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Thermo Scientific Mercury Freedom® System: An Overview of Field Results

ICAC/MARAMA Webinar

Jeremy Whorton

July 26, 2011

Top 4 Categories of MARAMA Questions

- Working principle of the Thermo Scientific Mercury Freedom System (5 min)
- Measurement of low-level Mercury (3 min)
- Field results – Power, Cement and Waste Incinerator (10-15 min)
- Reliability (up-time)
- Summary and conclusions

Thermo Scientific Mercury Freedom® System Overview

Model 82i Probe Controller

Model 80i Mercury Analyzer

Model 81i Mercury Calibrator

Zero air supply
Optional Nitrogen Generator

Model 83i Inertial Probe

Proven performance in multiple CEMS applications

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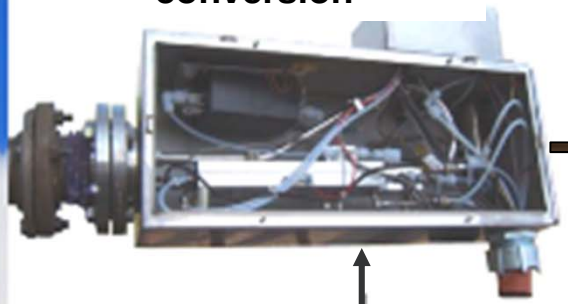
Wet-basis dilution, dry conversion and direct CVAF

Sample extraction and conversion



Sample transport

Model 80i Analyzer (Direct CVAF)

Model 82i Probe Controller

Model 81i Calibrator

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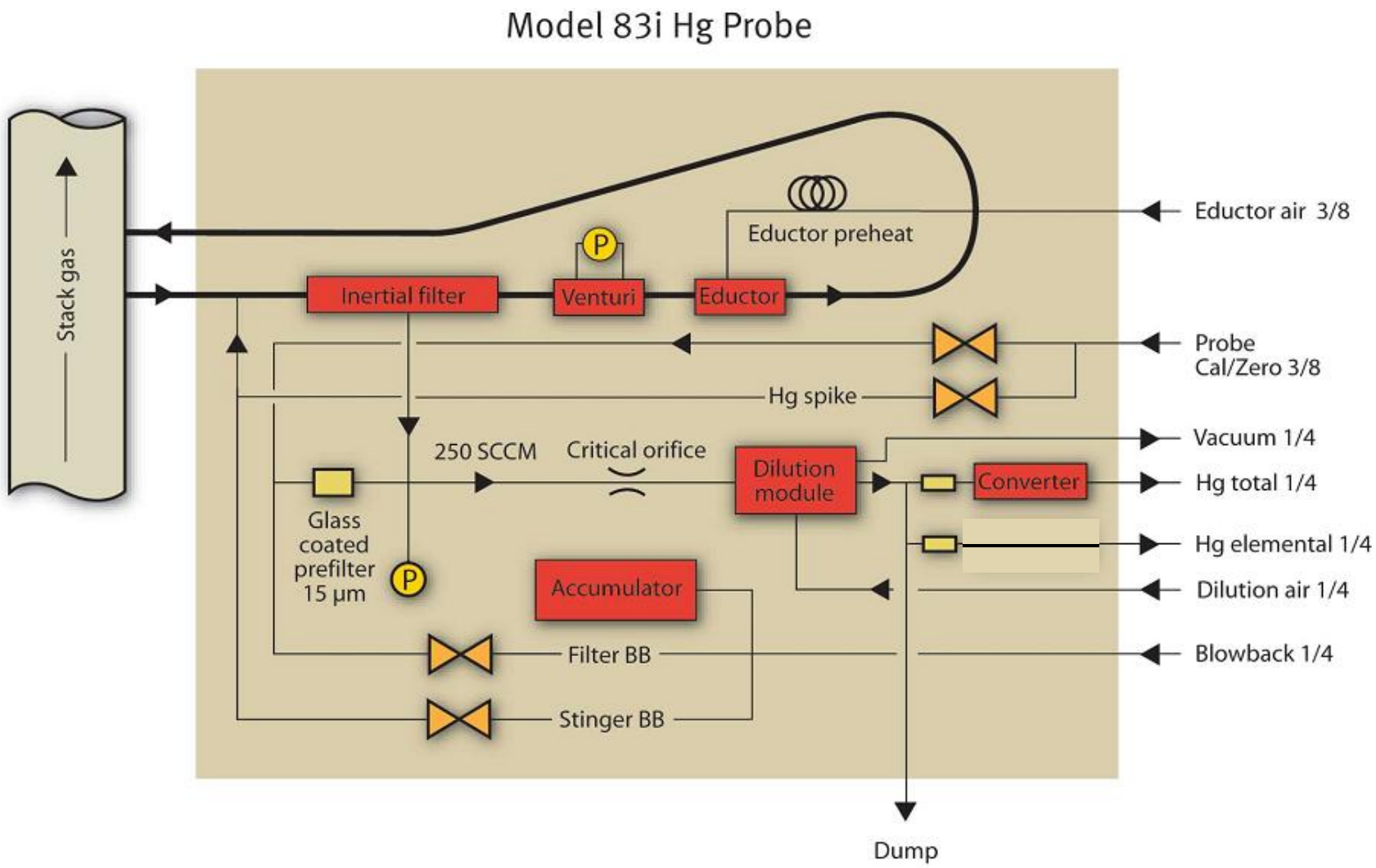
Model 83*i* Probe/Converter Flow Scheme



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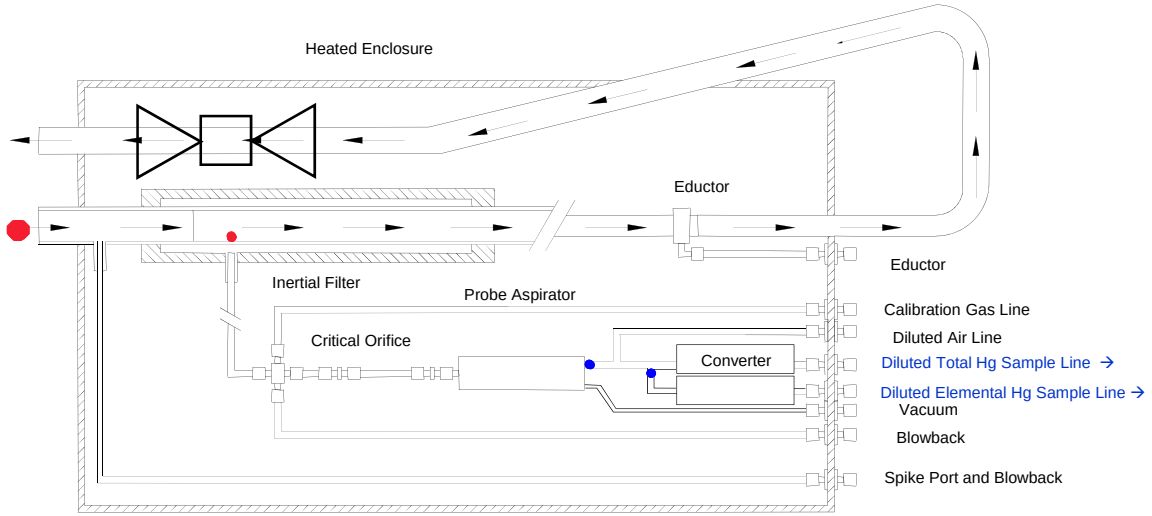
Model 83*i* Inertial Filter Probes

- Material: Silica Coated Stainless Steel or Hastelloy C-276
- Design Flow Rate (lpm): 10 – 50 liters/minute
- Heated Filter/Inlet Stinger/Outlet Stinger Blowback
- Inertial Separation Mechanism separates Vapor Hg from Particulate Matter



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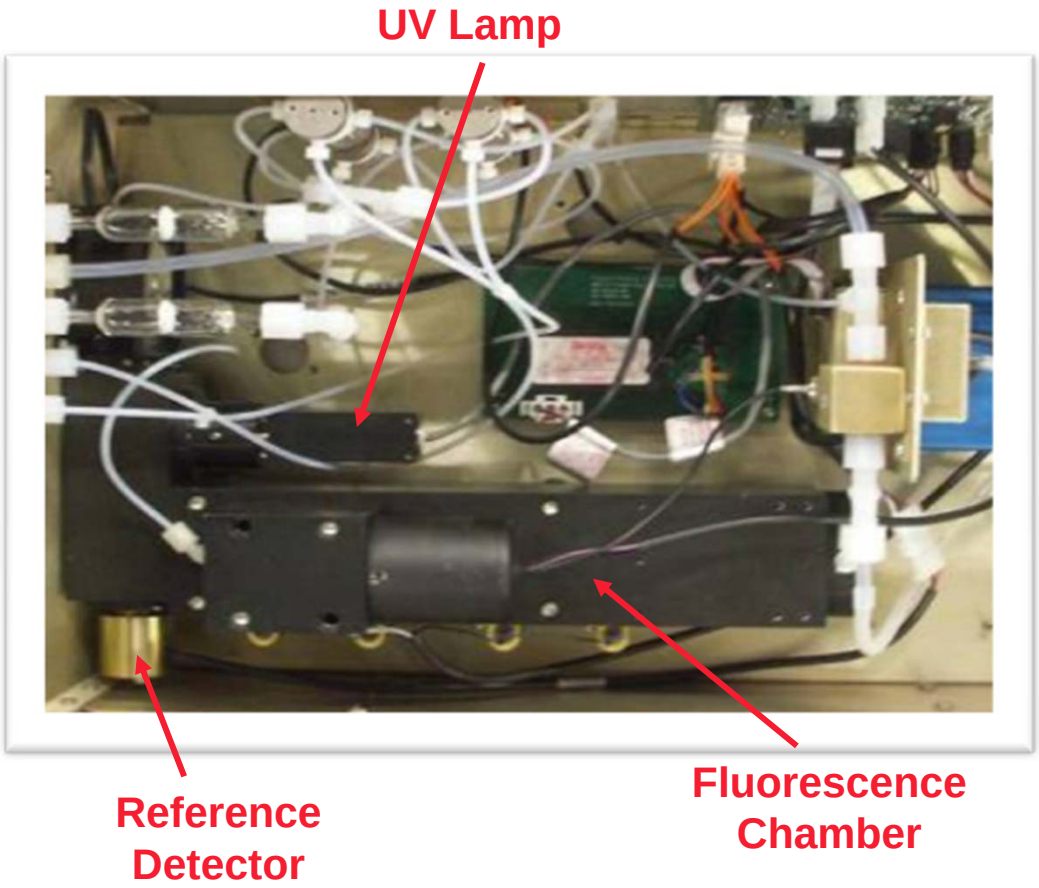
Model 80*i* Hg Analyzer

- Direct Measurement CVAF
  - Continuous measurement
  - No additional gases required
- Uses Diluted Sample
  - Lower moisture, less reactive
- Capable of Speciation
  - Measures either Hg^T or Hg^0
- Analyzer Detection Limit:
  ~1 ng/m^3 (~0.1 ppt)
- No cross interference with SO_2



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Hg Fluorescence

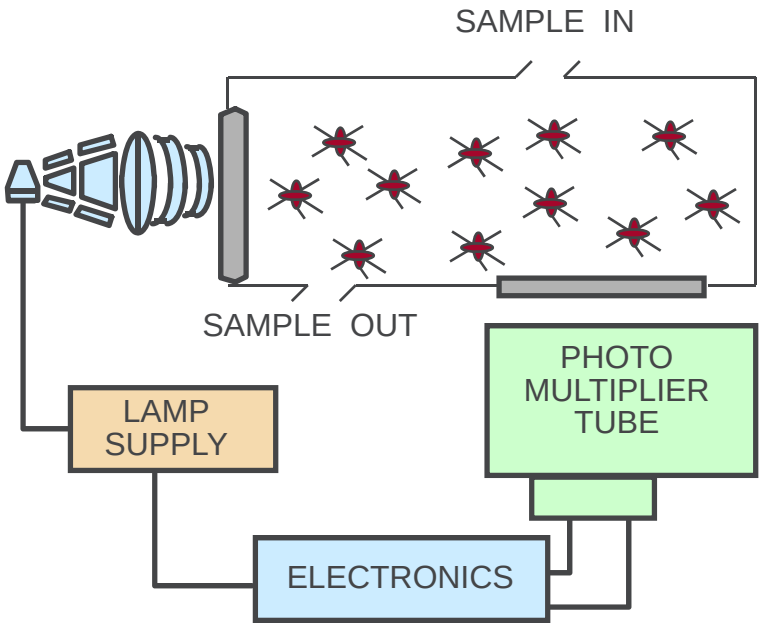
$$Hg + h\nu\,(253.7\ nm) \xrightarrow{I_a} Hg^*$$

$$Hg^* \xrightarrow{K_f} Hg + h\nu\,(253.7\ nm)$$

$$I_a = I_o[I - e^{-\{ax(Hg)\}}]$$

$$I_f \; ; \; I_o ax(Hg) \text{ or } K(Hg)$$

High Intensity Hg Lamp
Reflective Filtering
Enhanced Light Baffling
Bandpass Filter



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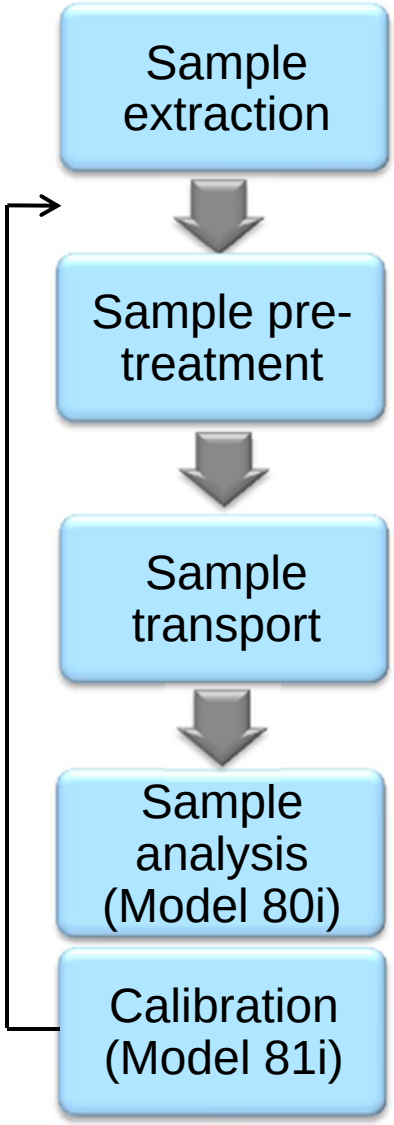
Combining Performance with Ease of Use



- Probe with high flow inertial filter is proven to work in high dust applications
- Dry conversion at stack avoids potential loss or chemistry changes of oxidized mercury in the sample line
- Dry conversion requires no wet chemistry or water supply
- Direct measurement CVAF ensures linearity over broad range and avoids interferences with SO_2
- High bench sensitivity eliminates need for expensive carrier gas and gold trap replacements
- Real-time monitoring with 10 second response time over entire range is ideal for process control
- *i*-Series platform offers modular design, enhanced interface capabilities with seamless integration into plant data flow

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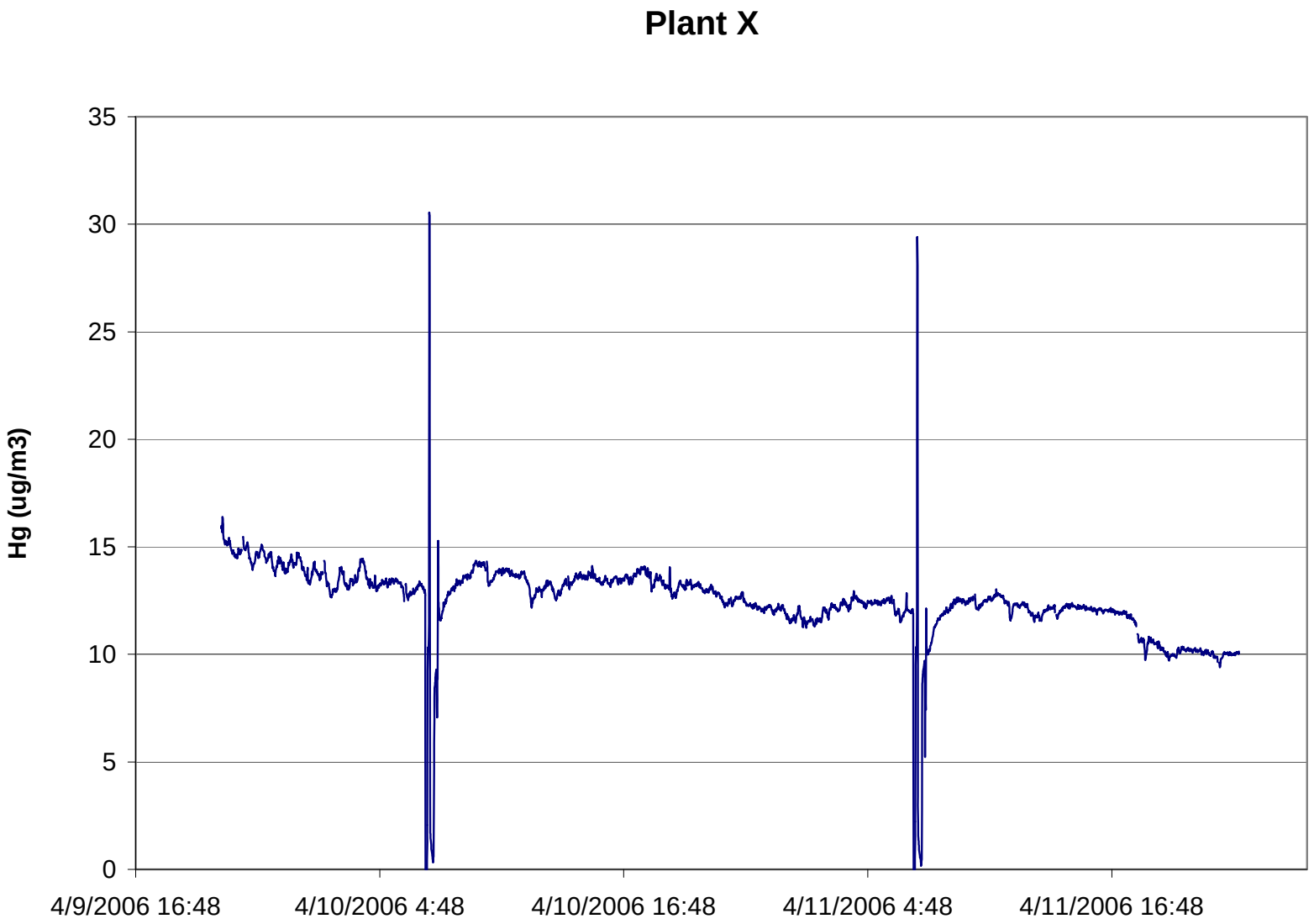
Typical Mercury Levels, Then……2006



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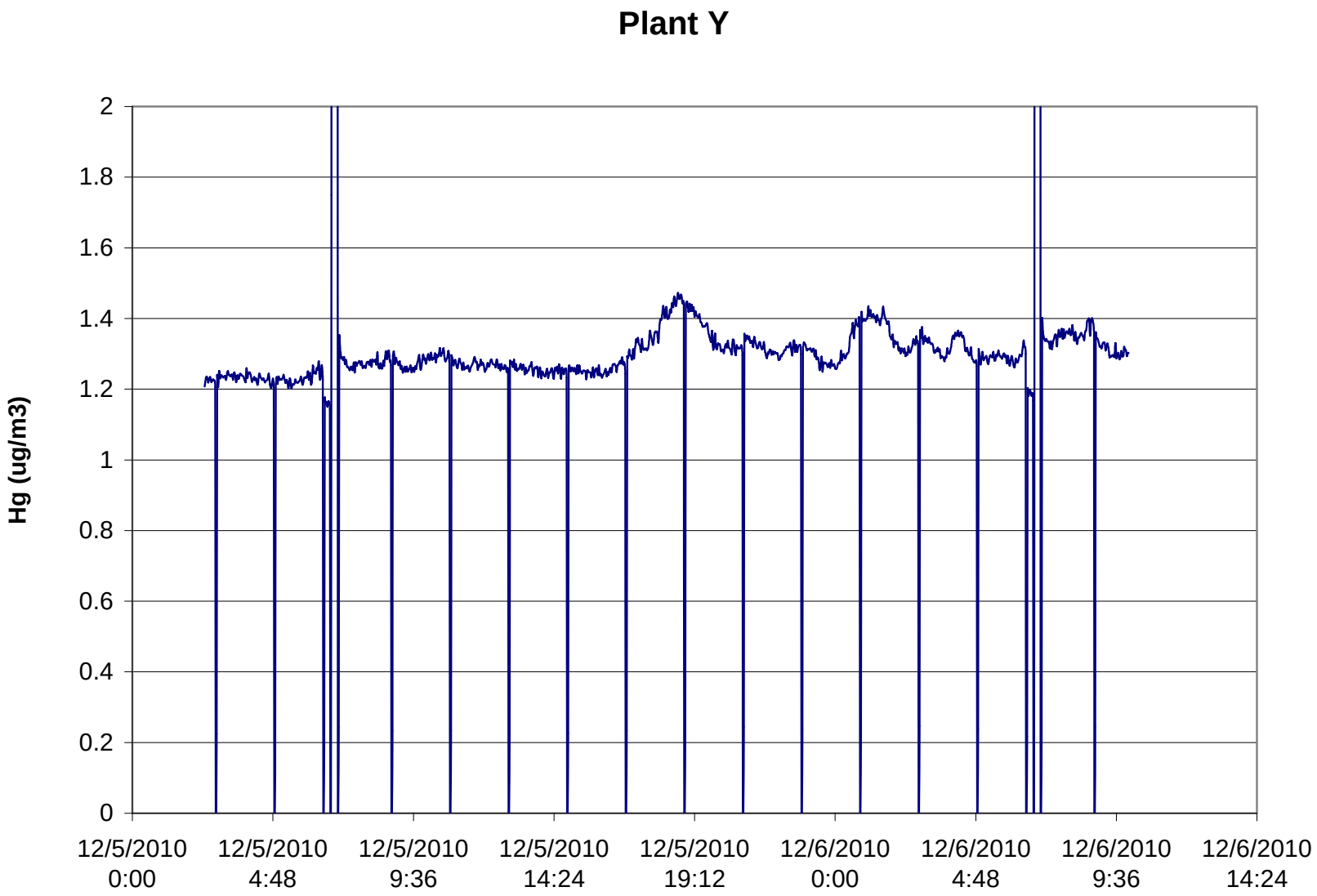
Typical Mercury Levels, Currently 2010



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Dilution with Nitrogen for low level measurements

- For Total Hg stack concentrations < 1 µg/m^3
  - Nitrogen dilution system
  - Zero Air feed to Nitrogen generator
  - 0.2 ng/m^3 analyzer MDL @ 40:1 system dilution
  - MDL ~ 0.008 µg/m^3

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Circulating Fluidized Bed Unit

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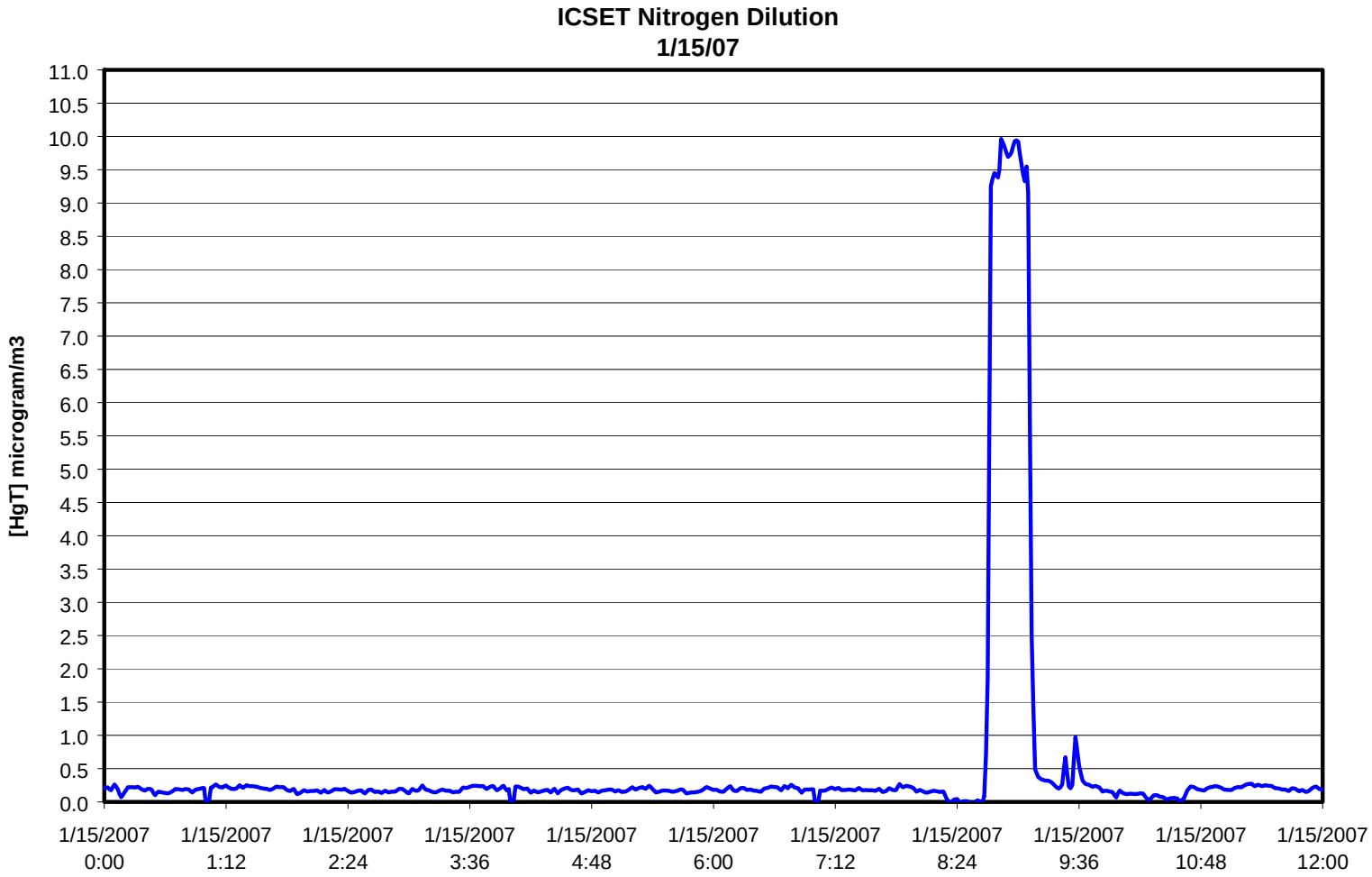
ICSET Nitrogen Dilution Testing



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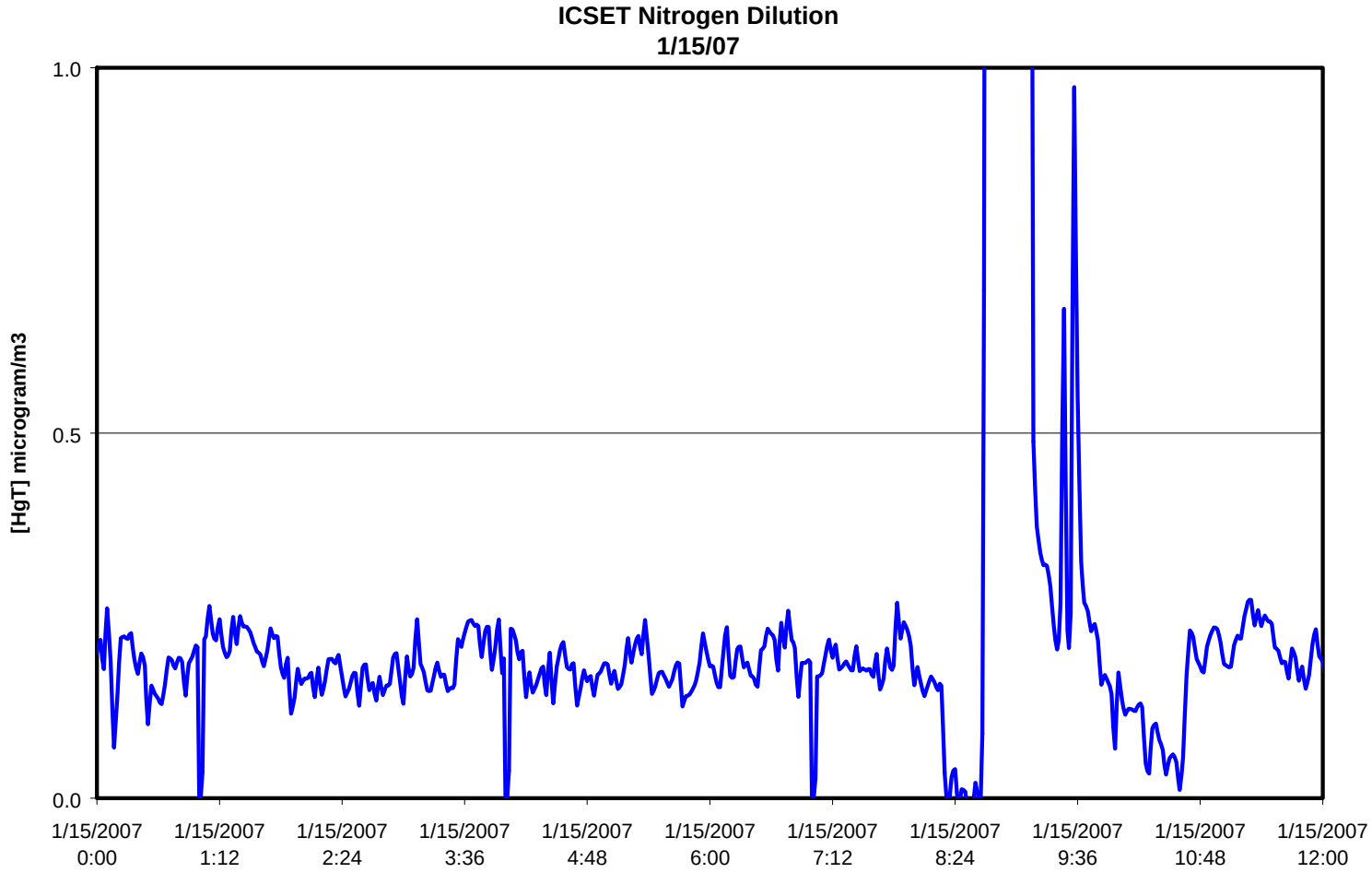
ICSET Nitrogen Dilution Testing



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Southwest plant: RATA results at 0.6 to 3 µg/m³

Facility						Test Date: 11/4 and 11/5/2008		
Unit Number:						Project #: M22M0486		
Test Location: Stack						Site Name:		
Monitor / Calibrator: Model 80i / Model 81i						Serial Numbers: 0803527419 / 0803527425		
	Test Run	Date	Start Time	End Time	Reference Method Hg µg/scm	CEM Output Hg µg/scm	(RM-CEM) Difference (di)	Difference^2 (di^2)
1	1	11/04/08	1522	1552	3.0	2.8	0.15	0.02
1	2	11/04/08	1615	1645	3.0	2.8	0.13	0.02
1	3	11/05/08	1027	1057	1.3	1.2	0.09	0.01
0	4	11/05/08	1117	1147	0.6	1.0	-0.39	0.15
1	5	11/05/08	1203	1233	0.8	0.9	-0.09	0.01
1	6	11/05/08	1246	1321	0.9	0.9	0.05	0.00
1	7	11/05/08	1340	1430	0.7	0.9	-0.14	0.02
1	8	11/05/08	1545	1631	0.7	0.7	0.02	0.00
1	9	11/05/08	1646	1729	0.6	0.7	-0.06	0.00
1	10	11/5/2008	1749	1819	0.9	0.8	0.08	0.01

Standard Deviation	0.101	su
Confidence Coefficient	0.078	CC
Relative Accuracy based on % of RM Value	7.8	%
Relative Accuracy based on difference	0.0	Mean Difference
Calculated Bias Adjustment Factor	1.000	BAF
Default BAF (Hg <5.0 ug/scm)	1.000	BAF

Meets specifications for annual RA

Utility Field Results

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Northwest plant: RATA results at 0.6 to 1.6 µg/m^3

Hg RATA Test Data and Results Report

			Plant:				Site Name:			
			Parameter:	Hg			Monitor ID:			
			Test Date:	10/24/2007	10/26/2007					
				Level:	High					
Reference Method Used:		30B		Use of RATA:				Confidence Coefficient:		0.045
Mean of RM Values:		1.209		Mean of Monitor Data:		1.196		Mean Difference:		-0.001
Relative Accuracy:		3.77		Mean Int. Gross Load:		0		Statistical Bias:		1.001
Total Runs:		10		Standard Deviation:		0.062		Bias Adjustment Factor:		Pass
Tabulated t-value:		2.262								

Run#	Test Run Used	Date	Start Time	End Time	Reference Method (RM) Value (ug/scm)	DAHS Value	(RM-DAHS) difference	difference^2	Load	% Difference
1	1	10/24/2007	7:27	8:37	1.64	1.54	0.100	0.010		6.1%
2	1	10/24/2007	9:28	10:38	1.45	1.48	-0.030	0.001		2.1%
3	1	10/24/2007	11:47	12:57	1.35	1.45	-0.100	0.010		7.4%
4	0	10/24/2007	13:38	14:48	1.16	1.35	-0.190	0.036		16.4%
5	1	10/24/2007	15:32	16:42	1.38	1.34	0.040	0.002		2.9%
6	1	10/24/2007	17:14	18:24	1.22	1.22	0.000	0.000		0.0%
7	1	10/25/2007	6:17	7:27	1.18	1.23	-0.050	0.003		4.2%
8	1	10/25/2007	8:12	9:22	0.96	1.04	0.090	0.008		9.4%
9	1	10/26/2007	10:00	11:10	0.84	0.87	-0.030	0.001		3.6%
10	0	10/27/2007	11:43	12:53	0.58	0.73	-0.150	0.023		25.9%
11	0	10/25/2007	13:25	14:35	0.96	1.06	-0.100	0.010		10.4%
12	1	10/25/2007	15:16	16:26	0.97	1.00	-0.030	0.001		3.1%
13	1	10/25/2007	16:55	18:05	1.10	1.10	0.000	0.000		0.0%

Utility Field Results

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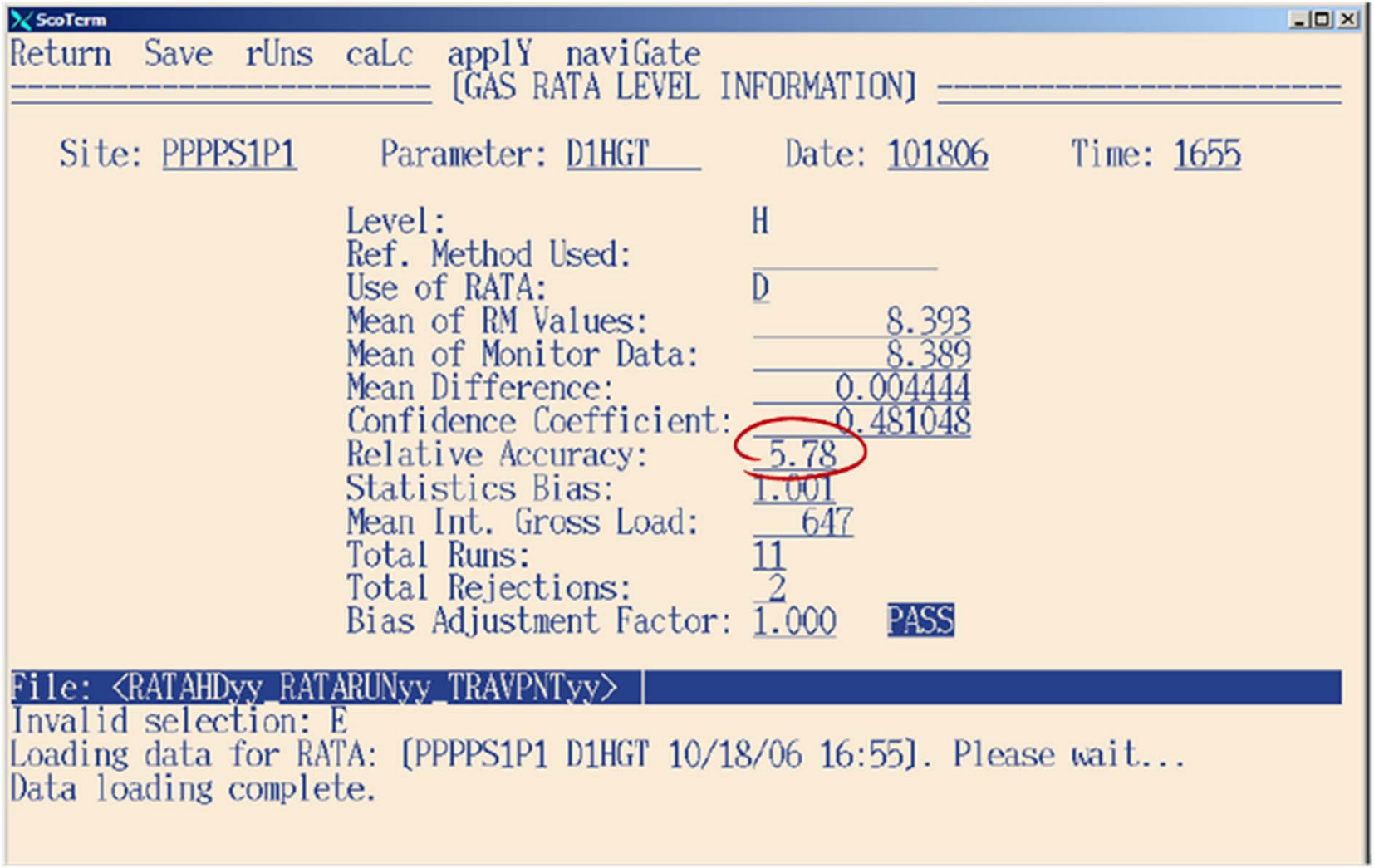
Northwest plant II: RATA results at 5.78%



Reference method used was Ontario Hydro

US plant: RATA results at 3 to 5 µg/m³

Client: Thermo Scientific
Plant:
Project #: M080805
Location: Stack
Date: 2/20/08 and 2/21/08
Test Method: Sorbent Hg (30B)

CEM Monitor Information

Hg Monitor/Model:			Model 80i		Hg Serial # :		0711321958	
1=accept 0=reject	Test Run	Test Date	Start Time	End Time	RM ug/wscm	CEM ug/wscm	(RM-CEM) Difference (di)	Difference² (di²)
1	1	02/20/08	12:05	12:35	3.31	3.66	-0.35	0.123
1	2	02/20/08	13:05	13:35	3.30	3.59	-0.29	0.084
1	3	02/20/08	13:50	14:20	3.18	3.57	-0.39	0.152
1	4	02/20/08	14:30	15:00	3.42	3.48	-0.06	0.004
1	5	02/20/08	13:32	14:02	3.01	3.46	-0.45	0.203
1	6	02/21/08	06:53	07:23	3.50	3.74	-0.24	0.058
0	7	02/21/08	07:35	08:05	4.17	4.03	0.14	0.020
0	8	02/21/08	08:20	08:50	4.55	4.44	0.11	0.012
0	9	02/21/08	09:00	09:30	5.06	4.53	0.53	0.281
1	10	02/21/08	09:40	10:10	4.56	4.41	0.15	0.022
1	11	02/21/08	10:20	10:50	4.10	4.29	-0.19	0.036
1	12	02/21/08	11:00	11:30	4.69	4.26	0.43	0.185
1	13	02/21/08	11:40	12:10	4.58	4.25	0.33	0.109

n	10	
t(0.025)	2.262	
Mean Reference Method Value	3.765	RM avg
Mean CEM Value	3.871	CEM avg
Sum of Differences	-1.060	di
Mean Difference	-0.106	d
Sum of Differences Squared	0.975	di^2
Standard Deviation	0.310	sd
Confidence Coefficient 2.5% Error (1-tail)	0.221	cc
Relative Accuracy	8.70	RA
Bias Adjustment Factor	1.000	BAF

Utility Field Results

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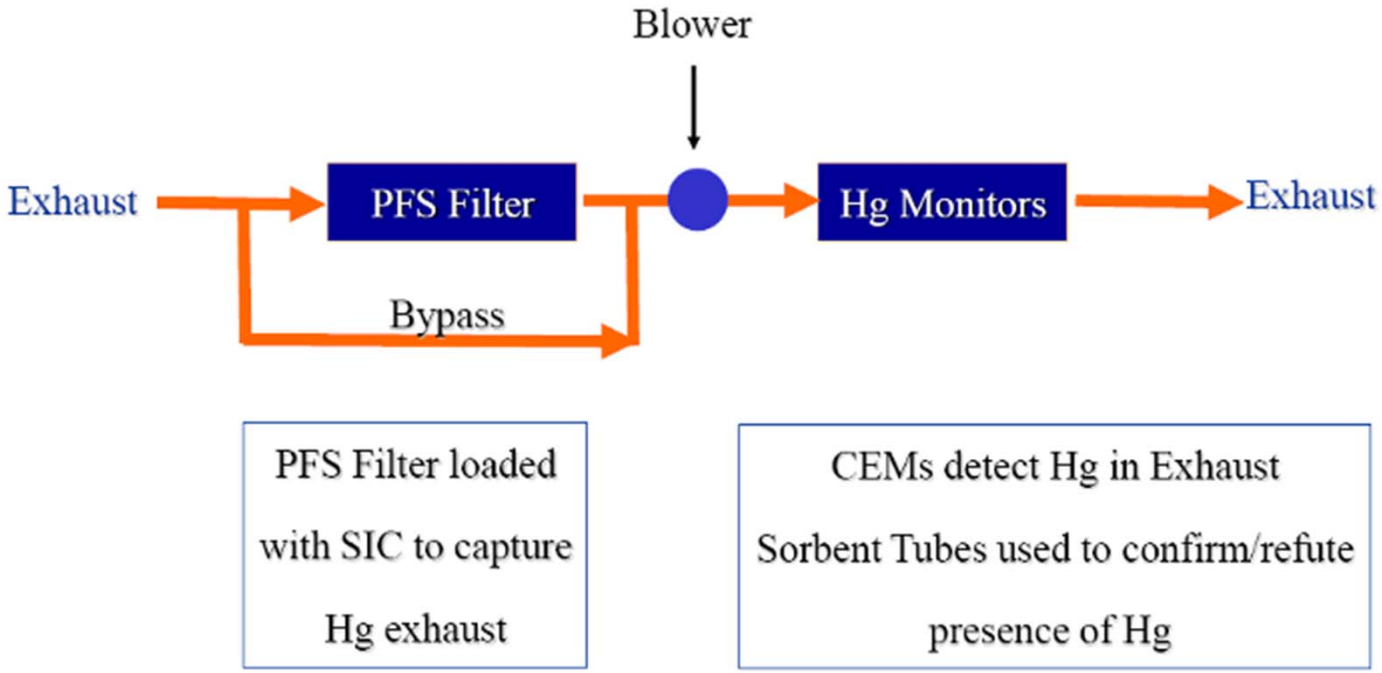
Umatilla Chemical Agent Disposal Facility Hg CEMS

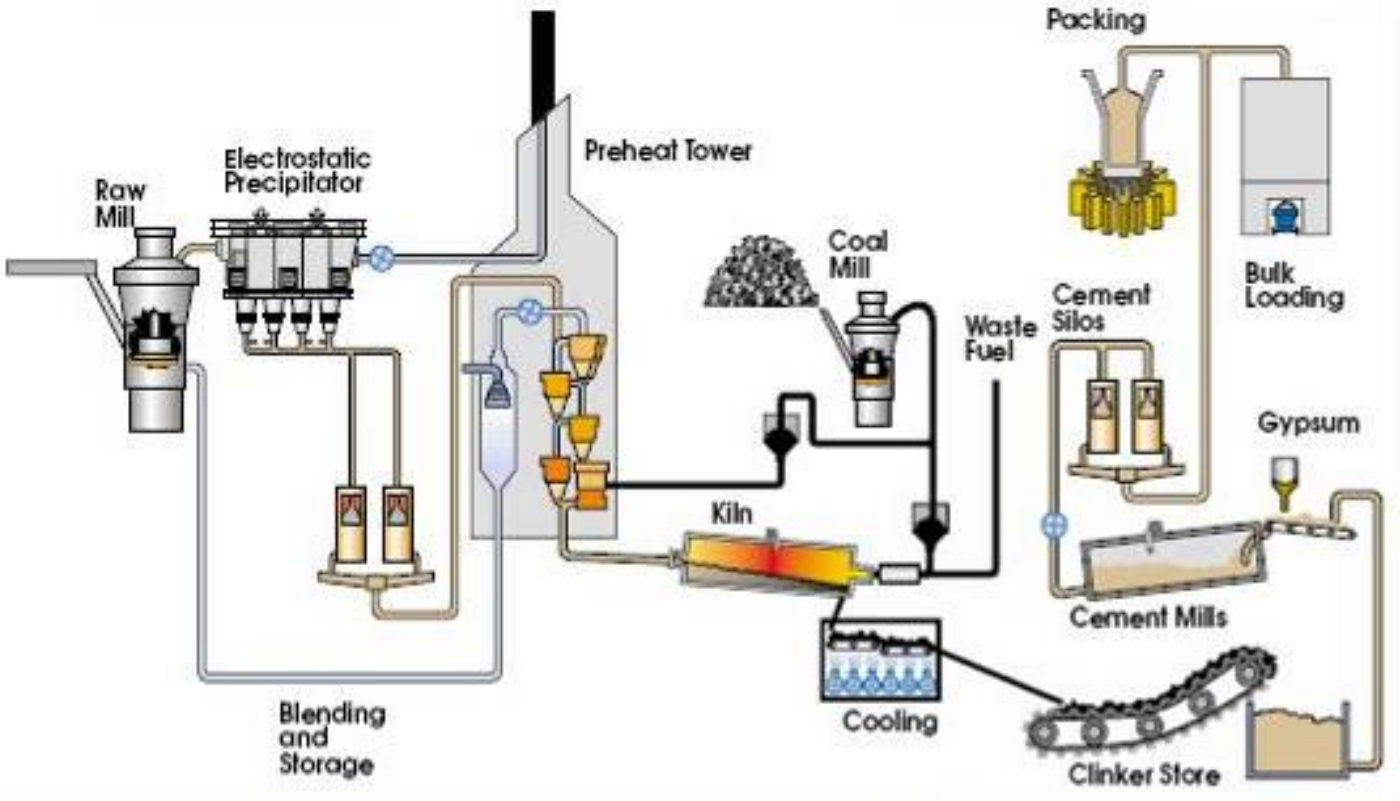
- UMCDF evaluated options to flag Mercury contamination from their HD Ton Containers



Source:
PPT at: http://events.awma.org/it32011/presentations.html (Section 14)

"UMCDF Hg CEMS system has proved to be very reliable"

Cement Process has Distinct Hg Monitoring Needs



- Large swings in Hg levels when raw mill switches states
- Wide array of raw materials and fuels contribute to mercury emissions
- High particulate levels and moisture can affect mercury content

Cement Field Results

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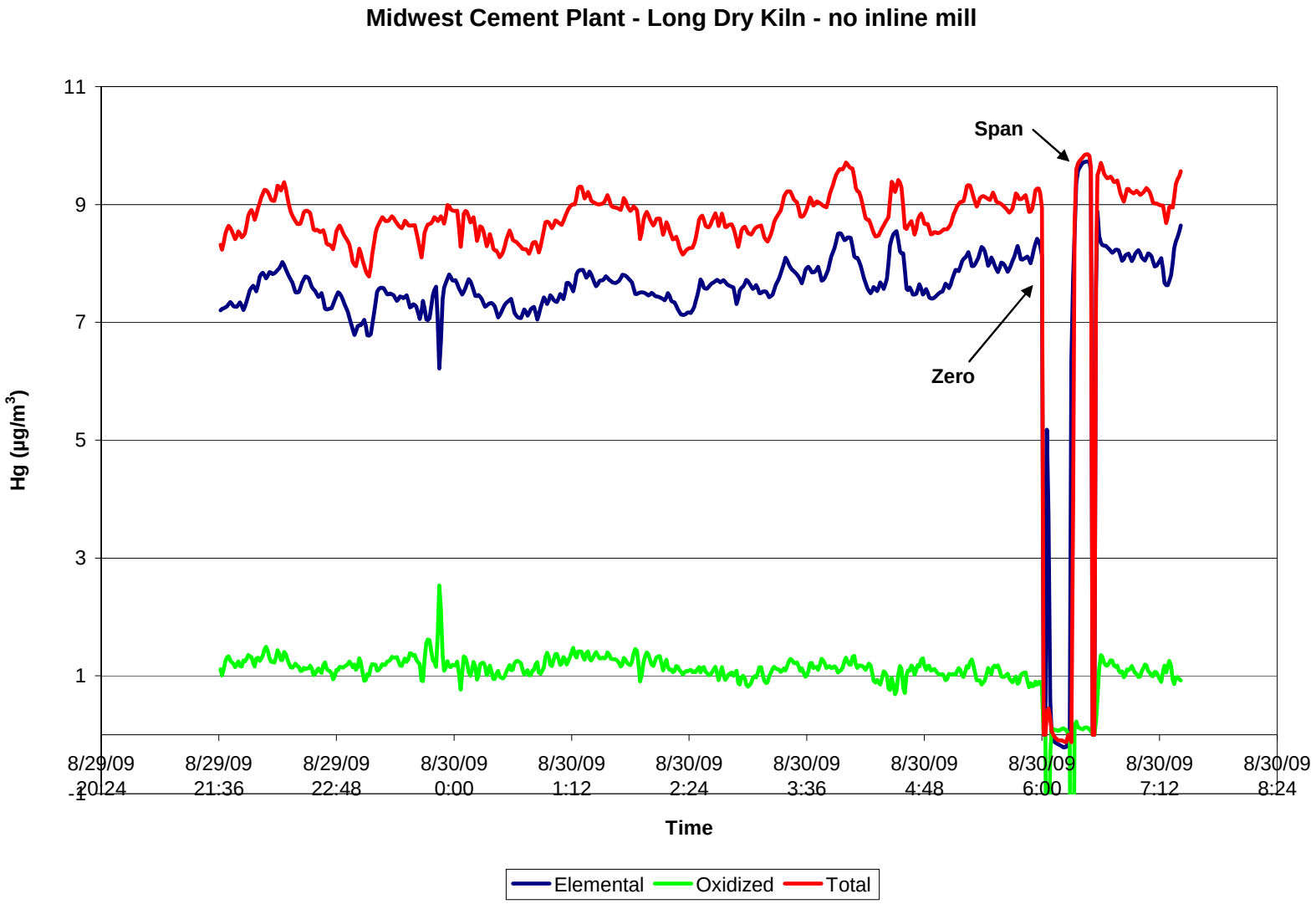
Midwest Plant - Dry, Horizontal Kiln without inline mill

Midwest Plant – Installed Mercury Freedom® System

Cement Field Results

Data – Midwest Cement Plant – no inline mill



Cement Field Results

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RATA Results at Midwest Plant

	Test Run	Date	Start Time	End Time	Reference Method Hg µg/scm	CEM Output Hg µg/scm	(RM-CEM) Difference (di)	Difference^2 (di^2)
1	1	09/22/09	0945	1015	12.1	11.7	0.35	0.13
1	2	09/22/09	1053	1123	11.2	11.4	-0.23	0.05
0	3	09/22/09	1148	1218	12.5	11.5	1.01	1.02
1	4	09/22/09	1251	1321	12.1	11.3	0.82	0.67
1	5	09/22/09	1354	1424	10.3	10.8	-0.47	0.22
1	6	09/22/09	1446	1516	11.7	11.8	-0.05	0.00
1	7	09/22/09	1545	1615	12.0	12.0	0.03	0.00
1	8	09/22/09	1638	1708	11.4	12.1	-0.73	0.53
1	9	09/22/09	1730	1800	12.1	11.9	0.19	0.03
1	10	9/23/2009	0855	0925	9.7	9.6	0.06	0.00

n	9	
t(0.025)	2.306	
Mean RM Value	11.396	RM
Mean CEM Value	11.400	CEM avg
Sum of Differences	-0.035	di
Mean Difference	-0.004	d avg
Sum of Differences^2	1.638	di^2
Standard Deviation	0.452	sd
Confidence Coefficient	0.348	CC
Relative Accuracy based on % of RM Value	3.1	%
Relative Accuracy based on difference	0.0	Mean Difference

Cement Field Results

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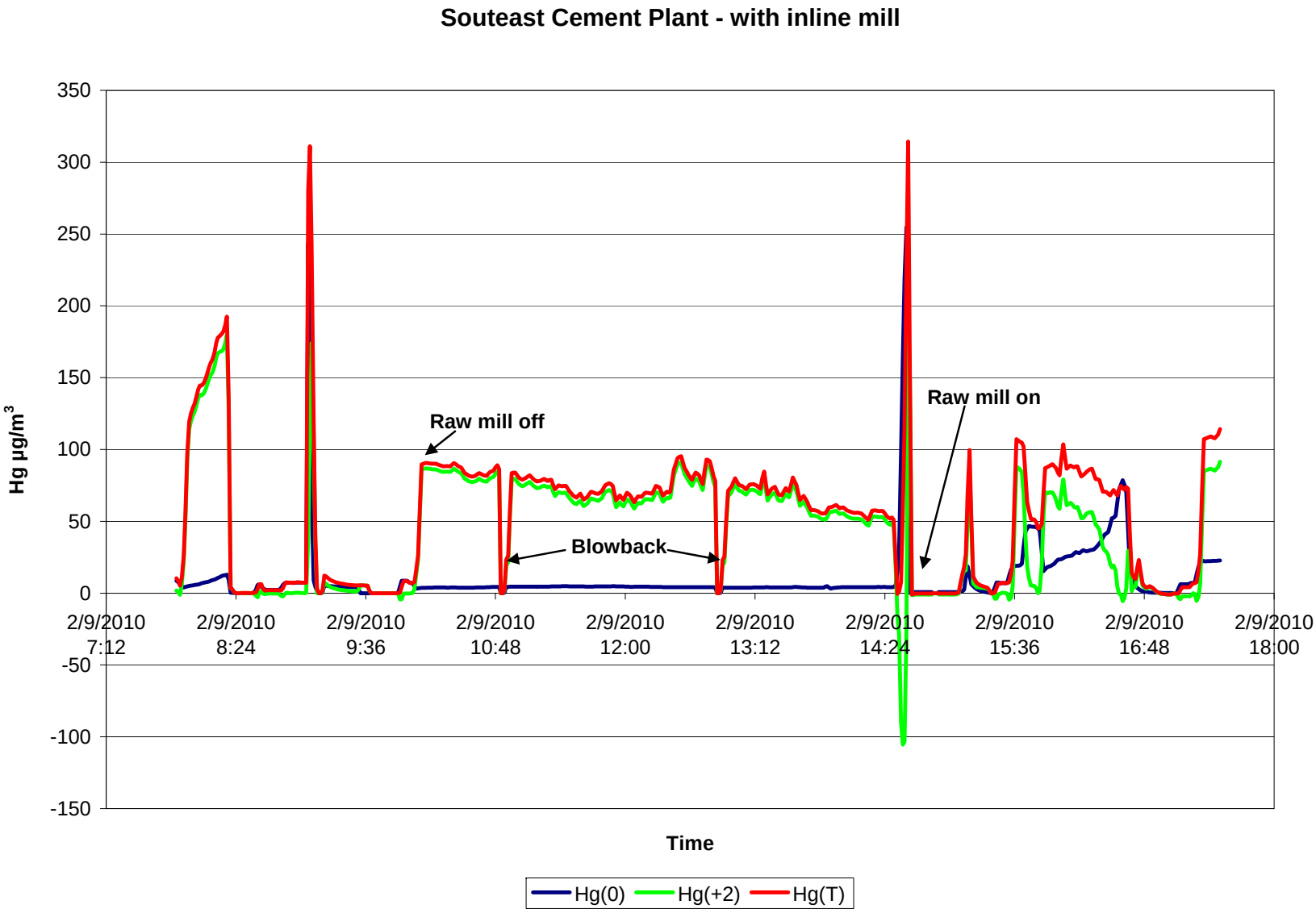
Midwest plant: Relatively Stable Mercury Levels

- Observed mercury concentrations were consistently in the range 3 to 15 µg/m^3 in the absence of an inline raw mill
- Current Model 81i Calibrator is adequate for this type of application
- Elemental Hg formed more than 90% of the total reading
- Thermo Scientific Mercury Freedom System passed RATA @ 3.1% and performed very well in this application
- Likely first instance of 30B traps tested against a real-time, continuous Mercury CEMS on a cement kiln

Southeast Cement Plant – with inline Raw-mill

Data – Southeast Cement Plant – with inline mill



Cement Field Results

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Southeast plant: Raw Mill Impacts Mercury levels

- Observed mercury concentrations wildly varied from <1 to >300 µg/m^3
  - Variability of readings clearly correlated to raw mill status
- Results confirm need for high-level Hg calibrator (0-500+ µg/m^3)
  - Mass Flow Controller changes
  - Hg reservoir temperature increase
- Planning NIST certified Vendor Prime at calibration point of 353 µg/m^3
- Oxidized mercury formed more than 90% of total reading
- Thermo Scientific Mercury Freedom System performed well over a broad range

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Long Term Reliability

- 6 years of data on hundreds of systems have enabled strong understanding of long term reliability (Hg sources)
- Thermo Scientific Mercury Freedom System has been used both for monitoring and process control
- Many systems installed in coal-fired power plants in 2006 are still running today

<u>At a Cement Kiln:</u>

- The customer and consultant had a concern in regards to long term exposure of the converter to the kiln effluent – Kilns are NOT boilers

- Presence of an in-line raw mill creates a need for high level calibration

- After 6 months of continuous exposure to the stack gas, we ran an oxidized linearity to challenge the system:
  - The system passed a 3-point oxidized linearity check after long term exposure to the kiln effluent

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Summary

- Mercury levels are decreasing as control devices are implemented or optimized
- Performance of existing CEMS can be optimized by ensuring:
  - A stable N_2 concentration
  - A good zero air supply (maintenance)
  - Using qualified lamps
  - Increasing averaging time
- A properly maintained Thermo Scientific Mercury Freedom System has a detection limit of 0.008 µg/m^3
- A low-level Mercury Calibrator is in development to support calibrations at lower concentrations (down to 0.2 µg/m^3)

Successful performance in multiple applications

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Thank you

anand.mamidipudi@thermofisher.com

jeremy.whorton@thermofisher.com

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