Update and Discussion on Advances in Mercury CEMS, Real World Experiences and Lessons Learned

MARAMA ICAC Meeting
Exton, PA
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Agenda July 10 MARAMA ICAC Meeting

- Overview of Thermo Fisher Scientific
- Clean Air Mercury Rule
- Overview of Mercury Freedom System
- Low Level Monitoring Experiences
- Certification Preparation Experiences
- Summary
ThermoFisher Mercury CEMS Capabilities

- Thermo Fisher has shipped 450+ Hg CEMS- some direct and others through systems integrators.

- Commitment to Power Generation Industry, EPRI, and EPA
  - Supplier of instrumentation to EPA and Utilities since Early 1970’s

- Deep Instrumentation & CEMS Applications Design Expertise
  (~35 Engineers Contributing to Development)
  - Critical to Meeting Requirements of Very Challenging Application

- Modern Manufacturing Facilities and Processes
  - Key To Meeting Significant Market Demand
Clean Air Mercury Rule

- EPA is required to regulate mercury emissions, as mandated by the Clean Air Act Amendments of 1990
- The final “CAMR” rule was signed on March 15, 2005
  - Established a cap-and-trade program
  - Required most units to continuously monitor Hg emissions.
- Update- Feb 8- Rule is thrown Out, but many states still require monitoring. CEMS Installation activities are still moving forward.
The Mercury Freedom System

- Dilution based measurement
- Inertial Filter Sample Conditioning or Conventional Dilution Probe
- Conversion at the Stack
- Direct Measurement CVAF
- High sensitivity
- True real-time monitoring
- Modular design
- iSeries platform
Mercury Freedom™ System
Key Components

- Sample Extraction (Probe)- 2 types
  - Inertial Separation Filter for extreme particulate loading
  - Conventional Filtration Probe
- Sample Pretreatment (Conversion/Scrubbing)
  - Dry Thermal Converter
- Sample Transport (Umbilical)
  - Heated Teflon coupled with dilution
- Mercury Analyzer
  - Continuous CVAF
- Mercury Analyzer Calibration System
  - Elemental Hg via vapor pressure/mass flow control
Model 83i Probe/Converter

- Designed for serviceability
- Integrated Converter and Mercuric Chloride Generator
- Can be installed UPSTREAM of particulate control device, i.e. baghouse, precipitator, etc.
- Can be used to verify operation of activated carbon injection system performance.
Converter/Inertial Filter Probe

- Thermal converter
- Mounting Flange
- Heated Al Clamshell
Inertial Filter/Dilution Module

- Fast loop
- Critical Orifice
- Dilution Module
- Cal Filter
Fast Loop Inertial Filter
Total Mercury Converter
Model 83i GC Probe- For Wet Stack Applications
Model 83i GC Extraction/Dilution Module
Inertial Filter vs. 83i-GC
Trend of BBSES Unit 1 Hg

Hg (µg/sm$^3$)

- CEM
- STM

Dates from 10/20/05 to 11/17/05
Model 82i Probe Controller

- Automates Probe calibration via Calibrator Microprocessor
- Automates both filter and stinger blowback
- Electronic Pressure Regulation
- Electronic Pressure Transducers
Model 80i Hg Analyzer

- Direct Measurement CVAF
  - Continuous measurement
  - No additional gases required

- Diluted Sample
  - Lower moisture, less reactive

- Speciating
  - Measures either Hg\textsuperscript{T} or Hg\textsuperscript{0}

- Analyzer Detection Limit:
  Currently $\sim$1 ng/m\textsuperscript{3} (\sim0.1 ppt)

- No cross interference with SO\textsubscript{2}
Model 80i Hg Analyzer
Model 80i Hg Analyzer Flow Scheme

Model 80i Hg Analyzer

Exhaust
Flow
Polarizing Beam Splitter
Reference detector
PMT assy
Rejection mirror
Hg lamp source

S1 (Total)
S2 (Elemental)
S3 (Sample)
S4 (Z/S)

Total
Elemental
Zero air
Cal gas
Hg Fluorescence

\[
\text{Hg} + h\nu \ (253.7 \text{ nm}) \xrightarrow{K_f} \text{Hg}^* \\
\text{Hg}^* \xrightarrow{\text{Hg} + h\nu \ (253.7 \text{ nm})}
\]

\[I_a = I_o[I_e^{-\alpha_x(Hg)}]\]

\[I_f \propto I_o \alpha_x(Hg) \text{ or } K(Hg)\]

High Intensity Hg Lamp
Reflective Filtering
Enhanced Light Baffling
Bandpass Filter
Model 81i Hg Calibrator

- Hg Vapor Generator
  - Now NIST Traceable with Interim Traceability Protocol
  - Used to calibrate directly to analyzer and across probe filter
  - Check dilution ratio
  - Using Peltier Cooler/vapor pressure control and mass flow controller
    - 1 µg/m³ to 50 µg/m³
Model 81i Hg Calibrator Flow Scheme

Model 81i Hg Calibrator

CDA (20-40 psig)

Regulator Set to 25 psig

MFC 1 0-50 sccm

Bypass solenoid

Temp control

MFC 2 0-20 lpm

Hg source

1.5 l/m orifice

Pump on/off

Hg scrubber

Zero air to analyzer

Cal gas to probe
Zero air to probe

Rest

Exhaust

Calibration gas to analyzer
NIST Traceability

- All Thermo elemental generators leaving the factory are checked against a NIST traceable Vendor Prime
- Bracketing procedure “3 x 3”

"User Prime" vs. Vendor Prime Comparison

<table>
<thead>
<tr>
<th>Instrument Information</th>
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<tbody>
<tr>
<td>DATE</td>
</tr>
<tr>
<td>&quot;User Prime&quot; S/N</td>
</tr>
<tr>
<td>Vendor Prime S/N</td>
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<table>
<thead>
<tr>
<th>Test Information</th>
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<tbody>
<tr>
<td>Generator Set Point (ug/m3)</td>
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<tr>
<td>2.7</td>
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<tr>
<td>5.7</td>
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<tr>
<td>8.1</td>
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20 Degrees C, 1 ATM

Rev. A.0
Elemental Hg, Oxidized Hg, and the Weekly Integrity Test

- The Thermo 81i Mercury Calibrator generates Elemental Mercury Calibration gas.
- Daily span checks are required with elemental Mercury.
- CAMR required a “Weekly Integrity Test” with Oxidized Mercury.
- Thermo provides the “Mercuric Chloride Generator” for this test.
- A 3-point Oxidized Linearity is required for initial certification of Hg CEMS.
HgCl₂ Generator Module - For the weekly Integrity Test
HgCl$_2$ Generator System Flow
PIPP Multi-Level HgCl₂ Generation 3/12/07

PIPP Outlet Run 4 Tuesday

Time

Hg (ug/m³)
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15

15 µg/m³ Hg⁰
10 µg/m³ Hg⁰
5 µg/m³ Hg⁰

Hg(0) Hg(T) Hg(2+)
Installation Activities

- Low Level Monitoring Experiences
  - Nitrogen Generator

- Certification Preparation Experiences
  - The challenges of emission rate variability.
ICSET Nitrogen Dilution Testing 1/15/06
Low Concentration Hg Measurements

- For Total Hg stack concentrations > 0.5 µg/m³
  - Standard dilution system
  - Use Zero Air
  - 1 ng/m³ analyzer MDL
  - 40:1 system dilution - CEMS MDL ~ 0.04 µg/m³

- For Total Hg stack concentrations < 0.5 µg/m³
  - Nitrogen dilution system
  - Use Zero Air feed to Nitrogen generator
  - 0.2 ng/m³ analyzer MDL
  - 40:1 system dilution - CEMS MDL ~ 0.008 µg/m³
Hg Fluorescence

Mercury Fluorescence, Pressure Dependence for Samples at constant Mixing Ratio

Mercury in Nitrogen

Mercury in Air

Raleigh scattering

CEMS MDL = 0.008 microgram/m³

CEMS MDL = 0.040 microgram/m³

Sample Chamber Pressure, atmospheres absolute

Relative Fluorescence Intensity

Relative Background Signal

0.0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0

0.00 0.10 0.20 0.30 0.40 0.50 0.60 0.70 0.80 0.90 1.00
Linearity using Nitrogen

\[ y = 0.99358x - 0.00193 \]
\[ R^2 = 0.99997 \]
• Cooperative Certification Preparation study performed at Sheldon Station- NPPD

• Nitrogen Generators needed for low level monitoring.

• RATAs are still expensive, even Method 30B.

• Hg RATAs and Hg CEMS are still new to many people.

• We are showing all the test results, operational data, good practices to help other users pass RATAs
Host Site is Nebraska Public Power Sheldon Station
View when standing on Unit 2 Stack Looking at Unit 1
Sheldon Station Details

Sheldon Unit 1 (1963) - 120 MWg

Sheldon Unit 2 (1968) - 135 MWg

- Two units, each B&W boiler w/ 3-cyclones
- Pulse jet baghouses added 2000.
- No scrubbers or SCR
- PRB Coal for fuel
- Precipitators de-energized but still in gas stream to capture large ash particles.
Prior to Testing, both systems have been installed for several weeks.
What does it read on Flue Gas? - Typical Levels of Hg on Unit 1

NPPD Sheldon #1 Load vs. MW - 36 hrs

36 hrs - MW varies from 80-120 MW
Typical Levels of Hg on Unit 2 – Much Lower than U1

NPPD Sheldon #2 Load vs. MW - 36 hrs

36 hrs - MW varies from 80-130 MW
Why are these levels so low?
Preparing for RATA- There are lots of things you can do.

For ANY Hg CEMS:

a) 30B Traps vs. Gas Generator
b) CEM Calibration Results
c) Linearity Report
d) 7-day Drift Test
e) Cycle Response Test
f) Temp and Pressure QA
g) Cross check your Gas Generator
h) Plant Operations Data Evaluation (i.e. load vs. Hg)
i) Calibrator QA
j) System Integrity Check
k) Confirm Moisture Correction
l) DAS Command & Control

Specific to Thermo Hg System:

a) Pressure, Temp, and Lamp Compensation
b) Nitrogen Generator Check
c) Backup of config for all analyzers
d) QC the LREC file
NPPD Sheldon #2 7-day CET Results
NPPD Sheldon #2 Linearity Results

- HgT
- abs diff
- 0.8 ug
- % diff
- 10%
- Hg81

Linearity Sheldon Unit 2
Collect Traps from your gas generator- If you Can

These are 30B Carbon Traps set up to sample the gas coming out of the 81i Calibrator.

We think you should pull some samples and connect the traps in this manner before each RATA.
**NPPD Sheldon 81i Calibrator Traps- Both Units**

**Burn Traps against the Calibrator BEFORE the RATA!**

<table>
<thead>
<tr>
<th>System</th>
<th>81i Value</th>
<th>Trap #1</th>
<th>Trap #2</th>
<th>30B Trap Average</th>
<th>Difference</th>
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<tr>
<td>3.0</td>
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<td>9.09</td>
<td>1.01</td>
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</table>
Cross Check Your Gas Generator- If you Can

- Connect the output of one calibrator to another.
- We connected the calibrator for Unit 1 to Unit 2 and vice versa.
- Then we ran a span check to see what happened.
Other Plant Data Cross Check Plot

NPPD Sheldon #1 Boiler Parameters vs. HgT

- CO2/2.5
- HgT
- MW/30
- Nox*5
- SO2/125

Hours

1 3 5 7 9 11 13 15 17 19 21
Weekly System Integrity Checks Chlorine Setup
Relative Accuracy Summary Sheldon Unit 1-PASSED!

NPPD Sheldon 1 RATA Results

9 Runs - Mean Diff of 0.2 ug

- Dashed line: HgT
- Red line: CEM Ave
- Green line: 30B
- Black line: run diff
- Yellow line: allowed
- Yellow line: 9-run mean diff
Relative Accuracy Summary Sheldon Unit 2- PASSED!

NPPD Sheldon 2 RATA Results

9 runs - Mean Diff of 0.1 ug

- HgT
- CEM Ave
- 30B
- run diff
- allowed
- 9-run mean diff
RATA Challenges with Method 30B constraints

- Mercury Concentrations in the stack dropped from 2.4 to 0.9 ug/m³ during the 2-day period of the Unit 2 RATA.

- If the Hg concentration in the flue gas changes during the RATA, one needs to ensure that 30B QA checks, specifically including spike targets and permissible sample mass range, are within tolerance. Even concentration changes that seem insignificant could be very important.

- If the concentration had fallen another 0.2 ug, a new spike target would have to be used, doubling the amount of QA testing required.
• The Method 30B QA of the trap is very specific to the initial concentration values when choosing the sampling parameters.

• If the concentration values shift from the initial, one cannot assume that the QA is valid. At lower concentrations, shifts have a larger impact on staying within the boundaries of the method QA limits.

• At concentrations just above 1.0 ug, paired train agreement can be challenging.
Lessons Learned Summary: Things to Check and Know

**For ANY Hg CEMS**

a) 30B Traps vs. Gas Generator  
b) CEM Calibration Results  
c) Linearity Report  
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**Specific to Thermo Hg System:**

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- Method 30B offers advantages because you can check the output of the Calibrator (Gas Generator).
- A 30B RATA can be conducted in 2 working days- even with low concentrations in the flue gas.
Mercury Freedom™ System

- Thermo has been a key supplier of air pollution monitoring solutions for 30+ years

- The Hg CEMS development is an extension of Thermo experience and expertise

- Thermo-owned, proprietary technology affords a seamless integration of components and ease of operation

- System is designed, engineered, manufactured, and supported by Thermo Fisher Scientific
Thanks

Questions?