

Analysis of Wet FGD Wastewaters

*overcoming matrix interferences and complying
with discharge regulations for metals*

Michelle Briscoe
Vice President of Analytical Services
Brooks Rand Labs



Presented June 16, 2011

McIlvaine Company "Hot Topics Hour" Webinar Series

Background



2010 Effluent Limitation Guidelines (ELGs)

- EPA to revise standards for metals in water discharges from power plants
- Primary focus on coal-fired power plants:
 - Generate most of the pollutant loads
 - Coal dominates forecasted future power generation

Key Waste Streams

- The **FGD** wastewater from new SO₂ controls
- Ash pond discharges

Current Status of ELGs



Detailed and comprehensive study 2007-2009

- Data collection included
 - Questionnaire (9 different companies)
 - Wastewater sampling & split study by UWAG
 - Site visits

Primary metals of concern for Env. & HH Risk

Mercury (Hg)

Selenium (Se)

Arsenic (As)

**EPA: Unregulated toxic metals are present,
but CAN be reduced**

Success of Treatment Technologies Depends on Accurate Data

Assumption:

EPA Method + Accredited Lab = Accurate Data

NOT ALWAYS TRUE

FGD Waters are Complex and Variable

Total suspended solids	< 10 mg/L – 17%
Total dissolved solids	4000 – 68,000 mg/L
pH	4.5 - 9
Sulfate	450 – 22,000 mg/L
Chloride	1,000 – 28,000 mg/L
Calcium	600 – 5,700 mg/L
Magnesium	400 – 7,700 mg/L
Sodium	20 – 4,800 mg/L
Total organic carbon	5 – 1100 mg/L

Risk of Inaccurate Data due to Matrix Interferences

What is an Interference?

Common Interferences in FGD Waters:

- Physical (e.g., high levels of solids)
- Spectral (due to analytical method)

Mass spectral **polyatomic interferences** with
EPA Method 200.8 (ICP-MS)

Analytical Interference Example

Arsenic (As) - only one isotope at mass **75**

- major interference: $^{40}\text{Ar}^{35}\text{Cl}^+ = \text{mass } 75$

Similar polyatomic interferences for Se, Cr,
and other metals

Overcoming Interferences



- Specialty methods can be used
 - Developed with support from EPRI
 - Modification of EPA 200.8 for ICP-MS
- Specialty trace metals labs can be utilized
 - Cutting-edge instrumentation and methods
 - Analysts with advanced analytical chemistry skills



ELECTRIC POWER
RESEARCH INSTITUTE



EPRI Technical Update Report #1017978 (2009):

“Trace Metals Determination in Flue Gas Desulfurization Waters: Optimization of Dynamic Reaction Cell ICP-MS”

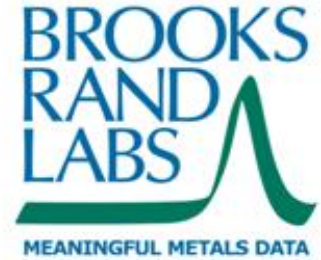
Principal Investigator: M. Briscoe, Brooks Rand Labs

EPRI Project Manager: N. Goodman

More accurate data for:

As, Cd, Cr, Cu, Fe, Ni, Sb, Se, V, and Zn

Arsenic Interferences



90-99% of reported concentration can be due to an INTERFERENCE

Actual FGD Wastewater Treatment System **Effluent** Data:

Site ID	Regular ICP-MS	DRC Method
1	26	2
2	510	18
3	110	11
4	3200	21

All results are in units of ppb or $\mu\text{g/L}$

Chromium Interferences

97-99% of reported concentration can be due to an INTERFERENCE

Actual FGD Wastewater Treatment System **Effluent** Data:

Site ID	Regular ICP-MS	DRC Method
1	30.6	< 0.23
2	267	2.73
3	222	< 1.2
4	96.8	3.37

All results are in units of ppb or $\mu\text{g/L}$

Selenium Interferences

20-55% of reported concentration can be due to an INTERFERENCE

Actual FGD Wastewater Treatment System **Effluent** Data:

Site ID	Regular ICP-MS	DRC Method
1	151	102
2	6740	5460
3	750	504
4	14100	6220

All results are in units of ppb or $\mu\text{g/L}$

Validation of DRC Method

Selenium

Site ID	DRC Method	HR-ICP-MS
1	102	115
2	5460	5580
3	504	550
4	6220	6270

All results are in units of ppb or $\mu\text{g/L}$

And What About Mercury?

- Method 1631
 - Cold Vapor Atomic Fluorescence
 - Detection Limit = 0.15 ng/L
- Watch out for Suppression
 - Matrix Spikes
 - Analysis at Multiple Dilutions



In Conclusion...

- New Regulations for FGD Wastewaters
- FGD Wastewaters are Complex
 - Bias due to Interferences is a RISK
- Accurate data is achievable
 - Careful selection of method

Metals Speciation in FGD WW

Selenium: Se(IV), Se(VI),
SeCN, SeSO₃, others

Arsenic : As(III), As(V),
MMAs, DMAs, others

Mercury: MeHg, Hg(II), Hg⁰



Thank you!

Questions?

Contact Info:

Michelle Briscoe

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

206-632-6206, ext. 117

michelle@brooksrands.com