Hg CEMs: A Researcher's Perspective

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Hg CEMs: Potential Applications

- **Research**
- **Source Characterization**
- **Process optimization/control**
- **Regulatory**

Hg CEMs: Research Applications

- **Understanding Hg species is key to understanding Hg control**
  - **Fundamental studies**
    - **Hg chemistry in combustion processes**
    - **Fundamental control research**
  - **Control technology evaluations**
    - **Pilot-plant and Field studies**
- **Source Characterization**
  - **Emission profiles**
  - **Source variability**

Total vs. Speciating?

- **Most Hg CEMs measure total Hg**
- **Speciating Hg CEM valuable**
  - **Research tool**
  - **Process monitor**
- **Speciation by difference (total – elem.)**
- **Speciated Hg meas. more complicated**

Hg CEMs: State-of-the-Art

- **Hg CEMs routinely used in Europe**
- **In US, Hg CEMs primarily used for research purposes**
  - **Diverse measurement environments**
  - **Majority prototype systems**
  - **Commercial systems current focus of performance testing**
- **Many vendors now exist**
- **Recent field test programs have done much to advance the technology**

Wet vs. Dry Conversion Systems

- **Wet chemistry reduction systems most proven**
  - **Intensive to operate**
  - **Chemical handling issues**
- **Dry systems less proven, but have much greater advantages**

ORD/NRMRL Hg CEM Research

- **Hg CEMs needed to support our research**
- **Data quality critical**
- **Main areas of emphasis:**
  - **Development of diagnostic and QA/QC tools**
  - **Investigation of measurement issues (biases, interferences, etc)**
  - **Performance testing (Pilot-scale and field)**

Development of QA/QC Tools

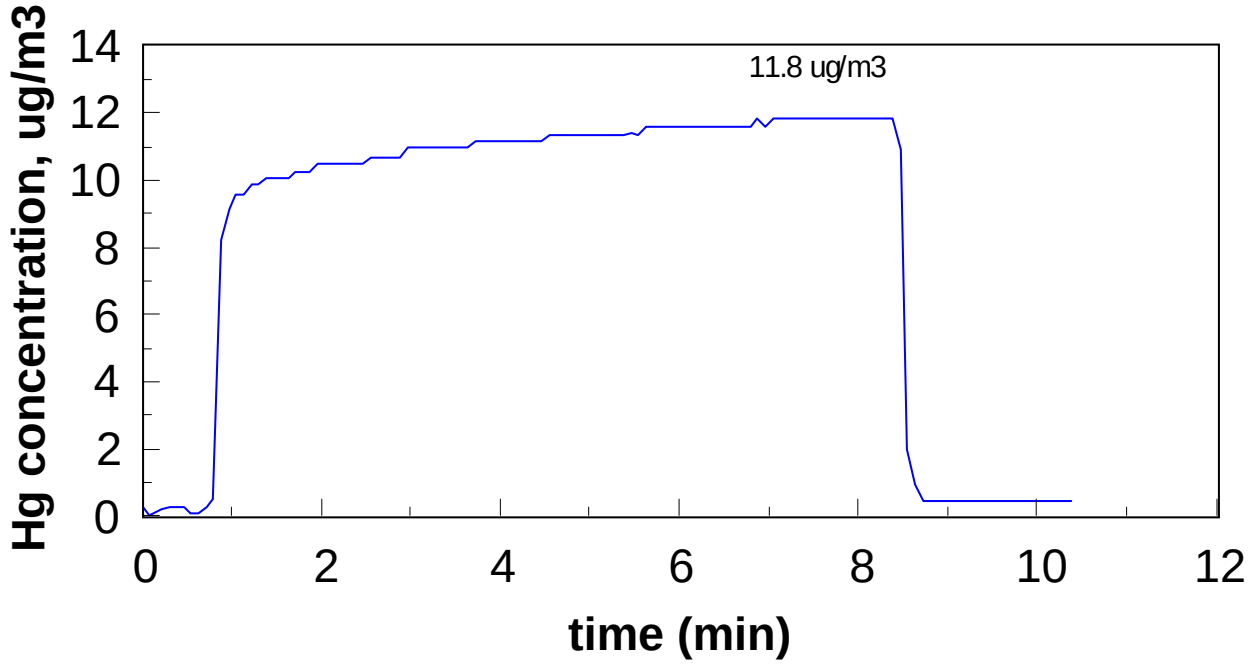
- **Elemental Hg gas standard**
  - **Drift checks, system bias, calibration**
- **Oxidized Hg (HgCl2) gas standard**
  - **System bias checks, sample transport, converter efficiency, etc**

Elemental Hg Gas Standard

- **Tank stability**
- **Tank concentration**
- **Delivery issues**

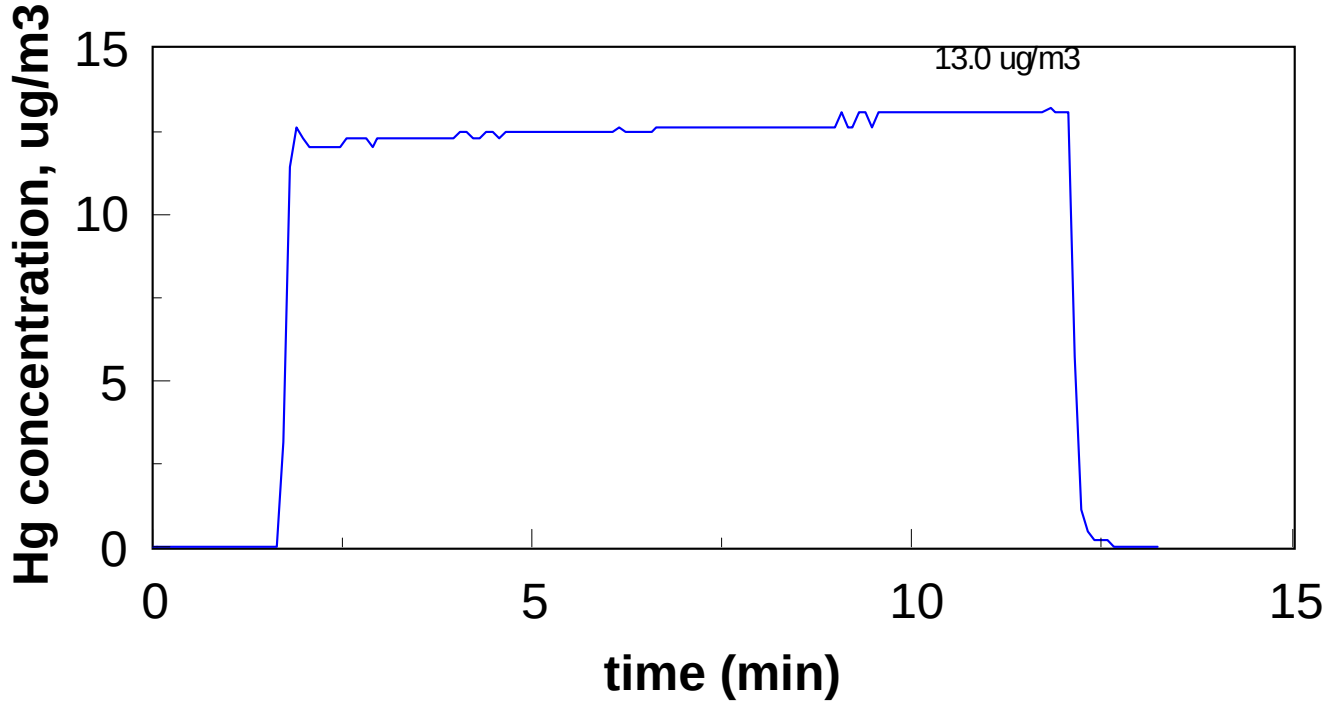
efelder response to Hg tank (CC19870), 16 ug/N

range 0-20 ug/m3



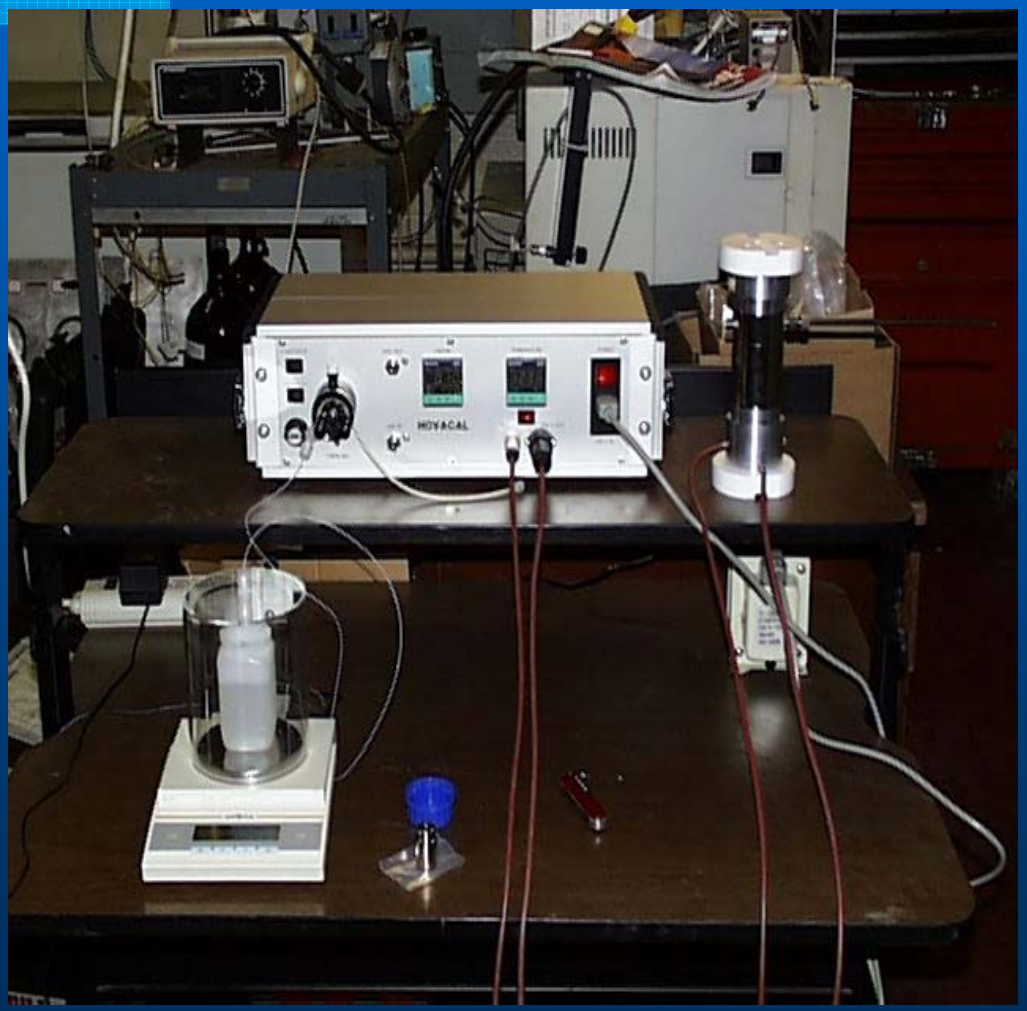
Seefelder response to Hg tank (CC19931), 16 u

range 0-20 ug/m3



$HgCl_2$ Gas Standard

- **Hg species**
- **Stability**
- **Accuracy**
- **Transport**



$HgCl_2$ Gas Standard

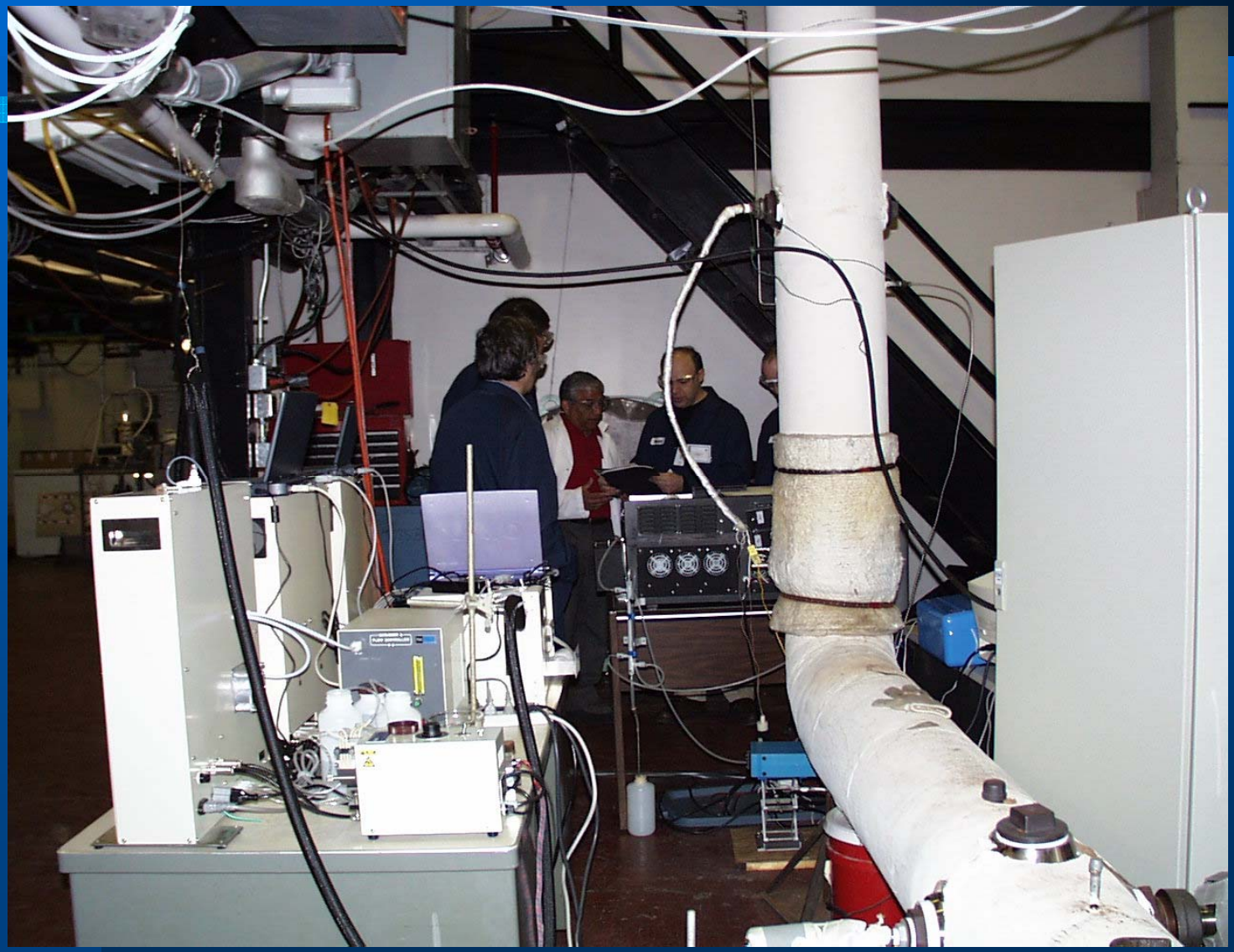
Investigation of Measurement Issues

- **Interferences**
  - **SO_2, SO_3, Cl_2, HCl, NO_x, NH_3, PM**
- **Biases**
  - **Sample transport/reactivity of oxidized forms**
  - **Conversion efficiency**
  - **Particulate-phase capture/oxidation**

Performance Testing

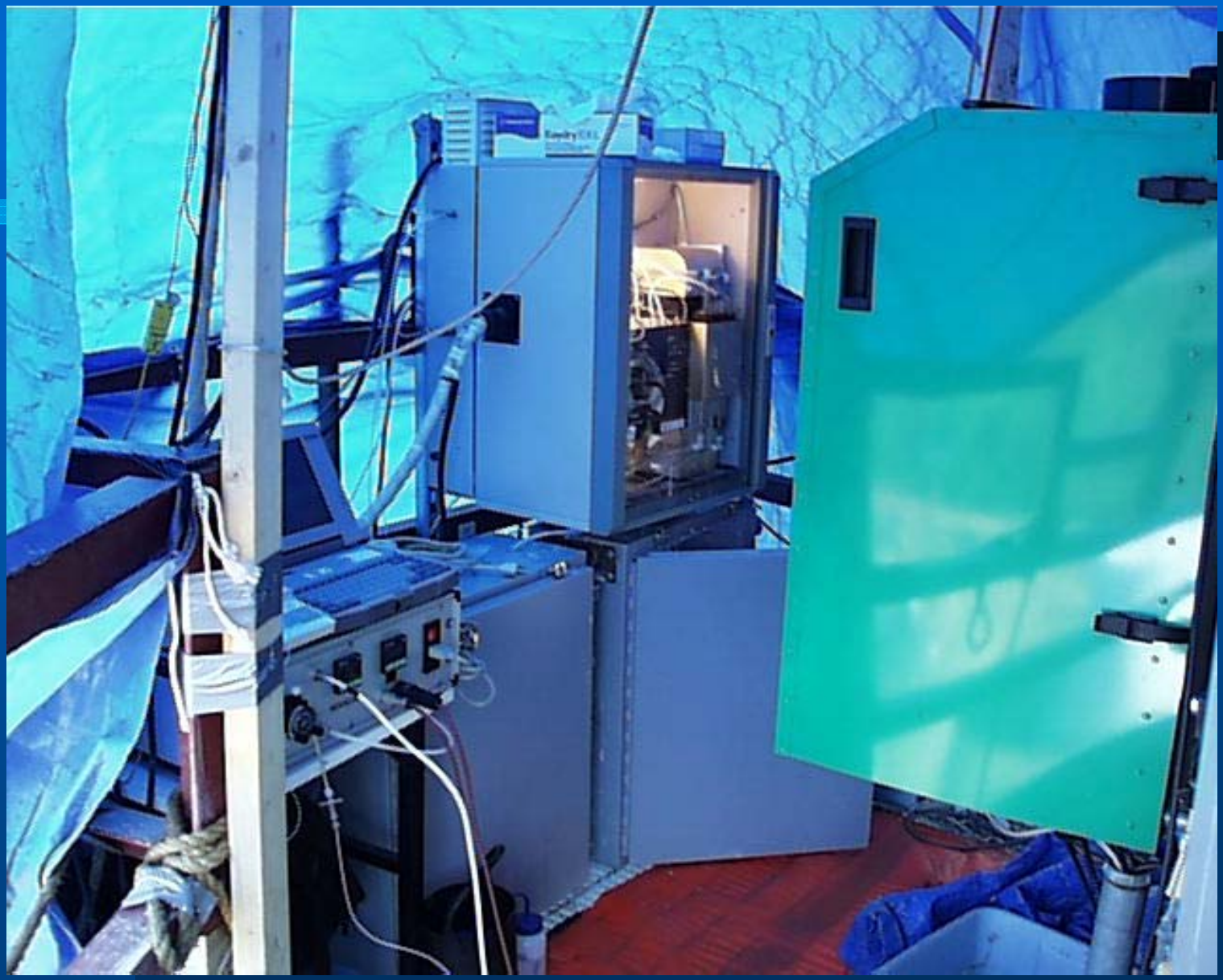
- **Focus on commercial systems**
- **Research application issues consistent with other applications**
- **Collaboration is key**
- **NRMRL/ETV Pilot-Scale Tests**
- **ETV/DOE MWFA Incinerator Tests**
- **EPA/OAQPS Coal Utility Tests**

NRMRL/ETV Hg CEM Tests



OAQPS Field Hg CEM Tests


CAUTION
CAUTION



Future Plans

- **Continued field testing**
- **Focus on APCD inlet environments**
- **Evaluation of inertial PM probes**
- **Evaluation of dry thermal/catalytic conversion systems**

Message

- **Continued field testing of Hg CEMs critical to development**
- **Opportunities limited**
- **Current OAQPS tests represent majority of commercially available systems**

Field Evaluation of Mercury CEMS: Coal-fired Electric Utilities

Bill Grimley & Barrett Parker
Emissions Measurement Center (EMC),
EMAD, OAQPS, OAP, USEPA

Jeff Ryan
APPCD, NRMRL, ORD, USEPA

Outline

- **Positive Findings to date**
- **Project Background**
  - Regulatory need
  - Mercury monitoring: Options and CEMS
- **EMC Activities**
  - **Phase 1 and Phase 2 field work**
  - **Phase 3 Plans**

Positive Findings to Date

- **Elemental (Hg^0) calibration cylinders proved very useful to check CEMS calibration and verify sampling system.**
- **"HOVACAL" $HgCl_2$ standards generator proved very useful to challenge CEMS converters, and verify sampling system.**

Findings, cont.

- **Wet converter CEMS passed second RATA on 10 of 15 runs with RA of 9.5%.**
- **Dry converter CEMS #2 modifications, (between first and second RATAs) materially improved performance on second RATA, for about a week.**

Background: Regulatory Need

- **2 Potential regulatory pathways**
  - **CAA / Utility MACT**
  - **NEP / multi-pollutant legislation**
- **Utility MACT finding on Dec 2000**
  - **Propose regs by Dec 2003**
  - **Promulgate regs by Dec 2004**
  - **Compliance date of Dec 2007**

Background: Mercury Monitoring Options

- **Mercury CEMS**
- **Manual stack testing**
- **Extended Period Integrated Sampling - using absorption media**
- **Material Balance by (Hg in fuel) – (Hg in non-gaseous combustion by-products)**

Background: Mercury CEMS

- **Europe has applied certified mercury CEMS**
- **But lack of field demonstration data on sources with co-pollutant mix typical of US sources**
- **Decision to focus on total gaseous mercury**
- **Existence of Draft PS - 12**

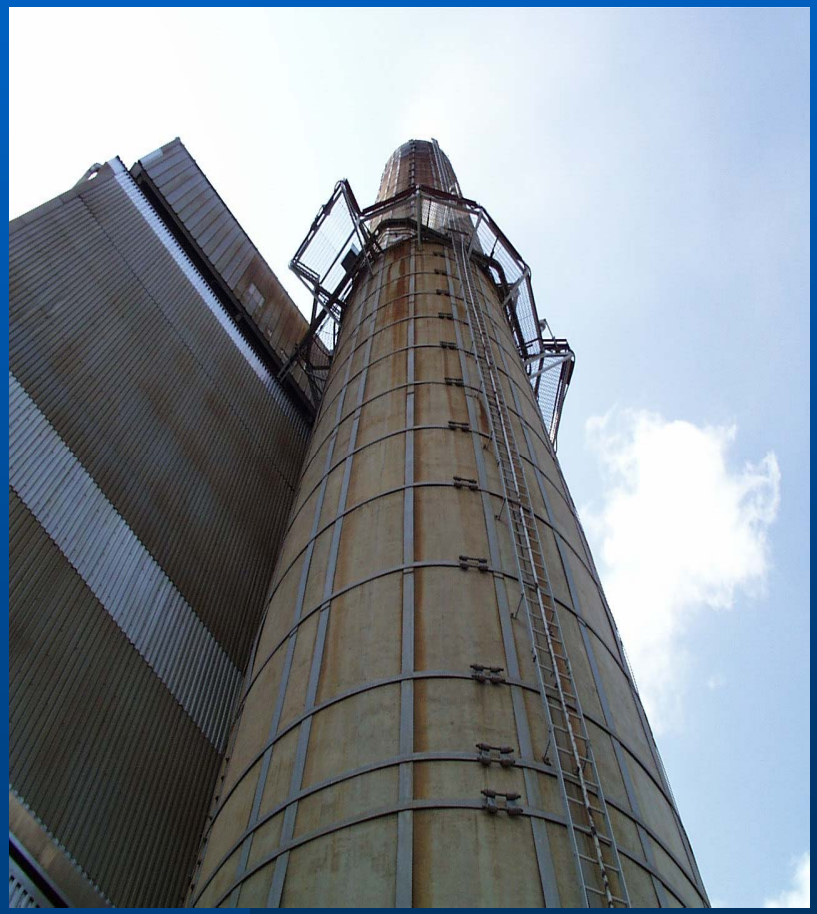
EMC Activities

- **Evaluate CEMS for Application to Coal-fired Electric Utilities**
  - **Site selection: 140 MW tangentially-fired pulverized coal boiler with cold-side ESP, burning eastern bituminous**
  - **Calibration of detectors and sample handling system with mercury standards**
  - **Conduct RATAs with “Ontario Hydro”**
  - **Collect Data for 3 months on performance criteria**

First Phase

- **May - Jul 01: Contact Vendors**
  - **“Dry” versus “Wet” ionic Hg converters**
  - **Other factors**
- **Aug – Sept 01: Installation, begin CEMS operation**
  - **Direct calibration with cylinder standards**
  - **Sampling system check with cylinder standards and “HOVACAL”**

Sampling Location



- **Sample routing: Probe to cal/bias manifold; to 120’ TFE Teflon sample line; to sample manifold in trailer; all maintained @ 360 ° F**
- **All fittings interior TFE-coated**
- **Sample line changed to PFA Teflon Oct 01**
- **Sampling bias check “up and back”**

Sampling Location

First Phase cont.

- **Oct 01: First RATA**
  - 12 runs
- **Nov 01: Vendors service units**
  - catalytic converter issues
  - mechanical problems

First Phase cont.

- **Jan 02: APPCD, NRMRL Installs a Third CEMS**
  - **Wet Converter CEMS, “on stack” location**
- **Mar 02: Second RATA Series**
  - **15 “Ontario Hydro” Runs versus 12**
  - **Coal: Source Change**

First Phase, CEMS manifold

First Phase, temperature controls

First Phase cont.

- **CEMS challenged by**
  - **Elemental mercury cylinder gas**
  - **$HgCl_2$ generated by a “Hovacal” (see right)**
    - **$HgCl_2$ produced using precision mass flowrate controller**

First Phase cont.

- **Dry conversion CEMS # 1**
  - **Catalyst converts oxidized to elemental mercury**
  - **Cold vapor atomic adsorption UV photometer detects mercury**

First Phase cont.

- **Dry Conversion CEMS # 2**
  - **Catalyst coverts oxidized to elemental mercury**
  - **Cold vapor atomic adsorption UV photometer detects mercury**

First Phase cont.

- **APPCD's Wet conversion CEMS added to test**
  - **Converter unit illustrated**
  - **Located near stack port**

First Phase Results

- **Standards, sampling system field verified**
- **Wet conversion system RATA**
- **Ontario Hydro confirms expected Hg species split**
- **Vendor awareness increased**

RATA #2: Wet Converter CEMS

Run #	CEMS	RM	Diff.
1	4.5	3.9	-0.6
2	4.4	4.3	-0.1
8	9.1	8.0	-1.1
9	8.6	7.7	-0.9
10	9.4	9.1	-0.3
11	7.8	7.8	0.0

RATA #2: Wet Converter CEMS

Run #	CEMS	RM	Diff.
12	8.3	8.5	0.2
13	9.8	11.5	1.7
14	9.5	10.1	0.6
15	7.0	8.5	1.5
Avg.	7.8	7.9	0.1
S.D.			0.9
C.C.			0.7

Relative Accuracy: 9.5 %

RATA #2: Dry Converter CEMS # 2

Run #	CEMS	RM	Diff
1	5.2	3.9	-1.3
2	6.6	4.3	-2.3
3	5.2	3.7	-1.5
4	3.1	3.6	0.5
5	3.8	4.2	0.4
6	3.6	4.3	0.7
7	4.0	3.3	-0.7

RATA #2: Dry Converter CEMS # 2

Run #	CEMS	RM	Diff
8	5.3	8.0	2.7
9	5.4	7.7	2.3
10	7.3	9.1	1.8
11	1.3	7.8	6.5
12	3.2	8.5	5.3
13	3.4	11.5	8.1
14	1.8	10.1	8.3
15	1.3	8.5	7.2

Second Phase

- **June 02: resurveyed vendors to locate more participants**
- **Aug 02: acquired and installed 2 “new” dry converter CEMS, arrangements made to further modify old dry converter CEMS #2**
- **Sept ’02: relocated wet converter CEMS to trailer**

Second Phase, cont.

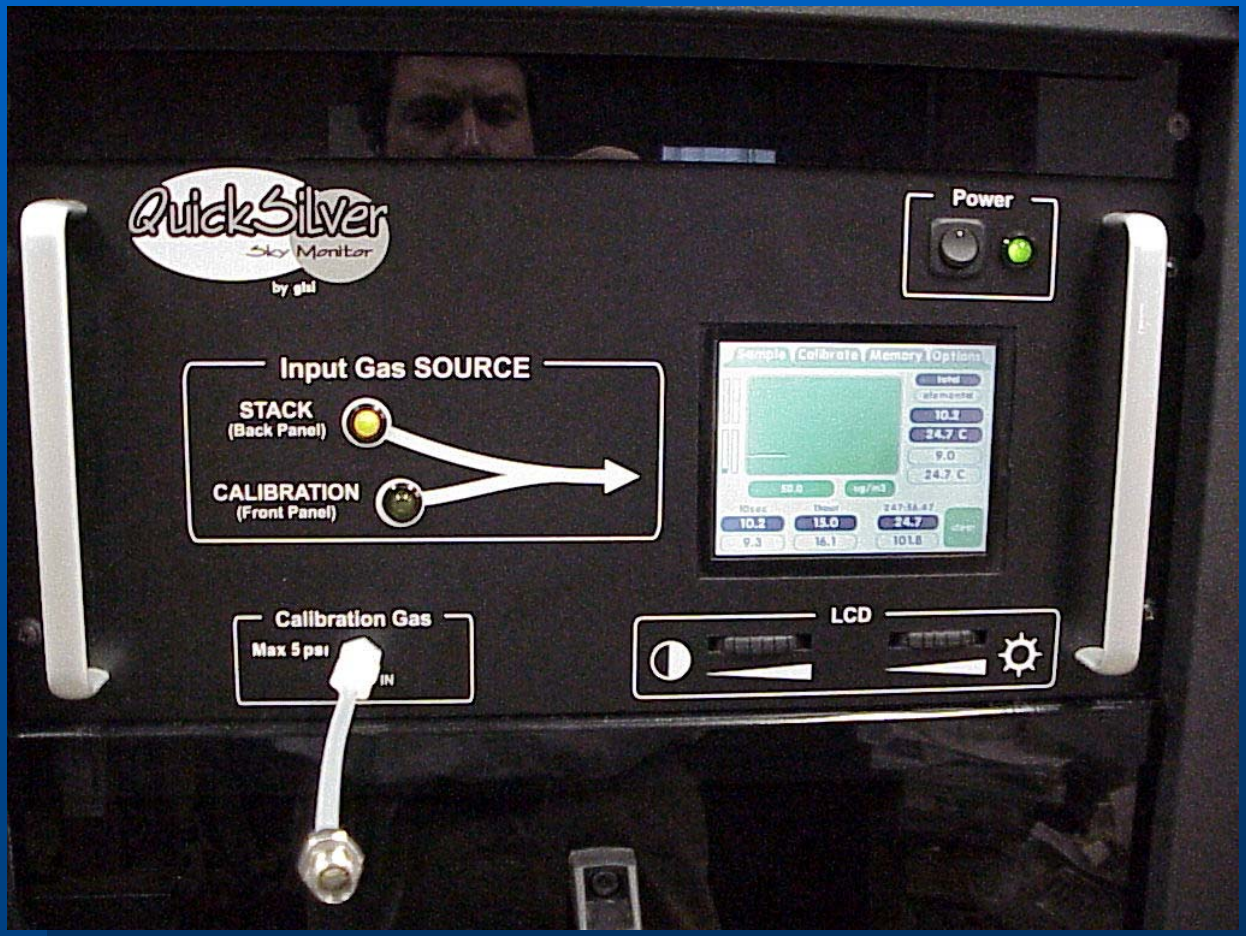
- **Sept 02: added EPRI integrated sample monitoring system**
- **Sept 02: completed third RATA series**
- **Oct 02: added two additional dry converter CEMS, one with “new” measurement technology**
- **Dec 02: fourth RATA series planned**

Second Phase, cont.

Second Phase, cont.

Second Phase, cont.

Second Phase, cont.


QuickSilver
Sky Monitor
by gtsi
Power
Input Gas SOURCE
STACK
(Back Panel)
CALIBRATION
(Front Panel)
Calibration Gas
LCD

Second Phase, cont.

Second Phase, cont.

Current Evaluation Status

- **Hg Standards**
- **Sampling System**
- **RATA Test Results**
- **CEMS Availability**

What's Next ?

- **Electric Utility MACT**
  - **Assess Mercury Limit & Standard**
    - **Total vs. Speciated**
    - **Percent Reduction vs. Limit**
  - **Prepare Monitoring & Testing Recommendations**
    - **Proposal or Request for Comment**

What's Next ? (continued)

- **Electric Utility MACT (continued)**
  - **Adjust draft PS-12 as needed**
  - **Conduct Phase III if required**
    - **Bituminous with wet scrubber and ESP**
    - **Adsorbent injection with hot side ESP**
    - **Subbituminous with SCR (or SNCR)**

What's Next ? (continued)

- **Multipollutant Legislation**
  - **Track Progress and Content**
    - **Administration, Jeffords, Others**
    - **Instrument Mandate, Trading Provisions, Speciated Limits, Implementation Schedule**
- **Consent Decrees for Hg CEMS**
  - **Offer Advice and Assistance**
    - **PSEG Mercer (NJ) & Others**

What's Next ? (continued)

- **Hazardous Waste Combustors**
  - **Review ETV Results from Oak Ridge**
- **Mercury Cell Chlor-Alkali Plants**
  - **Develop Test Program with Chlorine Institute**
- **State Regulations**
  - **Share Information with Massachusetts and Others**

Acknowledgements

- **Bill Maxwell & Bob Wayland, ESD**
- **Ralph Roberson, RMB Consultants**
- **Utility site personnel**
- **CEMS vendors**
- **MRI and Arcadis personnel**