EPA METHOD 324

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Development Team

- EPRI
- EPRI Solutions
- Frontier Geosciences
- ADA-ES
- Apex Instruments
- SparkWorks

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Key Applications for M-324

- Low-cost mercury emission monitor
  - RATA tests
  - CEM performance evaluation during startup
  - Backup system for CEMs
  - More appropriate for small sized units

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Other Method 324 Facts

- We expect theupdated method will be detailed and inclusive so that high quality laboratories can apply the method – it will not be a single laboratory method
- CVAFS verses CVAA – currently only validated using CVAFS

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Fluegas Mercury Sorbent Method and Measurements Supported Since 1991 by:

- EPRI (PISCES Project + Others)
- US-DOE FETC
- USEPA
- European Union – MOE Project
- State Agencies
- Electric Utilities
- Industry – Alcoa, Noranda, Consol + others
- Research Institutions – EERC, MSE Technologies.

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Brief Milestones for Sorbent Total Mercury (STM) by CVAFS in Coal Fluegas

- First used as early as 1991 for EPRI (Bloom, 1993). Provided good coal utility mass balances and helped to show that EPA Method-29 was under reporting total Hg (See for example EPRI (1996) publication TR-107695).
- MESA Method used for total Hg and speciated Hg in coal fluegas for the EPRI PISCES program (Prestbo and Bloom, 1995, Chu and Porcella, 1995) and performance tested for total Hg in EPRI-EPA Method 301 study (Nott et. al, 1994, Nott et al, 1995).
- MESA Method evaluated for speciated Hg in coal fluegas (Laudal et. al, 1996 and Laudal et. al, 1997). Total Hg results are within acceptable limits for sensitivity, accuracy and precision. (Laudal et. al, 1996, Prestbo and Tokos, 1997).

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Sorbent Total Mercury Method Description

- Using standard fluegas sampling equipment and clean-handling techniques, a known volume of fluegas is drawn through a series of sorbent traps. The traps are kept above the water condensation by either placing in a heated probe or directly into the fluegas stream.

- The quantification of total Hg in the fluegas is dependent on a well-characterized, low-blank carbon-based sorbent trap, with historical applications of either KCl/soda lime (MESA Method) or KCl/quartz (FAMS Method) and quartz fiber filters to also separate and determine the speciation as needed.

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Select Published Articles and Proceedings

- Bloom, N.S. (1993) "Mercury Speciation in Flue Gases: Overcoming the Analytical Difficulties." *Managing Hazardous Air Pollutants: State of the Art.* (W. Chow and K. Connor, Eds.), EPRI TR-10189, Lewis Publishers, Boca Raton, USA p. 148.
- Prestbo E.M. and Bloom N.S. 1995. "Mercury Speciation Adsorption (MESA) Method for Combustion Flue Gas: Methodology, Artifacts, Intercomparison and Atmospheric Implications," *Wat. Air Soil Pollut.,* **80:**145.
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- Prestbo E.M. and Bloom N.S., *Mercury Speciation Adsorption (MESA) Method Intercomparison Results in Combustion Flue Gas*, Proceedings Coal-Energy and the Environment, 11th Annual Pittsburgh Coal Conference, Vol. 1, pp. 557-562, U. of Pittsburgh, PA, September 12-16, 1994.
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- Laudal D., Nott B., Brown T. and Roberson R., (1997) "Mercury Speciation Methods for Utility Flue Gas," *Fresenius J. Anal. Chem.*, 358:397.
- Laudal D.L., Heidt M.K., Brown T.D., Nott B.R. and Prestbo E.M. (1996) *Mercury Speciation: A Comparison Between EPA Method 29 and Other Sampling Methods,* proceedings of the Air & Waste Mngmt Assoc. Annual Meeting, #96-WA64A.04.

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Select Reports and Standard Operating Procedures

- DOE, National Energy Technology Laboratory (2001) "Comparison of Sampling Methods to Determine Total and Speciated Mercury in Flue Gas," CRADA 00-F038 Final Report DOE/NETL-2001/1147, Pittsburgh, USA.
- USEPA, EERC, Frontier Geosciences (2001) "A Validation Study at the EERC of the Fluegas Mercury Sorbent Speciation (FMSS) Method," Draft Final Report (Contact James Kilgroe at Kilgroe.Jim@epa.gov or Eric Prestbo at ericp@frontiergeosciences.com).
- Electric Power Research Institute, (1994) Electric Utility Trace Substances Synthesis Report. Volume 1 to 4: See specifically Appendix O, Mercury in the Environment in Volume 3. EPRI TR-104614-V1 to V4.
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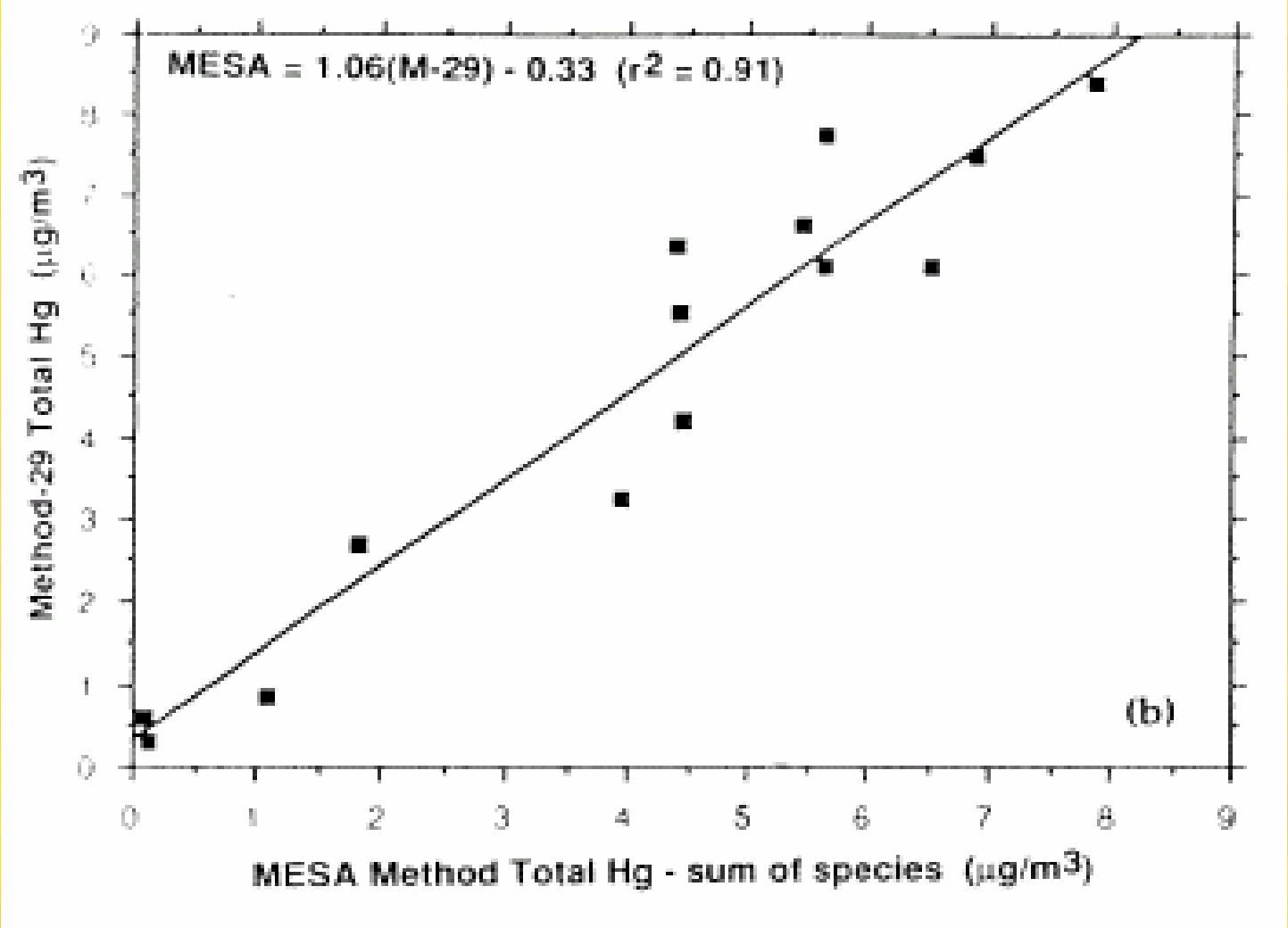
Intercomparison of Total Mercury at Comanche Power Plant (~1994)

Prestbo E.M. and Bloom N.S. 1995. "Mercury Speciation Adsorption (MESA) Method for Combustion Flue Gas: Methodology, Artifacts, Intercomparison and Atmospheric Implications," *Wat. Air Soil Pollut.*, **80:**145.



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EPA and EPRI Fluegas Total Mercury Method 301 Validation

Nott B.R., Huyck K.A., DeWees W., Prestbo E.M., Olmez I, and Tawney C.W. (1994). "Evaluation and Comparison of Methods for Mercury Measurement in Utility Stack Gas," *J. Air & Waste Mngmt. Assoc.*, #94-MP6.02.
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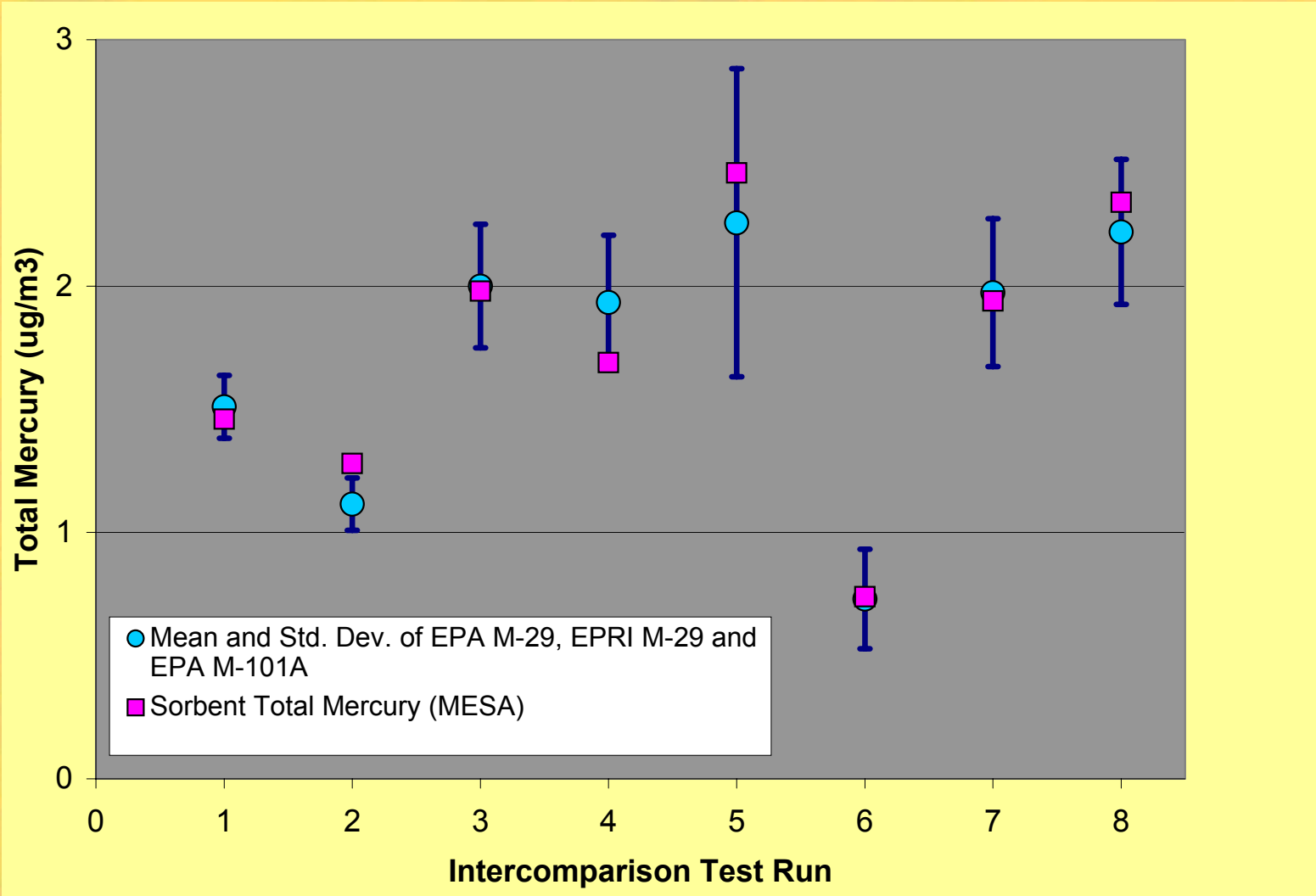

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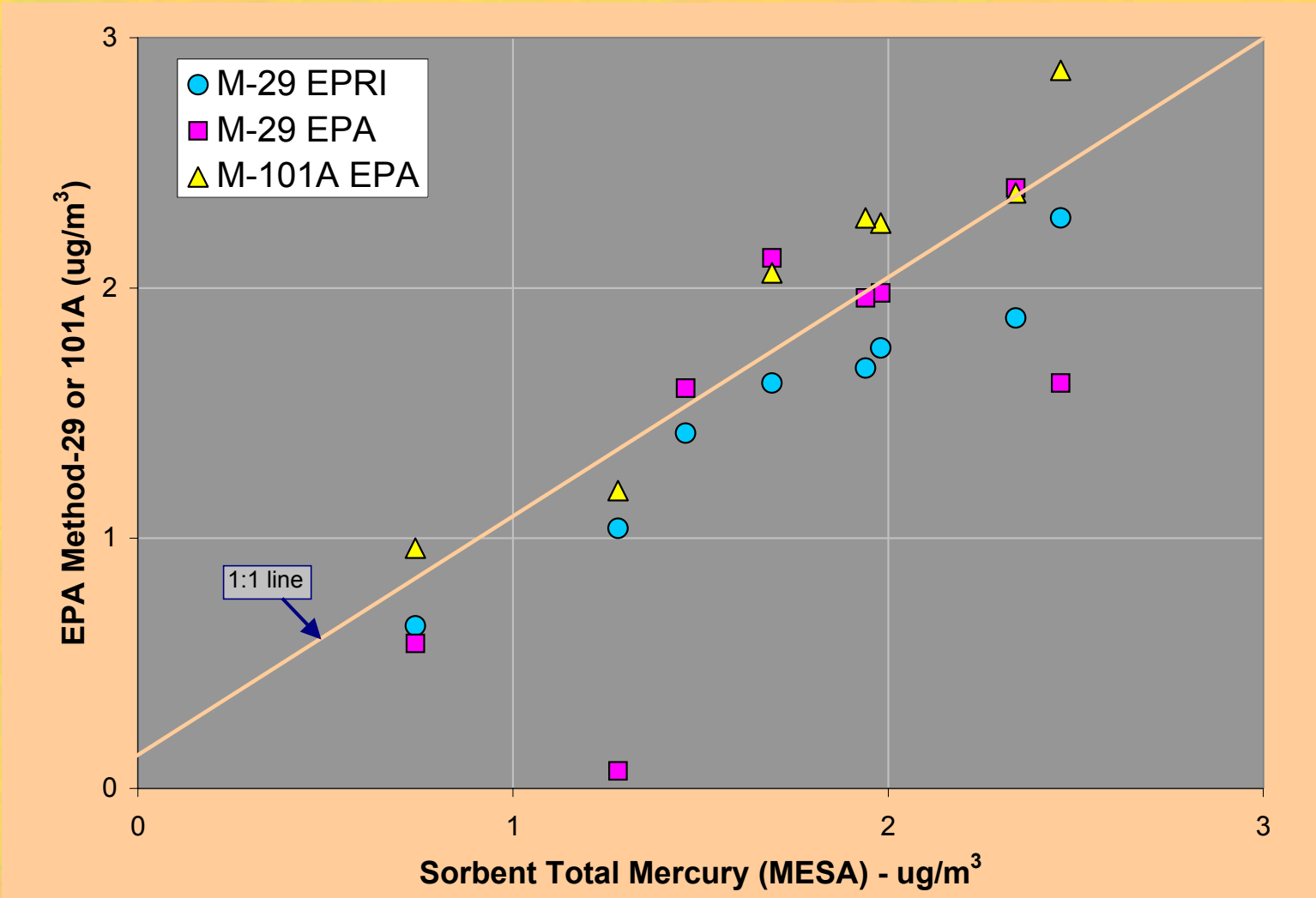

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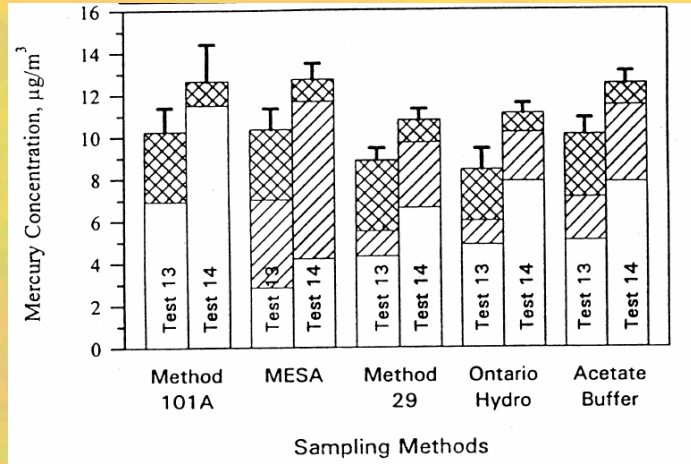
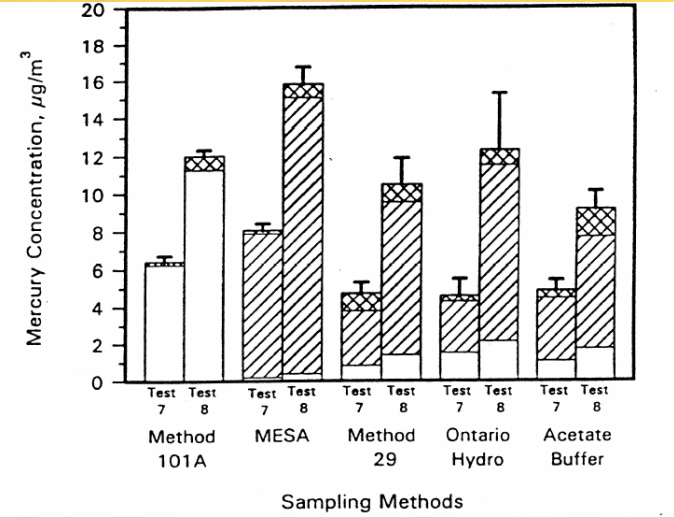
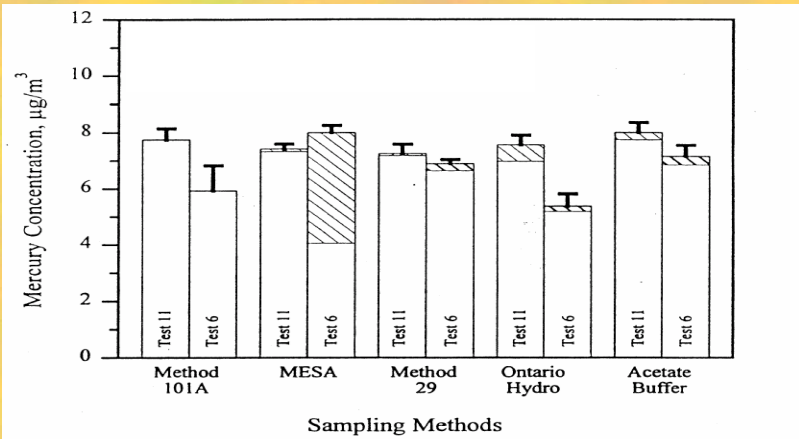
EERC 1996 Method Evaluation

1) Laudal D., Nott B., Brown T. and Roberson R., (1997) "Mercury Speciation Methods for Utility Flue Gas," *Fresenius J. Anal. Chem.*, 358:397.
2) Laudal D.L., Heidt M.K., Brown T.D., Nott B.R. and Prestbo E.M. (1996) *Mercury Speciation: A Comparison Between EPA Method 29 and Other Sampling Methods,* proceedings of the Air & Waste Mngmt Assoc. Annual Meeting, #96-WA64A.04.

- Compare Total Mercury Values – the Sorbent Total Mercury is labeled as MESA in these figures







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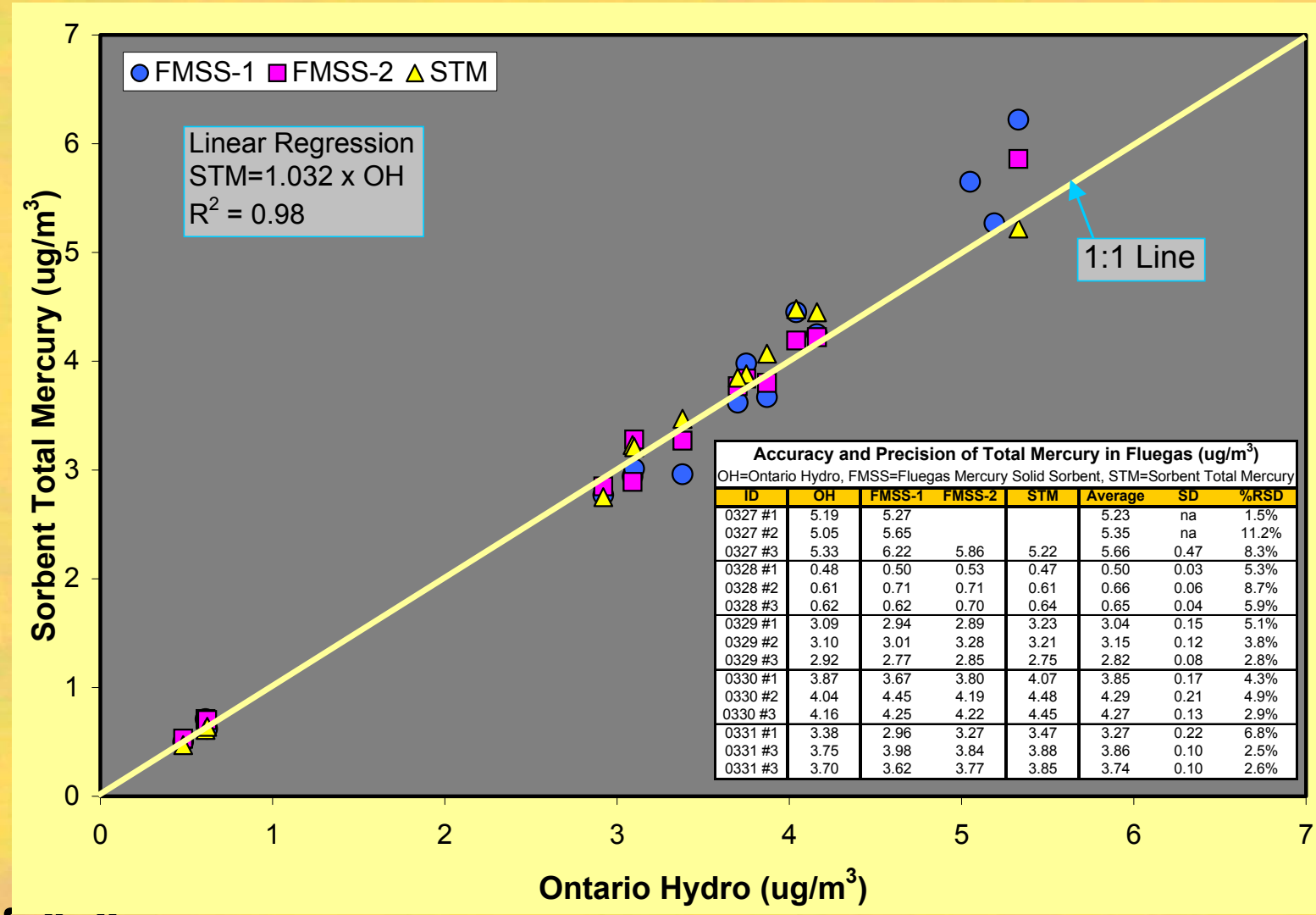
DOE, National Energy Technology Laboratory (2001)

"Comparison of Sampling Methods to Determine Total and Speciated Mercury in Flue Gas," CRADA 00-F038 Final Report DOE/NETL-2001/1147, Pittsburgh, USA.

OH=Ontario Hydro, FMSS=Fluegas Mercury Solid Sorbent, STM=Sorbent Total Mercury



Accuracy and Precision of Total Mercury in Fluegas (ug/m^3)

OH=Ontario Hydro, FMSS=Fluegas Mercury Solid Sorbent, STM=Sorbent Total Mercury

ID	OH	FMSS-1	FMSS-2	STM	Average	SD	%RSD
0327 #1	5.19	5.27			5.23	na	1.5%
0327 #2	5.05	5.65			5.35	na	11.2%
0327 #3	5.33	6.22	5.86	5.22	5.66	0.47	8.3%
0328 #1	0.48	0.50	0.53	0.47	0.50	0.03	5.3%
0328 #2	0.61	0.71	0.71	0.61	0.66	0.06	8.7%
0328 #3	0.62	0.62	0.70	0.64	0.65	0.04	5.9%
0329 #1	3.09	2.94	2.89	3.23	3.04	0.15	5.1%
0329 #2	3.10	3.01	3.28	3.21	3.15	0.12	3.8%
0329 #3	2.92	2.77	2.85	2.75	2.82	0.08	2.8%
0330 #1	3.87	3.67	3.80	4.07	3.85	0.17	4.3%
0330 #2	4.04	4.45	4.19	4.48	4.29	0.21	4.9%
0330 #3	4.16	4.25	4.22	4.45	4.27	0.13	2.9%
0331 #1	3.38	2.96	3.27	3.47	3.27	0.22	6.8%
0331 #3	3.75	3.98	3.84	3.88	3.86	0.10	2.5%
0331 #3	3.70	3.62	3.77	3.85	3.74	0.10	2.6%

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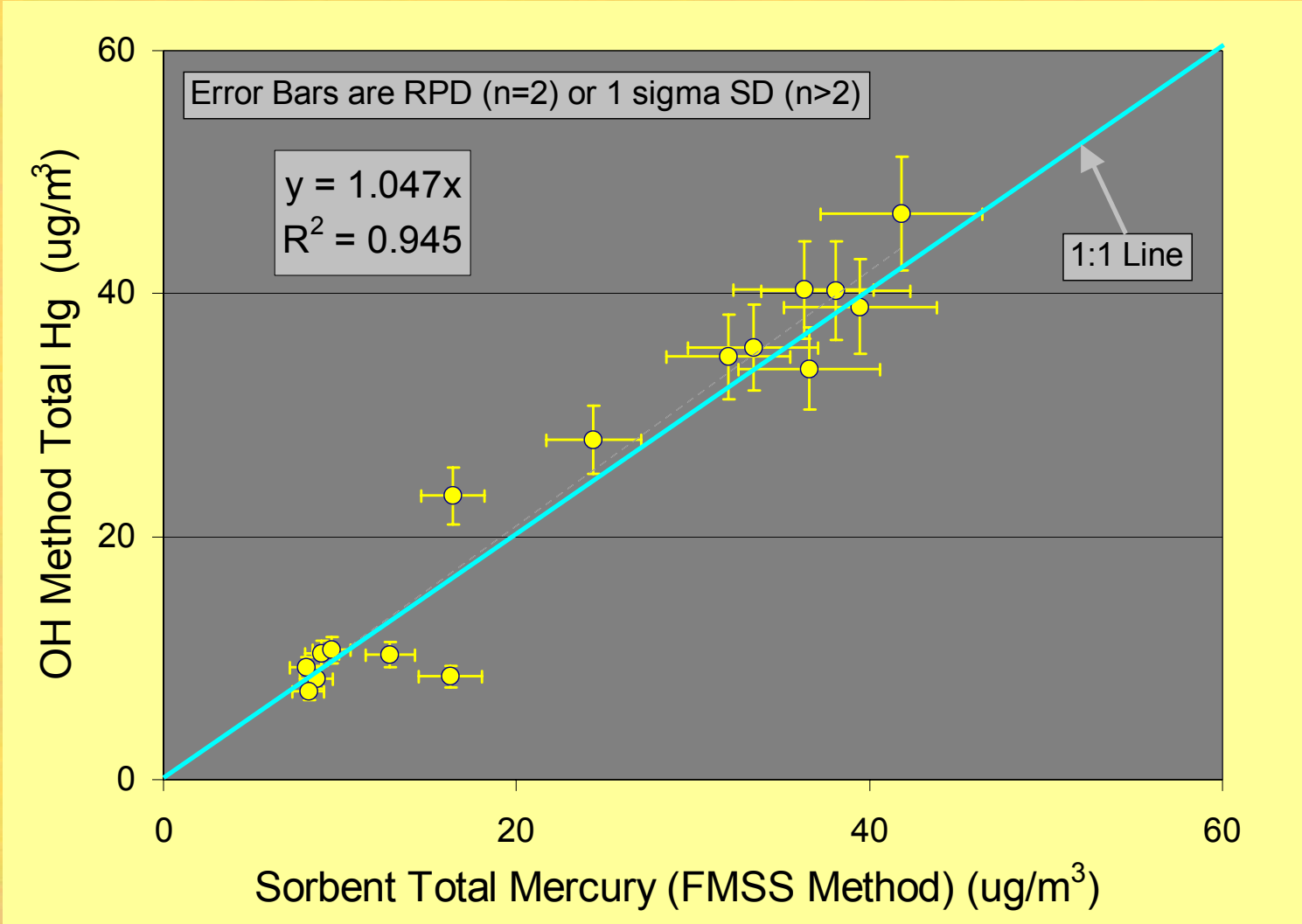
EERC/EPA PBMS Intercomparison (2001)

USEPA, EERC, Frontier Geosciences (2001) "A Validation Study at the EERC of the Fluegas Mercury Sorbent Speciation (FMSS) Method," Draft Final Report (Contact James Kilgroe at Kilgroe.Jim@epa.gov or Eric Prestbo at ericp@frontiergeosciences.com).



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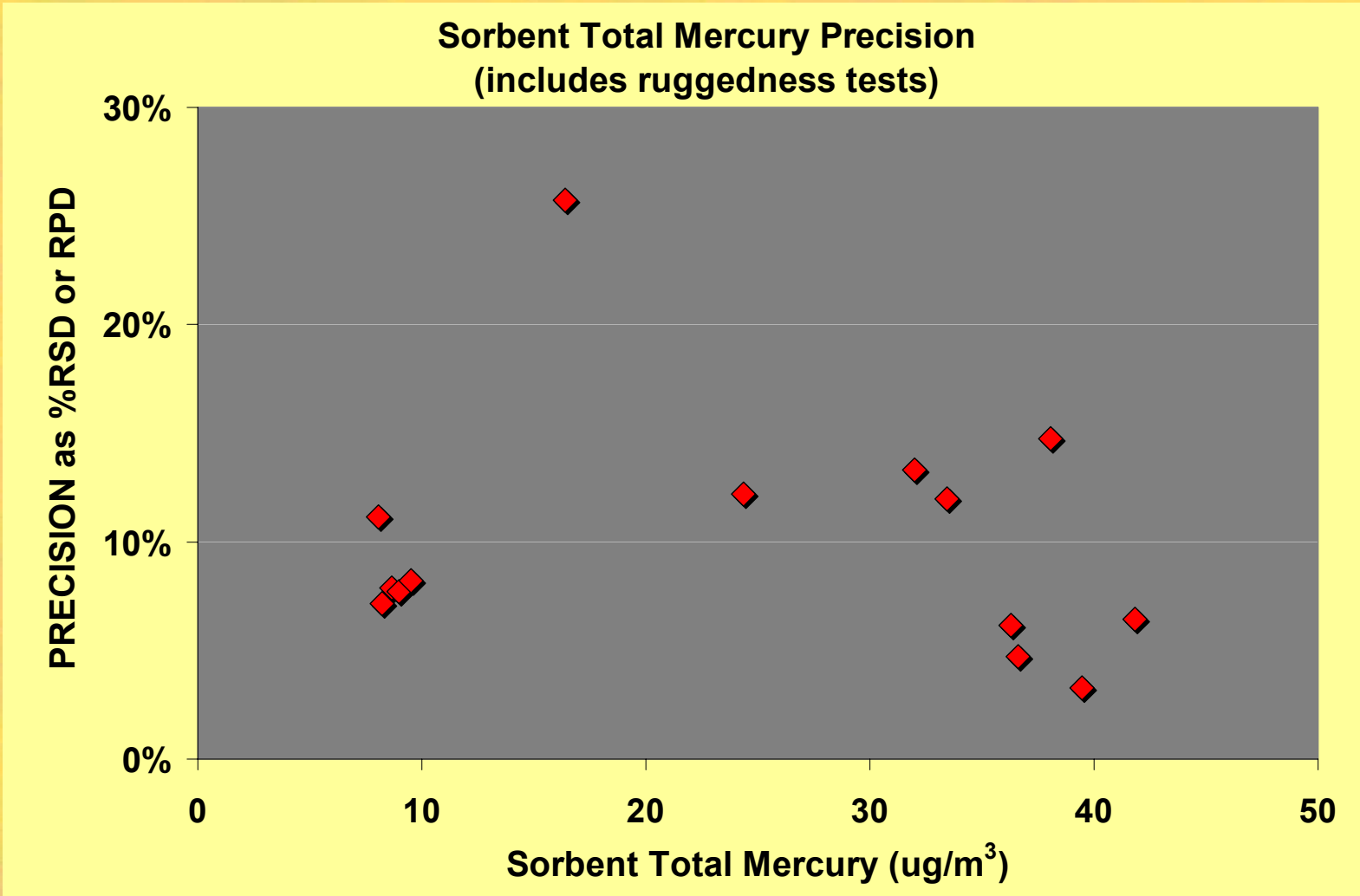

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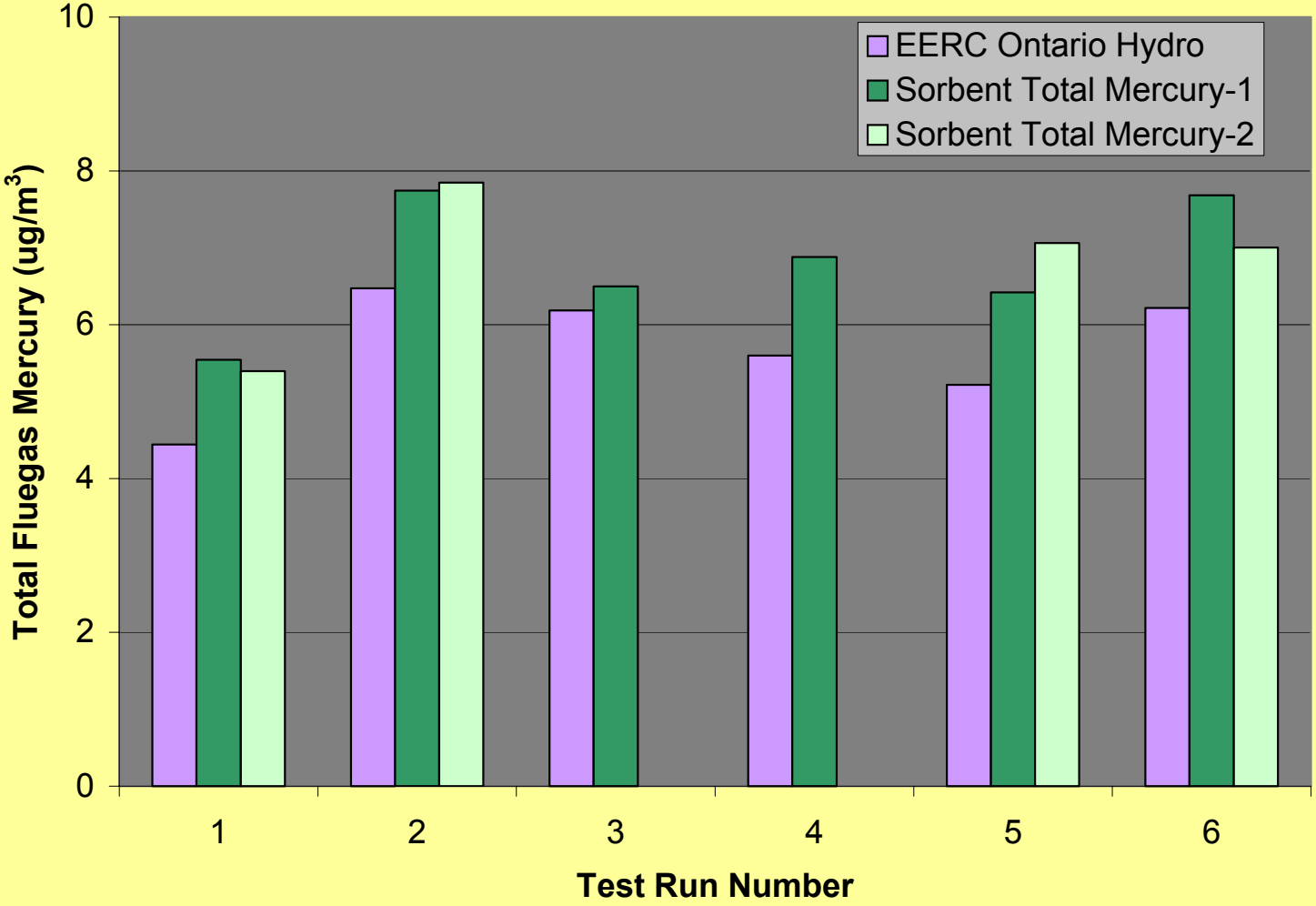
Intercomparison of Total Hg by Sorbent Total Mercury and Ontario Hydro Methods in Coal Utility Fluegas, Fall 2002

Note the precision of the STM duplicates



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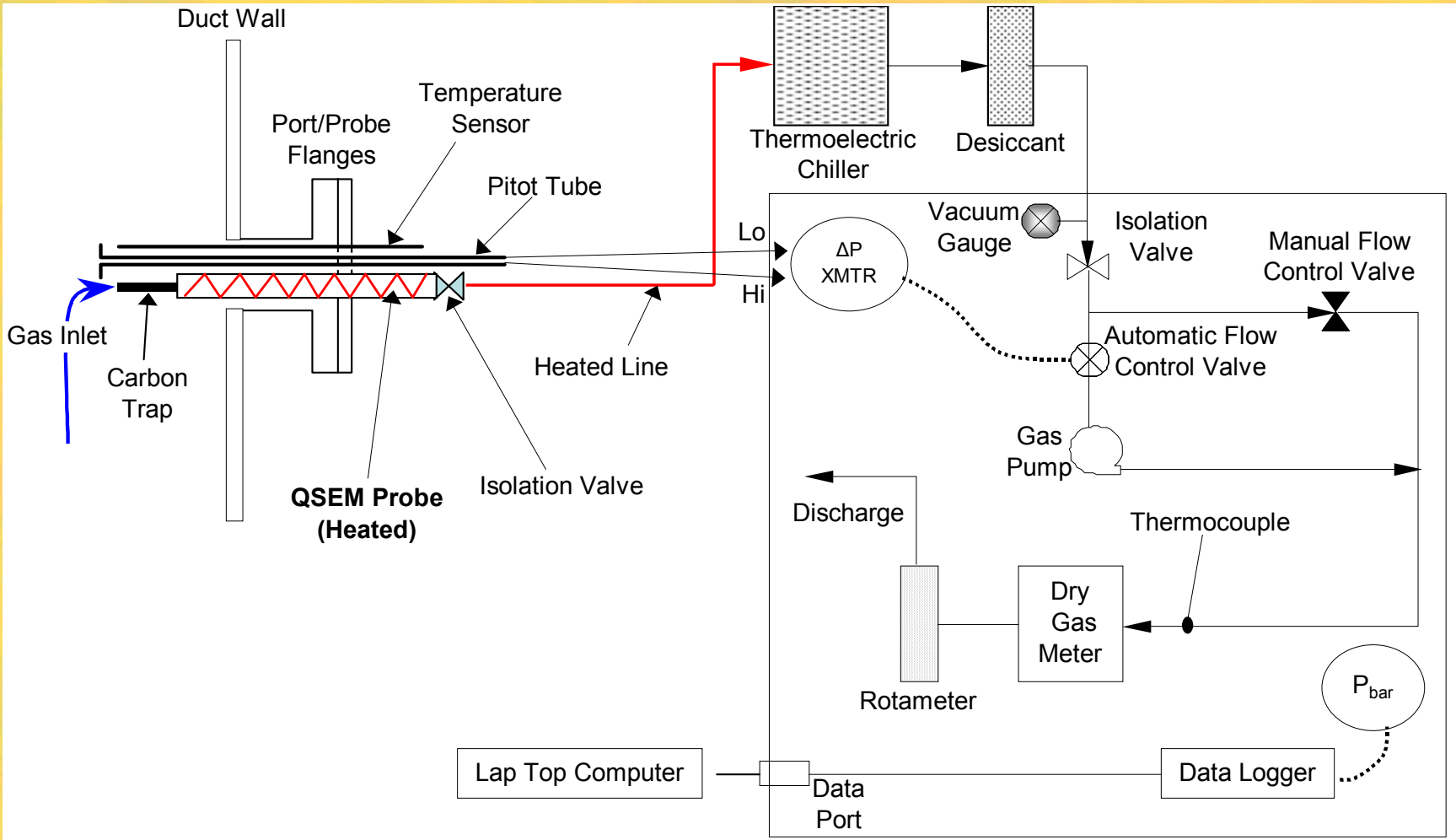
Method-324 Schematic

QSEM=Quicksilver Emission Monitor



QSEM Console (Rev D)

Upgraded Flow-Following Equipment

- Automatic sample flow control
- Adjust sample flow rate based upon duct flow
  - Pitot on sampling probe or signal from stack CEM
- Report total flow at standard conditions
- Team with equipment vendor to minimize period between development and availability

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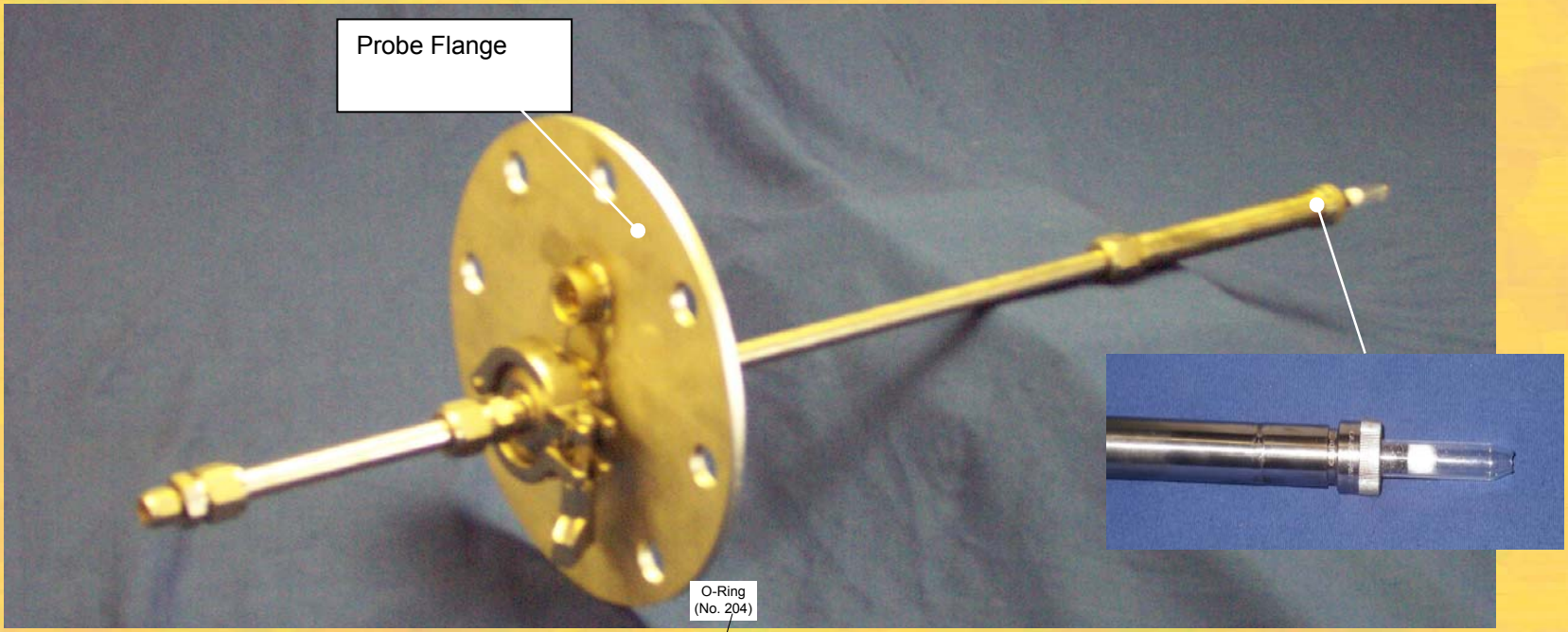
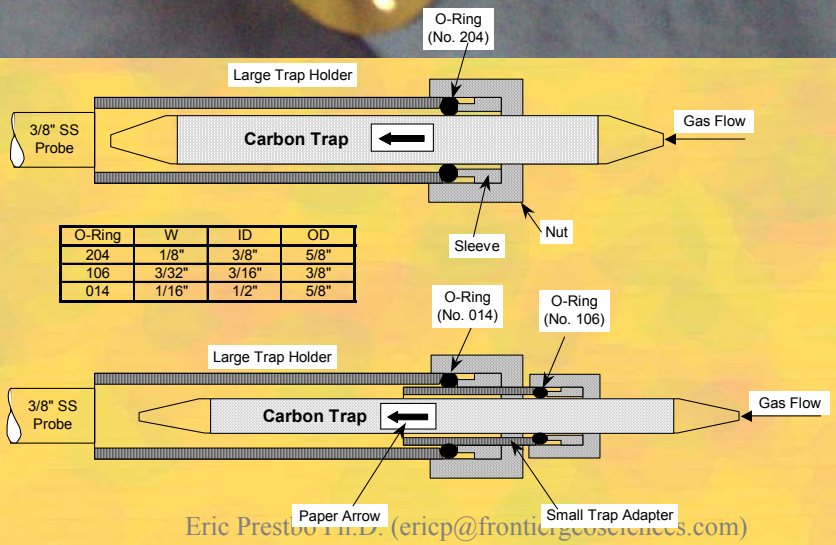
M-324 Probe





O-Ring	W	ID	OD
204	1/8"	3/8"	5/8"
106	3/32"	3/16"	3/8"
014	1/16"	1/2"	5/8"

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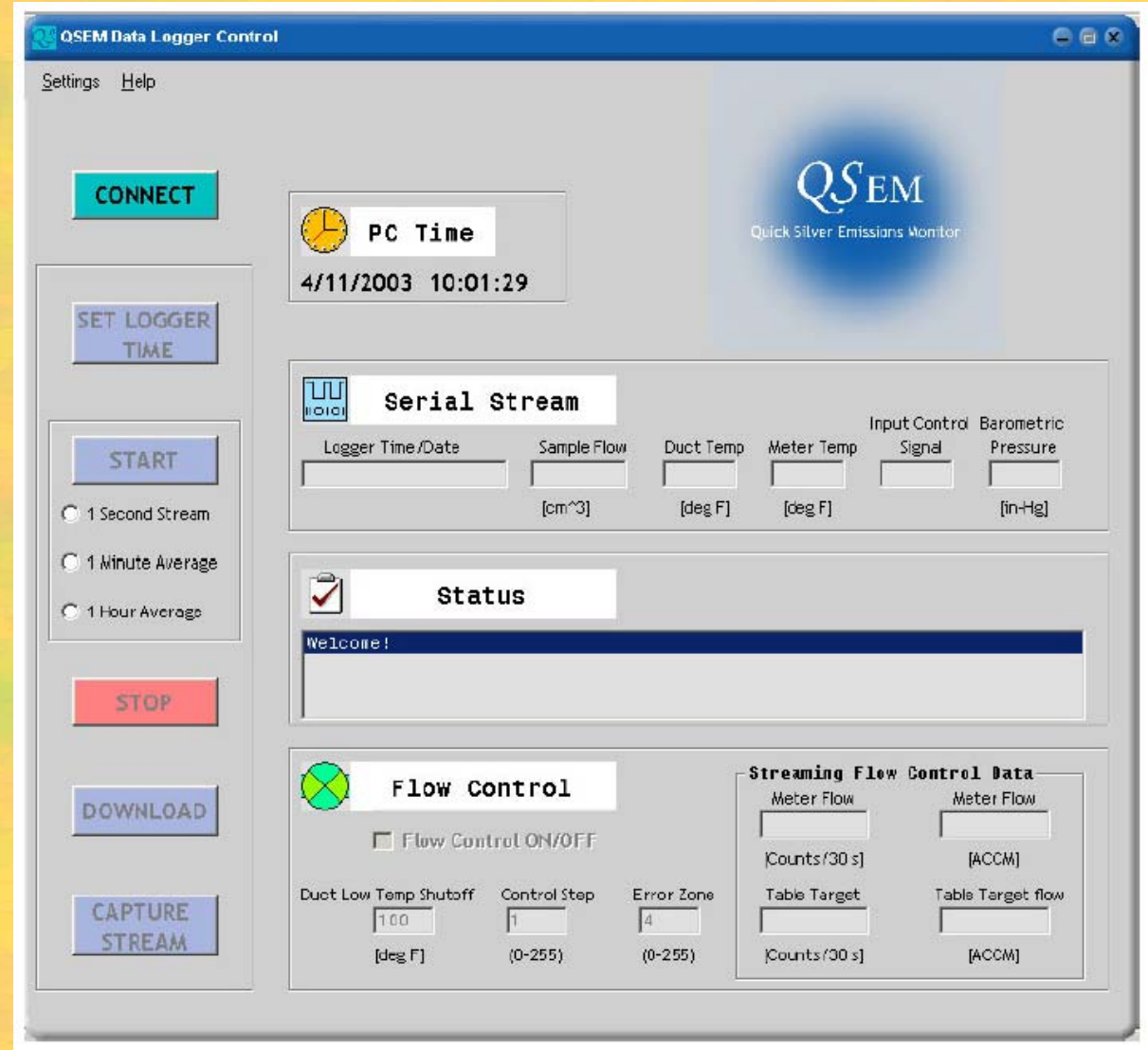
HMI Screen



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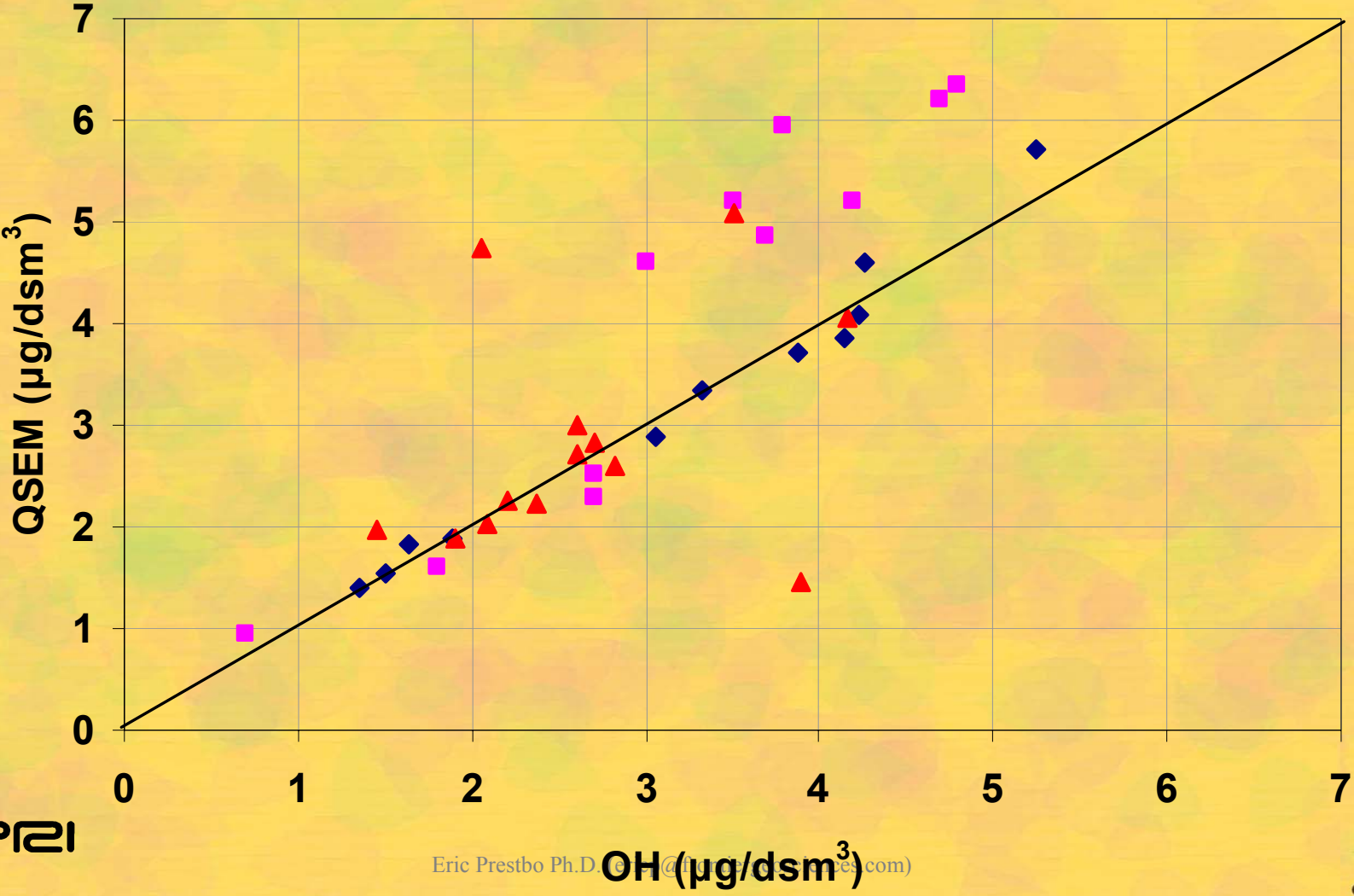
Ontario Hydro Comparisons, 3 sites



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M-324 Relative Accuracy Table

M-324 and OH

	All Runs	Best 9
Site 1	54 %	4.8 %
Site 2	9.5 %	1.6 %
Site 3	7.0 %	5.9 %

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QA/QC for Method-324

QA/QC specification	Acceptance Criteria	Frequency	Corrective Action
Reagent blank	<5 ng/digest and a standard deviation of 1.0 ng/digest. (n=3)	3 per analysis set of 20 sorbent traps	Reanalyze, investigate source of high levels
Sorbent Trap Blank	<5 ng/digest and a standard deviation of 1.0 ng/digest. (n=3)	Not required, but recommended for low sample trap loadings (<100 ng/digest) or if field blanks or the Trap Quality Indicator (Table 324-1) are above their acceptance criteria	A high sorbent trap blank may result in a positive bias. A blank correction may be applied using the sorbent trap blank as described in section 9.2. Investigate trap blank source and correct
Sorbent trap field blank	<5 ng/trap or < 5% of average Hg collected on the traps.	1 per 10 field samples collected	Notify field personnel of sample handling issue, retrain. Also possible that the sorbent trap blank is contributing, investigate
B-Trap Bed Analysis	<2% of A trap bed value or < 5 ng/trap	Every Sample	Investigate sample collection parameters, retrain, digest and analyze unused traps to check variability and background Hg levels, replace trap lot
Paired train Results	Same as section 8.6.6 of PS-12A of 40 CFR Part 60, Appendix B	As required	Report higher value if discrepancy between values <20% RPD; use average if within 20% RPD
Calibration Curve Correlation Coefficient (minimum of 5	$r \geq 0.995$, linear regression forced through zero	Beginning of analytical day, every 12 hours thereafter	Recalibrate
Initial/Continuing Calibration Verification (ICV/CCV)	80-120% recovery	Following every calibration, 1 per 10 analytical cycles	Halt analysis, reanalyze, recalibrate if necessary (ICV) or rerun all samples since last valid CCV (CCV)
Initial/Continuing Calibration Blank (ICB/ CCB)	Individual limit of < 0.25 ng/L (Instrument blanks are not blank corrected)	Following every calibration, 1 per 10 analytical cycles	Halt analysis, reanalyze, recalibrate if necessary (ICB) or rerun all samples affected by high blank (CCB)
Laboratory analytical and analytical spike duplicate (AS/ASD)	75-125% recovery with RPD $\leq$ 25 1 per analytical batch ? 20 samples	1 per batch of 20 samples	Reanalyze, halt analysis and investigate possible instrumental causes of error, flag data if not resolvable
Laboratory analytical duplicate (AD)	? 25 RPD/RSD	1 per batch of 20 samples	Reanalyze, halt analysis and investigate possible instrumental causes of error, flag data if not resolvable

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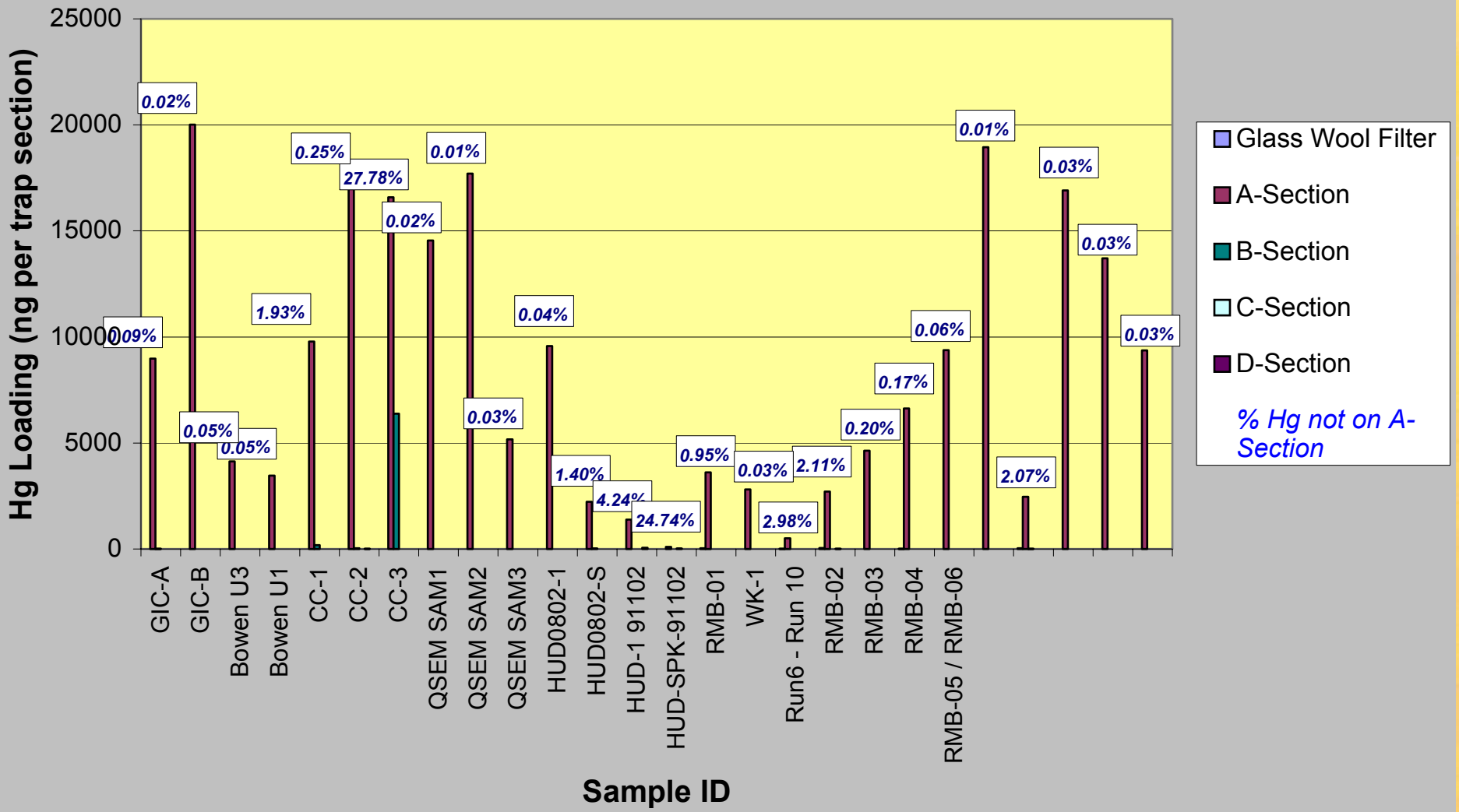
Where does the Hg collect? Is the iodated carbon efficiently capture on the leading edge of the iodated carbon trap with no breakthrough with the high loadings and long sampling time? Note, virtually no Hg observed after the B-Section of the trap!



Coal-Fired Power Plants with M-324 Data

- ~8 plants with long sample time testing
- ~15 plants with short term (<24 hr) testing for fluegas Hg characterization
- ~3 plants with wet-scrubbers

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Technical Solutions

- Customize for high dust and wet-scrubber applications
- Improvements made in volume measurement accuracy
- More field-spike results forthcoming
- Proportional sampling testing

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Summary

- Reliable operation by various groups
  - Could be operated by on-site personnel
- Portable
- Low maintenance
- Low-cost equipment
- Method 301 validation Fall ’03
- Issued as EPA Draft M324 December ‘03

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