Development and Evaluation of Method Guidance for the Analysis of Flue Gas Desulfurization Wastewater by ICP-CRC-MS

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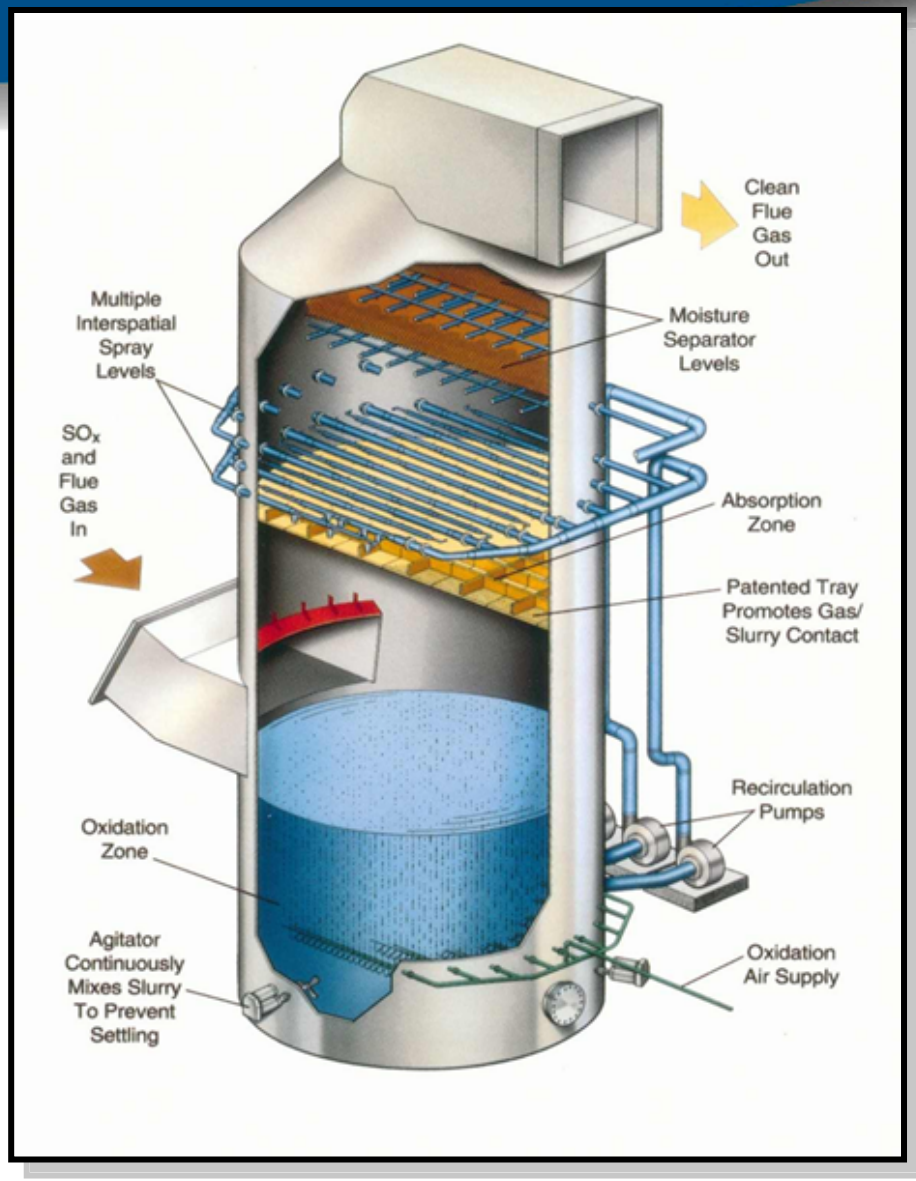
Outline

- Introduction
- Characteristics of Flue Gas Desulfurization (FGD) Wastewaters
- Interferences for FGD Wastewaters using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) Methods
- Development of guidance for Inductively Coupled-Collision/ Reaction Cell-Mass Spectrometry (ICP-CRC-MS) analysis of Wastewaters
- Round Robin Study Design
- Summary and Conclusions
- Next Steps

Project Background

- Flue gas desulfurization (FGD) system
  - Used to remove sulfur dioxide from flue gas at coal-fired power plants
  - Must be periodically purged (blown down) to reduce dissolved salts, avoid corrosion



Characteristics of FGD Wastewaters

- FGD purge waters have high levels of major constituents
  - Ca, Mg, Na, Sr, Si, B, Cl, SO_4
  - Some elements can remain elevated after water treatment
- No "typical" sample composition

Parameter	Concentration mg/L
Calcium	680 – 5,700
Chloride	1,100 – 23,000
Magnesium	210 – 5,800
Sodium	50 – 1,900
Sulfate	1.2 – 13,000
Total dissolved solids (TDS)	5,000 – 42,000
Total suspended solids (TSS)	6.0 - 65

Challenges in FGD Water Analysis

- Trace metal levels from these streams are typically very low
  - Very sensitive analytical methods are needed to measure levels accurately
- Matrix is highly challenging for ICP-MS
  - Elevated concentration of dissolved salts (e.g., Cl, Ca)
  - High variability among FGD systems, and over time speciation of elements (e.g., selenium) can impact recovery during sample digestion
  - Multiple polyatomic interferences on some metals

EPA Response to Challenges

- **May 2011: Draft U.S. Environmental Protection Agency (EPA) FGD ICP/MS Standard Operating Procedure: Inductively Coupled Plasma/Mass Spectrometry for Trace Element Analysis in Flue Gas Desulfurization Wastewaters (DCN SE03835)**
  - **Intended as an adjunct to EPA Method 200.8**
  - **Approved for monitoring under 40 CFR Part 136**
  - **Referenced in the Effluent Limitations Guidelines and Standards for the Steam Electric Power Generating Point Source Category (June 7, 2013)**

Why is Additional Guidance Needed?

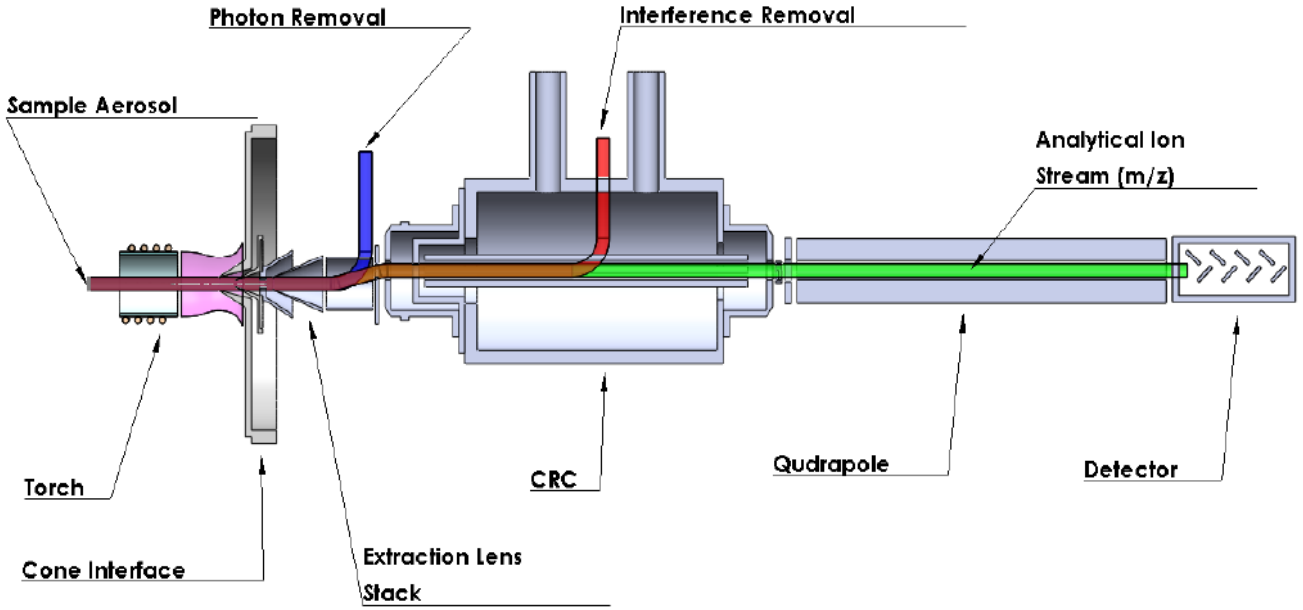
- EPA's Draft SOP lacks procedures for:
  - Bottle cleaning
  - Digestion procedures for difficult samples
  - Sample dilutions
  - Detailed instrument settings
  - Instrument cleaning
  - Analytical sequence
  - Matrix for method detection limit study
- Quality control should be more stringent

Project Objectives

- Assist laboratories in improving ICP-CRC-MS competency for analyzing FGD wastewater
  - Use in conjunction with EPA Methods 200.8 and EPA SOP
  - Enable laboratories to obtain more accurate and consistent measurements of trace-level metal concentrations in FGD wastewater

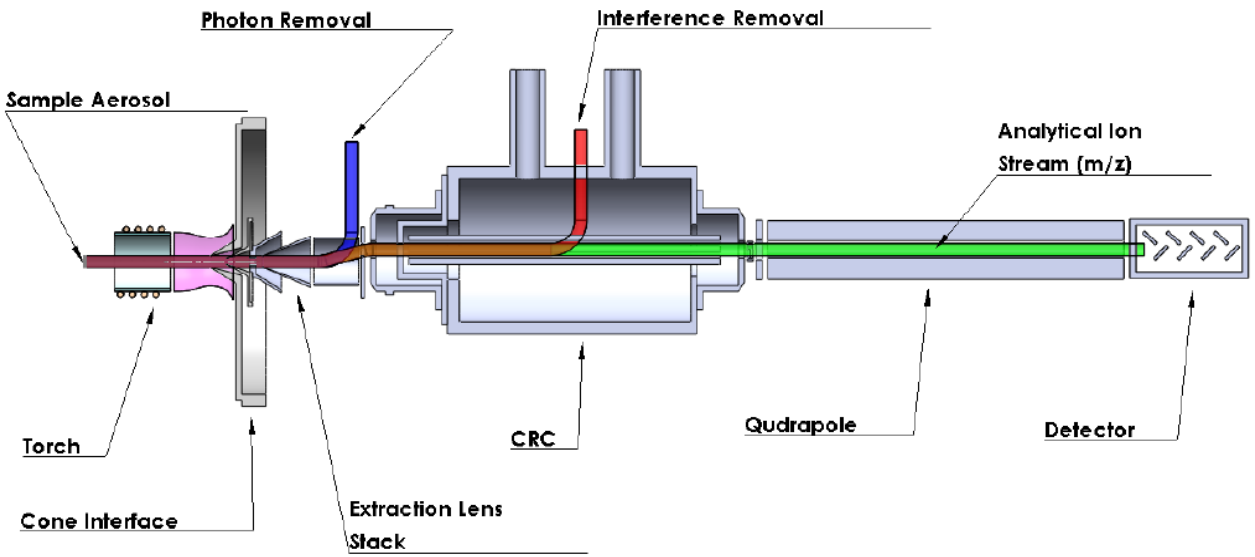
ICP-MS and CRC Description

- Acid digested sample nebulized into an aerosol and introduced into a radio frequency (RF) plasma field
  - Argon carrier gas
- Inside the plasma, sample atomized and converted to charged ions
- Metal ions transferred from plasma to high vacuum region and then into the CRC
  - Removal of molecular interferences through use of cell gases

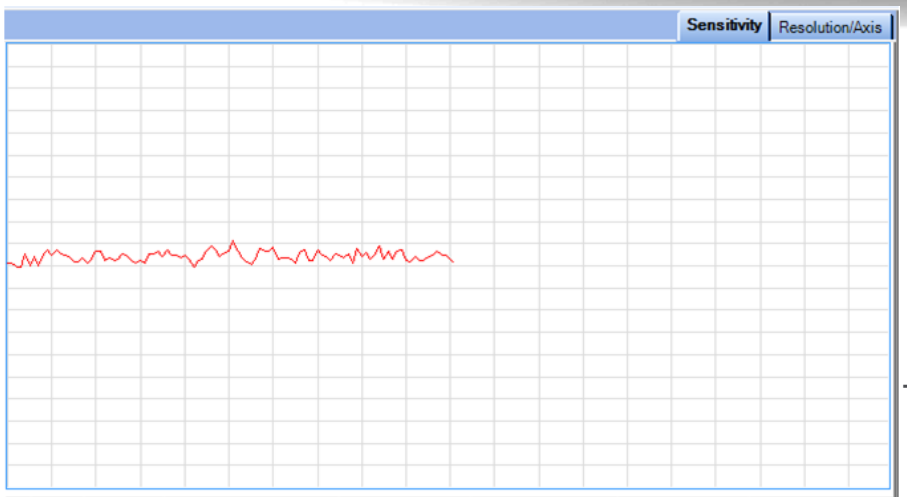


ICP-MS and CRC Description

- CRC acts as an active ion guide, using cell rods with negative voltage
- Surviving ions transferred to quadrupole mass spec
  - Separated according to mass-to-charge (m/z) ratio by magnetic field
  - Ions with target m/z are detected by an electron multiplier producing a signal proportional to number of ions hitting detector per unit of time



ICP-MS and CRC Description



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	☐	45	2.0E6	1695545	1672685.9	1.88
	☐	72	5.0E5	312513	310932.2	1.75
	☐	103	5.0E6	2057962	1967438.3	1.84
	☐	115	5.0E6	2254958	2169241.8	1.58
	☐	125	5.0E4	32237	31896.8	1.59
	☐	159	5.0E5	157497	176862.1	31.28
	☐	175	5.0E5	343592	375505.6	19.93
	☐	209	2.0E6	1807117	1822412.3	1.75

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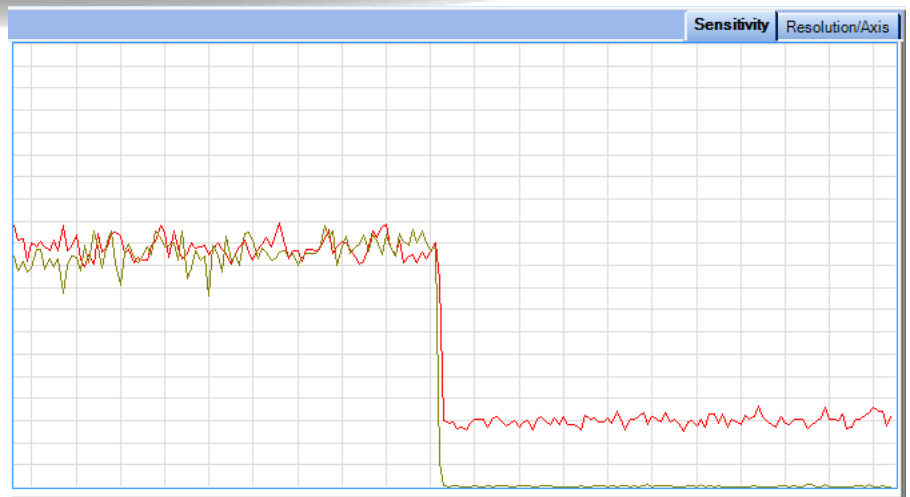

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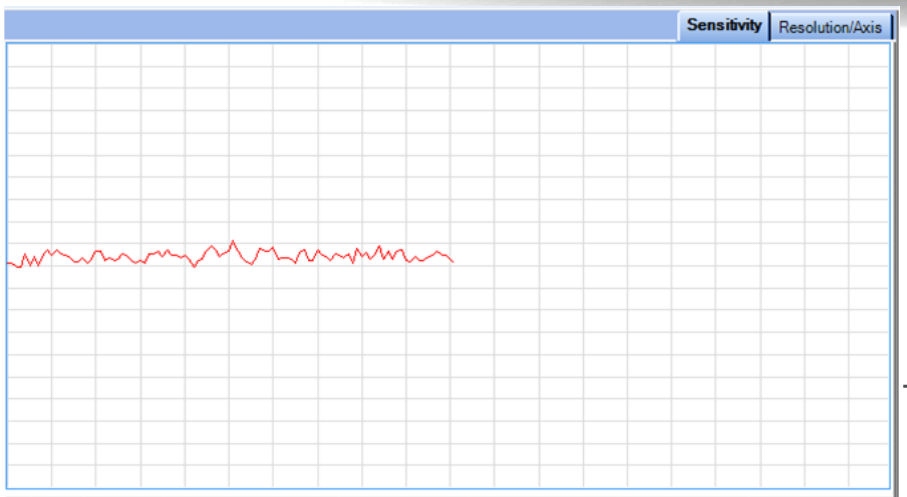
	☐	52	5000	1935	6366.4	71.86
	☐	63	1000	897	813.8	12.96
	☐	60	50	21	44.4	65.48
	☑	78	1000	0	258.0	102.82
	☐	51	1.0E4	5132	9421.4	46.73
	☐	66	50	33	32.1	30.96

- **Matrix blank comparison between no gas mode and gas mode**

ICP-MS and CRC Description



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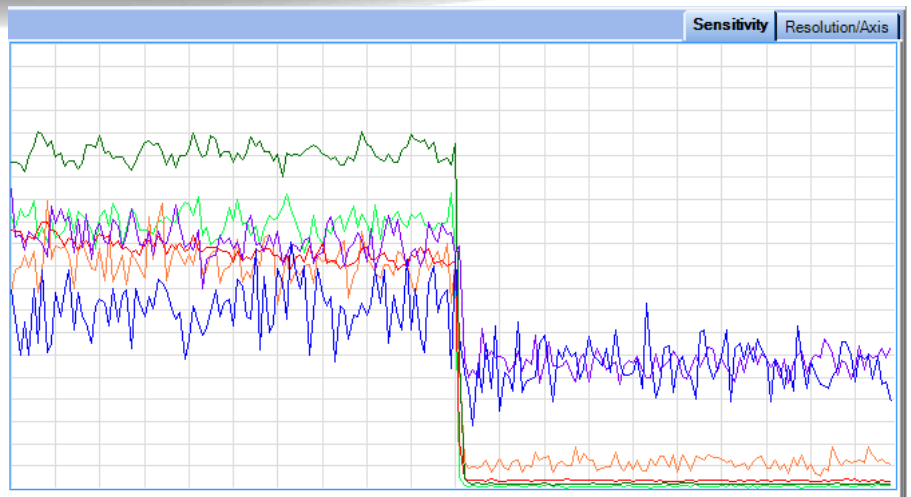

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	☑	59	500	27	144.3	79.02
	☑	52	2.0E4	294	5645.5	92.19
	☑	63	1000	317	425.7	33.48
	☑	60	200	39	68.4	25.10
	☐	78	1000	4	297.5	96.92
	☑	51	2.0E4	200	7817.5	95.35
	☐	66	50	13	23.4	50.58

- **Matrix blank comparison between no gas mode and gas mode**

Study Approach

- **Priority pollutants under the Clean Water Act and known to suffer from interferences in ICP-MS analysis**
  - **Aluminum (Al)**
  - **Arsenic (As)**
  - **Cobalt (Co)**
  - **Chromium (Cr)**
  - **Copper (Cu)**
  - **Nickel (Ni)**
  - **Selenium (Se)**
  - **Vanadium (V)**
  - **Zinc (Zn)**

Study Approach

- Guidance was tested through the use of actual FGD wastewater samples
  - Verify that recommendations could be followed successfully
- Results were compared to data from laboratories utilizing alternative interference control methods
  - Used to evaluate the accuracy, precision, and sensitivity of ICP-CRC-MS
- Feedback was provided regarding the practicality and ease of understanding of the guidance to further improve the process

Interferences for FGD Wastewaters using ICP-MS Methods

- Two greatest interferences are polyatomic and physical
- Polyatomic interferences are formed when more than one element combine
  - Form a m/z similar to analyte of interest
  - $^{40}Ar^{35}Cl^{+}$ interferes with $^{75}As^{+}$

Element Polyatomic Interferences

Aluminum

- Challenging to due wide range of concentrations
  - Range from low parts-per-billion (ppb, µg/L) to high parts-per-million (ppm, mg/L)
- Monoisotopic at mass 27 m/z
- Potential interferences of $^{12}C^{15}N^{+}$ and $^{13}C^{14}N^{+}$
  - Typically not seen due to carbon's high first ionization potential (IP)
- Another potential interferent that is problematic is $^{11}B^{16}O^{+}$
  - This stems from the high level of boron that can be present in these systems
- Aluminum can also be biased high due to ease of contamination through sampling and lab prep

Arsenic

- Typically found in concentrations of below detection limit to low ppb levels
- Monoisotopic at mass 75 m/z
  - Chloride greatest cause of concern through formation of $^{40}Ar^{35}Cl^{+}$, $^{38}Ar^{37}Cl^{+}$, and $^{40}Ca^{35}Cl^{+}$
  - CRC use essential for accurate measurement

Cobalt

- Typically found in sub-ppb to ppb concentration
- Monoisotopic at mass 59 m/z
  - Calcium poses greatest risk through formation of $^{43}Ca^{16}O^{+}$ and $^{42}Ca^{16}O^{1}H^{+}$
  - CRC extremely sensitive to cobalt

Chromium

- Concentration typically below detection limit to low ppb level
- Two useful masses at 52 and 53 m/z
  - Spectral overlap with transition metals eliminate 50 and 54 m/z
- Carbon and chloride interferences most common
  - Carbide ($^{40}Ar^{12}C^{+}$) stemming from carbon additives in the FGD system
  - Also from methanol or acetic acid for improved charge transfer
  - $^{35}Cl^{16}O^{1}H^{+}$ another potential interference from high chloride content
- Method blanks, field blanks, and laboratory duplicates can help identify any possible contamination sources

Copper

- Typically found in low ppb concentrations in FGD wastewater
- Two abundant isotopes at mass 63 and 65 m/z
  - $^{40}Ar^{23}Na^{+}$ most common interference
- Contamination is a common problem

Nickel

- Typically found in low ppb concentrations in FGD wastewater
- Five naturally abundant isotopes at masses 58, 60, 61, 62, and 64 m/z
  - $^{44}Ca^{16}O^{+}$ and $^{23}Na^{37}Cl^{+}$ most common interferences
- Mass 60 m/z is the preferred isotope for ICP-MS due to its high relative abundance

Selenium

- Concentrations vary widely in FGD waters
  - Can range from low ppb to ppm
- Naturally abundant isotopes at masses 74, 76, 77, 78, 80, & 82 m/z
- Mass 78 m/z preferred, 80 m/z typically monitored
  - High relative abundance
  - Lack of spectral overlap for krypton
- Formation of argon dimers poses the greatest analytical challenge
  - $^{38}Ar^{40}Ar^{+}$ and $^{40}Ar^{40}Ar^{+}$
- Can be prevented through the use of ultra high purity (UHP) argon
  - Ensure a low krypton background as well

Vanadium

- Typically found in low ppb concentrations in FGD wastewater
- Two naturally abundant isotopes at masses 50 and 51 m/z
- Mass 51 m/z is the preferred isotope due to high relative abundance and lack of spectral overlap with other metals
- Chloride poses greatest risk with possible formation of $^{35}Cl^{16}O^{+}$

Zinc

- Typically found in low ppb concentrations in FGD waters
- Five naturally abundant isotopes at masses 64, 66, 67, 68, and 70 m/z
  - 66 m/z preferred isotope → lack of spectral overlap and high relative abundance
- Sulfur poses the greatest risk of polyatomic formation
  - $^{34}S^{16}O_2^+$ and $^{34}S^{32}S^+$ due to the high amount of sulfate typically found in FGD waters
- Can be biased high due to ease of contamination through sample handling

Development of Guidance Document

- Developed to accompany EPA 200.8 and EPA Draft SOP
- Uses EPA Method 200.8 as a fundamental structure
- Recommends procedures for successful analysis of FGD wastewaters
- Includes some instrument-specific recommendations for CRC equipped instruments
  - Intended to apply to all current ICP-MS instruments
  - Defers to vendor documentation for hardware-related operational issues

Round Robin Study Design

- Inter-laboratory study to evaluate performance of the ICP-CRC-MS method using EPRI guidance
- Four labs (SRI and 3 volunteer utility labs) analyzed samples following EPRI guidance
- Three commercial labs analyzed samples using different ICP-MS techniques
  - ICP-CRC-MS by 200.8 without EPRI guidance
  - ICP-MS using dynamic reaction cell (DRC) technology
  - High resolution ICP-MS used as reference method

Round Robin Study Samples

- Nineteen samples of FGD wastewater from coal-fired power plants
  - Plants burning a range of coal types
  - Using a variety of FGD system types, treatment processes
  - Included high dissolved solids samples to test the robustness of the EPRI procedures
- Synthetic FGD Water sample included to provide a check on the quality of the results

Sample Preparation/Collection

- Sample preserved to a final 2% nitric acid concentration
  - Heated to 85°C for two hours to ensure complete metal dissolution
- Filtered through a series of decreasing size filters
- Aliquot pre-screened for trace metals of interest
  - Samples with elements below detection limits were fortified using high purity stock standards
- Samples distributed as digestates using modified EPA 3015A
  - Samples digested at 15 minute heat ramp to 170°C, 10 minute hold at 170°C, followed by 5 minute cool down
- Sample sources/concentrations were not communicated to labs
  - Provided with TSS and conductivity in order to select proper dilution

Laboratories, Instruments, and Methods

Code	Laboratory	Instrument	Technique
A	SRI	Agilent 7700	ICP-CRC-MS and Appendix A
B	Laboratory B	Agilent 7700	EPA Method 200.8
C	Laboratory C	Perkin Elmer Elan DRC II	ICP-DRC-MS
D	Reference Laboratory D	Thermo Element 2	High resolution ICP-MS
E	Utility Lab A	Agilent 7700	ICP-CRC-MS and Appendix A
F	Utility Lab B	Agilent 7700	ICP-CRC-MS and Appendix A
G	Utility Lab C	Thermo X-Series	ICP-CRC-MS and Appendix A

Sample Concentration Ranges

- Concentration ranges of the fortified digestates
- Designed for all elements of interest to be above detection limits of all labs

Element	Expected Range
Aluminum	30 – 15,000 ppb
Arsenic	2 – 50 ppb
Cobalt	0.5 – 75 ppb
Chromium	4 – 25 ppb
Copper	0.5 – 20 ppb
Nickel	5 – 1,000 ppb
Selenium	20 – 4,000 ppb
Vanadium	1 – 40 ppb
Zinc	5 – 2,000 ppb

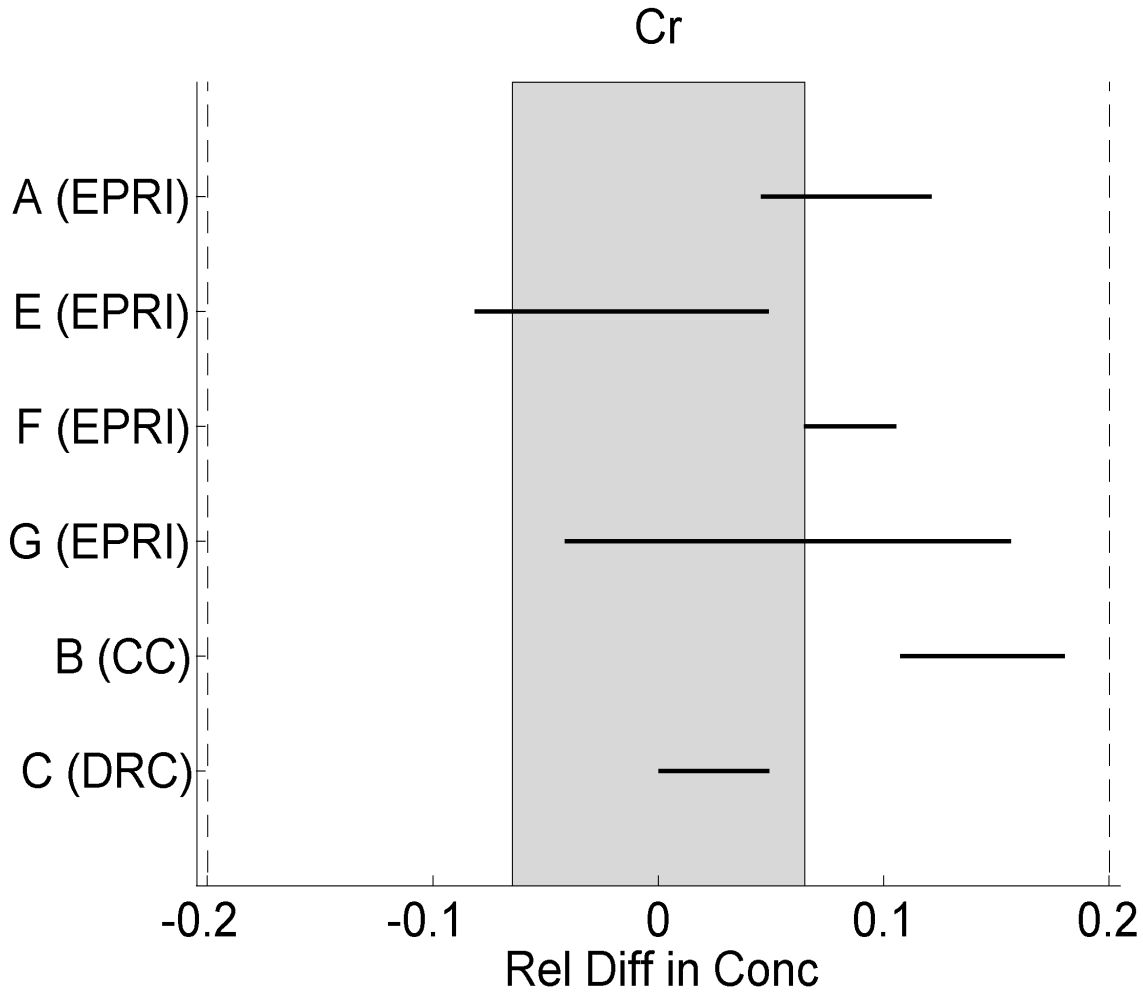
Statistical Evaluation of Round Robin Study

- Understand impact of EPRI guidance on method performance
- Not intended to provide a comprehensive precision and bias statement for the method
  - Needs larger number of laboratories
  - Analysis of samples with a range of spike concentrations
- Statistical measures
  - Relative difference from High-Resolution ICP-MS (reference method) – bias/accuracy
  - Relative percent difference of replicates – single-lab precision
  - Method detection limits – measure of sensitivity

Round Robin Study Results

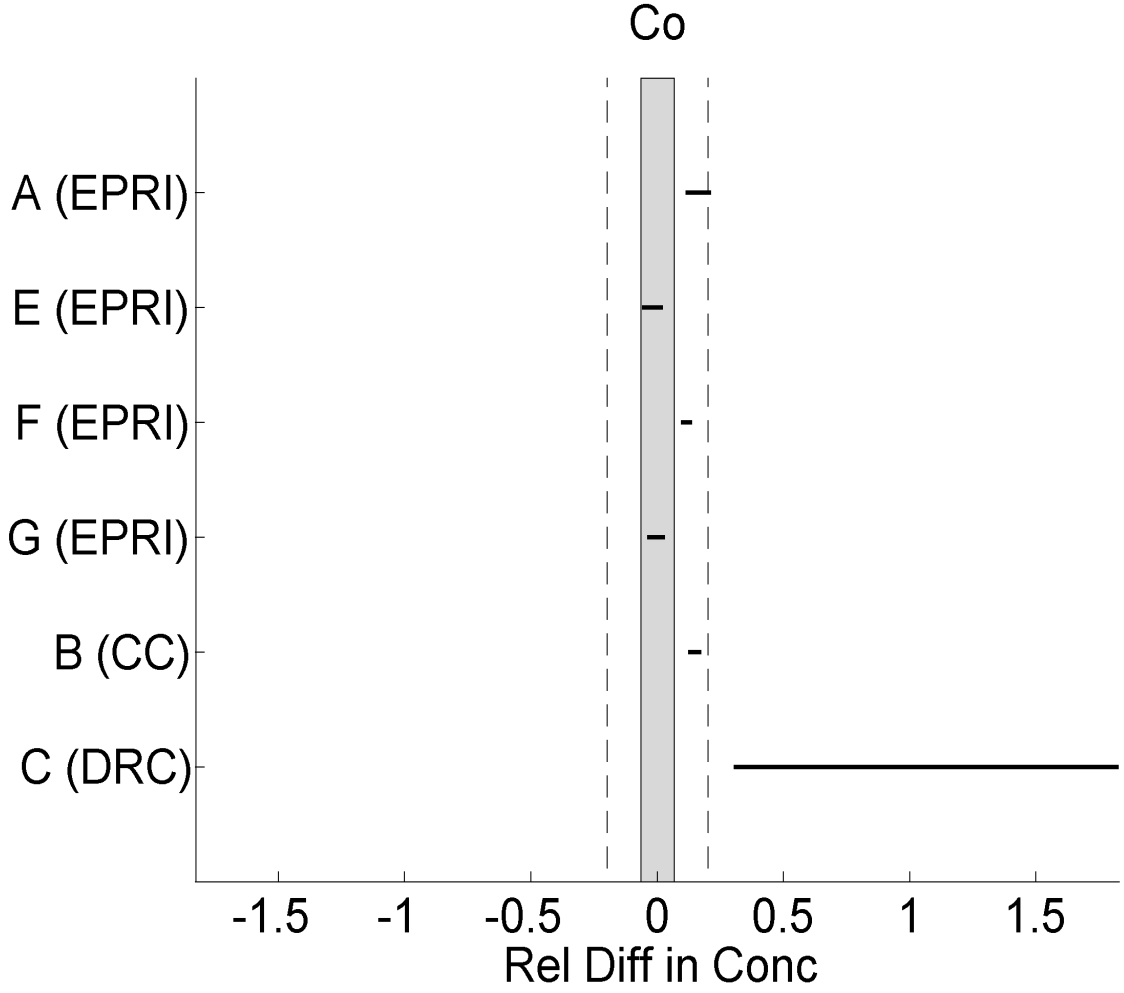
- EPRI guidance vs. EPA 200.8 (Lab B)
  - Labs using EPRI guidance were closer to the reference method for four of nine elements (Cr, Co, Ni, Se) than lab using 200.8 alone
  - Lab using 200.8 alone was closer to the reference method for Cu
  - Remaining metals did not exhibit significant difference
- EPRI guidance vs. DRC (Lab C)
  - Lab using DRC was not significantly different from labs using EPRI guidance for eight metals (Al, As, Cr, Cu, Ni, Se, V, and Zn)
  - DRC lab had significant high bias for Co

Chromium Relative Difference vs. High-Resolution ICP-MS



Black lines: 95% CI of the Mean RD
Gray box: ±6.5% RD
Dashed line, ±20% RD

Cobalt Relative Difference vs. High-Resolution ICP-MS



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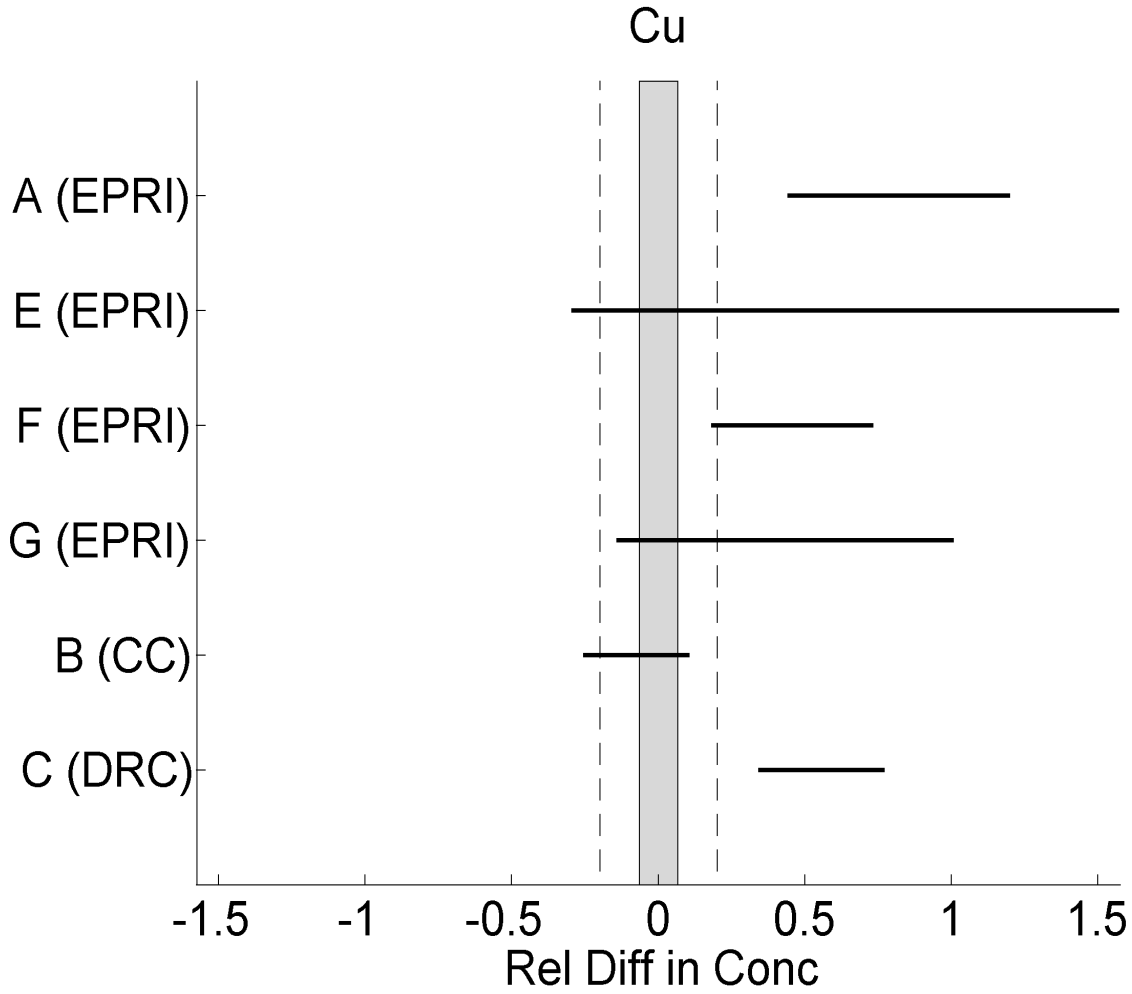
Copper Relative Difference vs. High-Resolution ICP-MS



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Gray box: ±6.5% RD
Dashed line, ±20% RD

Method Detection Limit Studies

- Laboratories were instructed to use synthetic high-ionic strength matrix for MDL studies
  - Some used clean water instead
  - Dilution factors were not always provided to study organizer
- Large range of MDLs reported for low-resolution instruments
  - Example: arsenic MDLs ranged from 0.004 µg/L to 0.75 µg/L
- Reporting limit calculation procedures were not consistent among labs

Summary and Conclusions

- Application of EPRI guidance improved accuracy over EPA Method 200.8 alone for some elements
- Cobalt had a significant high bias using a DRC method
- Method detection limits were extremely variable among laboratories
- Sample preparation and digestion procedures were not evaluated in round robin study (digestates were sent to labs), but following EPRI guidance should enhance interlaboratory precision

Next Steps for Method Improvement

- **Provide the EPRI Guidance to labs analyzing FGD samples**
  - **Guidance included in EPRI comments to proposed Effluent Guidelines rulemaking (Appendix F2 of Docket Item EPA-HQ-OW-2009-0819-4499)**
  - **Study report can be purchased at www.epri.com, Report 1023787**
- **Continue method improvement**
  - **As more laboratories adopt CRC technology, a larger round robin study to support a formal precision and accuracy statement for the method would be helpful.**
  - **As FGD systems and analytical instrumentation continue to evolve, the EPRI guidance may need to be revisited**

A Special Thanks

- 2014 National Environmental Monitoring Conference
- Electric Power Research Institute
  - Naomi Goodman
- Southern Research Institute
  - Mark Berry
  - Robert Strange
- Mark Kelinske