EPA Update on the Development of Alternative Reference Methods for Mercury and Testing Equipment

Jeff Ryan
US EPA ORD
ryan.jeff@epa.gov
(919) 933-2998

2007 Measurement Technology Workshop
September 11, 2007

Topics

- Method 30A (IRM) approach
- IRM field testing
- Development of IRM equipment
- Method 30B (sorbent trap) approach
- Sorbent Trap RM laboratory and field testing

Overall Approach to New RMs …

- Performance-based
- Test program-specific (site) and matrix-specific performance verification
- Use of “Method of Standard Addition” for matrix-specific performance verification
  - Gaseous dynamic spiking for IRM
  - Gaseous static spiking for STRM

Method 30A - Mercury Instrumental Reference Method (IRM)

- Timely (real-time)
- Performance-based
  - Amenable to multiple and new technologies
  - Site/Test program-specific verification of data quality
  - FR Notice of Intent (62 FR 52098, 10/6/97)
- Consistent w/ SO_x & NO_x instrumental methods
- Key elements
  - Interference test (optional)
  - Calibration error/linearity (Hg^0)
  - System integrity/drift ($HgCl_2$)
  - System response time
  - Dynamic spiking ($HgCl_2$)

Dynamic Spiking

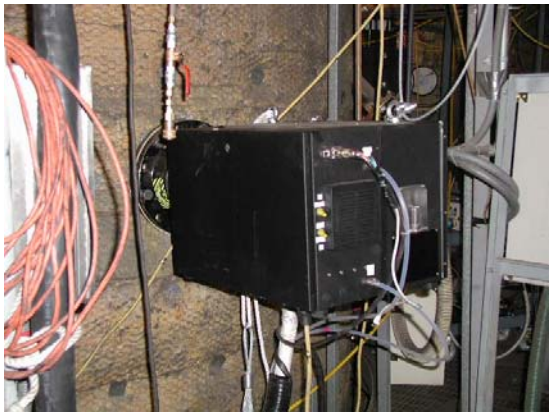
- Nothing new
- Included in revisions to Methods 6C and 7E (optional)
- Gaseous method of “standard addition”
- Introduce known quantities of $HgCl_2$ into probe sampling stack gas
- Spike flow minor (<20%) relative to sample flow
- Requires knowing sample flow rate or dilution ratio

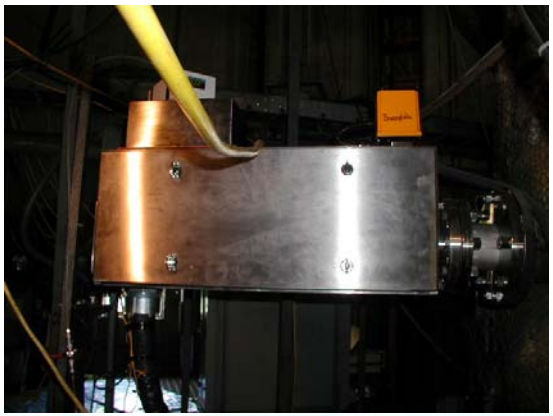
Lehigh Univ. Field Test

- Implement Conceptual (2/28/06) IRM on 4 available systems
- Use one common set of Hg gas standards for our calibrations
  - Vendors still calibrated/configured their systems the way they wanted
- Determine whether performance criteria pass/fail, but without corrective action – get what we get
- Did not perform Part 75 pre-certification tests, but IRM tests very similar

Available Systems

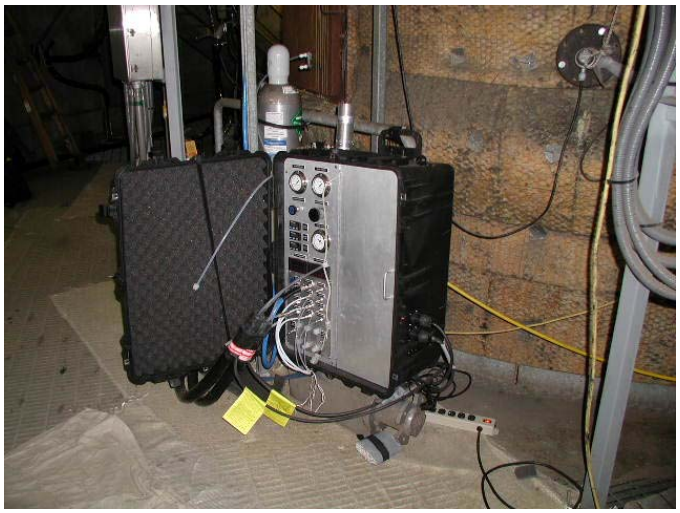
- 3 “stationary” Hg CEMS
  - GE/PSA
  - Tekran
  - Thermo



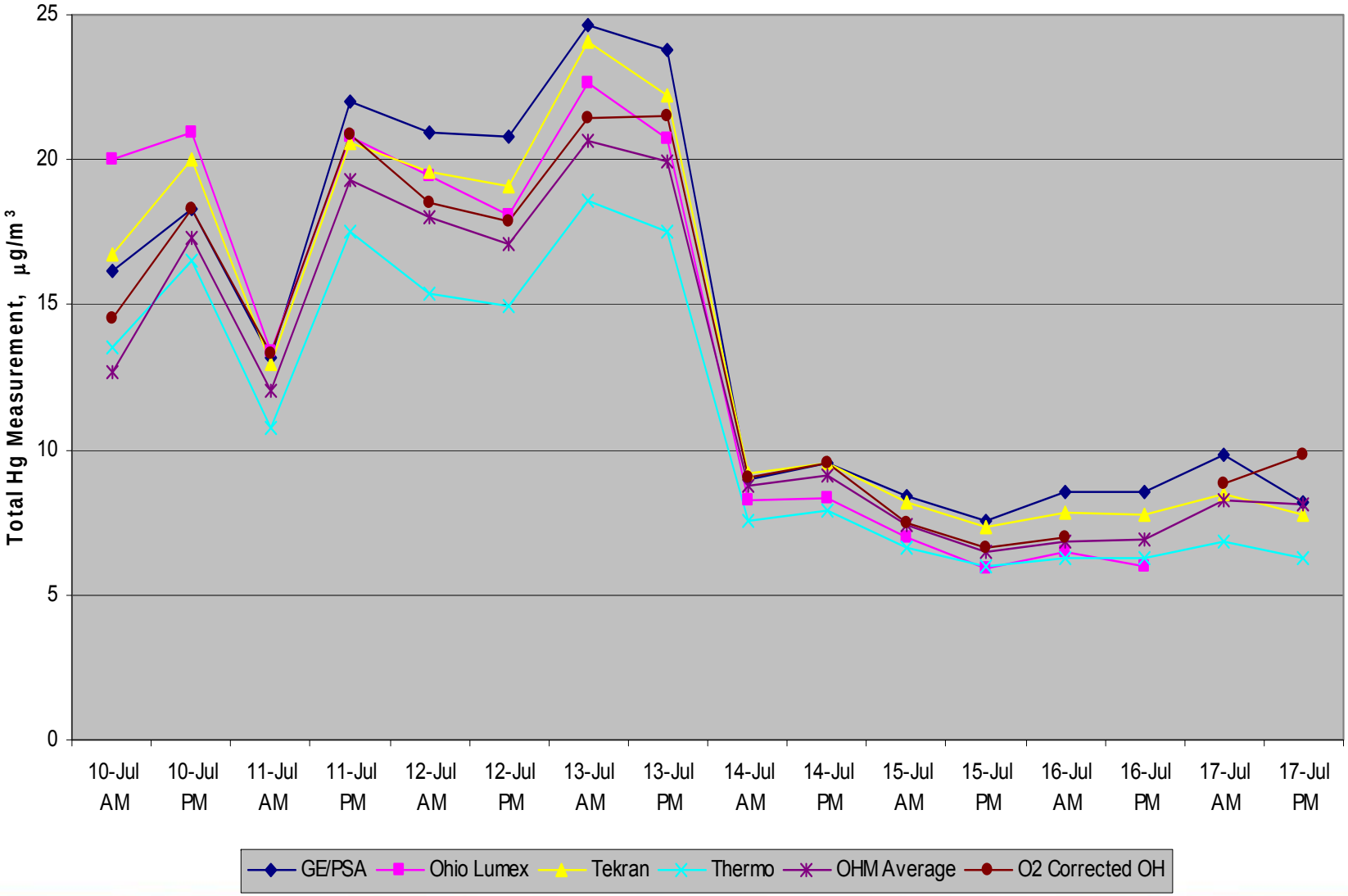


Available Systems

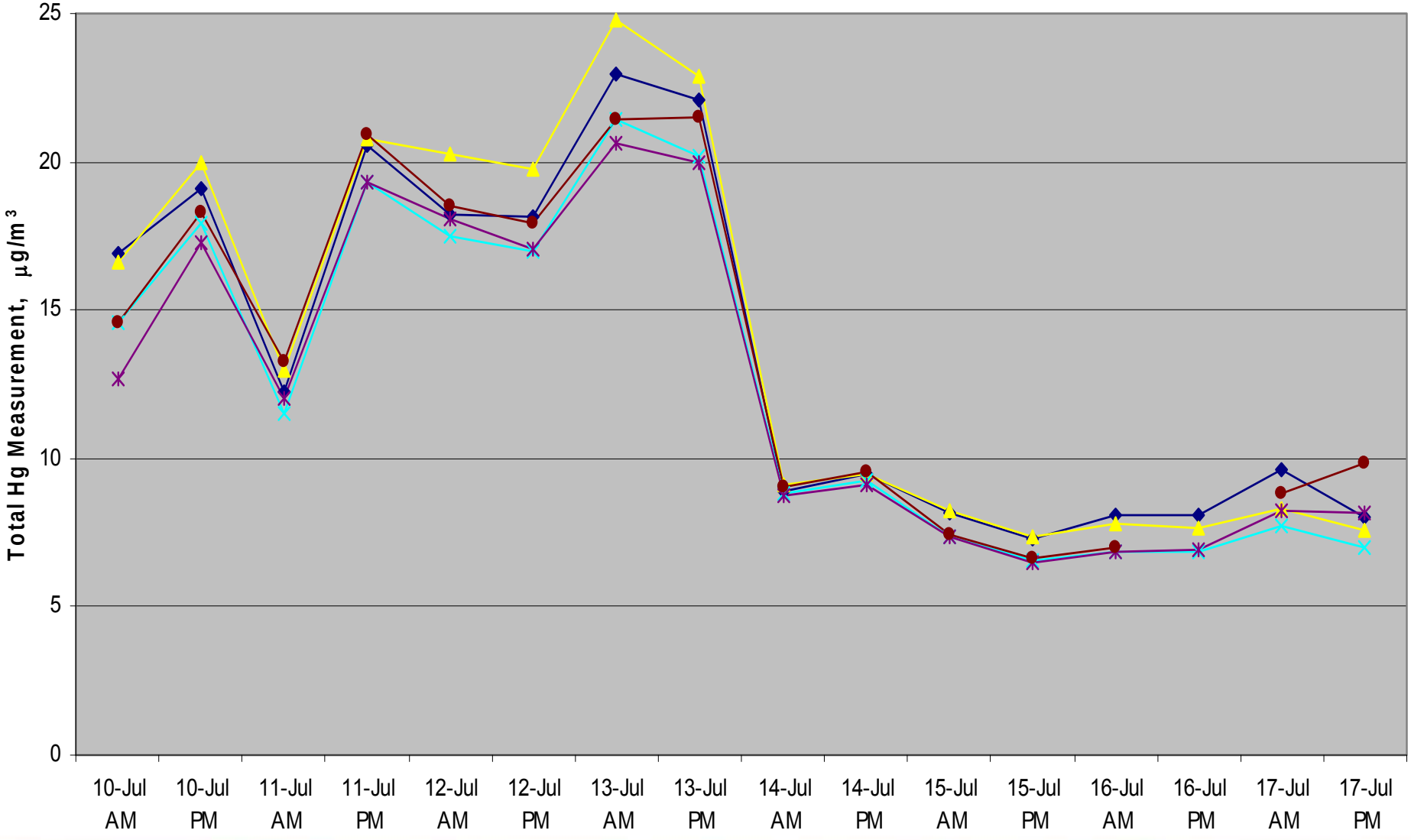
- 1 “portable” Hg CEMS
  - Ohio Lumex (fixed mount)



Total Hg Measurements, Normalized for Oxidized Cal Error



Total Hg Measurements, Normalized for Drift



Dynamic Spiking Data Sheet (Drift Corrected)

Facility name:	Armstrong	Date:	18-Jul-06 Time: 9:12
Unit(s) tested:	Unit 2	Test personnel:	JEB, NFR
Analyzer make & model:	[redacted]	Estimated native Hg concentration:	6.6 $\mu g/m^3$
Serial number:		Estimated unspiked sample flow rate:	48.25 slpm
Calibration span	20 $\mu g/m^3$	Estimated spike gas flow rate:	4.7 slpm

Preliminary Data

Target Level	C_{target} ($\mu g/m^3$)		C^*_{spike} ($\mu g/m^3$)		Selected C_{spike} Value ($\mu g/m^3$)	Expected[1] C_{ss} ($\mu g/m^3$)
	Upper	Lower	Upper	Lower		
High	13.2	11.9	75	61	69	12.7
Low	10.6	9.3	47	34	46	10.5

[1]Calculated from the selected spike gas concentration, using Equation 6

Spiking Data

Target Level	Q_{probe} (lpm)	Q_{spike} (lpm)	C_{ss} ($\mu g/m^3$)	C_{native} ($\mu g/m^3$)			% Spike Recovery
				Pre	Post	Avg.	
High	48.22	4.66	11.55	5.98	6.54	6.26	X 104.2% X
	48.08	4.66	11.45	6.54	6.76	6.65	X 94.3% X
	48.29	4.66	12.97	6.76	7.01	6.89	103.10%
	48.31	4.67	14.09	7.01	7.49	7.25	102.95%
	48.42	4.67	14.48	7.49	7.67	7.58	103.86%
	48.26	4.67	13.80	7.67	7.51	7.59	X 93.2% X
						Avg.	103.3%
						RSD	0.5%
Low	48.33	4.66	12.93	7.51	8.42	7.97	X 111.7% X
	48.34	4.65	12.59	8.42	8.20	8.31	X 96.6% X
	48.35	4.66	13.05	8.20	8.37	8.29	107.17%
	48.23	4.66	13.24	8.37	8.85	8.61	103.80%
	48.37	4.66	14.04	8.85	9.46	9.16	109.41%
						Avg.	106.8%
						RSD	2.6%

RATA of [redacted] Normalized to Integrity/Drift Checks

Concentrations corrected to 20°C, wet basis

Test #	Date	Times	[redacted] µg/wsm³	OH µg/wsm³	Difference µg/wsm³	Status
3	10-Jul	09:33-11:15	16.62	12.66	3.96	Discarded
4	10-Jul	14:00-15:38	19.96	17.29	2.67	Excluded
5	11-Jul	09:00-10:35	12.99	12.02	0.97	Included
6	11-Jul	14:00-15:30	20.78	19.28	1.50	Included
7	12-Jul	09:05-10:45	20.24	18.04	2.20	Included
8	12-Jul	14:00-15:37	19.72	17.08	2.64	Included
9	13-Jul	09:13-10:47	24.77	20.65	4.12	Excluded
10	13-Jul	13:55-15:30	22.85	19.98	2.88	Excluded
11	14-Jul	09:17-11:02	9.12	8.73	0.39	Included
12	14-Jul	14:08-15:45	9.49	9.11	0.38	Included
13	15-Jul	09:30-11:05	8.22	7.38	0.84	Included
14	15-Jul	14:00-15:35	7.35	6.49	0.87	Included
15	16-Jul	09:40-11:20	7.79	6.83	0.96	Included
16	16-Jul	13:10-14:48	7.67	6.90	0.77	Included
17	17-Jul	09:15-10:52	8.30	8.25	0.05	Included
18	17-Jul	14:08-15:46	7.57	8.14	-0.57	Included
Arithmetic Mean of all runs			**13.97**	**12.43**	**1.54**	µg/wsm³

			Arithmetic Means		
Total valid runs	**15**	**[redacted]**	**OH**	**Difference**	
		13.79	**12.41**	**1.38**	**µg/wsm³**
Bias Test:	**Passed**	**Confidence Coeff.**		**0.70**	**µg/wsm³**
Factor:	**0.90**	**Relative Accuracy**		**16.76%**	

			Arithmetic Means		
Runs included in RA calculation	**12**	**[redacted]**	**OH**	**Difference**	
		11.61	**10.69**	**0.92**	**µg/wsm³**
Bias Test:	**Passed**	**Confidence Coeff.**		**0.56**	**µg/wsm³**
Factor:	**0.92**	**Relative Accuracy**		**13.82%**	

			Arithmetic Means		
Runs with Hg below 10 µg/wsm³	**8**	**[redacted]**	**OH**	**Difference**	
		8.19	**7.73**	**0.46**	**µg/wsm³**
Bias Test:	**Passed**	**Confidence Coeff.**		**0.44**	**µg/wsm³**
Factor:	**0.94**	**Relative Accuracy**		**11.63%**	

			Arithmetic Means		
Runs with Hg above 10 µg/wsm³	**7**	**[redacted]**	**OH**	**Difference**	
		20.19	**17.76**	**2.43**	**µg/wsm³**
Bias Test:	**Passed**	**Confidence Coeff.**		**0.94**	**µg/wsm³**
Factor:	**0.88**	**Relative Accuracy**		**18.95%**	

Study Conclusions …

- Not all systems passed all IRM performance criteria, but all criteria capable of being achieved
- For the most part, minimal Hg CEM measurement biases relative to OHs (<±10%)
  - Consistent with dynamic spiking recoveries
  - Lack of bias is intended outcome of dynamic spiking procedure – **dynamic spiking served its purpose!**
- Drift correction of data improved IRM data quality
  - Consistent with existing methods (7E, 6C)
- Test results supportive of proposed Method 30A performance criteria

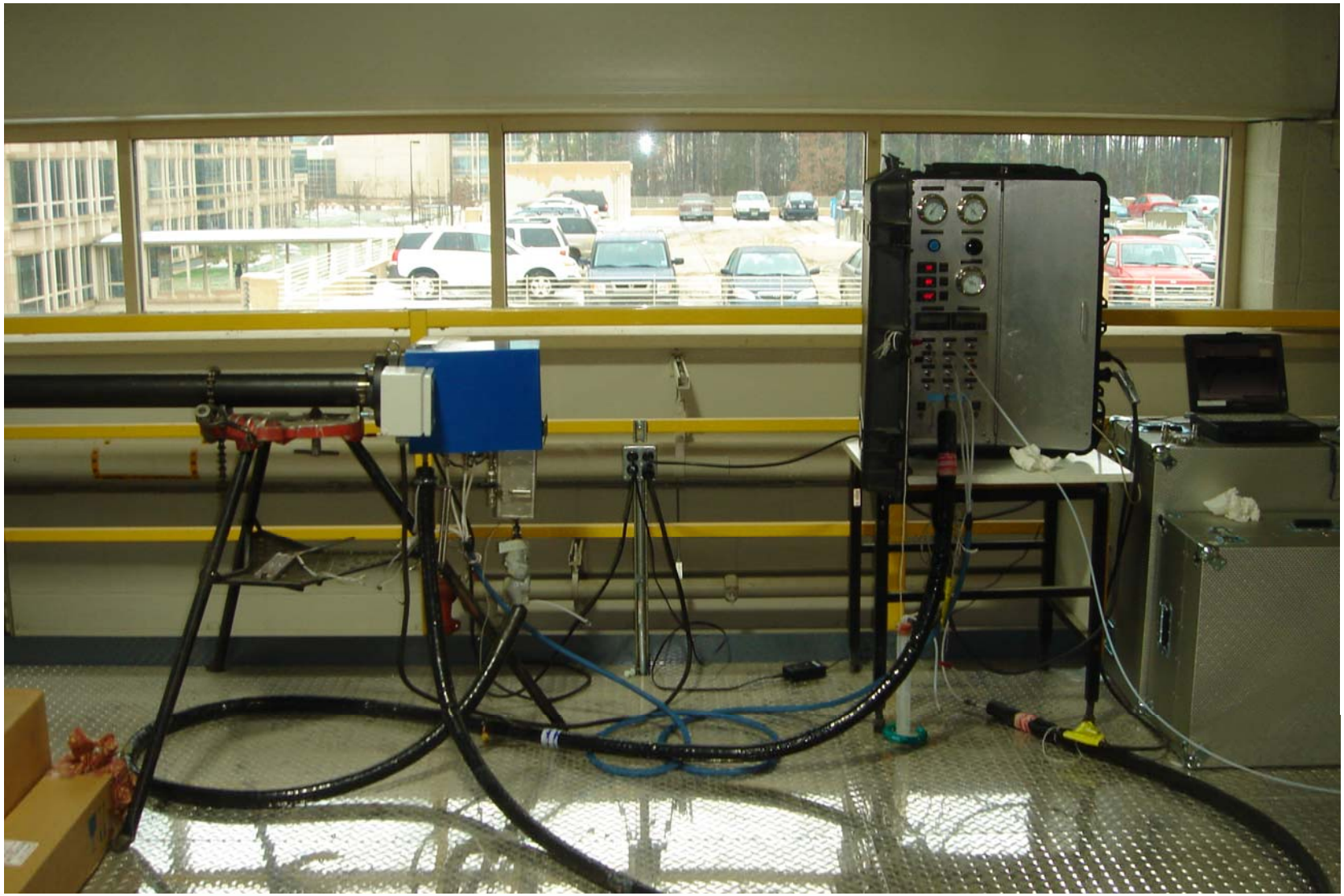
Lehigh Tests - Practical Issues …

- Spent significant amount of time trying to perform procedures on analyzers that aren't optimized for doing IRM
  - Not conducive to dynamic spiking (probe, flow, spiking, etc)
- Test Equipment:
  - Not capable of traversing
  - Required considerable set-up time
  - Certainly not portable!
- IRM-specific test equipment is needed to make Method 30A viable

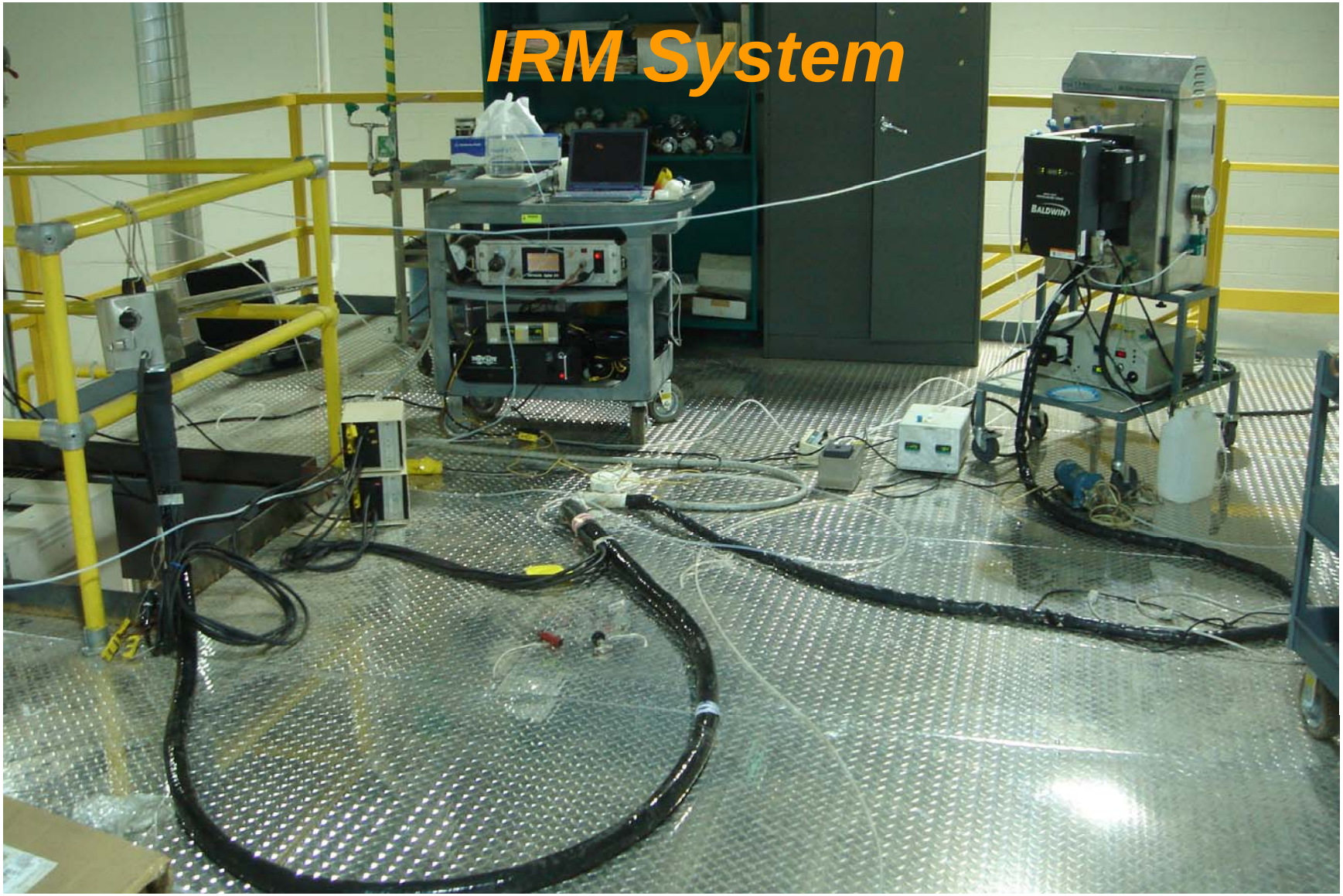
Current Focus

- Develop IRM-Specific Equipment
  - Simple
  - Portable
  - Practical
  - Traversable Probes
  - Less expensive
  - Working with Multiple Vendors
- Perform Stratification Testing
- Perform IRM testing at multiple test sites
- **Objective: Fully perform (successfully) IRM in <2 days**

Lumex/M&C IRM System



EPA/APEX/PSA/THERMO IRM System



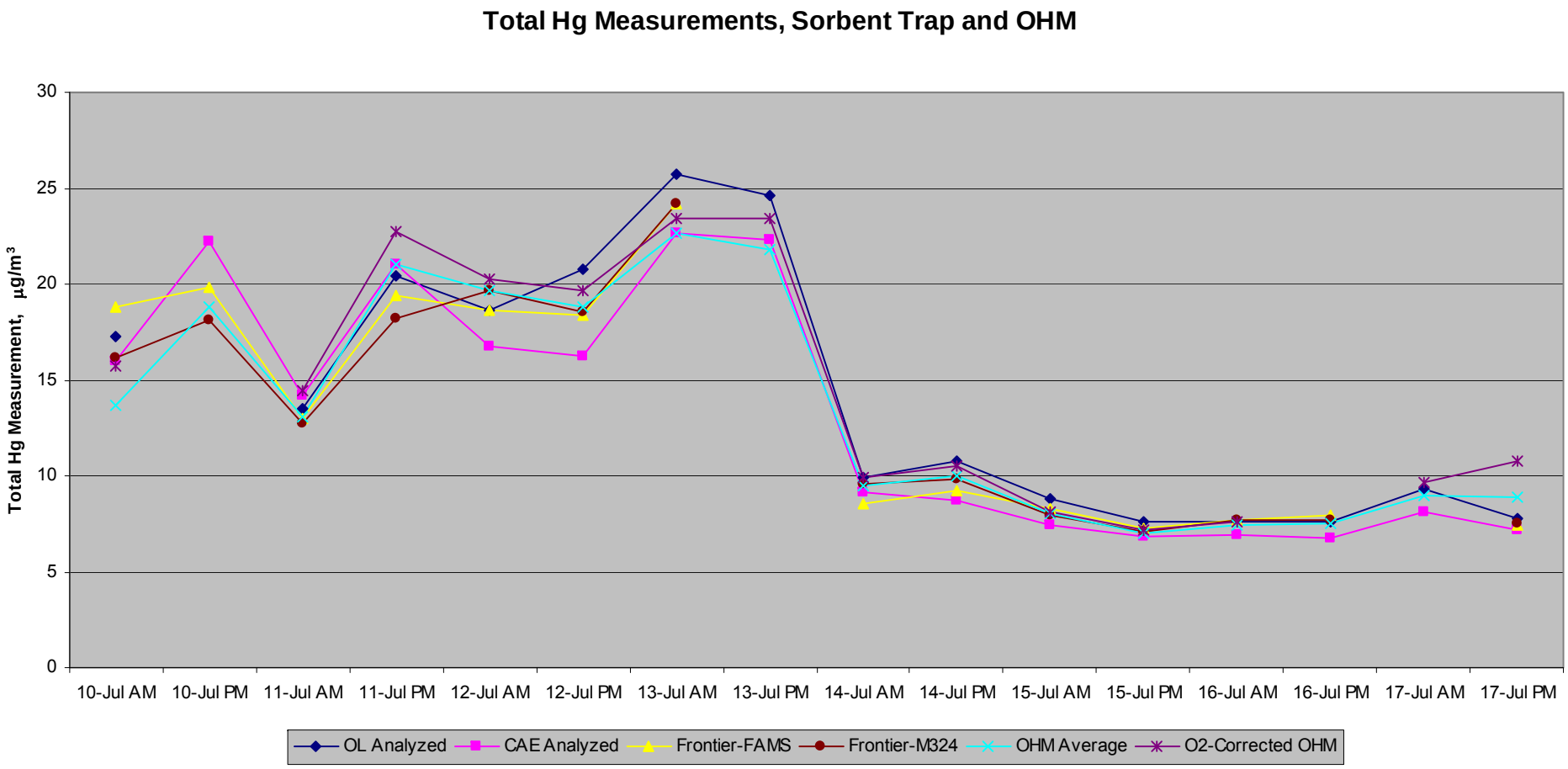
Field Testing Status …

- Well … We're getting there …
- Tracer gas approach works well
- Successful dynamic spiking with new probes
- Stratification testing still a challenge due to equipment limitations
- Still struggling with equipment issues – All minor yet annoying
  - Drift
  - Filter
  - Orifice dilution ratio
- Still early in the field testing stage
- We're relying on vendors to develop necessary IRM equipment for us to test!

Development of Hg Method 30B Sorbent Trap Reference Method

- Field data with Appendix K RATA tests very supportive
- Rapid advances of “Thermal” analysis techniques
- Increased understanding of “Wet” analysis techniques
- Reliable Hg^0 spiking techniques

Sorbent Traps vs. OHM



Method 30B - Sorbent Trap Reference Method for Mercury

- Performance-based
  - Amenable to new sorbents, equipment, and analytical technologies
    - Lab verification of sorbent performance and analysis
    - Site/Test program-specific verification of data quality
- Capability for timely results
- Minimization of trap spiking, especially in the field
- Description
  - Known volume of stack gas is sampled through paired, in-stack 2-section sorbent traps (e.g., iodated carbon)
  - Analysis by any suitable system that can meet performance criteria (e.g., leaching, digestion, thermal desorption/direct combustion coupled with UV AF, UV AA, XRF)

Method 30B - Sorbent Trap Reference Method for Mercury, cont

- Key QA Elements
  - Laboratory
    - Matrix interference test (for leaching analysis)
    - Minimum sample mass determination
    - Analytical bias test
  - Field (for each test)
    - Field recovery test (assess bias by static spiking)
    - Paired train agreement (assess precision)
    - Trap second section breakthrough

Approach

- Overall focus is how to determine just how much sample must be collected that can be measured reliably
- Largely about characterizing your analytical capabilities
  - How low can you go?
  - Can you measure accurately at that level?
  - Are there any measurement interferences?
  - How does that compare to your background levels?
- Tests and criteria for characterizing measurement performance

Analytical Tests

- Analytical Matrix Interference Test
  - For “wet” analysis technique only
  - Serial dilution test to determine minimum dilution ratio (if any)
  - One time

Analytical Tests

- Minimum Sample Mass Determination
  - Purpose is to identify the lowest Hg mass (or concentration) that you can measure reliably that can be used to target the mass of Hg you need for sampling
    - Falls within your calibration curve (≥2x lowest point)
    - Factors in liquid sample volumes, sample dilutions, etc.
    - Considers your detection limits, trap background levels
    - Serves as lower bound for Analytical Bias Test
    - Used to estimate target sample collection volumes and run times

Analytical Tests

- Analytical Bias Test
  - Purpose is to confirm that the minimum sample mass you've identified can be measured accurately by your intended analytical technique
  - Confirm acceptable recovery of Hg^0 *and* $HgCl_2$
  - Done at two levels that define the lower and upper bound that actual samples must fall within
  - One time
  - Can expand when needed

Field Testing

- Field Recovery Test
  - Purpose is a test-specific assessment of overall measurement performance (bias)
  - Based on Field Recovery Test in Method 18
  - Confirm acceptable recovery of Hg^0 from 3 pairs of spiked/unspiked trains
  - Analogous to dynamic spiking-the static method of standard addition
  - Potential for Field Recovery Test runs to qualify as RATA runs too
  - Does not have to be performed before collecting field samples, but must be successfully performed for each RATA or field test

Field Testing

- Test Runs
  - Use target sample mass, estimated stack concentration and nominal sample rate to estimate target sample volume and run time
  - Minimum run time of 30 min
  - For RATA testing, run time relief for stack concentrations <0.5 µg/m^3
  - Paired train agreement:
    - ≤10% RD for Hg concentrations >1 µg/m^3
    - ≤20% RD for Hg concentrations <1 µg/m^3 or ≤ 0.2 µg/m^3 absolute difference

Sample Analysis

- Section 1 analyses must be within valid calibrated range
- Sample analyses must be bracketed by valid Continuing Calibration Verification checks
- Section 1 analyses must also be within bounds of Analytical Bias Test
- Sorbent trap Section 2 breakthrough/background
  - ≤10% of Section 1 Hg mass for Hg concentrations >1 $\mu g/m^3$
  - ≤20% of Section 1 Hg mass for Hg concentrations >1 $\mu g/m^3$
- Additional guidance for estimating Hg levels below lowest point in calibration
  - Section 2
  - Section 1 where stack Hg <0.5 $\mu g/m^3$

Examples and Field Data

- EPA/ORD Thermal Analysis
  - MDL ~1 ng
  - Lowest point in cal curve = 10 ng
  - Minimum sample mass = 20 ng
  - Recoveries within 90-110% for Hg^0 and $HgCl_2$
  - Nominal sample flow rates: 400, 800 cc/min
  - Estimated run time for 0.5 µg/m^3 stack Hg @ 400 cc/min sample rate = 100 min
  - Estimated run time for 0.5 µg/m^3 stack Hg @ 800 cc/min sample rate = 50 min

Field Recovery Tests

- Quad probes, paired spiked/unspiked trains at 400, 800cc/min, 1 hour runs
- Recoveries: avg = 104%, range 97-114%, n = 8
- Average stack Hg concentration = 0.79 µg/m^3
  - Average @ 400 cc/min = 0.78 µg/m^3
  - Average @ 800 cc/min = 0.75 µg/m^3
  - Average unspiked = 0.76 µg/m^3
  - Average spike subtracted = 0.81 µg/m^3
- RDs: All RDs <10% and < 0.2 µg/m^3 absolute dif.
- Breakthroughs <2%
- Analyses were **not** performed in the field!

What Should You Know?

- Focus on RM performance criteria
  - Most is consistent with existing RMs
  - Method 30B is largely analytically-oriented
- Guidance and training will come!
  - CAMD training
  - Web sites for guidance documents and lessons learned
  - Data reports

Questions …

- IRM?
- IRM Equipment?
- Sorbent Trap RM?
- Other?