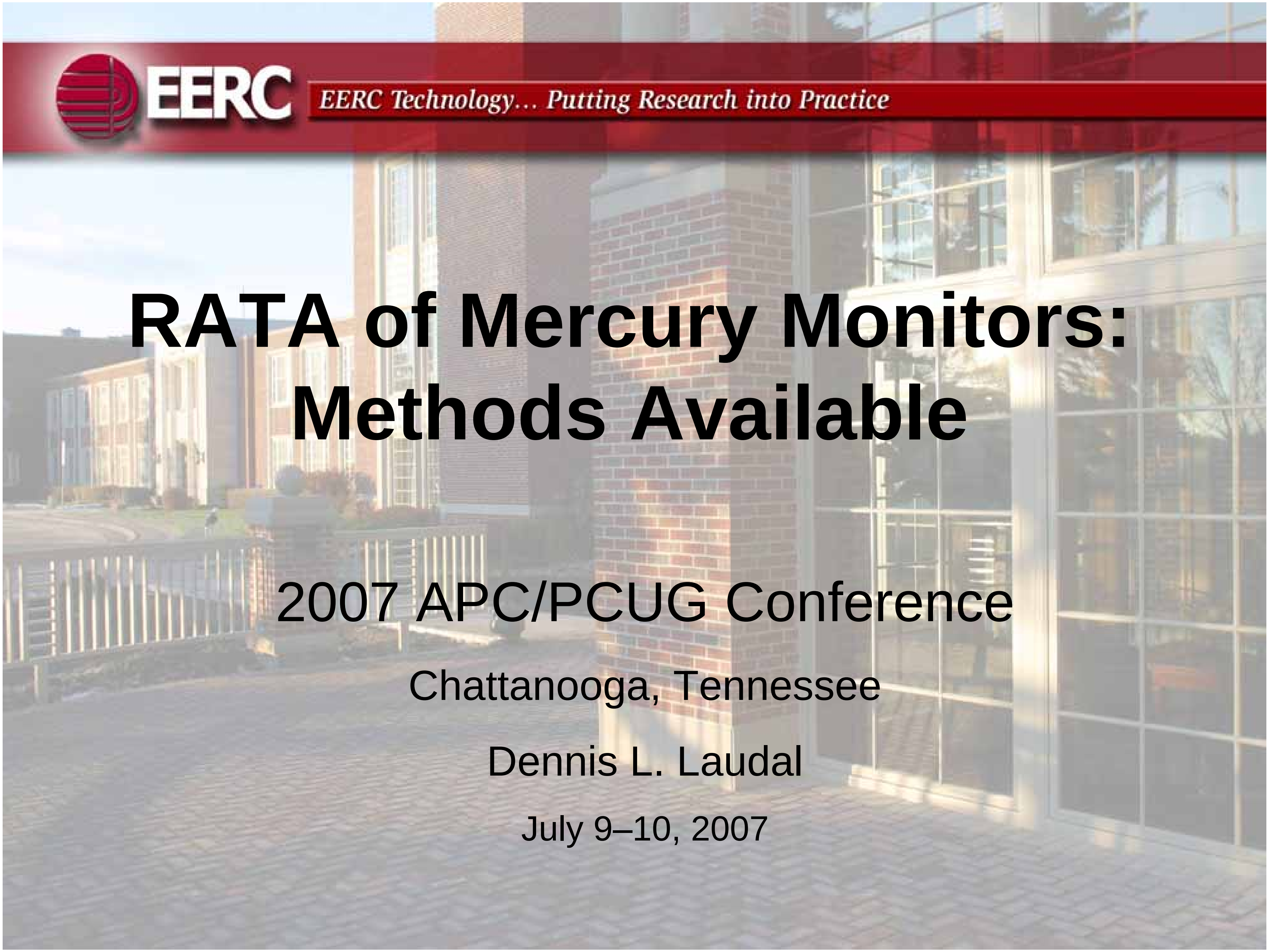
Reinhold Environmental Ltd.

2007 APC Round Table & Expo Presentation

July 8-10, 2007
Chattanooga, TN
Hosted by TVA



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RATA of Mercury Monitors: Methods Available

2007 APC/PCUG Conference

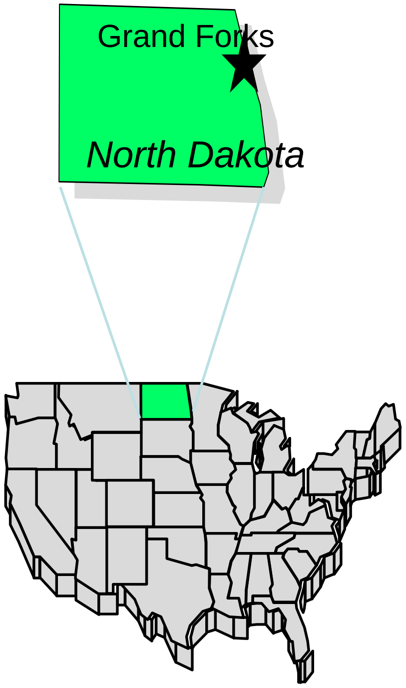
Chattanooga, Tennessee

Dennis L. Laudal

July 9–10, 2007

EERC Mercury Measurement Experience

- The EERC validated the Ontario Hydro (OH) mercury speciation method, ASTM International Method D6784-02.
- The EERC has over 20 years of experience in characterization and measurement of mercury.
- The EERC has done extensive mercury sampling at 60 different power plants over the past 8 years.
- The EERC has more than 15 years of experience with continuous mercury monitors (CMMs).
- The EERC has been testing sorbent traps as a reference method (RM) for the past 2 years and have completed four relative accuracy test audits (RATA's) using EPA Method 30B protocols.



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Mercury Measurement Under CAMR

- 40 CFR Part 60 Appendix B – Performance Specifications 12A
  - Procedures for sitting and installing continuous mercury monitors (CMMs).
  - Certification of CMMs (upscale drift and zero drift).
  - RATA.

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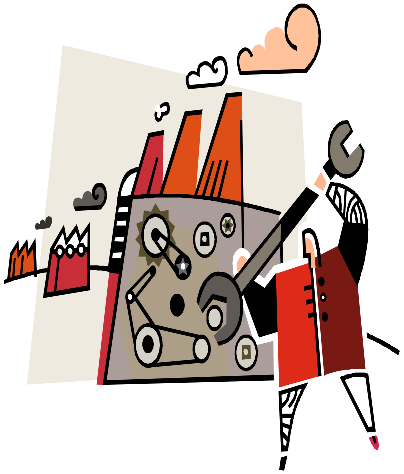
Mercury Measurement Under CAMR

- Current RATA requirements
  - Must be done during instrument certification and then annually thereafter.
  - Currently the only recognized methods are the Ontario Hydro (OH) Method and EPA Method 29.
  - Other RMs are being proposed including sorbent trap methods, Draft EPA Method 30B and Instrumental Reference Methods (IRMs), Draft EPA Method 30A.

RATA Procedure

- Use paired reference method (RM) samples.
- Conduct a minimum of nine valid paired RM test runs.
- More than nine RM tests can be conducted but only a maximum of three valid sets of test results can be rejected.



- Report all data, including rejected data.
- Run RM long enough to ensure a sufficient mass of mercury is collected for analysis. RM data must meet the relative difference (RD) criteria.

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RATA Procedure

Paired Samples: Relative difference (RD)

$$RD = 100\% \times \frac{\left|(C_a - C_b)\right|}{(C_a + C_b)}$$

Where,

C_a and C_b are concentration values determined from each of the two samples, respectively**.**

Relative Accuracy Test Procedure

- The minimum performance criteria are:
  - RD ≤ 10% for Hg concentrations >1.0 µg/m^3
  - RD ≤ 20% for Hg concentrations ≤ 1.0 µg/m^3
- Pairs of data that do not meet these criteria are eliminated from the data set used to determine relative accuracy (RA).

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Relative Accuracy Test Procedure

Calculate RA using:

$$RA = \frac{\left|\bar{d}\right| + \left|cc\right|}{RM} \times 100\%$$

Where,

$\bar{d}$ = The sum of the differences between the RM values and the corresponding CMM values

cc = The value of the confidence coefficient

RM = Arithmetic mean of the reference method values

Relative Accuracy Test Procedure

Calculate the confidence coefficient (one tailed) of a data sets using:

$$cc = t_{0.025} \frac{S_d}{\sqrt{n}}$$

Where,

$t_{0.025}$ = Student t value (use statistical tables)

S_d = Standard deviation

n = Number of data points

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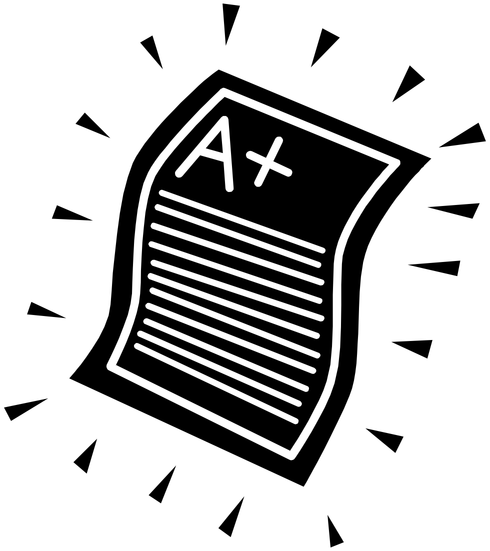
Relative Accuracy Test Procedure

The CMM passes the RATA if:



- The Hg concentration as measured by the reference method is >5.0 µg/m^3 and the RA is ≤ 20.0%
- The Hg concentration is ≤5.0 µg/m^3 and the absolute difference between the RM and CMM is ≤ 1.0 µg/m^3.

Relative Accuracy Test Procedure

Bias Test

Bias Adjustment Factor (BAF) is zero if:

$$\bar{d} \leq |cc|$$

Relative Accuracy Test Procedure

BAF is defined by:

$$BAF = 1 + \frac{\left|\bar{d}\right|}{CMM_{avg}}$$

Where,

CMM_{avg} = Mean of the data values provided by the CMM during the failed bias test

Relative Accuracy Test Procedure

The RATA data sets are evaluated for bias using:

$$\mathrm{CMM}_i^{\mathrm{Adjusted}} = \mathrm{CMM}_i^{\mathrm{Monitor}} \times \mathrm{BAF}$$

Where,

$\mathrm{CMM}_i^{\mathrm{Monitor}}$ = Data provided by the monitor at time i

$\mathrm{CMM}_i^{\mathrm{Adjusted}}$ = Data value, adjusted for bias, at time i

BAF = Bias adjustment factor, calculated to the nearest thousandth

Ontario Hydro Mercury Speciation Method

ASTM D6784-02

Standard Test Method for Elemental, Oxidized, Particle-Bound, and Total Mercury in Flue Gas Generated from Coal-Fired Stationary Sources (Ontario Hydro Method)

www.astm.org

Advantages of the OH Method or EPA Method 29

- Proven at a number of sites and under a wide variety of conditions.

- Provides good results with a high level of sensitivity, <0.5 µg/Nm^3.

- Currently, the only mercury measurement methods considered to be a RM by EPA.

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Limitations

But …

- A high level of quality assurance/quality control (QA/QC) and well-trained personnel required.
- In many cases a 2-week or more turnaround time is needed for results; in other words, no real-time data.
- It is expensive.
- There is simply not enough certified organizations to complete the number of RATAs that will be needed by January 1, 2009.

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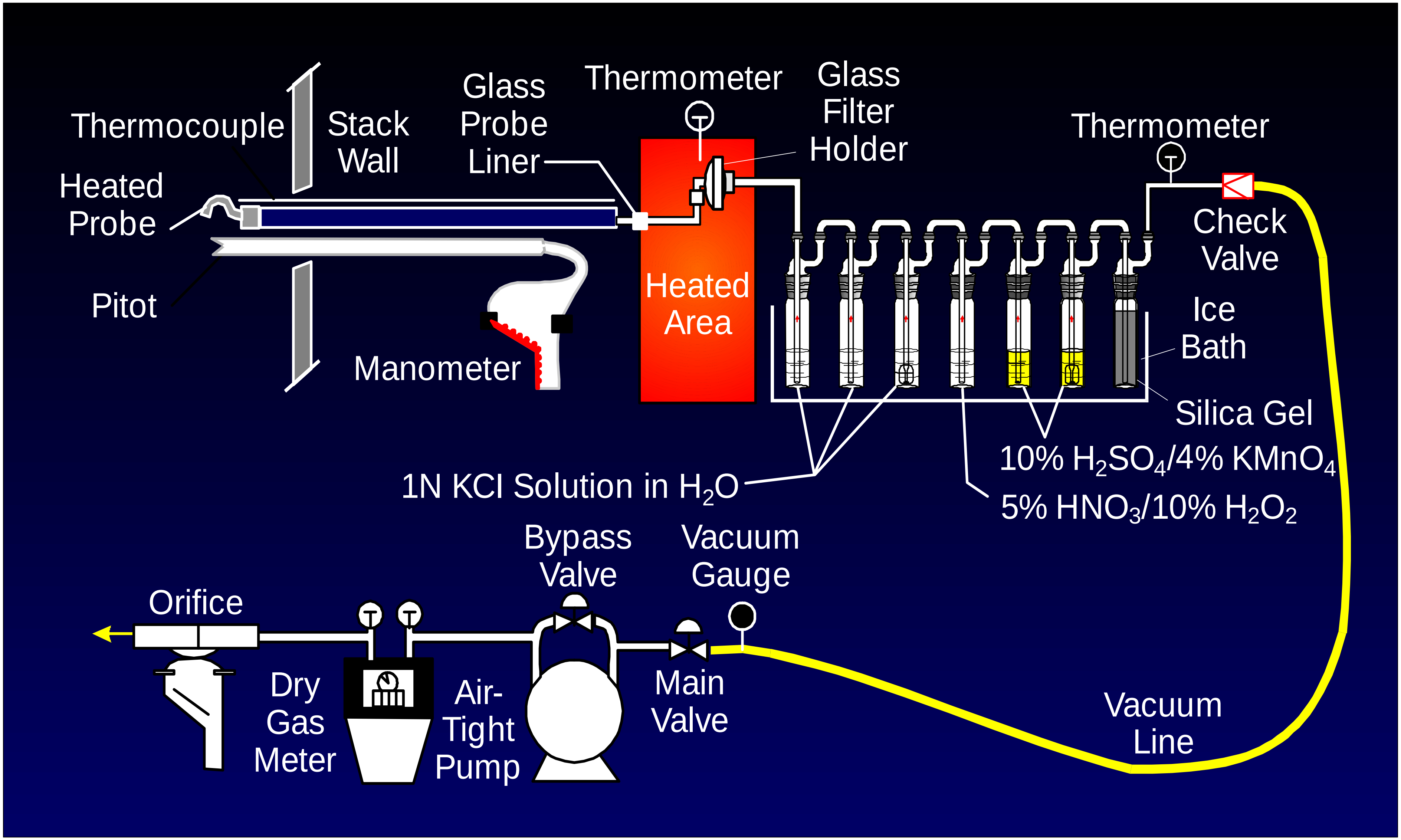
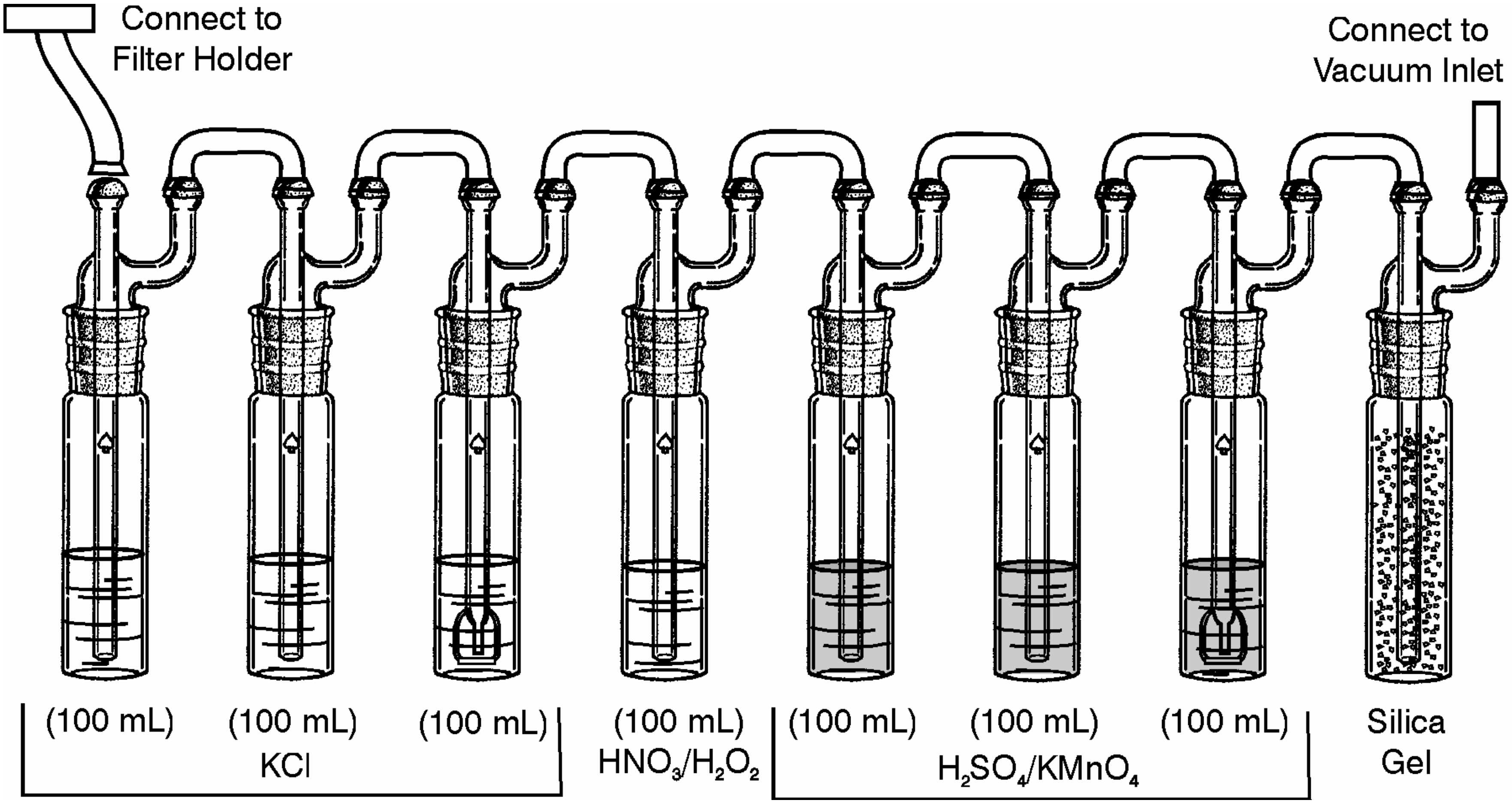
OH Impinger Train



OH Impinger Train



Other Potential Reference Methods

- IRM – EPA Draft Method 30A
- Determination of Total Vapor-Phase Mercury Emissions from Coal-Fired Combustion Sources Using Carbon Sorbent Traps– EPA Draft Method 30B

- The draft of both methods can be found at the following website:

http://www.epa.gov/ttn/emc/prelim.html

Sorbent Traps as a RM and for Appendix K

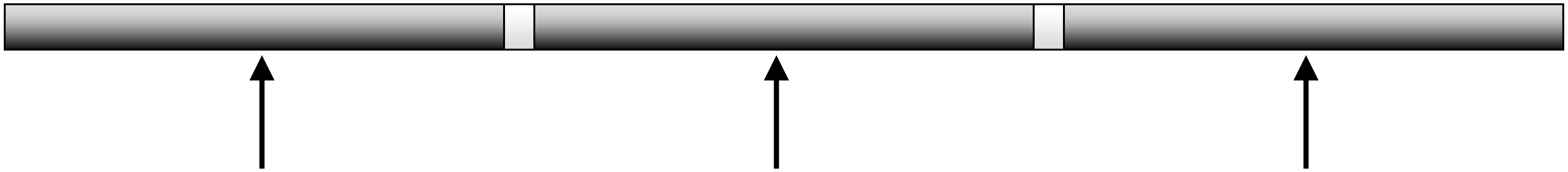
- Both are sorbent trap methods
- Both are procedural not proscribed methods

But:

- A RM is designed to certify or prove another method is working properly. In this case a CMM.
- Appendix K is a CMM.

Differences Between the RM and Appendix K Carbon Traps

Appendix K trap



Section 1

Primary Section

Section 2

Secondary Section

Section 3

Spiked Section

RM Trap

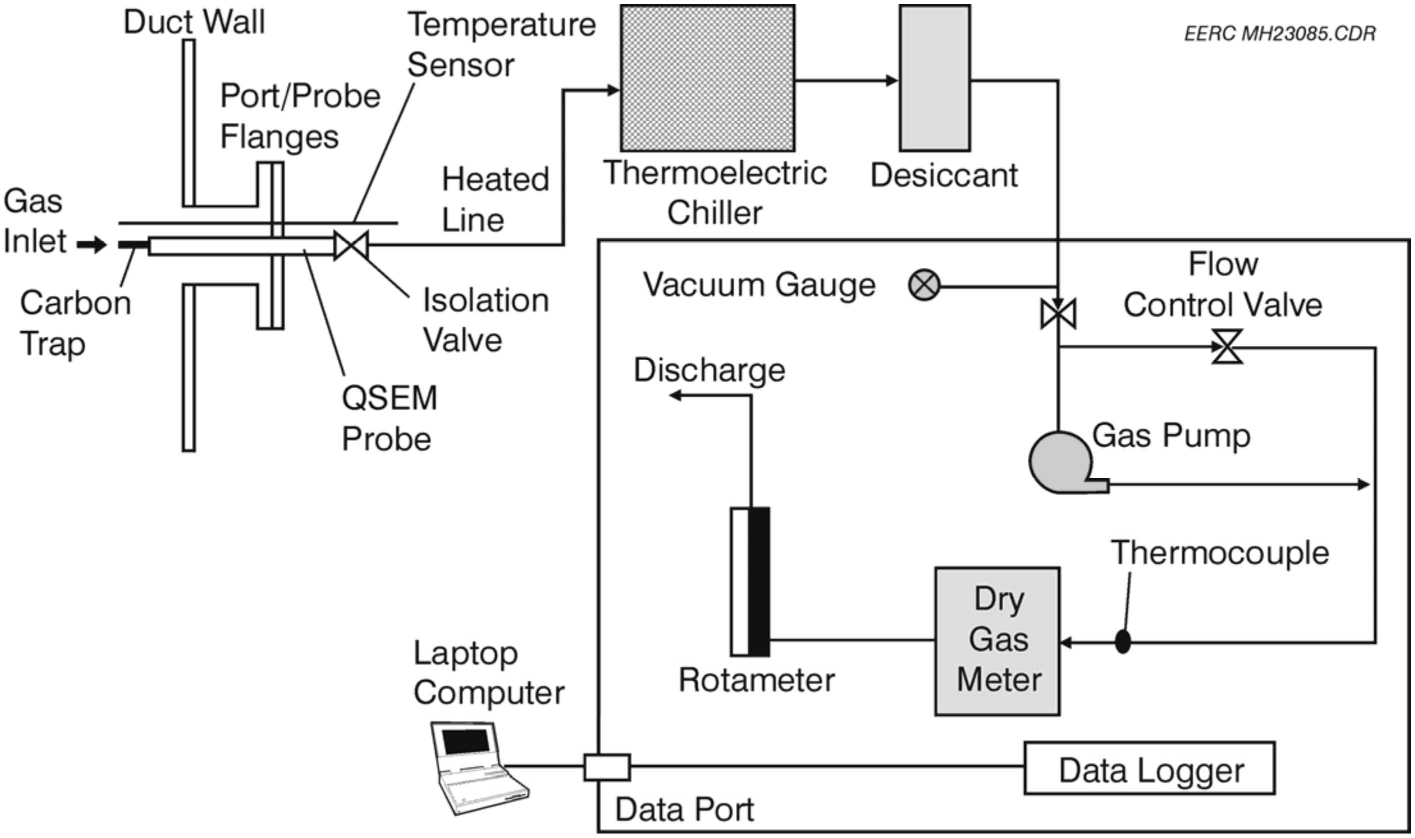
Section 1

Primary Section
(Spiked for Field
Recovery Test)

Section 2

Secondary Section

Example of Sorbent Trap Sampling System



Dual-Trap Probe Design

EPA Method 30 B

Determination of Total Vapor-Phase Mercury Emissions from Coal-Fired Combustion Sources Using Carbon Sorbent Traps

- Sample point selection
- Measurement system performance tests
- Sampling procedures
- Sampling handling
- Analytical procedures
- QA/QC

Sample Point Selection

- Do a 12-point traverse for the RATA or,
- Conduct a 12-point stratification test for vapor-phase total Hg prior to the RATA.

Stratification Test

Hg concentration at each traverse point differs from the mean by:

- ≤5% or ≤0.2 µg/m^3
  - Unstratified
  - Single point RATA allowed
- ≤10% or ≤0.5 µg/m^3
  - Minimally stratified
  - Short-line traverse allowed
- >10%
  - Stratified
  - Long-line traverse required

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Measurement System Performance Tests

- Determination of minimum mass of Hg to be collected
- Analytical matrix test
- Hg^0 and $HgCl_2$ analytical bias test
- Field recovery test

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Determination of Minimum Mass of Hg to Be Collected

- Perform a multipoint calibration of the analyzer at a minimum of three points (the linear coefficient r^2 must be ≥0.99).
- All field samples analyzed must fall within the range of the calibration curve.
- Lowest point in your calibration curve must be ≥10, the minimum detection limit of your instrument (MDL).
- Select a calibration check standard that is >2 times the lowest concentration in your calibration curve.
- Minimum sample time is 30 minutes.

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Determination of Minimum Mass of Hg to Be Collected

Example calculation assuming the following:

- Instrument MDL is 1 ng.
- Instrument was calibrated at 10, 20, 50, 100, and 200 ng.
- Estimated Hg concentration in the stack is 3 µg/m^3.
- 2 ng Hg is measured in the blank sorbent traps.
- A sample rate of 0.3 L/min is chosen.

Determination of Minimum Mass of Hg to Be Collected

With a 2-ng Hg concentration in the blank level to meet the criteria of ≤5% of the total mass of Hg in the second section requires the following:

- A minimum of 40 ng Hg must be collected, requiring 44.4 min of sample time.
- Therefore, it would be recommended that 60 ng be collected at a sampling rate of 0.5 L/min, requiring a sample time of 40 min.

Analytical Matrix Test

- Only required if you use a sample digestion analytical approach, and only done once for each type of sorbent material to be used.

- Digest and analyze a mass of sorbent material similar to what will be used in the field.

- Use standard addition analytical procedures to determine any matrix effects (see example in Section 8.2.1.3 of Method 30B).

Hg^0 and $HgCl_2$ Analytical Bias Test

- This test defines the bounds within which the field samples must be to be valid.

- Only done once for each sorbent type or instrument

- Analyze the front section of three sorbent traps spiked with Hg^0 at the lower and upper concentrations (must be spiked with vapor-phase Hg^0).

- Analyze the front section of three sorbent traps spiked with $HgCl_2$ at the lower and upper concentrations (liquid standards may be used).

- To be valid, the average recovery of each set of three samples must be between 90% and 110% of the known value.

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Field Recovery Test

- Done once for each unit tested
- Requires three sets of dual train tests using one Hg^0-spiked trap (first section) paired with a nonspiked trap.
- Based on the Hg mass to be collected on the first section of the trap, the spike must be within 50% to 150% of this mass.
- Sample the stack gas and analyze traps using the same sampling procedures and analytical methods as for the standard field samples (discussed later).

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Field Recovery Test

Determine the fraction of the spike recovered using the equation:

$$C_{rec} = \frac{m_s}{v_s} - \frac{m_u}{v_u}$$

Where:

C_{rec} = Concentration of spike compound measured

m_s = Total mass of Hg measured on Section 1 of the spiked trap

m_u = Total mass of Hg measured on Section 1 of the unspiked trap

v_s = Volume of gas sampled, spiked trap

v_u = Volume of gas sampled, unspiked trap

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Field Recovery Test

- The average of the percentage of the spike recovered must be between 85% and 115% to begin the RATA.
- It is acceptable to perform the field recovery test concurrent with the actual test run using a quad probe.
- It is also acceptable to use field recovery test data as part of the RATA if the difference between the spiked and unspiked samples after subtracting out the spike has an RD of ≤10%.

Sampling Procedures

- Pretest leak check – must not exceed 4% of the target sampling rate.
- Determine and record flue gas characteristics
  - Temperature stack and gas meter
  - Barometric pressure and meter pressure
  - Moisture (at least one EPA Method 4 must be done for each test run)
- Insert probe (with traps installed) into duct
- Record sample data (i.e., sorbent trap ID, date, time, operator)

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Sampling Procedures

- Record initial gas flowmeter reading, meter temperature, and sample system vacuum readings
- Set flow rate to obtain desired rate.
- At the end of the predetermined time period, record the final gas meter reading and final value of all other essential parameters.
- Conduct post test leak check with sorbent traps in place but plugged.
- Recover samples by removing traps from probe and sealing both ends. Wipe any deposited material from the outside of the traps and place in an appropriate sample storage container.

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Sample Handling

BE CAREFUL

- ASTM D6911-03 – Guide for Packaging and Shipping Environmental Samples for Laboratory Analysis
- ASTM D4840-99 – Standard Guide for Sampling Chain-of-Custody Procedures

Analytical Procedures

- Modified EPA Method 1631 Digestion Procedures followed by analysis using cold-vapor atomic fluorescence (CVAF)
- Thermal desorption – Ohio Lumex RA-915+ Hg analyzer with RP-324 attachment
- Thermal combustion – Leeman, Leco, Milestone

Analytical Procedures

- Daily multipoint calibration (minimum of three points)
  - All field recovery samples must be within the bounds of the calibration.
  - May require a low and a high calibration curve.
  - $r^2 \geq 99\%$.
  - Analyzer response must be ±10% of the reference value at each calibration point.
- Following calibration, an independent check standard is analyzed and must be ±10% of the expected value.
- For every 10 samples, a check standard is analyzed and again must be ±10% of the expected value.

Field Recovery Data

	Hg Conc. $\mu g/m^3$				Hg Conc. $\mu g/m^3$			
Sample	Spiked Sample	Spike Meas.	Spike Actual	Spike Recovery %	Unspiked Sample	Spiked Sample with Spike Subtracted	Avg.	RD %
1	5.24	2.32	2.37	98.04	2.92	2.87	2.90	0.79
2	4.42	1.06	1.80	58.98	3.36	2.62	2.99	12.31
3	6.01	0.29	2.56	11.33	3.05	3.45	3.25	6.16
4	5.02	1.39	2.54	54.47	3.64	2.48	3.06	19.00
5	6.25	2.91	2.59	112.47	3.34	3.66	3.50	4.61
6	6.75	3.00	2.95	101.73	3.75	3.80	3.77	0.68

🟨 Spiked field recovery samples used (90 ng).

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Status of Draft EPA Method 30B

- Not yet approved
- Has been fast tracked
- Assuming not glitches should be approved later this year.

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Comparison of Sorbent Traps to the OH Method

Test	Sorbent Traps, µg/m^3	OH Method, µg/m^3	RA, %
1	9.47	8.47	18.17
2	2.19	2.14	9.24
3	0.20	0.29	45.71
4	3.91	4.28	17.31

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Instrumental Reference Method

- Can provide real-time results.
- Would be less costly and time consuming

  than an OH method RATA.
- Can be done in conjunction with other continuous emission monitor (CEM) RATAs.
- Is highly desired by the utility industry.

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IRM Concerns

- Current specification is only a draft method (Draft EPA Method 30A).
- No instruments have passed all of the requirements.
- Traversing of some sort will be required; this is very difficult with CMMs; therefore, an IRM must be greatly simplified.

IRM Concerns

- Variations in stack mercury concentrations may be a concern.
- National Institute of Standards and Technology (NIST)-traceable calibration gases are not yet available.
- Most likely an IRM will not be available to meet the initial requirements for certification of CMMs by January 1, 2009 as required by CAMR.

EERC Recommendations

- Read Draft EPA Method 30B and fully understand the requirements before testing.

- If you have a wet stack, you will have to shroud your probe and provide extra heat. In addition you may have to reduce your flow rate (requiring more sample time) because of potential plugging.

- There are enough things that can go wrong that it is essential that the results are obtained quickly. Most likely will require analysis in the field.

- Although optional in the method, you must do blank samples.

EERC Recommendations

- Talk to your vendor about obtaining the carbon sorbent in bulk for doing check standards.
- Make sure you have good communications with the CMM operator when doing the RATA.
- Most likely, it will be necessary to have a high and low calibration curve.

Contact Information

Energy & Environmental Research Center
University of North Dakota
15 North 23rd Street, Stop 9018
Grand Forks, North Dakota 58202-9018

World Wide Web: **www.undeerc.org**
Fax No. (701) 777-5181

Dennis L. Laudal
(701) 777-5138
dlaudal@undeerc.org

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