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Assessment of Bias in Measurement of Mercury Emissions from Coal Fired Power Plants – Comparison of Electronic CEMS and Sorbent Traps

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> > **McIlvaine Hot Topic Hour**

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# What might contribute to differences in Hg measurement in two methods?

- Hg on PM Hg CEMS don't include Hg<sup>P</sup>, but Sorbent Traps do
  - From EPA Method 30B: "This method is only intended for use only under relatively low particulate conditions (e.g., sampling after all pollution control devices)." - <u>30B assumes Hg<sup>P</sup> can be neglected</u>
  - 2001 ICR data showed Hg<sup>P</sup> ranging from non-detect to 0.93μg/Nm<sup>3</sup> on uncontrolled units, but typically a small part of total Hg.
- What about when <u>high</u> Br is added to flue gas?
  - URS and EERC have reported some effect
- Random or otherwise unexplained measurement errors
  - Especially important for field measurements!

Contribution of Hg<sup>P</sup> for Uncontrolled Units Hg<sup>P</sup> is mostly captured in ESP on an uncontrolled unit and is generally a very small part of total Hg



# Effect of Controlling Hg on Hg<sup>P</sup>

Br helps oxidize Hg<sup>0</sup> making it easier to capture on PM or in a scrubber, ACI captures Hg as Hg<sup>P</sup> - Which increases the Hg content of the fly ash!



# Hg concentration on PM

Mercury tends to be on fly ash that is most difficult to capture – more concentrated in small size fraction that escapes PM control device

- from ESP inlet: 1.0925 mg/kg (ppm)
- inside ESP:
- from ESP outlet:

Mercury concentration (mg/kg or ppm) in fly ash particles at ESP outlet

0.6615 mg/kg (ppm)

7.5303 mg/kg (ppm)

- Higher concentration on smaller particles
- Would expect concentration of Hg in activated carbon to be significantly higher

	Dust diameter (µm)			
Dia. µm	0-3	3-10	10-24	24-45
Hg, mg/kg	9.0827	6.2917	3.6420	1.0657

Jedrusik, M., and Swierczok, A., "The influence of unburned carbon particle on electrostatic precipitator collection efficiency", 13<sup>th</sup> International Conference on Electrostatics, Journal of Physics: Conference Series 301 (2011) 012009

# Hg in PM, PM emission rate and difference in gaseous and total Hg – how they relate



### How could Br impact Hg CEMS? Aside from the Hg<sup>P</sup> effect discussed earlier

- Surface reaction on probe filter (stinger) or probe internal surfaces
  - Corrosion, particulate build up, or inadequately coated surfaces
  - If reactive surface is available, the fastest and easiest reaction
- "Interference" with thermal converters?
  - Suggested by some, but thermodynamics suggests otherwise.
- Residual Br after converter and reformation of Hg<sup>2+</sup> between converter and analyzer
  - Possible, but suppliers take measures to avoid this

# **Actual Field Data**

- Without Br added
- With Br added

Comparison of Tekran Continuous Mercury Monitor (CMM) versus Sorbent Trap from Coal Power Plant RATAs (no bromine added)



# Data from four units over four years, with Br added

- Annual RATAs over a four-year period
  - Tekran Hg CEMS
  - Method 30 B reference method
- Units use wet scrubber for PM & SO2 control
- Use ACI and also add bromine for Hg control
  - Have varied bromine injection rate (but don't have data on ACI rates)
  - Due to proprietary nature of additive, bromine vapor concentrations are not known. Results shown for bromine rates are normalized based upon rate of injection.
  - Don't know if any HBr makes it past the wet scrubber!

#### **Results four units, four years** comparison of CEMS to 30B, Br addition varied each year



## Effect of Bromine Addition (stdev shown)

Difference, 30B minus MEMS



# What does this data tell us?

- Differences in measurement are clearly explainable by Hg<sup>P</sup> for all RATAs with one *possible* exception
- That one RATA at highest Br rate suggests *possible* effect of Br, but . . .
  - These were not well-controlled experiments. There could be something else going on, such as higher PM emissions.
  - How much HBr makes it past a wet scrubber? If there was little HBr there, it was due to other effects.
  - Might be increased Hg<sup>P</sup> conversion
  - Could be other effects not explored here

# Summary

- For controlled units <u>expect</u> some difference between electronic CEMS and Sorbent Traps due to effect of Hg<sup>P</sup>
  - This effect can be significant at MATS compliance levels
  - Br addition or ACI should increase this effect
- Brominated PAC does not appear to impact electronic CEMS
- At most bromine addition rates, no impact observed
  Difference can be explained by Hg<sup>P</sup>
- At sufficiently "high" bromine addition rates, difference may increase
  - Impact was not enough to affect RATA

# **Practical Implications**

 Method 30B includes Hg<sup>P</sup>, which results in overestimation of gaseous Hg that <u>may</u> be significant at MATS Hg levels

- But not enough to impact RATA pass or fail

- Differences in Hg<sup>T</sup> up to about 0.50 ug/Nm3 (typically less, but sometimes more) may be explained by Hg<sup>P</sup> when controlling Hg with ACI and/or Br
  - Will vary somewhat by coal Hg levels, PM emissions, ACI injection, etc.
- Bromine "interference" should not be a concern except possibly under extremely high furnace Br injection rates and is not a concern for brominated activated carbon
- With field measurements there are many other variables at play that could explain differences.

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