Hg CEMS Improvements and Updates

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Agenda

• Mercury CEMS overview
• Sample transport at lower temperatures
• Linearity across a wide concentration range
• QC checks with Hg Permeation
• Bromine injection and Low Level Measurements
• Probe Update
Hg CEMS Overview: Model 80i Hg Analyzer
Hg CEMS Overview: Model 81i Hg Generator

- Hg Vapor Generator
  - Calibrates analyzer and probe
  - Provides concentrations for Low/Mid/High (1 \( \mu g/m^3 \) to 50 \( \mu g/m^3 \))
  - Uses a Peltier Cooler to control vapor pressure of Mercury source
  - Uses mass flow controllers to vary output concentration
  - NIST Traceable
Hg CEMS Overview: Zero Air / N$_2$ Generator

- Compressed Air In
- Coalescing Filters
- Heatless Air Dryer
- Surge Tank
- Chemical Scrubbers
- Nitrogen Generator
Speciation provides valuable information for Hg control
Sample Transport

- Sample lines on Thermo Scientific Mercury Freedom CEM Systems have been heated to 120 °C since the product was developed.

- Since conversion of oxidized Hg occurs in the probe, only elemental Hg is transported, not oxidized.

- Sample is transported at low pressure (nominally 60 mmHg) and sample is diluted ~ 40:1

- Testing was needed to prove that a lowered line temperature did not effect performance
RATA Results at Midwest Cement Plant

Using a “cold” spare line, not the heated sample line.
Overview of the Test Group

With the help of Spectrum Systems and various Utilities the following test group of 10 was selected:

- Qty. 5 CEMS at a Power Utility in the Southeast
- Qty. 3 CEMS at a Power Utility in the North
- Qty. 1 CEMS at a Power Utility in the West
- Qty. 1 CEMS at a Cement Plant in the Midwest

Wet stacks, dry stacks in warm and cold climates, 100 to 500 ft lines
Results and Summary

• Operation of Thermo Scientific Mercury Freedom Sample line temperature at 50° C is proven acceptable based on this study.

• The lines were lowered to 50° C for the study, but it is recommend to operate at 70° C

• The sample line needs temperature control, not self limiting types

• These results are largely qualitative, but since the study began in 2011, many more operators have lowered their line temperatures and have not reported any adverse effects on accuracy (RATA) or precision (daily zero and span).
Hg Measurement over a Large Range

- Coal Fired Power Plant mercury emissions vary depending on what is happening in the process
  - Plant On: X $\mu$g/m$^3$
  - Occasional/rare process upset: XX $\mu$g/m$^3$

- Cement Kiln mercury emissions vary dramatically depending on what is happening in the process
  - Mill On X $\mu$g/m$^3$
  - Mill Off XXX $\mu$g/m$^3$

- Fortunately, Atomic Fluorescence is linear over a wide range of concentrations
Typical Variation at a Power Plant
“Typical” Variation at a US Cement Kiln

Southeast Cement Plant - with inline mill

<table>
<thead>
<tr>
<th>Time</th>
<th>Hg µg/m³</th>
</tr>
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<tbody>
<tr>
<td>2/9/2010 7:12</td>
<td>0</td>
</tr>
<tr>
<td>2/9/2010 8:24</td>
<td>50</td>
</tr>
<tr>
<td>2/9/2010 9:36</td>
<td>100</td>
</tr>
<tr>
<td>2/9/2010 10:48</td>
<td>150</td>
</tr>
<tr>
<td>2/9/2010 12:00</td>
<td>200</td>
</tr>
<tr>
<td>2/9/2010 13:12</td>
<td>250</td>
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<tr>
<td>2/9/2010 14:24</td>
<td>300</td>
</tr>
<tr>
<td>2/9/2010 15:36</td>
<td>350</td>
</tr>
<tr>
<td>2/9/2010 16:48</td>
<td>400</td>
</tr>
<tr>
<td>2/9/2010 18:00</td>
<td>450</td>
</tr>
</tbody>
</table>

Graph showing variation in Hg µg/m³ over time. Peaks labeled 'Raw mill on' and 'Raw mill off' and a peak labeled 'Blowback'.
Variation at a Cement Kiln outside the US

Cement Kiln Outside of the US

Hg(mg/m3)

8:24 9:36 10:48 12:00 13:12 14:24 15:36 16:48 18:00

5/16/11 5/16/11 5/16/11 5/16/11 5/16/11 5/16/11 5/16/11 5/16/11 5/16/11

Hg(o) Hg(t)
Linearity with a used “stock” Mercury system
Linearity with a used “stock” Mercury system

System Span Linearity

\[ y = 1.0473x - 0.1897 \]

\[ R^2 = 0.9999 \]

<table>
<thead>
<tr>
<th>Expected Conc (μg/m³)</th>
<th>Measured Conc (μg/m³)</th>
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</thead>
<tbody>
<tr>
<td>7.5</td>
<td>6.8</td>
</tr>
<tr>
<td>11.1</td>
<td>10.6</td>
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<tr>
<td>20.3</td>
<td>20.9</td>
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</tr>
<tr>
<td>52.9</td>
<td>55.8</td>
</tr>
<tr>
<td>106.1</td>
<td>112.4</td>
</tr>
<tr>
<td>226.3</td>
<td>236.0</td>
</tr>
</tbody>
</table>
QC Checks using a Permeation Source

In order to comply with the 2009 Interim Elemental Mercury Gas Traceability Protocol, a Quarterly Audit is required:

Option A: Field Reference Generator
Option B: Permeation Tube
Option C: Sorbent Tube
Option D: Cylinder Gas

Interim Elementary Mercury Gas Traceability Protocol -- July 01, 2009

Interim EPA Traceability Protocol for Qualification and Certification of Elemental Mercury Gas Generators

7.0 QUALITY ASSURANCE
QC Checks using a Permeation Source

- Thermo has developed a Mercury Permeation Source (Model 84i) that integrates into existing and new Mercury CEMS in order to meet the requirements of Section 7.

- Done at the instrument, **NOT** through the system, to check the precision of the NIST traceable 81i mercury generator.
Bromine Injection Testing

The primary goal of the project: Determine the effects of bromine on the accuracy and precision of CMMs at mercury concentrations < 1.0 μg/Nm³.

Boiler → Baghouse (BH)

- HBr Injection
- AC Injection
Mercury Freedom System Test Results

Natural Gas

Thermo Results, µg/Nm³ on a wet basis vs. Sorbent Trap Data, µg/Nm³ on a wet basis

- HBr, 5 ppm
- HBr, 25 ppm
- BAC
- AC + HBr, 5 ppm
- AC + HBr, 25 ppm

EERC DL43820 CDR
Mercury Freedom System Test Results

Wyoming PRB Coal

Thermo Results, µg/Nm³ on a wet basis vs. Sorbent Trap Data, µg/Nm³ on a wet basis

- AC
- BAC
- AC + HBr, 5 ppm
- AC + HBr, 25 ppm
Bromine and Mercury Conclusion

• Hydrogen Bromide does react with elemental mercury, there were no signs of a measurement bias at 5 or 25 ppm HBr injection or Brominated AC with the TFS Mercury System

• Using the standard TFS oxidizer and converter, Mercuric Bromide behaves similarly to Mercuric Chloride, both in oxidation and reduction

• System Integrity Testing using Mercuric Bromide, show that the converter efficiency is >95%

• No measurement bias detected with the use of HBr or Brominated AC in the TFS system in this study
Probe Options

- We have partnered with M&C to provide another probe option
- Performance of the converter and oxidizer require testing on each unit to ensure quality and adherence to specifications
We would like to thank:

- **Spectrum Systems** (Sean Myrick and Reggie Davis) for providing a majority of the test information for the line temperature study.

- **EERC** (Dennis Laudal and Jeff Thompson) and **EPRI** (Chuck Dene) for the Bromine injection test data.