



### NTRODUCTION

flue gas desulfurization (FGD) waters using an ICP-MS with Dynamic Reaction Cell (DRC) technology and a high-performance sample introduction system. The method is optimized and validated for the quantification of Ag, As, Cr, Cu, Ni, Sb, Se, V, and Zn. Additional information is presented on the method development challenges related to the determination of AI and Co.

In response to the need for more accurate data for FGD waters than was available using standard ICP-MS methods, the Electric Power Research Institute (EPRI) contracted Brooks

Rand Labs (BRL) to develop an optimized analytical standard operating procedure (SOP) using the ICP-DRC-MS technology (Figure 1). The objective was to develop a method that would eliminate or reduce polyatomic interferences in this matrix, and that can be implemented by a commercial or utility laboratory.

High-resolution sector field ICP-MS (HR-ICP-MS) analyses were performed on the same samples by the Ohio State University. To determine whether a second laboratory could successfully implement the SOP, a portion of samples were analyzed by the University of Arizona (UA). All ICP-DRC-MS analyses were performed using the Perkin-Elmer ELAN<sup>®</sup> DRC<sup>™</sup> II ICP-MS and an ESI<sup>®</sup> SC-FAST<sup>™</sup> sample introduction system.



Figure 1 - Brooks Rand Labs Trace Metals Research *Group with Perkin Elmer*<sup>®</sup> *DRC*<sup>™</sup> *II ICP-MS and ESI*<sup>®</sup> SC-FAST<sup>™</sup> high performance sample introduction

## FGD WASTEWATER

Flue gas desulfurization is the process of removing the sulfur dioxide from the flue gas through the use of wet scrubber systems that utilize an alkali reagent, often limestone. Calcium carbonate slurry is contacted with the flue gas to convert gaseous sulfur dioxide to calcium sulfite. In most new limestone FGDs, air is used to further oxidize the calcium sulfite to calcium sulfate (gypsum). The slurry is then purged from the wet scrubber and the gypsum is separated from the resultant blowdown stream. This aqueous waste stream may then pass through a series of physical and chemical treatment processes before it is discharged (Figure 2).



The accurate quantification of metals at low concentrations is important for power plants that need to monitor for compliance with water discharge permits. The composition of FGD waters is highly variable from plant to plant and presents a challenging matrix for trace metal analysis, similar in difficulty to seawater.

FGD water samples are typically very high in dissolved solids, including chloride, bromide, carbon, sulfur, and other elements that may contribute to polyatomic interferences when analyzed by standard mode ICP-MS.

Elemental compositions of the unfiltered FGD water samples used in this project are shown in Table 1, which represents the average composition of nine samples taken from different points in the wastewater treatment process, ranging from primary solids removal (clarifier effluent) to physical/chemical treatment system effluent.

Conc. (mg/L)
0.147
364
1,850
7,810
< 1.5
129
3,700
23.1
1,070
9,630
31,300
375
71

Table 1

Approach

### Analytical Challenges

- internal standard solution

### Preparation

- in solution

### Introduction System



## INSTRUMENT CONDITIONING

resulted in acceptable stability.

Figure 4 - 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.

# An Optimized Method for Trace Metals Determination in Flue Gas Desulfurization Waters Using ICP-DRC-MS



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## **Approach & Analytical Challenges**

. Develop and optimize ICP-DRC-MS methods for Ag, Al, As, Co, Cr, Cu, Ni, Sb, Se, V, and Zn in FGD wastewater. 2. Validate method with high-resolution ICP-MS.

3. Prepare a draft Standard Operating Procedure (SOP). 4. Verify SOP in a second laboratory.

• mass spectral interferences  $\rightarrow$  refer to handout • FGD matrix loading  $\rightarrow$  high sample dilution and low sample introduction flow rate are

• changes in ionization efficiency of the plasma from sample-specific levels of carbon or high levels of chloride or bromine  $\rightarrow$  methanol and acetic acid were used as additions to the

### SAMPLE PREPARATION & INTRODUCTION SYSTEM

- All samples were preserved and prepared with a closed-vessel oven digestion.
- samples were acidified to 5% (v/v) with concentrated HNO<sub>2</sub>
- samples were digested under moderate pressure at 85 °C for a minimum of 8 hours • acidification of the sample digestate to 0.5% (v/v) with HCI was necessary to keep Ag and Sb

Use of the ESI<sup>®</sup> SC-FAST<sup>™</sup> Sample Introduction System (Figure 3) improved method

Figure 3 - Schematic of ESI<sup>®</sup> SC-FAST<sup>m</sup> high-performance sample introduction system coupled to the ICP-DRC-MS.

Signal stability had been one of the most challenging issues related to the analysis of FGD waters. The need for an instrument

conditioning period quickly became apparent Repeated analysis of an effluent sample

diluted to 0.5% TDS for a minimum of 1 hour (longer for some elements) prior to calibration





## **DRC METHOD DEVELOPMENT**

### **Method Optimization**

- Oxygen, ammonia, and methane were investigated in this study. • DRC gas flow rates of 0.2 – 2.0 mL/min were considered; 0.6 mL/min yielded acceptable results for all elements involved in this study (minimal loss of precision was noted by using the same flow rate for all elements and analysis time was greatly decreased by using a fixed flow rate value).
- RPq values of 0.2 0.85 were investigated; 0.70 0.85 optimal for all elements. • Sample flow rates from 100 µL/min to 1000 µL/min were investigated:
- 200 µL/min was optimal for elements using ammonia or methane 400 µL/min was optimal for analysis of arsenic and selenium using oxygen • Rh, In, Sc, Ga, Ge, and Tm were evaluated as internal standards; Rh and In were found to be
- the most appropriate internal standards for all of the elements in this study. • DRC optimization was performed and evaluated for each test sample and the suspected
- polyatomic interferences affecting each element.

### **Method Detection Limit Studies**

Method detection limit (MDL) studies for the FGD wastewater matrix were performed for all target metals following procedures specified in 40 CFR 136, part B.

The simulated FGD wastewater matrix was composed of 10 mg/L Ca, 1 mg/L Mg, 5% (v/v) concentrated HNO<sub>3</sub>, and 0.5 % (v/v)concentrated HCI.

The MDLs and MRLs for undiluted samples, those achieved in this study, are listed in Table 2.

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# Comparison of Standard Mode & DRC Mode ICP-MS

### Elements with Improvement

- As, Cr, and V the percent reduction in concentration due to interferences was large and
- Cu large and consistent reduction in concentration due to interferences for most
- Se and Sb the beneficial effects for interference reduction were consistent, but more moderate.

Sample 1 Sample 2 Sample 3 Sample 4

As Cr Cu Se V Sb

### **Elements with Matrix Specific or No Improvement**

- Zn a large percent reduction in interferences for half of the samples; moderate or no benefit for others.
- Ni no beneficial effects for most samples; inconsistent results, but no increases in concentrations.
- Al and Co slight increase in concentration for most samples with current method; DRC is not recommended.



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Analyte	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 2	*Not included in the SOP	

\*Not included in the SOP





The University of Arizona results compared well with the ICP-DRC-MS data produced at BRL. Noted exceptions were As and Zn in some samples (Figure 5).





samples.





# COMPARISON OF HR-ICP-MS & ICP-DRC-MS



A comparison of the ICP-DRC-MS and HR-ICP-MS results for the samples is presented in Figure 9. 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. Silver could not be compared because HR results were below detection limits in all samples. Arsenic could not be validated with HR-ICP-MS results because high resolution was unable to resolve the chloride interference in the FGD matrix.

### CONCLUSIONS

- The ICP-DRC-MS results were validated using HR-ICP-MS, and the usability of the developed SOP was verified by ICP-DRC-MS analyses at a second laboratory that had no experience in analyzing FGD waters. Based on this research, the procedures developed by BRL were found to be useful for reducing or eliminating polyatomic interferences that impact standard mode ICP-MS results for the following elements: arsenic, antimony, chromium, copper, selenium, vanadium. and zinc.
- For arsenic, some FGD water samples from certain power plants can exhibit high recoveries on matrix spike analyses if not diluted to a sufficient level.
- Copper and zinc exhibited more variability than the other elements in their response to DRC interferences removal. The reason for this discrepancy is unknown and appears to be matrixspecific; however, the ICP-DRC-MS results were in the same range as the HR-ICP-MS
- Nickel and silver do not benefit from DRC. However, these elements can be included in a multi-element analysis using DRC with no loss of accuracy.
- Cobalt and aluminum were evaluated; however, a beneficial ICP-DRC-MS method was not successfully developed. Analysis by ICP-DRC-MS is not recommended for these analytes.

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References

- Niki Masters, Project Coordinator at Brooks Rand Labs Colin Davies, President/Owner of Brooks Rand Labs
- Panayot Petrov, PhD, Research Chemist at Brooks Rand Lab Bryan Setzer, Communications Manager at Brooks Rand Labs
- Fremont Analytical Laboratory, Seattle, WA
- Dr. John Olesik and Anthony Lutton of Trace Elements Research Laboratory (TERL) at the Ohio State University Mary Kay Amistadi at the Arizona Laboratory for Emerging Contaminants (ALEC) at the University of Arizona

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Sample 4

Sample 1 Sample 2 Sample 3