/L** Co. The MDL spiking level was 10 times the achieved MDL. The method reporting limit (MRL) is set at 0.100 µg/L. BRL reports all sample concentrations down to the MDL.
This MDL study meets NELAC signal to noise ratio requirements.

Brooks Rand Labs MDL Report

Analyte: Co-1	**Prepared By: MFP**	**Analyzed By: MFP**
Matrix: FGD Wastewater	**Preparation Date: 08/16/2009**	**Analysis Date: 08/16/2009**
Method: EPA 1638 mod. with DRC HNO3 Oven Digestion	**Batch: B091075**	**Sequence: 0900650**

MDL Spike Recoveries

Sample ID	Result	Units	Spiking Level	Recovery
B091075-BS1	0.106	µg/L	0.1050	101
B091075-BS2	0.105	µg/L	0.1050	100
B091075-BS3	0.106	µg/L	0.1050	101
B091075-BS4	0.106	µg/L	0.1050	101
B091075-BS5	0.104	µg/L	0.1050	99
B091075-BS6	0.104	µg/L	0.1050	99
B091075-BS7	0.106	µg/L	0.1050	101
B091075-BS8	0.105	µg/L	0.1050	100

Average Recovery: 100% (Criteria = 50 - 150%)
Standard Deviation: 0.00089 µg/L
Achieved MDL: 0.0027 µg/L

Method Blank Results

SampleID	Result	Units
B091075-BLK1	0.002	µg/L
B091075-BLK2	0.002	µg/L
B091075-BLK3	0.002	µg/L
B091075-BLK4	0.003	µg/L

Average: 0.0023 µg/L
Standard Deviation: 0.0005 µg/L

IPR Spike Recoveries

SampleID	Result	Units	Spiking Level	Recovery
B091075-BS9	1.042	µg/L	1.053	99
B091075-BSA	1.066	µg/L	1.053	101
B091075-BSB	1.045	µg/L	1.053	99
B091075-BSC	1.052	µg/L	1.053	100
B091075-BSD	1.055	µg/L	1.053	100

Average Recovery: 100%
Standard Deviation: 1%

MDL Validation Spike Recoveries

SampleID	Result	Units	Spiking Level	Recovery
B091075-BSF	0.035	µg/L	0.03600	97
B091075-BSE	0.055	µg/L	0.05300	104

Brooks Rand Labs MDL Report

Analyte: Co-1	**Prepared By: MFP**	**Analyzed By: MFP**
Matrix: FGD Wastewater	**Preparation Date: 08/16/2009**	**Analysis Date: 08/16/2009**
Method: EPA 1638 mod. with DRC HNO3 Oven Digestion	**Batch: B091075**	**Sequence: 0900650**

Calibration Standards and Verification

SampleID	Result	Units	True Value	Recovery
0900650-CAL1	0.101	µg/L	0.100	101
0900650-CAL2	0.198	µg/L	0.200	99
0900650-CAL3	1.000	µg/L	1.000	100
0900650-CAL4	2.500	µg/L	2.500	100
0900650-CAL5	4.960	µg/L	5.000	99
0900650-CAL6	25.00	µg/L	25.000	100
0900650-CAL7	50.20	µg/L	50.000	100
0900650-CAL8	101.0	µg/L	100.000	101
0900650-CCV1	2.540	µg/L	2.500	102
0900650-CCV2	2.540	µg/L	2.500	102
0900650-CCV3	2.460	µg/L	2.500	98
0900650-CCV4	2.480	µg/L	2.500	99
0900650-CCV5	2.450	µg/L	2.500	98
0900650-CCV6	2.430	µg/L	2.500	97
0900650-CCV7	2.510	µg/L	2.500	100
0900650-CCV8	2.450	µg/L	2.500	98
0900650-ICV1	2.670	µg/L	2.500	107
0900650-SCV1	26.60	µg/L	27.060	98

Matrix Specific MDL Study: Copper in Flue Gas Desulphurization Wastewaters by Draft Method EPA 1638 (Modified) with Dynamic Reaction Cell (DRC) ICP-MS

August 16th, 2009

Brooks Rand Labs
3958 6th Avenue NW
Seattle, WA 98107

Objective. Determine the method detection limit (MDL) for copper (Cu) in flue gas desulphurization (FGD) wastewaters prepared with a 5% (v/v) nitric acid (HNO_3) closed-vessel oven digestion, using Draft EPA Method 1638 (modified) and 40 CFR 136 part B. The samples were analyzed using ICP-DRC-MS. As detailed below, the Cu MDL reported for this matrix is **0.020 µg/L**.

Analytical Method. A calibration was performed using EPA Draft Method 1638 (modified). Briefly, this method incorporates ionization of the sample in an inductively-coupled RF plasma, with detection of the resulting ions by mass spectrometer on the basis of their mass-to-charge ratio. In this method, all calibration standards and sample dilutions are prepared with 1% HNO_3: 0.5% HCl diluent. Ammonia (NH_4) gas is added to the DRC, which facilitates increased chemical resolution of the signal. Isotope 63 was used for this analysis. Prior to analyses, the samples were acidified to 5% (v/v) with concentrated HNO_3 and prepared with a closed-vessel digestion, heating for a minimum of 6 hours in an oven at 85 °C.

The MDL study consisted of the analysis of four method blanks, eight MDL samples spiked with 0.200 µg/L Cu, five initial precision and recovery (IPR) samples spiked with 2.000 µg/L Cu, and two MDL validation samples spiked at 0.072 and 0.105 µg/L. There were no statistical outliers. The samples were analyzed using NH_4 as the DRC gas with a flow rate of 0.6 mL/min and an RPq value of 0.75. The results of these measurements are found in the table on the next page, as well as in the raw data sheets archived in BRL's LIMS with sequence 0900650. This MDL study was prepared and analyzed by Michela Powell. The MDL and IPR results are reported ***corrected*** for the method blanks.

MDL Calculation. Using 40 CFR 136 part B, the MDL was calculated using the standard deviation of the spiked samples, with n = 8 replicates (7 degrees of freedom). In this case, the t value of 2.998 was used in the following equation, where σ is the standard deviation of the results obtained on samples spiked at a level near the MDL.

$$\mathbf{MDL = t^{*}\sigma}$$

The MDL calculated from these data is (2.998)*(0.00352) = 0.011 µg/L. The MDL has been elevated to **0.020 µg/L** Cu such that the low standard is no more than 10x the MDL. The MDL spiking level was 10 times the achieved MDL. The method reporting limit (MRL) is set at 0.200 μg/L. BRL reports all sample concentrations down to the MDL.

This MDL study meets NELAC signal to noise ratio requirements.

Brooks Rand Labs MDL Report

Analyte: Cu 63	**Prepared By: MFP**	**Analyzed By: MFP**
Matrix: FGD Wastewater	**Preparation Date: 08/16/2009**	**Analysis Date: 08/16/2009**
Method: EPA 1638 mod. with DRC HNO3 Oven Digestion	**Batch: B091075**	**Sequence: 0900650**

MDL Spike Recoveries

Sample ID	Result	Units	Spiking Level	Recovery
B091075-BS1	0.209	µg/L	0.2110	99
B091075-BS2	0.214	µg/L	0.2110	101
B091075-BS3	0.215	µg/L	0.2110	102
B091075-BS4	0.219	µg/L	0.2110	104
B091075-BS5	0.219	µg/L	0.2110	104
B091075-BS6	0.216	µg/L	0.2110	102
B091075-BS7	0.211	µg/L	0.2110	100
B091075-BS8	0.216	µg/L	0.2110	102

Average Recovery: 102% (Criteria = 50 - 150%)
Standard Deviation: 0.00352 µg/L
Achieved MDL: 0.0106 µg/L

Method Blank Results

SampleID	Result	Units
B091075-BLK1	-0.0009	µg/L
B091075-BLK2	-0.004	µg/L
B091075-BLK3	-0.002	µg/L
B091075-BLK4	-0.003	µg/L

Average: -0.0025 µg/L
Standard Deviation: 0.0013 µg/L

IPR Spike Recoveries

SampleID	Result	Units	Spiking Level	Recovery
B091075-BS9	2.138	µg/L	2.105	102
B091075-BSA	2.132	µg/L	2.105	101
B091075-BSB	2.125	µg/L	2.105	101
B091075-BSC	2.127	µg/L	2.105	101
B091075-BSD	2.133	µg/L	2.105	101

Average Recovery: 101%
Standard Deviation: 0%

MDL Validation Spike Recoveries

SampleID	Result	Units	Spiking Level	Recovery
B091075-BSF	0.077	µg/L	0.07200	107
B091075-BSE	0.108	µg/L	0.1050	103

Brooks Rand Labs MDL Report

Analyte: Cu 63
Matrix: FGD Wastewater
Method: EPA 1638 mod. with DRC
HNO3 Oven Digestion

Prepared By: MFP
Preparation Date: 08/16/2009
Batch: B091075

Analyzed By: MFP
Analysis Date: 08/16/2009
Sequence: 0900650

Certified Reference Material Recoveries

SampleID	SRM Name	Result	Units	Certified Level	Recovery
B091075-SRM1	NIST 1643e	22.60	µg/L	22.99	98

Calibration Standards and Verification

SampleID	Result	Units	True Value	Recovery
0900650-CAL1	0.197	µg/L	0.200	98
0900650-CAL2	0.410	µg/L	0.400	102
0900650-CAL3	2.050	µg/L	2.000	102
0900650-CAL4	5.050	µg/L	5.000	101
0900650-CAL5	9.970	µg/L	10.000	100
0900650-CAL6	49.80	µg/L	50.000	100
0900650-CAL7	99.00	µg/L	100.000	99
0900650-CAL8	194.0	µg/L	200.000	97
0900650-CCV1	5.070	µg/L	5.000	101
0900650-CCV2	5.040	µg/L	5.000	101
0900650-CCV3	4.880	µg/L	5.000	98
0900650-CCV4	4.930	µg/L	5.000	99
0900650-CCV5	4.890	µg/L	5.000	98
0900650-CCV6	4.850	µg/L	5.000	97
0900650-CCV7	4.930	µg/L	5.000	99
0900650-CCV8	4.830	µg/L	5.000	97
0900650-ICV1	5.440	µg/L	5.000	109
0900650-SCV1	22.40	µg/L	22.760	98

Matrix Specific MDL Study: Nickel in Flue Gas Desulphurization Wastewaters by Draft Method EPA 1638 (Modified) with Dynamic Reaction Cell (DRC) ICP-MS

December 24th, 2008

Brooks Rand Labs
3958 6th Avenue NW
Seattle, WA 98107

<u>Objective.</u> Determine the method detection limit (MDL) for nickel (Ni) in flue gas desulphurization (FGD) wastewaters prepared with a 5% (v/v) nitric acid (HNO_3) closed-vessel oven digestion, using Draft EPA Method 1638 (modified) and 40 CFR 136 part B. The samples were analyzed using ICP-DRC-MS. As detailed below, the Ni MDL reported for this matrix is **<u>0.062 µg/L</u>**.

<u>Analytical Method.</u> A calibration was performed using EPA Draft Method 1638 (modified). Briefly, this method incorporates ionization of the sample in an inductively-coupled RF plasma, with detection of the resulting ions by mass spectrometer on the basis of their mass-to-charge ratio. In this method, all calibration standards and sample dilutions are prepared with 1% HNO_3: 0.5% HCl diluent. Ammonia (NH_4) gas is added to the DRC, which facilitates increased chemical resolution of the signal. Isotope 62-1 was used for this analysis. Prior to analyses, the samples were acidified to 5% (v/v) with concentrated HNO_3 and prepared with a closed-vessel digestion, heating for a minimum of 6 hours in an oven at 85 °C.

The MDL study consisted of the analysis of four method blanks, eight MDL samples spiked with 0.200 µg/L Ni, five initial precision and recovery (IPR) samples spiked with 2.000 µg/L Ni, and two MDL validation samples spiked at 0.080 and 0.120 µg/L. There were no statistical outliers. The samples were analyzed using NH_4 as the DRC gas with a flow rate of 0.6 mL/min and an RPq value of 0.75. The results of these measurements are found in the table on the next page, as well as in the raw data sheets archived in BRL's LIMS with sequence 0801229. This MDL study was prepared and analyzed by Andrew Maizel. The MDL and IPR results are reported ***<u>corrected</u>*** for the method blanks.

<u>MDL Calculation.</u> Using 40 CFR 136 part B, the MDL was calculated using the standard deviation of the spiked samples, with n = 8 replicates (7 degrees of freedom). In this case, the t value of 2.998 was used in the following equation, where σ is the standard deviation of the results obtained on samples spiked at a level near the MDL.

$$\mathbf{MDL = t^{*}\sigma}$$

The MDL calculated from these data is (2.998)*(0.021) = **<u>0.062 µg/L</u>** Ni. The MDL spiking level was 3 times the measured MDL. The method reporting limit (MRL) is set at 0.200 µg/L. BRL reports all sample concentrations down to the MDL.

Brooks Rand Labs MDL Report

Analyte: Ni-1 62	**Prepared By: ACM**	**Analyzed By: ACM**
Matrix: FGD Wastewater	**Preparation Date: 12/11/2008**	**Analysis Date: 12/24/2008**
Method: EPA 1638 mod. with DRC **HNO3 Oven Digestion**	**Batch: B082299**	**Sequence: 0801229**

MDL Spike Recoveries

Sample ID	Result	Units	Spiking Level	Recovery
B082299-BS1	0.185	µg/L	0.2000	92
B082299-BS2	0.185	µg/L	0.2000	92
B082299-BS3	0.183	µg/L	0.2000	92
B082299-BS4	0.223	µg/L	0.2000	112
B082299-BS5	0.154	µg/L	0.2000	77
B082299-BS6	0.197	µg/L	0.2000	98
B082299-BS7	0.167	µg/L	0.2000	84
B082299-BS8	0.172	µg/L	0.2000	86

Average Recovery: 92% (Criteria = 50 - 150%)
Standard Deviation: 0.02078 µg/L
Achieved MDL: 0.062 µg/L

Method Blank Results

SampleID	Result	Units
B082299-BLK1	-0.024	µg/L
B082299-BLK2	-0.031	µg/L
B082299-BLK3	-0.028	µg/L
B082299-BLK4	-0.022	µg/L

Average: -0.026 µg/L
Standard Deviation: 0.004 µg/L

IPR Spike Recoveries

SampleID	Result	Units	Spiking Level	Recovery
B082299-BS9	2.266	µg/L	2.000	113
B082299-BSA	2.157	µg/L	2.000	108
B082299-BSB	2.187	µg/L	2.000	109
B082299-BSC	2.205	µg/L	2.000	110
B082299-BSD	2.314	µg/L	2.000	116

Average Recovery: 111%
Standard Deviation: 3%

MDL Validation Spike Recoveries

SampleID	Result	Units	Spiking Level	Recovery
B082299-BSF	0.109	µg/L	0.1200	91
B082299-BSE	0.063	µg/L	0.08000	79

Brooks Rand Labs MDL Report

Analyte: Ni-1 62
Matrix: FGD Wastewater
Method: EPA 1638 mod. with DRC
HNO3 Oven Digestion

Prepared By: ACM
Preparation Date: 12/11/2008
Batch: B082299

Analyzed By: ACM
Analysis Date: 12/24/2008
Sequence: 0801229

Calibration Standards and Verification

SampleID	Result	Units	True Value	Recovery
0801229-CAL1	0.209	µg/L	0.20	104
0801229-CAL2	0.360	µg/L	0.40	90
0801229-CAL3	2.140	µg/L	2.00	107
0801229-CAL4	4.980	µg/L	5.00	100
0801229-CAL5	10.10	µg/L	10.00	101
0801229-CAL6	50.10	µg/L	50.00	100
0801229-CAL7	99.70	µg/L	100.00	100
0801229-CAL8	197.0	µg/L	200.00	98
0801229-CCV1	5.160	µg/L	5.00	103
0801229-CCV2	5.130	µg/L	5.00	103
0801229-ICV1	5.220	µg/L	5.00	104
0801229-SCV1	62.80	µg/L	60.89	103

Matrix Specific MDL Study:
Selenium in Flue Gas Desulphurization Wastewaters by Draft Method EPA 1638 (Modified) with Dynamic Reaction Cell (DRC) ICP-MS

December 25th, 2008

Brooks Rand Labs
3958 6th Avenue NW
Seattle, WA 98107

Objective. Determine the method detection limit (MDL) for selenium (Se) in flue gas desulphurization (FGD) wastewaters prepared with a 5% (v/v) nitric acid (HNO_3) closed-vessel oven digestion, using Draft EPA Method 1638 (modified) and 40 CFR 136 part B. The samples were analyzed using ICP-DRC-MS. As detailed below, the Se MDL reported for this matrix is **0.019 µg/L**.

Analytical Method. A calibration was performed using EPA Draft Method 1638 (modified). Briefly, this method incorporates ionization of the sample in an inductively-coupled RF plasma, with detection of the resulting ions by mass spectrometer on the basis of their mass-to-charge ratio. In this method, all calibration standards and sample dilutions are prepared with 1% HNO_3: 0.5% HCl diluent. Oxygen (O_2) gas is added to the DRC, which facilitates increased chemical resolution of the signal. Isotope 78 was used for this analysis. Prior to analyses, the samples were acidified to 5% (v/v) with concentrated HNO_3 and prepared with a closed-vessel digestion, heating for a minimum of 6 hours in an oven at 85 °C.

The MDL study consisted of the analysis of four method blanks, eight MDL samples spiked with 0.050 µg/L Se, five initial precision and recovery (IPR) samples spiked with 0.125 µg/L Se, and two MDL validation samples spiked at 0.010 and 0.250 µg/L. There were no statistical outliers. The samples were analyzed using O_2as the DRC gas with a flow rate of 0.6 mL/min and an RPq value of 0.80. The results of these measurements are found in the table on the next page, as well as in the raw data sheets archived in BRL's LIMS with sequence 0801230. This MDL study was prepared and analyzed by Andrew Maizel. The MDL and IPR results are reported ***corrected*** for the method blanks.

MDL Calculation. Using 40 CFR 136 part B, the MDL was calculated using the standard deviation of the spiked samples, with n = 8 replicates (7 degrees of freedom). In this case, the t value of 2.998 was used in the following equation, where σ is the standard deviation of the results obtained on samples spiked at a level near the MDL.

$$\mathbf{MDL = t^{*}\sigma}$$

The MDL calculated from these data is (2.998)*(0.006) = **0.019 µg/L** Se. The MDL spiking level was 2.6 times the measured MDL. The method reporting limit (MRL) is set at 0.050 µg/L. BRL reports all sample concentrations down to the MDL.

Brooks Rand Labs MDL Report

Analyte: Se 78	**Prepared By: ACM**	**Analyzed By: ACM**
Matrix: FGD Wastewater	**Preparation Date: 12/24/2008**	**Analysis Date: 12/25/2008**
Method: EPA 1638 mod. with DRC **HNO3 Oven Digestion**	**Batch: B082297**	**Sequence: 0801230**

MDL Spike Recoveries

Sample ID	Result	Units	Spiking Level	Recovery
B082297-BS1	0.051	µg/L	0.05000	102
B082297-BS2	0.040	µg/L	0.05000	80
B082297-BS3	0.047	µg/L	0.05000	94
B082297-BS4	0.034	µg/L	0.05000	68
B082297-BS5	0.053	µg/L	0.05000	106
B082297-BS6	0.047	µg/L	0.05000	94
B082297-BS7	0.051	µg/L	0.05000	102
B082297-BS8	0.045	µg/L	0.05000	90

Average Recovery: 92% (Criteria = 50 - 150%)
Standard Deviation: 0.00635 µg/L
Achieved MDL: 0.0190 µg/L

Method Blank Results

SampleID	Result	Units
B082297-BLK1	0.016	µg/L
B082297-BLK2	0.006	µg/L
B082297-BLK3	0.010	µg/L
B082297-BLK4	0.007	µg/L

Average: 0.0098 µg/L
Standard Deviation: 0.0045 µg/L

IPR Spike Recoveries

SampleID	Result	Units	Spiking Level	Recovery
B082297-BS9	0.262	µg/L	0.2500	105
B082297-BSA	0.255	µg/L	0.2500	102
B082297-BSB	0.235	µg/L	0.2500	94
B082297-BSC	0.266	µg/L	0.2500	106
B082297-BSD	0.259	µg/L	0.2500	104

Average Recovery: 102%
Standard Deviation: 5%

MDL Validation Spike Recoveries

SampleID	Result	Units	Spiking Level	Recovery
B082297-BSF	0.026	µg/L	0.03000	87
B082297-BSE	0.013	µg/L	0.02000	65

Brooks Rand Labs MDL Report

Analyte: Se 78	**Prepared By: ACM**	**Analyzed By: ACM**
Matrix: FGD Wastewater	**Preparation Date: 12/24/2008**	**Analysis Date: 12/25/2008**
Method: EPA 1638 mod. with DRC HNO3 Oven Digestion	**Batch: B082297**	**Sequence: 0801230**

Certified Reference Material Recoveries

Sample ID	SRM Name	Result	Units	Certified Level	Recovery
B082297-SRM1	NIST 1643e	11.18	µg/L	11.97	93

Calibration Standards and Verification

SampleID	Result	Units	True Value	Recovery
0801230-CAL1	0.050	µg/L	0.050	100
0801230-CAL2	0.103	µg/L	0.100	103
0801230-CAL3	0.233	µg/L	0.250	93
0801230-CAL4	1.110	µg/L	1.000	111
0801230-CAL5	5.060	µg/L	5.000	101
0801230-CAL6	24.60	µg/L	25.000	98
0801230-CAL7	123.0	µg/L	125.000	98
0801230-CAL8	478.0	µg/L	500.000	96
0801230-CCV1	1.100	µg/L	1.000	110
0801230-CCV2	1.100	µg/L	1.000	110
0801230-CCV3	1.220	µg/L	1.000	122
0801230-CCV4	1.220	µg/L	1.000	122
0801230-CCV5	1.120	µg/L	1.000	112
0801230-ICV1	5.060	µg/L	5.000	101
0801230-SCV1	11.20	µg/L	11.970	94

Matrix Specific MDL Study: Silver in Flue Gas Desulphurization Wastewaters by Draft Method EPA 1638 (Modified) with Dynamic Reaction Cell (DRC) ICP-MS

December 24th, 2008

Brooks Rand Labs
3958 6th Avenue NW
Seattle, WA 98107

Objective. Determine the method detection limit (MDL) for silver (Ag) in flue gas desulphurization (FGD) wastewaters prepared with a 5% (v/v) nitric acid (HNO_3) closed-vessel oven digestion, using Draft EPA Method 1638 (modified) and 40 CFR 136 part B. The samples were analyzed using ICP-DRC-MS. As detailed below, the Ag MDL reported for this matrix is **0.004 µg/L**.

Analytical Method. A calibration was performed using EPA Draft Method 1638 (modified). Briefly, this method incorporates ionization of the sample in an inductively-coupled RF plasma, with detection of the resulting ions by mass spectrometer on the basis of their mass-to-charge ratio. In this method, all calibration standards and sample dilutions are prepared with 1% HNO_3: 0.5% HCl diluent. Ammonia (NH_4) gas is added to the DRC, which facilitates increased chemical resolution of the signal. Isotope 107 was used for this analysis. Prior to analyses, the samples were acidified to 5% (v/v) with concentrated HNO_3 and prepared with a closed-vessel digestion, heating for a minimum of 6 hours in an oven at 85 °C.

The MDL study consisted of the analysis of four method blanks, eight MDL samples spiked with 0.020 µg/L Ag, five initial precision and recovery (IPR) samples spiked with 0.101 µg/L Ag, and two MDL validation samples spiked at 0.012 and 0.008 µg/L. There were no statistical outliers. The samples were analyzed using NH_4 as the DRC gas with a flow rate of 0.6 mL/min and an RPq value of 0.80. The results of these measurements are found in the table on the next page, as well as in the raw data sheets archived in BRL's LIMS with sequence 0801229. This MDL study was prepared and analyzed by Andrew Maizel. The MDL and IPR results are reported ***corrected*** for the method blanks.

MDL Calculation. Using 40 CFR 136 part B, the MDL was calculated using the standard deviation of the spiked samples, with n = 8 replicates (7 degrees of freedom). In this case, the t value of 2.998 was used in the following equation, where σ is the standard deviation of the results obtained on samples spiked at a level near the MDL.

$$\mathbf{MDL = t^*\sigma}$$

The MDL calculated from these data is (2.998)*(0.001) = **0.004 µg/L** Ag. The MDL spiking level was 5 times the measured MDL. The method reporting limit (MRL) is set at 0.020 µg/L. BRL reports all sample concentrations down to the MDL.

Brooks Rand Labs MDL Report

Analyte: Ag 107	**Prepared By: ACM**	**Analyzed By: ACM**
Matrix: FGD Wastewater	**Preparation Date: 12/24/2008**	**Analysis Date: 12/24/2008**
Method: EPA 1638 mod. with DRC HNO3 Oven Digestion	**Batch: B082295**	**Sequence: 0801229**

MDL Spike Recoveries

Sample ID	Result	Units	Spiking Level	Recovery
B082295-BS1	0.017	µg/L	0.02000	85
B082295-BS2	0.019	µg/L	0.02000	95
B082295-BS3	0.020	µg/L	0.02000	100
B082295-BS4	0.020	µg/L	0.02000	100
B082295-BS5	0.019	µg/L	0.02000	95
B082295-BS6	0.021	µg/L	0.02000	105
B082295-BS7	0.020	µg/L	0.02000	100
B082295-BS8	0.017	µg/L	0.02000	85

Average Recovery: 96% (Criteria = 50 - 150%)
Standard Deviation: 0.00146 µg/L
Achieved MDL: 0.004 µg/L

Method Blank Results

SampleID	Result	Units
B082295-BLK1	-0.002	µg/L
B082295-BLK2	-0.002	µg/L
B082295-BLK3	-0.002	µg/L
B082295-BLK4	-0.002	µg/L

Average: -0.002 µg/L
Standard Deviation: 0.000 µg/L

IPR Spike Recoveries

SampleID	Result	Units	Spiking Level	Recovery
B082295-BS9	0.095	µg/L	0.1010	94
B082295-BSA	0.104	µg/L	0.1010	103
B082295-BSB	0.097	µg/L	0.1010	96
B082295-BSC	0.096	µg/L	0.1010	95
B082295-BSD	0.100	µg/L	0.1010	99

Average Recovery: 97%
Standard Deviation: 4%

MDL Validation Spike Recoveries

SampleID	Result	Units	Spiking Level	Recovery
B082295-BSF	0.014	µg/L	0.01200	117
B082295-BSE	0.013	µg/L	8.000E-3	162

Brooks Rand Labs MDL Report

Analyte: Ag 107	**Prepared By: ACM**	**Analyzed By: ACM**
Matrix: FGD Wastewater	**Preparation Date: 12/24/2008**	**Analysis Date: 12/24/2008**
Method: EPA 1638 mod. with DRC **HNO3 Oven Digestion**	**Batch: B082295**	**Sequence: 0801229**

Certified Reference Material Recoveries

SampleID	CRM Name	Result	Units	Certified Level	Recovery
B082295-SRM1	NIST 1643e	1.096	µg/L	1.062	103

Calibration Standards and Verification

SampleID	Result	Units	True Value	Recovery
0801229-CAL1	0.020	µg/L	0.02	100
0801229-CAL2	0.042	µg/L	0.04	105
0801229-CAL3	0.202	µg/L	0.20	101
0801229-CAL4	1.000	µg/L	1.00	100
0801229-CAL5	1.980	µg/L	2.00	99
0801229-CAL6	10.00	µg/L	10.00	100
0801229-CAL7	19.80	µg/L	20.00	99
0801229-CAL8	39.30	µg/L	40.00	98
0801229-CCV1	0.984	µg/L	1.00	98
0801229-CCV2	1.020	µg/L	1.00	102
0801229-ICV1	5.270	µg/L	5.00	105
0801229-SCV1	1.090	µg/L	1.06	103

Matrix Specific MDL Study: Vanadium in Flue Gas Desulphurization Wastewaters by Draft Method EPA 1638 (Modified) with Dynamic Reaction Cell (DRC) ICP-MS

December 24th, 2008

Brooks Rand Labs
3958 6th Avenue NW
Seattle, WA 98107

<u>Objective.</u> Determine the method detection limit (MDL) for vanadium (V) in flue gas desulphurization (FGD) wastewaters prepared with a 5% (v/v) nitric acid (HNO_3) closed-vessel oven digestion, using Draft EPA Method 1638 (modified) and 40 CFR 136 part B. The samples were analyzed using ICP-DRC-MS. As detailed below, the V MDL reported for this matrix is **<u>0.015 µg/L</u>**.

<u>Analytical Method.</u> A calibration was performed using EPA Draft Method 1638 (modified). Briefly, this method incorporates ionization of the sample in an inductively-coupled RF plasma, with detection of the resulting ions by mass spectrometer on the basis of their mass-to-charge ratio. In this method, all calibration standards and sample dilutions are prepared with 1% HNO_3: 0.5% HCl diluent. Ammonia (NH_4) gas is added to the DRC, which facilitates increased chemical resolution of the signal. Isotope 51 was used for this analysis. Prior to analyses, the samples were acidified to 5% (v/v) with concentrated HNO_3 and prepared with a closed-vessel digestion, heating for a minimum of 6 hours in an oven at 85 °C.

The MDL study consisted of the analysis of four method blanks, eight MDL samples spiked with 0.150 µg/L V, five initial precision and recovery (IPR) samples spiked with 1.500 µg/L V, and two MDL validation samples spiked at 0.060 and 0.090 µg/L. There were no statistical outliers. The samples were analyzed using NH_4 as the DRC gas with a flow rate of 0.6 mL/min and an RPq value of 0.80. The results of these measurements are found in the table on the next page, as well as in the raw data sheets archived in BRL's LIMS with sequence 0801188. This MDL study was prepared and analyzed by Andrew Maizel. The MDL and IPR results are reported ***<u>corrected</u>*** for the method blanks.

<u>MDL Calculation.</u> Using 40 CFR 136 part B, the MDL was calculated using the standard deviation of the spiked samples, with n = 8 replicates (7 degrees of freedom). In this case, the t value of 2.998 was used in the following equation, where σ is the standard deviation of the results obtained on samples spiked at a level near the MDL.

$$\mathbf{MDL = t^{*}\sigma}$$

The MDL calculated from these data is (2.998)*(0.005) = 0.014µg/L. The lowest calibration standard is set at 0.150 µg/L, and a criterion for the MDL is that it shall not be more than 10x lower than the MRL; therefore, the achieved MDL has been raised to **<u>0.015 µg/L</u>** V. The MDL spiking level was 9.4 times the measured MDL.

MDL Study Reports

The method reporting limit (MRL) is set at 0.150 µg/L. BRL reports all sample concentrations down to the MDL.

Brooks Rand Labs MDL Report

Analyte: V	**Prepared By: ACM**	**Analyzed By: ACM**
Matrix: FGD Wastewater	**Preparation Date: 12/11/2008**	**Analysis Date: 12/24/2008**
Method: EPA 1638 mod. with DRC HNO3 Oven Digestion	**Batch: B082299**	**Sequence: 0801229**

MDL Spike Recoveries

Sample ID	Result	Units	Spiking Level	Recovery
B082299-BS1	0.136	µg/L	0.1500	91
B082299-BS2	0.125	µg/L	0.1500	83
B082299-BS3	0.124	µg/L	0.1500	83
B082299-BS4	0.124	µg/L	0.1500	83
B082299-BS5	0.124	µg/L	0.1500	83
B082299-BS6	0.133	µg/L	0.1500	89
B082299-BS7	0.127	µg/L	0.1500	85
B082299-BS8	0.127	µg/L	0.1500	85

Average Recovery: 85% (Criteria = 50 - 150%)
Standard Deviation: 0.00457 µg/L
Achieved MDL: 0.014 µg/L

Method Blank Results

SampleID	Result	Units
B082299-BLK1	-0.004	µg/L
B082299-BLK2	-0.004	µg/L
B082299-BLK3	-0.005	µg/L
B082299-BLK4	-0.004	µg/L

Average: -0.004 µg/L
Standard Deviation: 0.001 µg/L

IPR Spike Recoveries

SampleID	Result	Units	Spiking Level	Recovery
B082299-BS9	1.270	µg/L	1.500	85
B082299-BSA	1.289	µg/L	1.500	86
B082299-BSB	1.279	µg/L	1.500	85
B082299-BSC	1.260	µg/L	1.500	84
B082299-BSD	1.292	µg/L	1.500	86

Average Recovery: 85%
Standard Deviation: 1%

MDL Validation Spike Recoveries

SampleID	Result	Units	Spiking Level	Recovery
B082299-BSF	0.081	µg/L	0.09000	90
B082299-BSE	0.047	µg/L	0.06000	78

Brooks Rand Labs MDL Report

Analyte: V	**Prepared By: ACM**	**Analyzed By: ACM**
Matrix: FGD Wastewater	**Preparation Date: 12/11/2008**	**Analysis Date: 12/24/2008**
Method: EPA 1638 mod. with DRC HNO3 Oven Digestion	**Batch: B082299**	**Sequence: 0801229**

Certified Reference Material Recoveries

SampleID	CRM Name	Result	Units	Certified Level	Recovery
B082299-SRM1	NIST 1643e	36.19	µg/L	37.86	96

Calibration Standards and Verification

SampleID	Result	Units	True Value	Recovery
0801229-CAL1	0.148	µg/L	0.15	99
0801229-CAL2	0.309	µg/L	0.30	103
0801229-CAL3	1.550	µg/L	1.50	103
0801229-CAL4	4.830	µg/L	5.00	97
0801229-CAL5	9.490	µg/L	10.00	95
0801229-CAL6	19.80	µg/L	20.00	99
0801229-CAL7	50.40	µg/L	50.00	101
0801229-CAL8	104.0	µg/L	100.00	104
0801229-CCV1	4.930	µg/L	5.00	99
0801229-CCV2	5.190	µg/L	5.00	104
0801229-ICV1	4.700	µg/L	5.00	94
0801229-SCV1	36.20	µg/L	37.86	96

Matrix Specific MDL Study: Zinc in Flue Gas Desulphurization Wastewaters by Draft Method EPA 1638 (Modified) with Dynamic Reaction Cell (DRC) ICP-MS

December 24th, 2008

Brooks Rand Labs
3958 6th Avenue NW
Seattle, WA 98107

Objective. Determine the method detection limit (MDL) for zinc (Zn) in flue gas desulphurization (FGD) wastewaters prepared with a 5% (v/v) nitric acid (HNO_3) closed-vessel oven digestion, using Draft EPA Method 1638 (modified) and 40 CFR 136 part B. The samples were analyzed using ICP-DRC-MS. As detailed below, the Zn MDL reported for this matrix is **0.028 µg/L**.

Analytical Method. A calibration was performed using EPA Draft Method 1638 (modified). Briefly, this method incorporates ionization of the sample in an inductively-coupled RF plasma, with detection of the resulting ions by mass spectrometer on the basis of their mass-to-charge ratio. In this method, all calibration standards and sample dilutions are prepared with 1% HNO_3: 0.5% HCl diluent. Ammonia (NH_4) gas is added to the DRC, which facilitates increased chemical resolution of the signal. Isotope 66-1 was used for this analysis. Prior to analyses, the samples were acidified to 5% (v/v) with concentrated HNO_3 and prepared with a closed-vessel digestion, heating for a minimum of 6 hours in an oven at 85 °C.

The MDL study consisted of the analysis of four method blanks, eight MDL samples spiked with 0.200 µg/L Zn, five initial precision and recovery (IPR) samples spiked with 2.000 µg/L Zn, and two MDL validation samples spiked at 0.080 and 0.120 µg/L. The Zn results for one MDL sample (B082299-BS6) and one IPR sample (B082299-BSA) were determined to be Grubb's Outliers and were omitted from use in the calculations described below. The samples were analyzed using NH_4 as the DRC gas with a flow rate of 0.6 mL/min and an RPq value of 0.80. The results of these measurements are found in the table on the next page, as well as in the raw data sheets archived in BRL's LIMS with sequence 0801229. This MDL study was prepared and analyzed by Andrew Maizel. The MDL and IPR results are reported ***corrected*** for the method blanks.

MDL Calculation. Using 40 CFR 136 part B, the MDL was calculated using the standard deviation of the spiked samples, with n = 7 replicates (6 degrees of freedom). In this case, the t value of 3.143 was used in the following equation, where σ is the standard deviation of the results obtained on samples spiked at a level near the MDL.

$$\mathbf{MDL = t^*\sigma}$$

The MDL calculated from these data is (3.143)*(0.009) = **<u>0.028 µg/L</u>** Zn. The MDL spiking level was 5.7 times the measured MDL. The method reporting limit (MRL) is set at 0.200 µg/L. BRL reports all sample concentrations down to the MDL.

Brooks Rand Labs MDL Report

Analyte: Zn-1 66
Matrix: FGD Wastewater
Method: EPA 1638 mod. with DRC HNO3 Oven Digestion

Prepared By: ACM
Preparation Date: 12/11/2008
Batch: B082299

Analyzed By: ACM
Analysis Date: 12/24/2008
Sequence: 0801229

MDL Spike Recoveries

Sample ID	Result	Units	Spiking Level	Recovery
B082299-BS1	0.197	µg/L	0.2000	98
B082299-BS2	0.195	µg/L	0.2000	97
B082299-BS3	0.190	µg/L	0.2000	95
B082299-BS4	0.183	µg/L	0.2000	92
B082299-BS5	0.205	µg/L	0.2000	102
B082299-BS7	0.207	µg/L	0.2000	104
B082299-BS8	0.188	µg/L	0.2000	94

Average Recovery: 97% (Criteria = 50 - 150%)
Standard Deviation: 0.00881 µg/L
Achieved MDL: 0.028 µg/L

Method Blank Results

SampleID	Result	Units
B082299-BLK1	-0.036	µg/L
B082299-BLK2	-0.044	µg/L
B082299-BLK3	-0.053	µg/L
B082299-BLK4	-0.040	µg/L

Average: -0.043 µg/L
Standard Deviation: 0.007 µg/L

IPR Spike Recoveries

SampleID	Result	Units	Spiking Level	Recovery
B082299-BS9	1.847	µg/L	2.000	92
B082299-BSB	1.884	µg/L	2.000	94
B082299-BSC	1.818	µg/L	2.000	91
B082299-BSD	1.910	µg/L	2.000	96

Average Recovery: 93%
Standard Deviation: 2%

MDL Validation Spike Recoveries

SampleID	Result	Units	Spiking Level	Recovery
B082299-BSE	0.142	µg/L	0.08000	178
B082299-BSF	0.119	µg/L	0.1200	99

Brooks Rand Labs MDL Report

Analyte: Zn-1 66	**Prepared By: ACM**	**Analyzed By: ACM**
Matrix: FGD Wastewater	**Preparation Date: 12/11/2008**	**Analysis Date: 12/24/2008**
Method: EPA 1638 mod. with DRC HNO3 Oven Digestion	**Batch: B082299**	**Sequence: 0801229**

Certified Reference Material Recoveries

SampleID	CRM Name	Result	Units	Certified Level	Recovery
B082299-SRM1	NIST 1643e	70.79	µg/L	76.50	93

Calibration Standards and Verification

SampleID	Result	Units	True Value	Recovery
0801229-CAL1	0.187	µg/L	0.20	94
0801229-CAL2	0.445	µg/L	0.40	111
0801229-CAL3	2.140	µg/L	2.00	107
0801229-CAL4	5.060	µg/L	5.00	101
0801229-CAL5	50.50	µg/L	50.00	101
0801229-CAL6	246.0	µg/L	250.00	98
0801229-CAL7	481.0	µg/L	500.00	96
0801229-CAL8	915.0	µg/L	1000.00	92
0801229-CCV1	5.090	µg/L	5.00	102
0801229-CCV2	5.310	µg/L	5.00	106
0801229-ICV1	5.210	µg/L	5.00	104
0801229-SCV1	70.60	µg/L	76.50	92

Outliers

SampleID	Result	Units	Spiking Level	Recovery
B082299-BS6	0.730	µg/L	0.2000	365
B082299-BSA	3.140	µg/L	2.000	157

The above results are determined to be Grubb's outliers at the 99% confidence interval and are therefore not included in any calculations.

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Electric Power Research Institute
3420 Hillview Avenue, Palo Alto, California 94304-1338 • PO Box 10412, Palo Alto, California 94303-0813 • USA
800.313.3774 • 650.855.2121 • askepri@epri.com • www.epri.com