REINHOLD ENVIRONMENTAL Ltd.

2012 APC Round Table
& Expo Presentation

July 16-17, 2012, in Baltimore, MD / Hosted by Duke Energy, Entergy, FirstEnergy, Southern Company & TVA

Low Level Mercury Monitoring using Sorbent Traps to meet MATS Monitoring Requirements

Jim Wright
Clean Air Engineering

July 17, 2012

Overview

- Why are we here?
- How did we get here?
- Where do we go from here?

MATS Limits

TABLE 3—EMISSION LIMITATIONS FOR COAL-FIRED AND SOLID OIL-DERIVED FUEL-FIRED EGUS

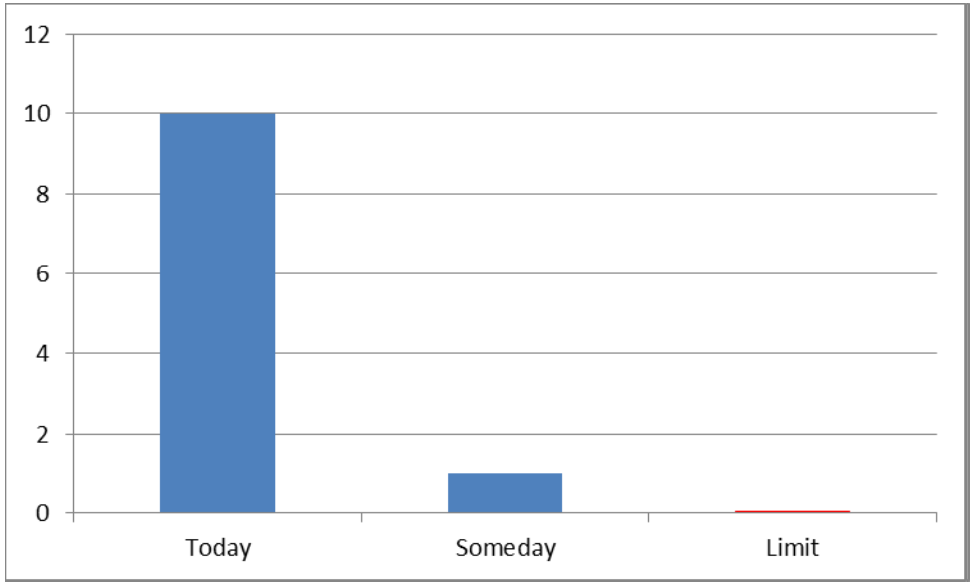
Subcategory	Filterable particulate matter	Hydrogen chloride	Mercury
Existing—Unit not low rank virgin coal	3.0E–2 lb/MMBtu. (3.0E–1 lb/MWh)	2.0E–3 lb/MMBtu. (2.0E–2 lb/MWh)	1.2E0 lb/TBtu. (1.3E–2 lb/GWh).
Existing—Unit designed low rank virgin coal	3.0E–2 lb/MMBtu. (3.0E–1 lb/MWh)	2.0E–3 lb/MMBtu. (2.0E–2 lb/MWh)	1.1E+1 lb/TBtu. (1.2E–1 lb/GWh). 4.0E0 lb/TBtu [a]. (4.0E–2 lb/GWh [a]).
Existing—IGCC	4.0E–2 lb/MMBtu. (4.0E–1 lb/MWh)	5.0E–4 lb/MMBtu. (5.0E–3 lb/MWh)	2.5E0 lb/TBtu. (3.0E–2 lb/GWh).
Existing—Solid oil-derived	8.0E–3 lb/MMBtu. (9.0E–2 lb/MWh)	5.0E–3 lb/MMBtu. (8.0E–2 lb/MWh)	2.0E–1 lb/TBtu. (2.0E–3 lb/GWh).
New—Unit not low rank virgin coal	7.0E–3 lb/MWh	4.0E–4 lb/MWh	2.0E–4 lb/GWh.
New—Unit designed for low rank virgin coal	7.0E–3 lb/MWh	4.0E–4 lb/MWh	4.0E–2 lb/GWh.
New—IGCC	7.0E–2 lb/MWh [b] 9.0E–2 lb/MWh [c]	2.0E–3 lb/MWh [d]	3.0E–3 lb/GWh [e].
New—Solid oil-derived	2.0E–2 lb/MWh	4.0E–4 lb/MWh	2.0E–3 lb/GWh.

Note: lb/MMBtu = pounds pollutant per million British thermal units fuel input.
lb/TBtu = pounds pollutant per trillion British thermal units fuel input.
lb/MWh = pounds pollutant per megawatt-hour electric output (gross).
lb/GWh = pounds pollutant per gigawatt-hour electric output (gross).
[a] Beyond-the-floor limit as discussed elsewhere.
[b] Duct burners on syngas; based on permit levels in comments received.

0.024 µg/dscm

NIST Calibrators

- Today
  0-10 µg/dscm
  low point of 2.7
- Someday
  0-1 µg/dscm
  low point of 0.2
- MATS Limit = 0.024



Source: EPRI CEMS, 2012, Thermo Supergroup

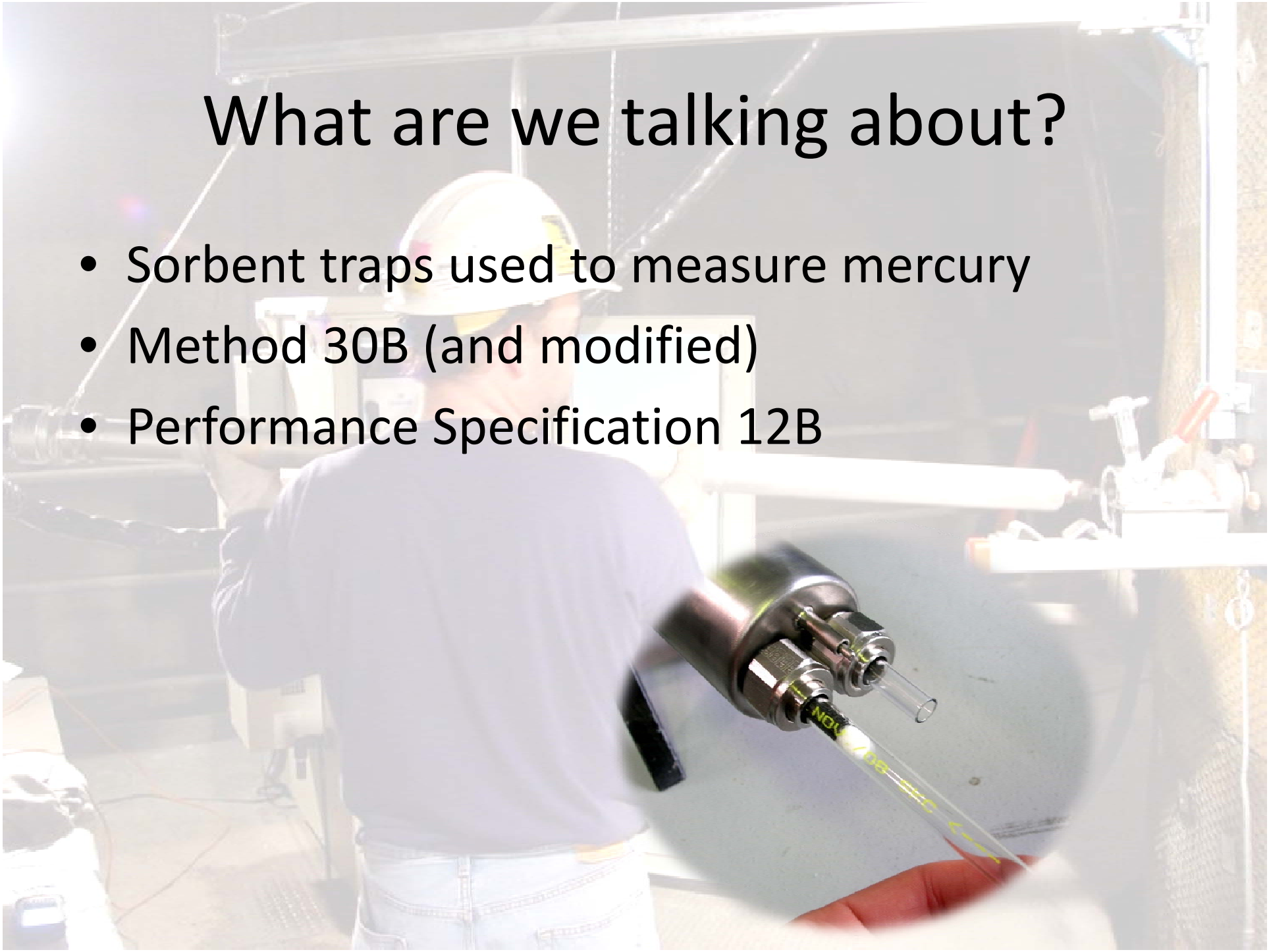
Two new units

- Permitted at 0.1 µg/dscm
- Sorbent trap monitoring
- Two primary and two back-up systems

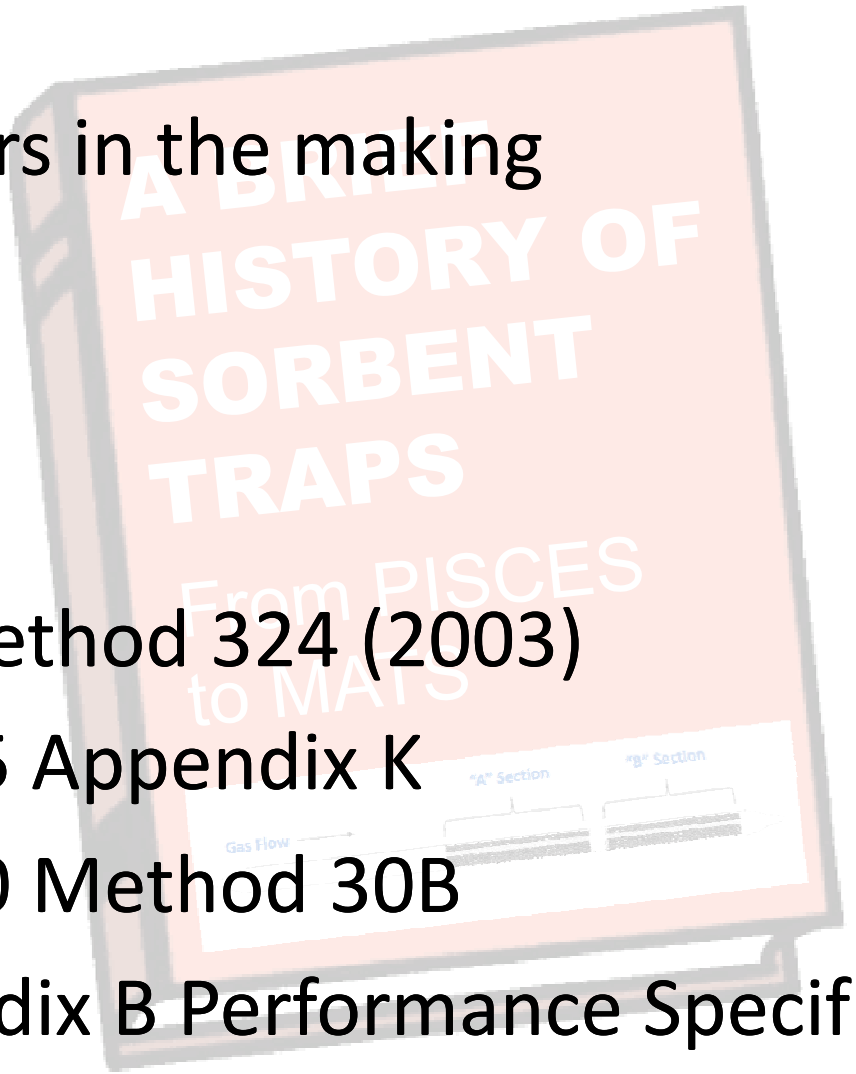
0.0035 µg/dscm

What are we talking about?

- Sorbent traps used to measure mercury
- Method 30B (and modified)
- Performance Specification 12B



The Journey



- 20 years in the making
- MESA
- FAMS
- QSEM
- EPA Method 324 (2003)
- Part 75 Appendix K
- Part 60 Method 30B
- Appendix B Performance Specification 12B

Players


FRONTIER
GEOSCIENCES
FRONTIER
GLOBAL SCIENCES


ADA
ENVIRONMENTAL SOLUTIONS


EERC
Energy & Environmental Research Center


OHIO LUMEX


EPRI
ELECTRIC POWER
RESEARCH INSTITUTE


U.S. DEPARTMENT OF
ENERGY


NETL


UNITED STATES
ENVIRONMENTAL PROTECTION AGENCY


CleanAir

What are sorbent traps used for?

Monitoring

Testing

Testing

- RATA
- MATS Planning
- LEE Evaluation
- Control Equipment Evaluation
- Permit Compliance

EPA Method 30B

Monitoring

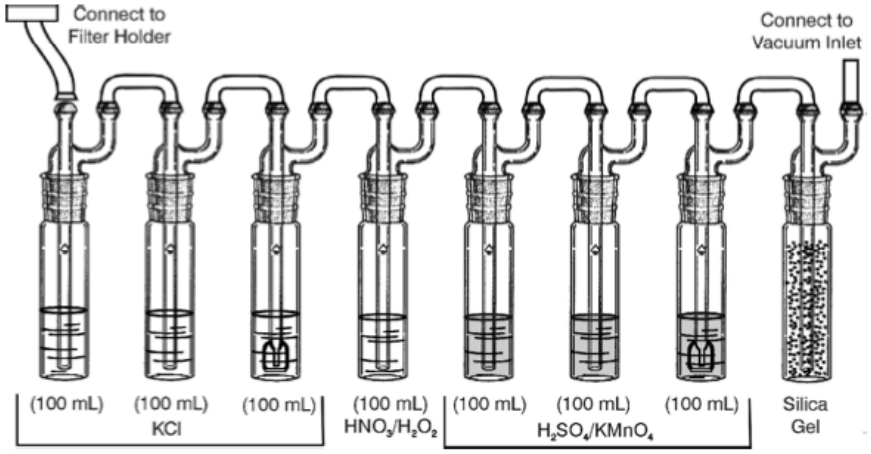
Hg CEMS
Back-up

Performance Specification 12B

Hg CEMS
Alternative

- Simplicity
- NIST-traceable
- It works
- Cost-effective

Method 30B
vs
Ontario Hydro Method



STMMS
vs
Hg CEMS

Simplicity

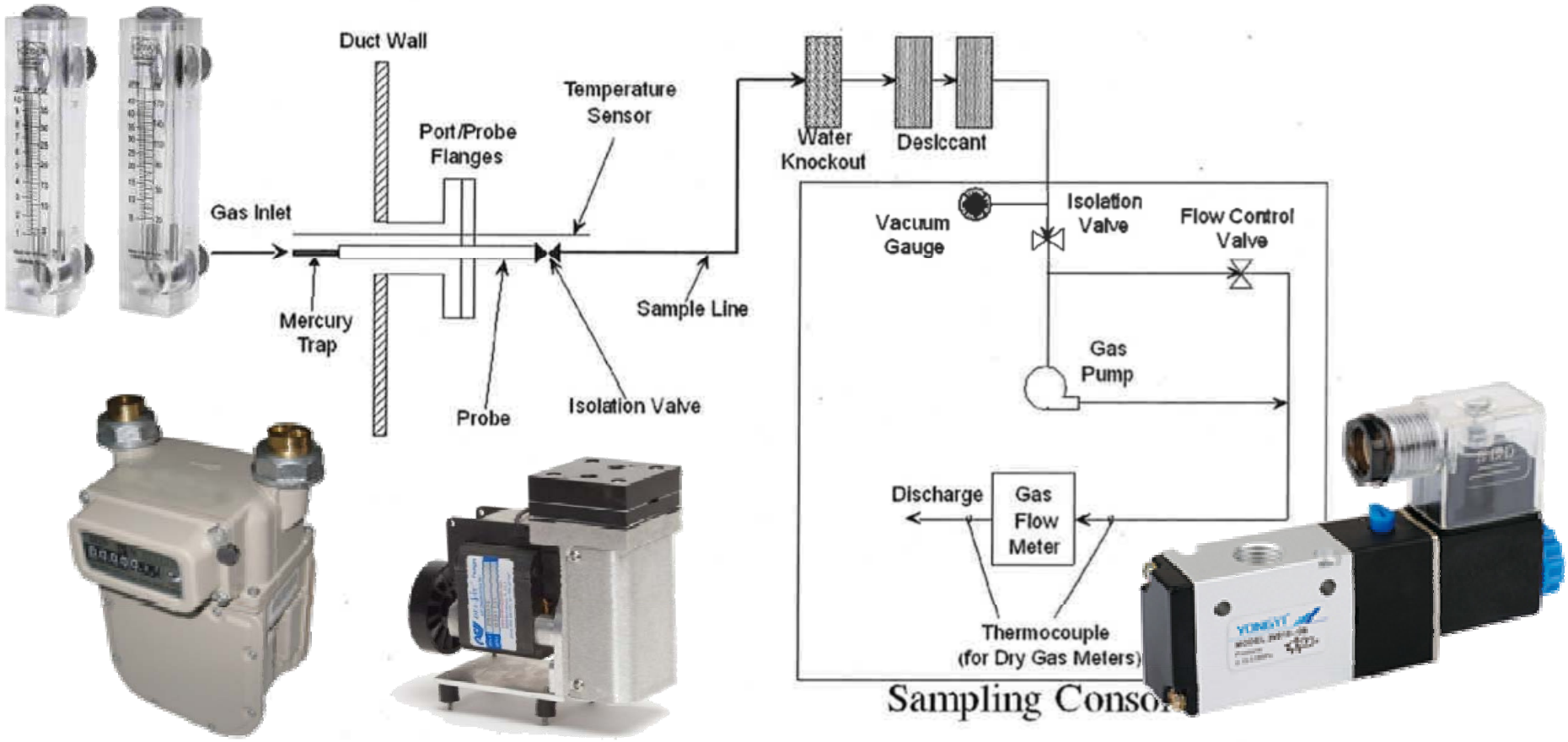
No hazardous chemicals

Simplicity

Simple to ship traps

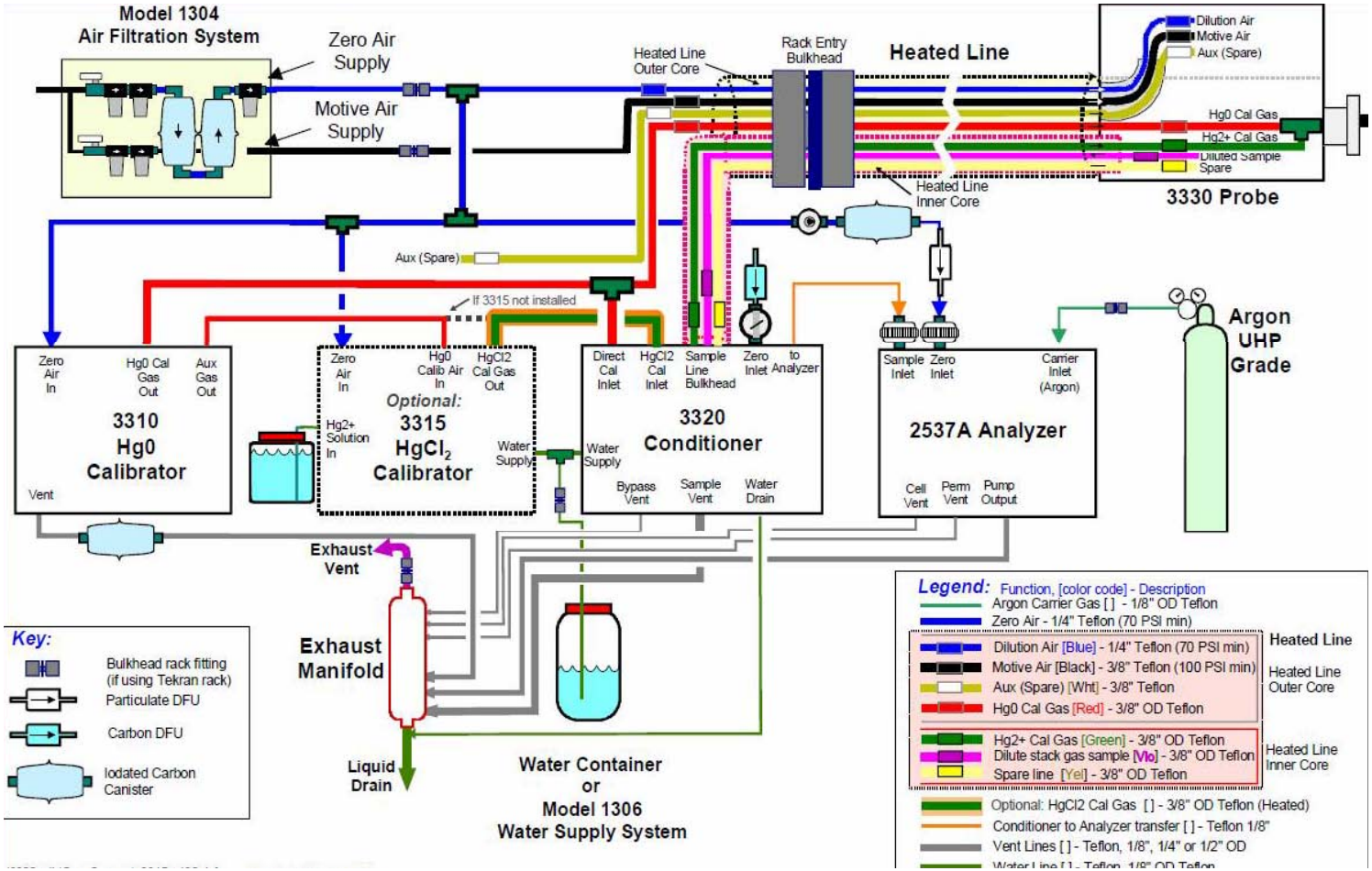
Simplicity

Simple mechanical equipment



Simplicity

Simple mechanical equipment

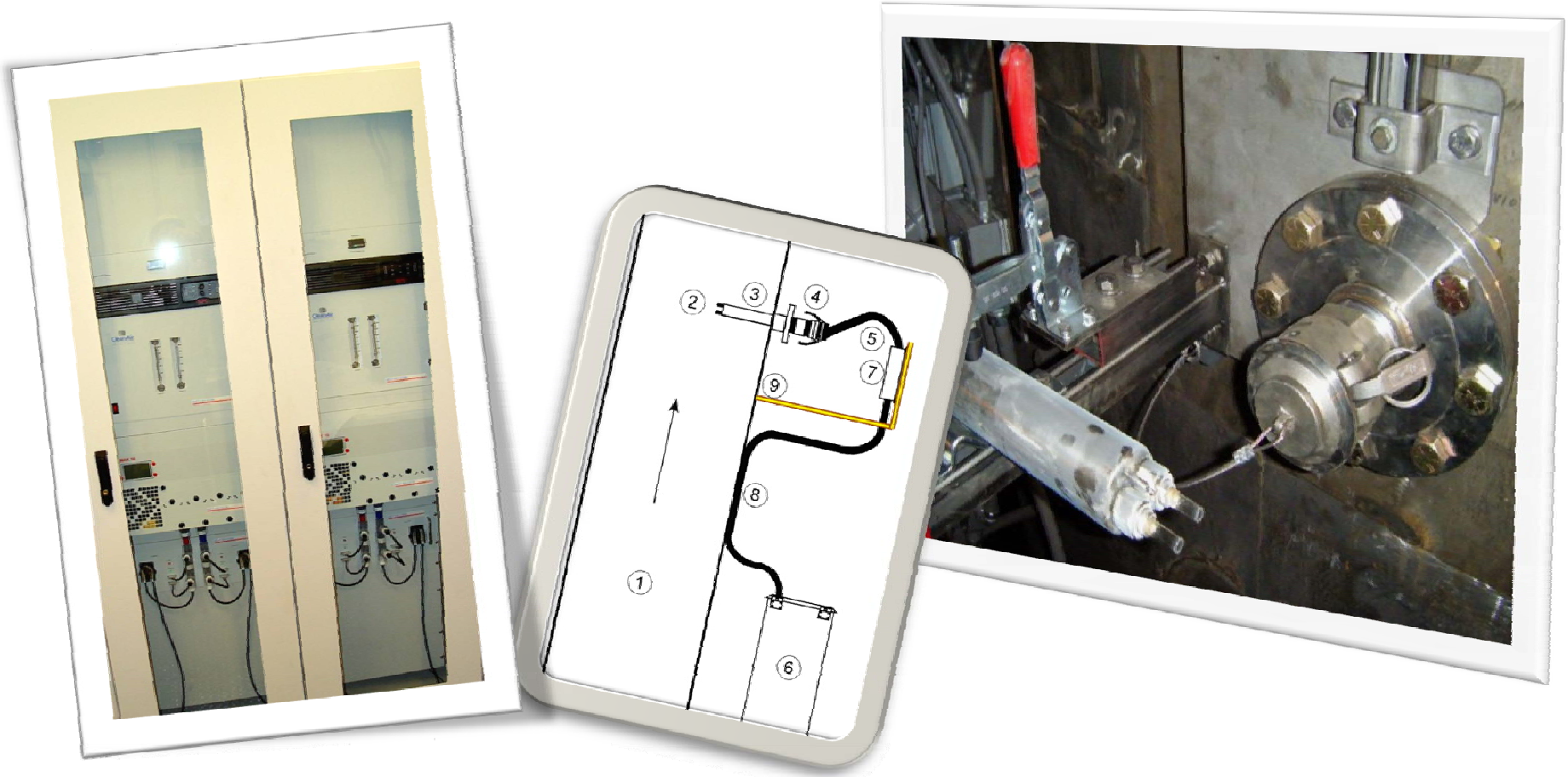


Simplicity

No on-site Hg calibration materials

Simplicity

Permanent systems install in 1-3 days

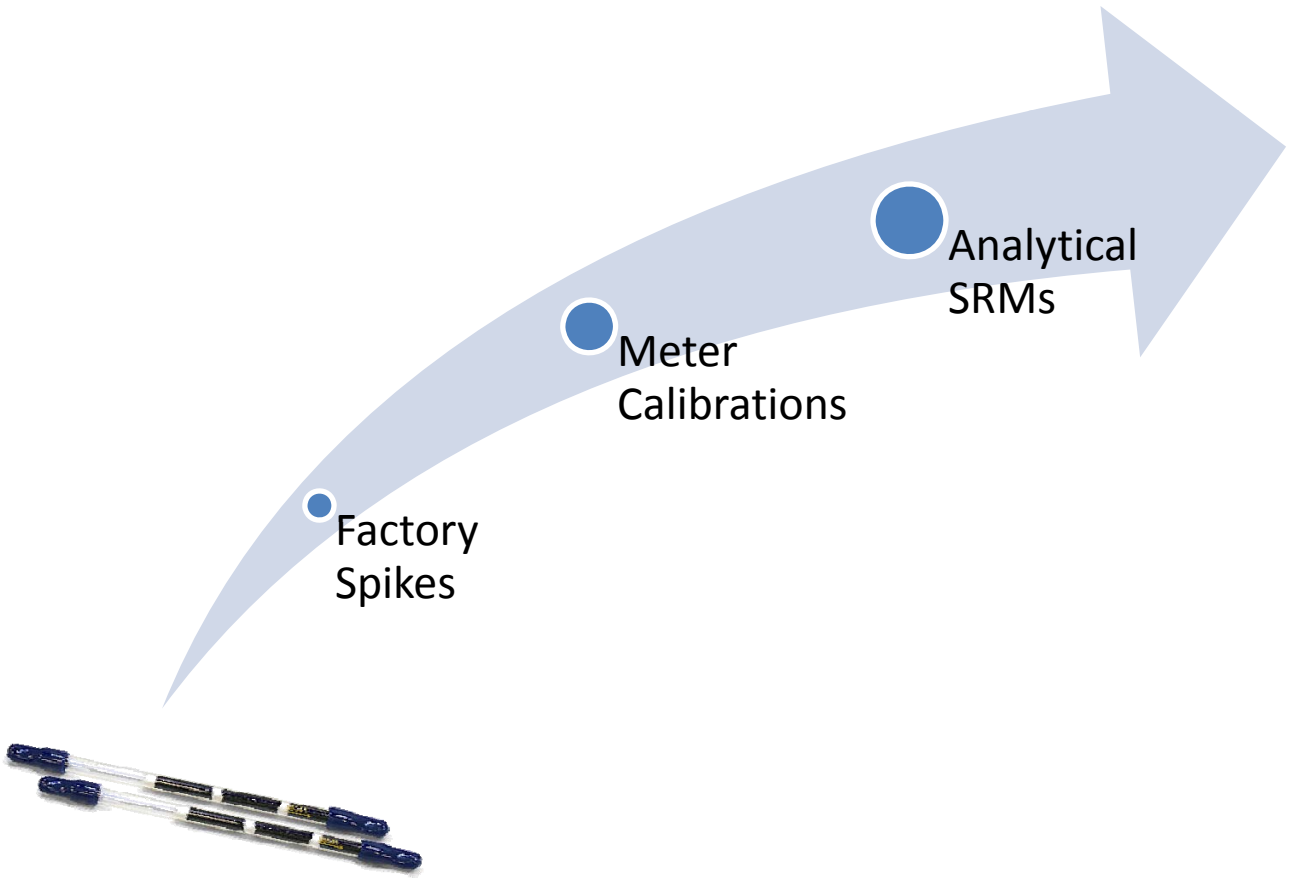


Certification Requirements
Hg CEMS versus STMMS

Hg CEMS	STMMS
7-day calibration error test	RATA
Linearity test	
3-level system integrity check	
Cycle time test	
RATA	

4.1.2 *Sorbent Trap Monitoring Systems.* For the initial certification of a sorbent trap monitoring system, only a RATA is required.

NIST-Traceable



NIST
National Institute of
Standards and Technology
U.S. Department of Commerce

It works

- No Hg transport issues
- Very low MDL possible
- Built-in QA/QC

$$MDL = \frac{mdl_a}{\dot{Q}_{sample} \times Time}$$

It works

- No Hg transport issues
- Very low MDL possible
- Built-in QA/QC

✓Spike recovery

✓Breakthrough

✓Paired trap agreement

✓Proportional sampling

It's cost-effective

…but not cheap.

- Hardware about ⅓ the cost of CEMS
- Operating costs about ½ cost of CEMS

	Type	EPA Estimate[b]	Reality[c]
Capital Costs	CEMS	$220,000	$300-400,000
	Sorbent trap	N/A	$100-150,000
Ongoing Costs[d]	CEMS	$77,000	$50-75,000
	Sorbent trap	N/A	$20-30,000

[a] Costs do not include stack or platform modifications

[b] From EPA CEMS Cost Model 03/07/07 w/ 10% inflation adjustment to 2012

[c] Vendor information

[d] Annual Costs. Without capital recovery

Sorbent Trap 101

- Total mercury *vapor*
  - Elemental vapor
  - Oxidized (Ionic) vapor

Hg^0 Hg^{2+} $Hg^0 + Hg^{2+}$

- Sometimes…Particle-bound – Hg_P
- Iodated activated carbon
- Paired sampling
- Atomic spectrometry analysis

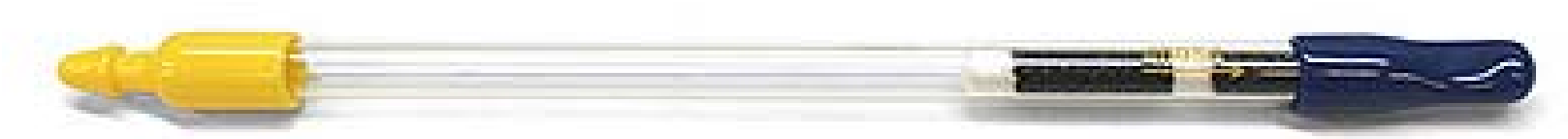
METHOD 30B – DETERMINATION OF TOTAL VAPOR PHASE MERCURY EMISSIONS FROM COAL-FIRED COMBUSTION SOURCES USING CARBON SORBENT TRAPS

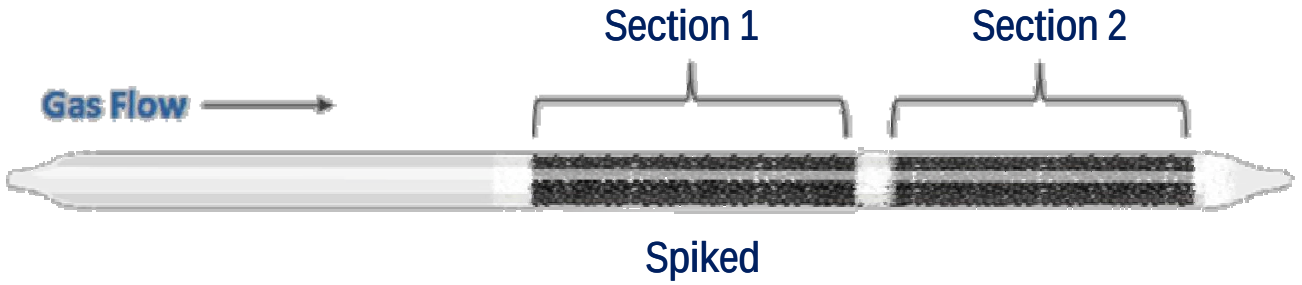
1.0 Scope and Application

What is Method 30B?

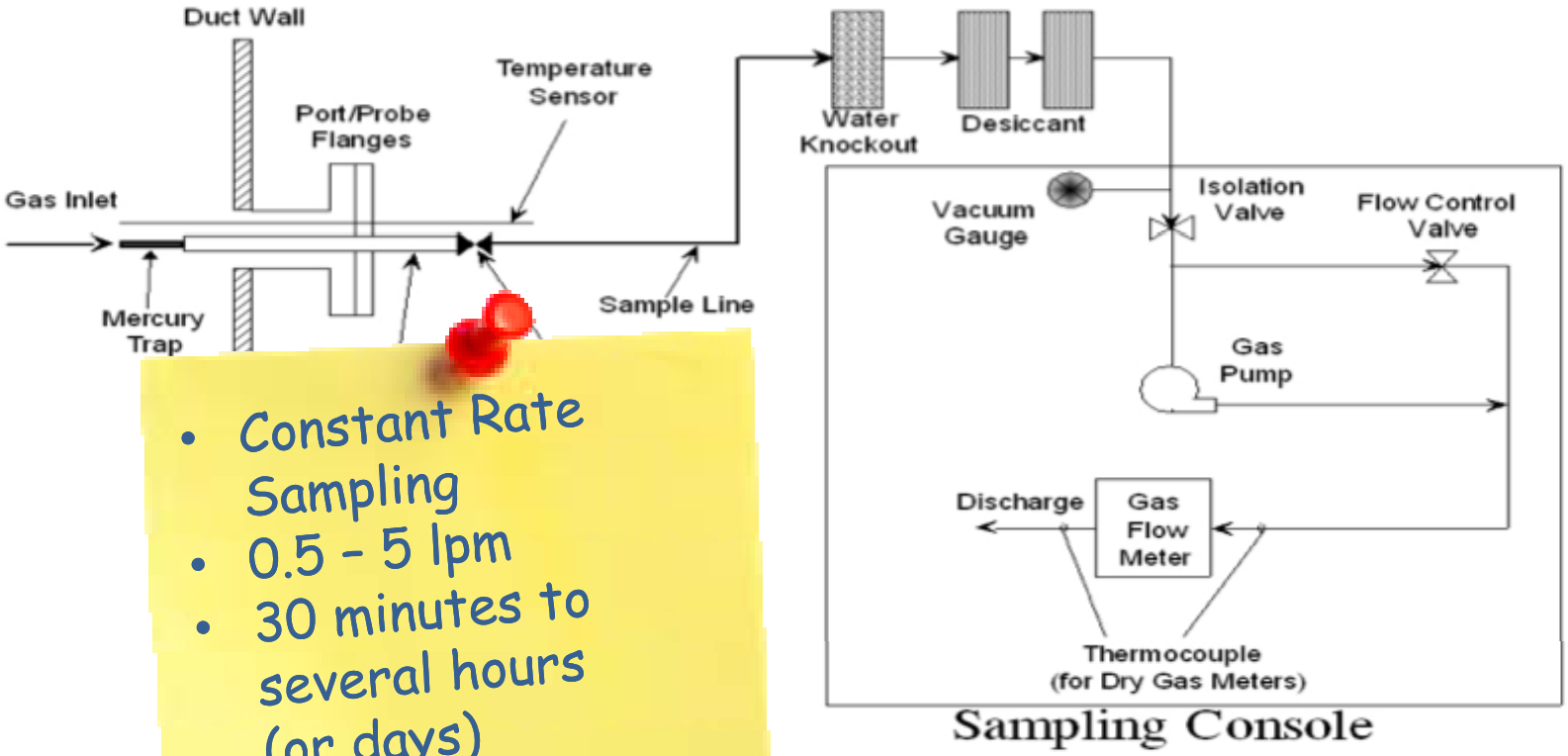
Method 30B is a procedure for measuring total vapor phase mercury (Hg) emissions from coal-fired combustion sources using sorbent trap sampling and an extractive or thermal analytical technique. This method is only intended for use only under relatively low particulate conditions (e.g., sampling after all pollution control devices). Quality assurance and quality control requirements are included to assure that you, the tester, collect data of known and acceptable quality for each testing program. This method does not completely describe all equipment, supplies, and sampling and

Method 30B Traps





Sampling



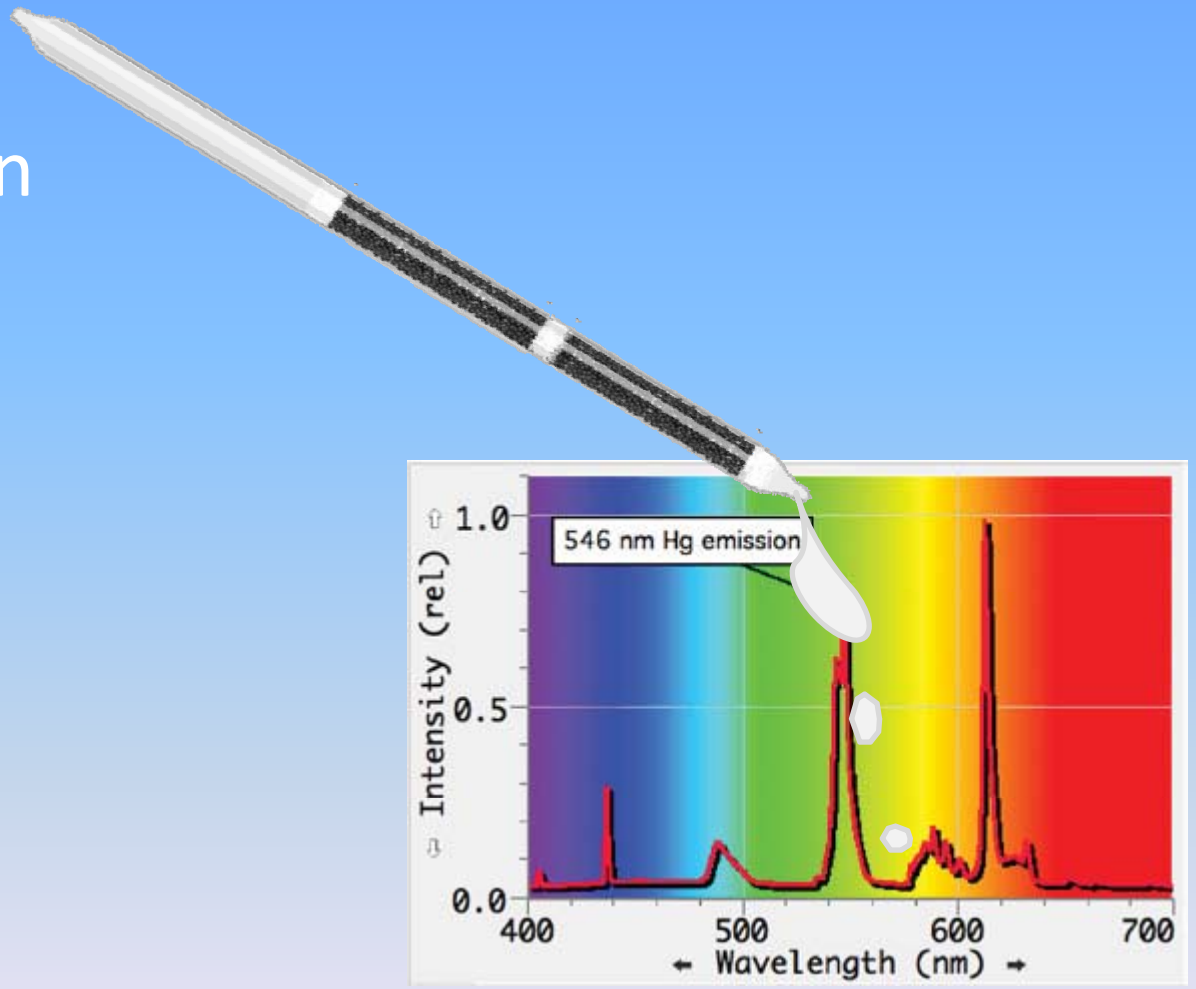
- Constant Rate Sampling
- 0.5 – 5 lpm
- 30 minutes to several hours (or days)
- Dry gas meter

Analysis

11.0 Analytical Procedures

The analysis of Hg in the field and quality control samples may be conducted using any instrument or technology capable of quantifying total Hg from the sorbent media and meeting the performance criteria in this method. Because multiple analytical approaches, equipment and techniques are appropriate for the analysis of sorbent traps, it is not possible to provide detailed, technique-specific analytical procedures. As they

1. Extraction
2. Analysis



3.9 *Thermal Analysis* means an analytical technique where the contents of the sorbent traps are analyzed using a thermal technique (desorption or combustion) to release the captured Hg in a detectable form for quantification.

3.10 *Wet Analysis* means an analytical technique where the contents of the sorbent tube are first leached or digested to quantitatively transfer the captured Hg to liquid solution for subsequent analysis.

Analysis – Thermal

Ohio Lumex Company, 2012

Thermal Mercury Analyzers

Ohio Lumex 915+ with RP-M324
Teledyne Leeman Labs Hydra II C
LECO AMA254
Milestone, Inc. DMA-80
Nippon Instruments MA-3000

Analysis – Wet

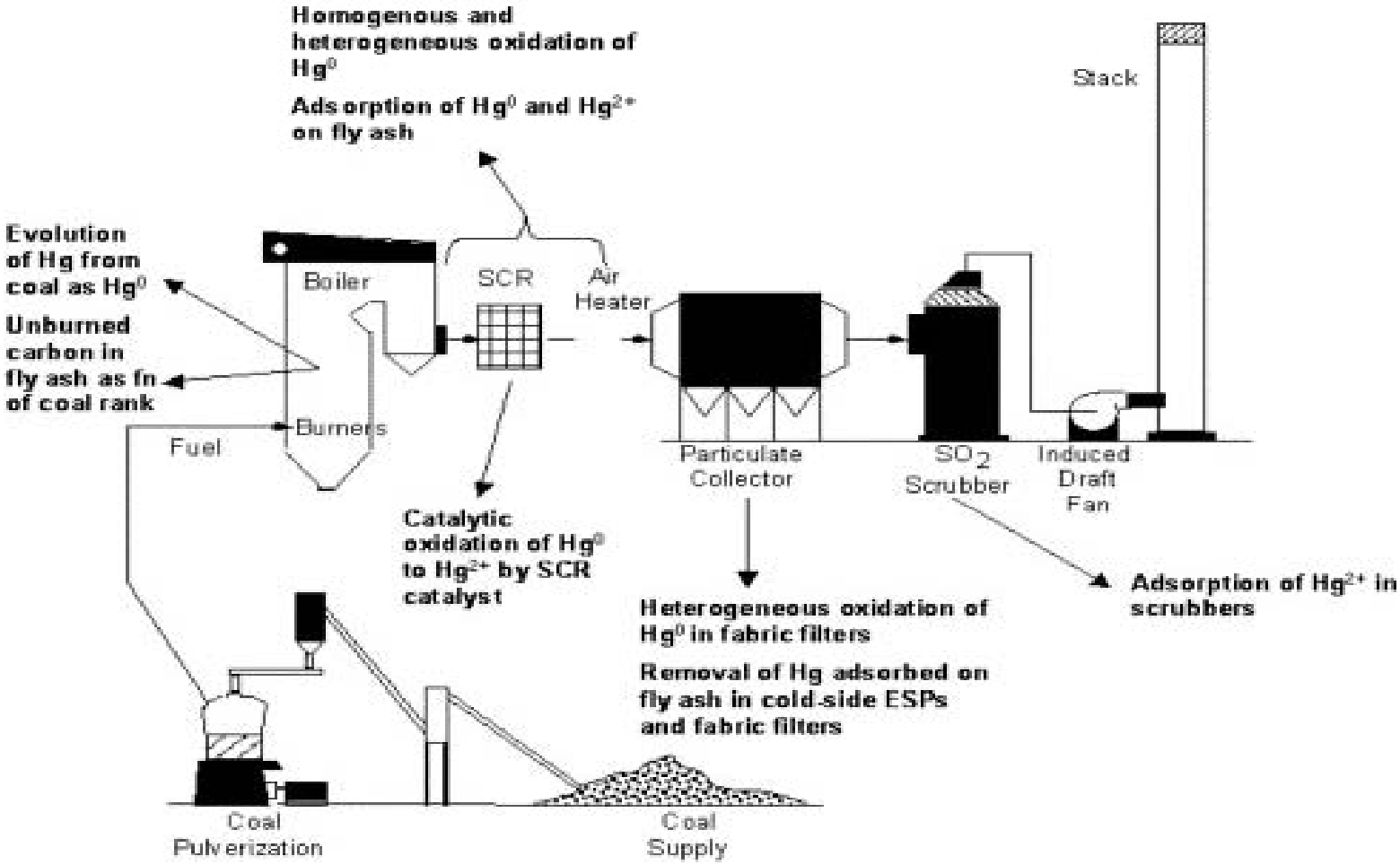
Brooks Rand Labs, 2012

Analyses

- Atomic fluorescence spectrometry (EPA Method 1631, Revision E)
- Atomic absorption spectrometry (EPA Method 7473)
- Gold amalgamation
- Zeeman-corrected AAS

Sorbent Trap 102 Speciation

Modified Method 30B



Description: FAMS (Modified US EPA Method 30B Trap – Speciation)

The FAMS method is very similar to EPA Method 30B. The FAMS method collects particulate bound mercury (PHg) on a filter and gaseous oxidized mercury Hg(II) and gaseous elemental mercury Hg(0) on solid sorbent media. While the FAMS method and Ontario Hydro method have undergone multiple side-by-side inter-comparison testing during US Department of Energy sponsored studies, there has never been a full EPA Method 301 validation of FAMS that would definitively assess its overall precision and bias.

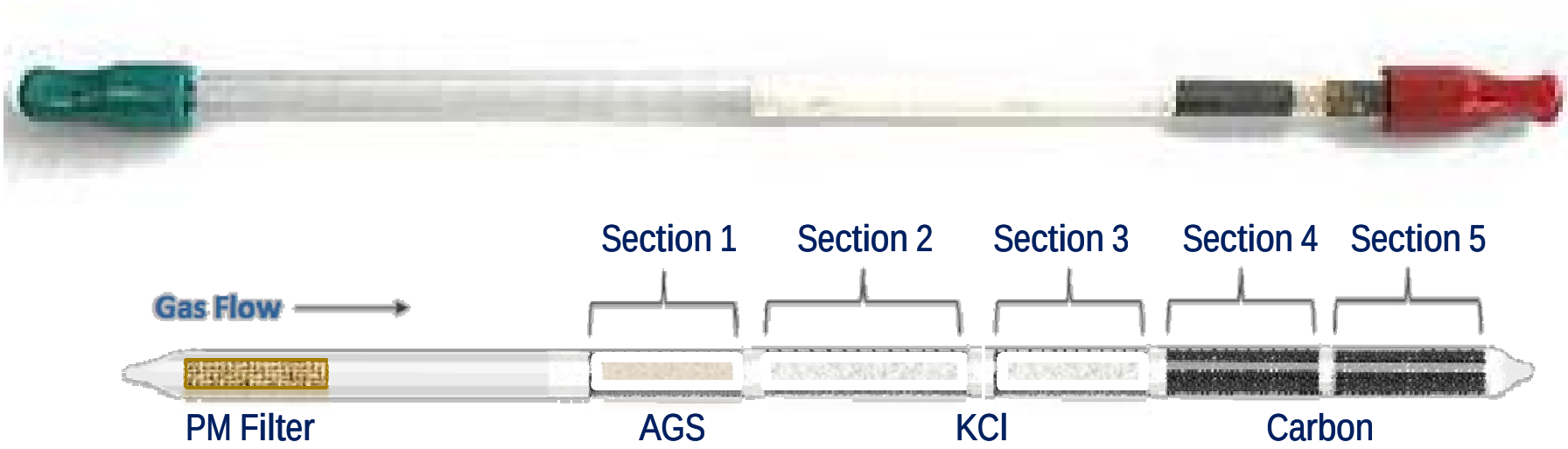
Modified US EPA Method 30B Trap – Speciation Version

(Flue gas Adsorbent Mercury Speciation (FAMS) Method)

Principle Of Operation:

The FAMS sorbent trap Hg speciation method is a modified version of the US EPA Method 30B sorbent trap total Hg emissions. This modified version employs a particulate trap and a specialized sorbent trap designed to selectively capture oxidized gaseous Hg and a sorbent trap to selectively capture elemental gaseous Hg. Thus, the FAMS method relies on sequential selective capture to separate and quantify three mercury species, particulate Hg (PHg), gaseous oxidized (Hg(II)g), and gaseous elemental (Hg0). The principle of the FAMS method has three simple steps: (1) Particulate bound Hg is captured on a pre-filter and the gas phase Hg(II) and Hg(0) pass through to the first sorbent trap section where (2) oxidized gaseous mercury is captured then finally the remaining Hg, gaseous elemental Hg is captured on the (3) EPA Method 30B trap section.

Speciation Traps



Speciation Trap Sections listed in direction from stack gas entry:

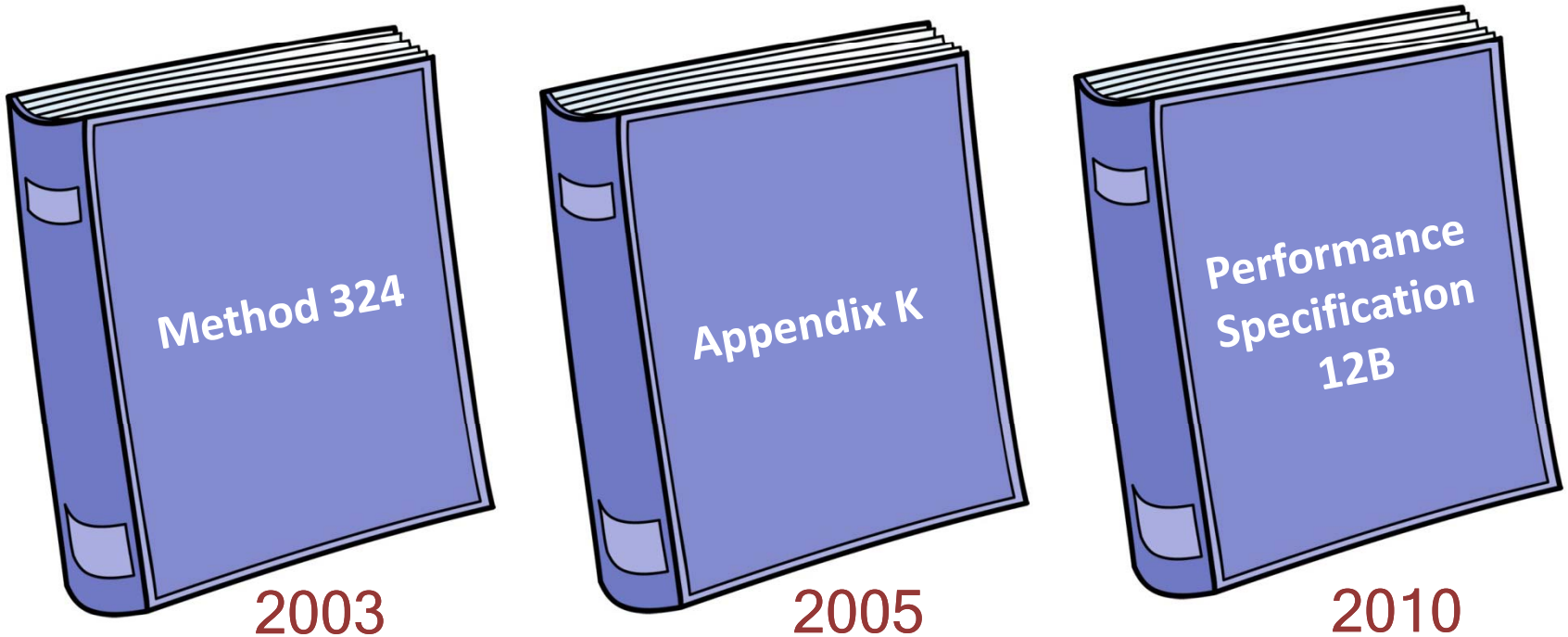
1. Acid Gas Scrubber (AGS)
2. Oxidized Mercury Analytical Bed
3. Oxidized Mercury Breakthrough Bed
4. Elemental Mercury Analytical Bed
5. Elemental Mercury Breakthrough Bed

Sorbent Trap 103 Monitoring

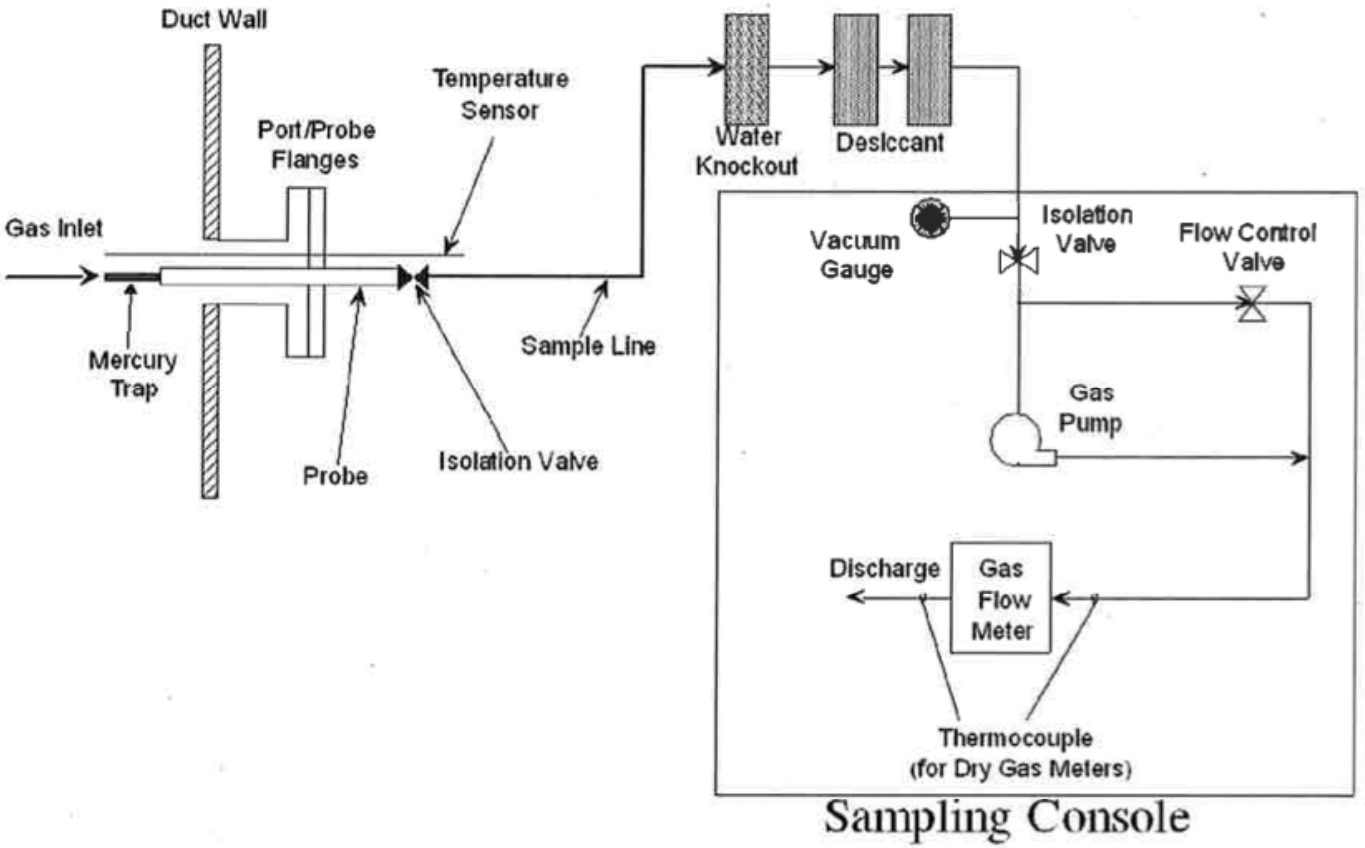
Performance Specification 12B – Specifications and Test Procedures For Monitoring Total Vapor Phase Mercury Emissions from Stationary Sources Using a Sorbent Trap Monitoring System

1.0 Scope and Application

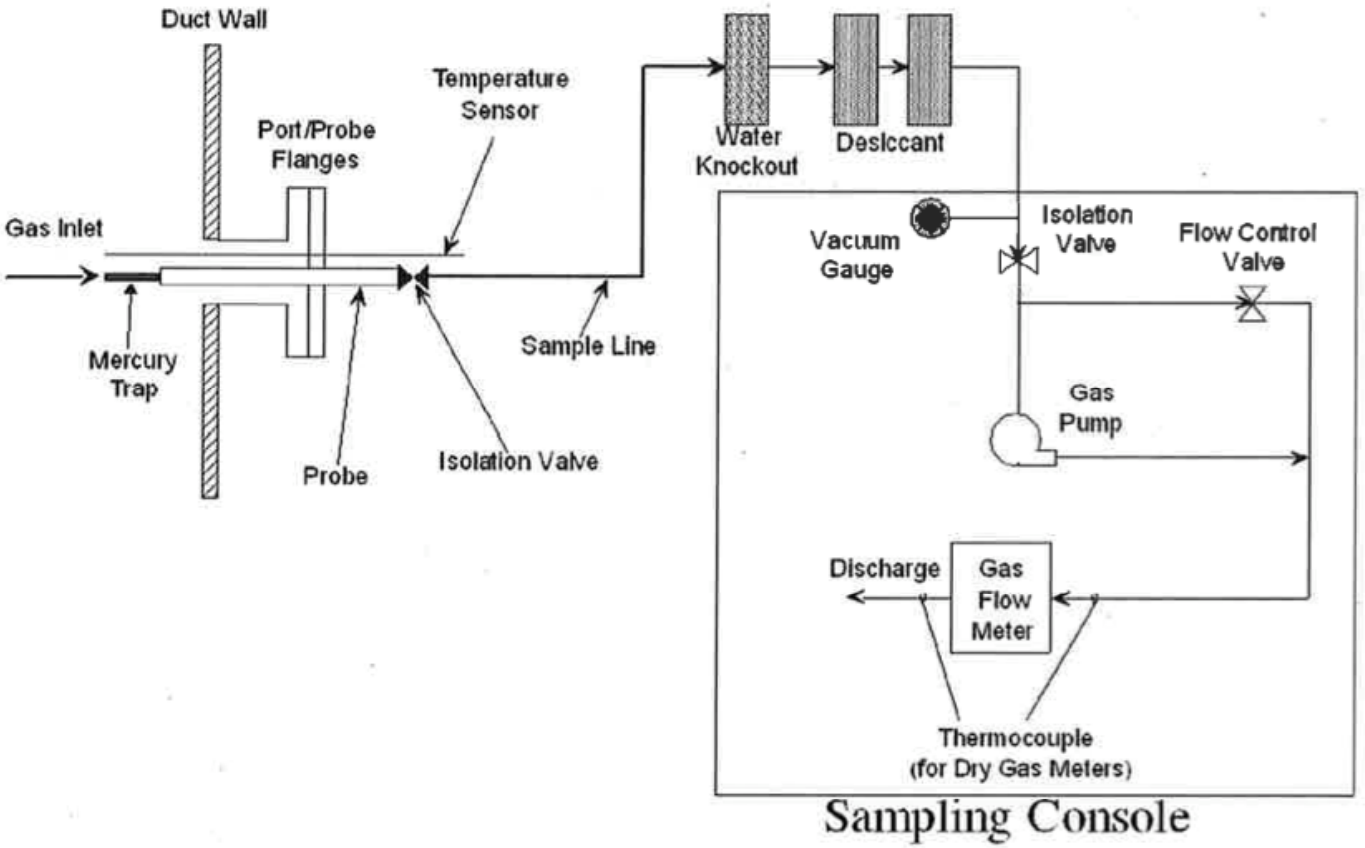
The purpose of Performance Specification 12B (PS 12B) is to establish performance benchmarks for, and to evaluate the acceptability of, sorbent trap monitoring systems used to monitor total vapor-phase mercury (Hg) emissions in stationary source flue gas streams. These monitoring systems involve continuous repetitive in-stack sampling using paired sorbent media traps with periodic analysis of the time-integrated samples. Persons using PS 12B should have a thorough working knowledge of Methods 1, 2, 3, 4, 5 and 30B in appendices A-1 through A-3 and A-8 to this part.


Method 324
Appendix K
Performance Specification 12B
2003
EU MACT
2005
CAMR
2010
PC MACT

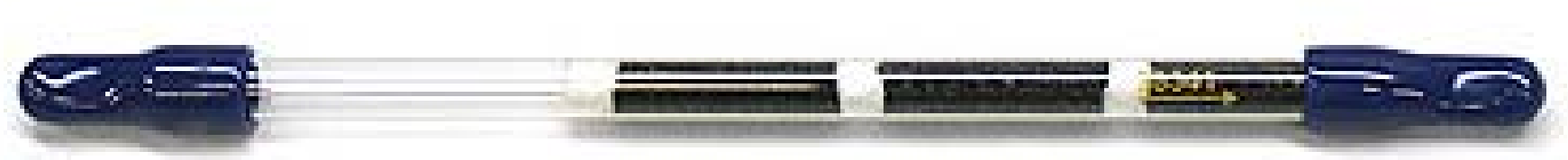
Testing – 30B

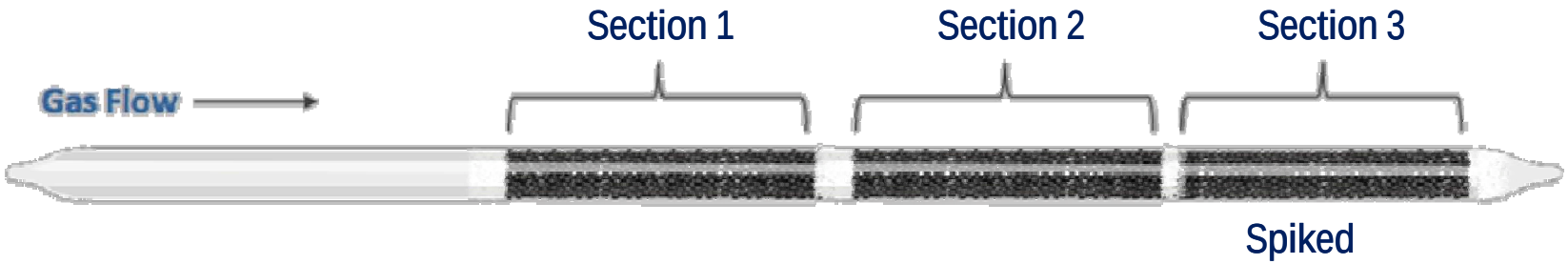

Duct Wall
Temperature Sensor
Port/Probe Flanges
Water Knockout
Desiccant
Gas Inlet
Vacuum Gauge
Isolation Valve
Flow Control Valve
Mercury Trap
Sample Line
Gas Pump
Probe
Isolation Valve
Discharge
Gas Flow Meter
Thermocouple (for Dry Gas Meters)
Sampling Console

Monitoring – 12B

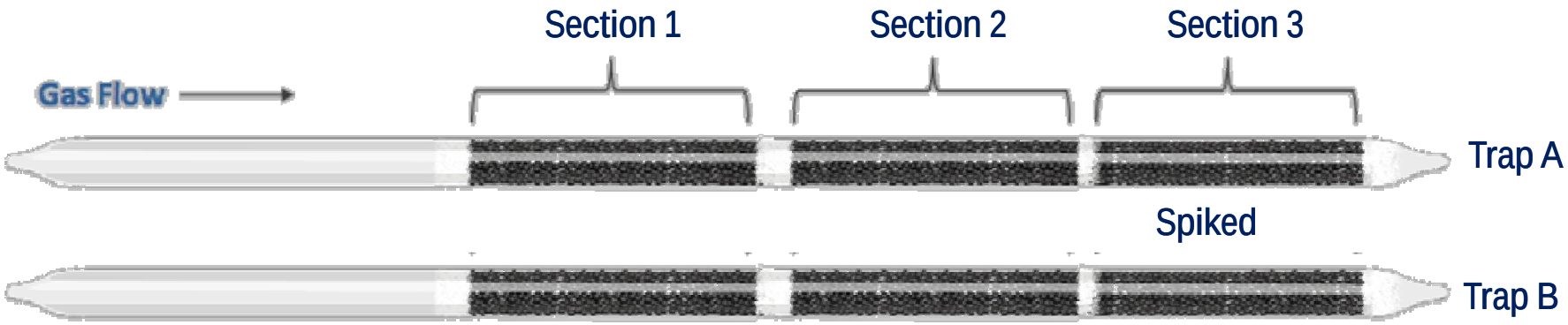


PS12B Sorbent Traps

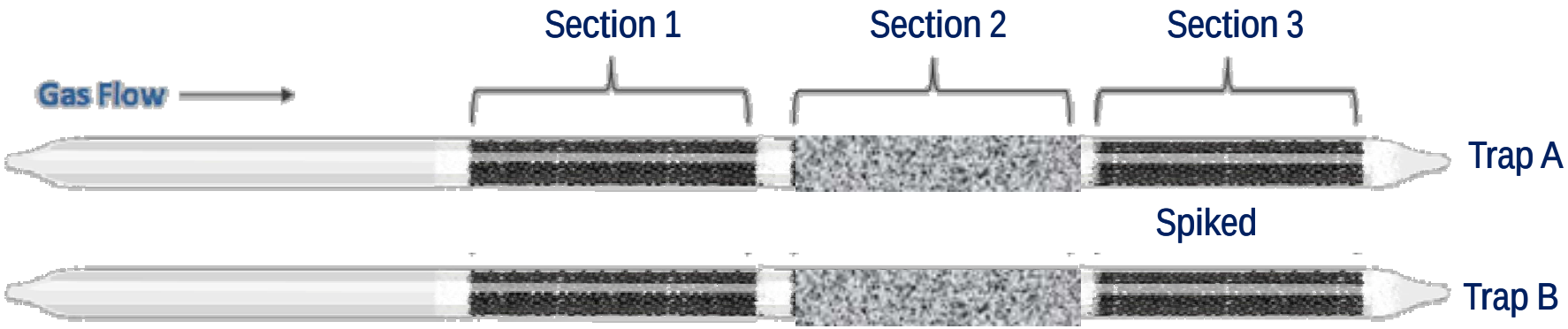




Quality Assurance



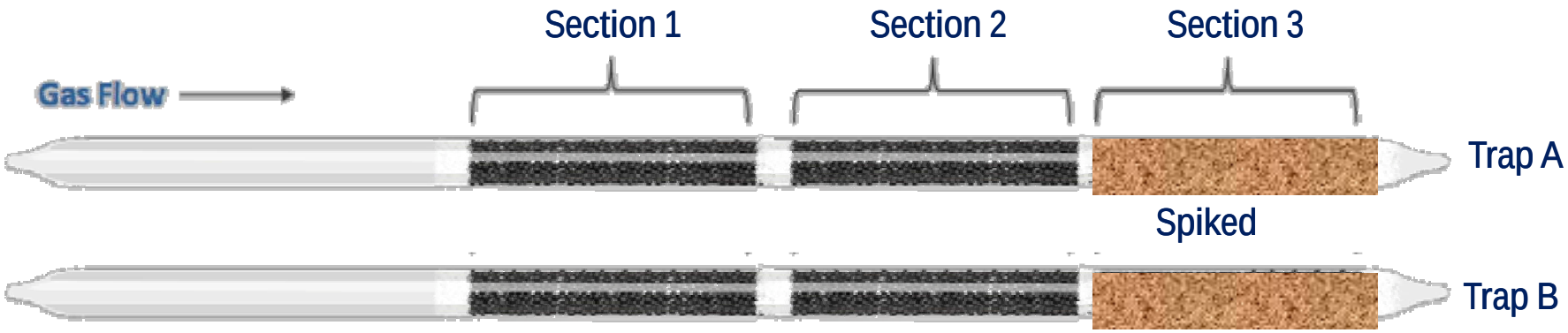
Quality Assurance



- Section 2 Breakthrough

$$\%B = \frac{M_2}{M_1} \times 100 \qquad \text{(Equation 12B-5)}$$

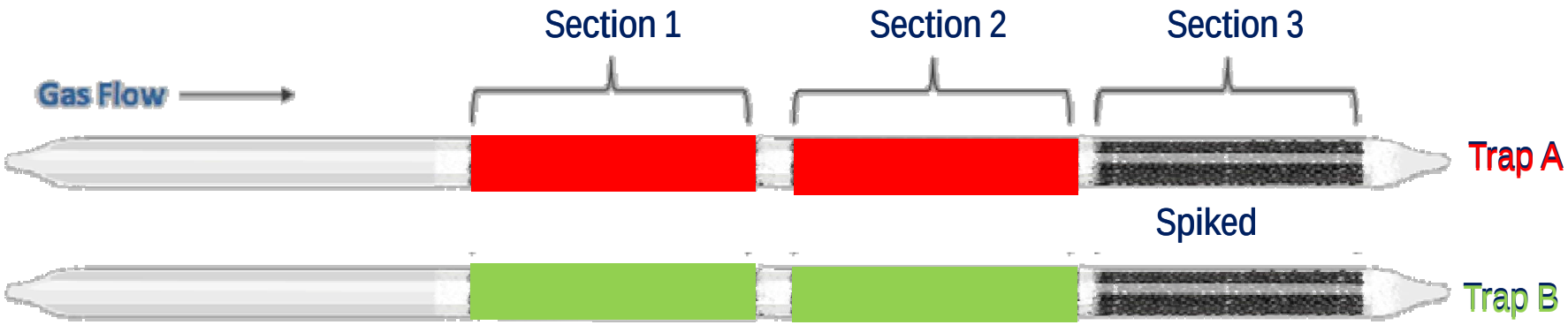
Quality Assurance



- Section 2 Breakthrough
- Section 3 Spike Recovery

$$\%R = \frac{M_3}{M_s} \times 100 \qquad \text{(Equation 12B-4)}$$

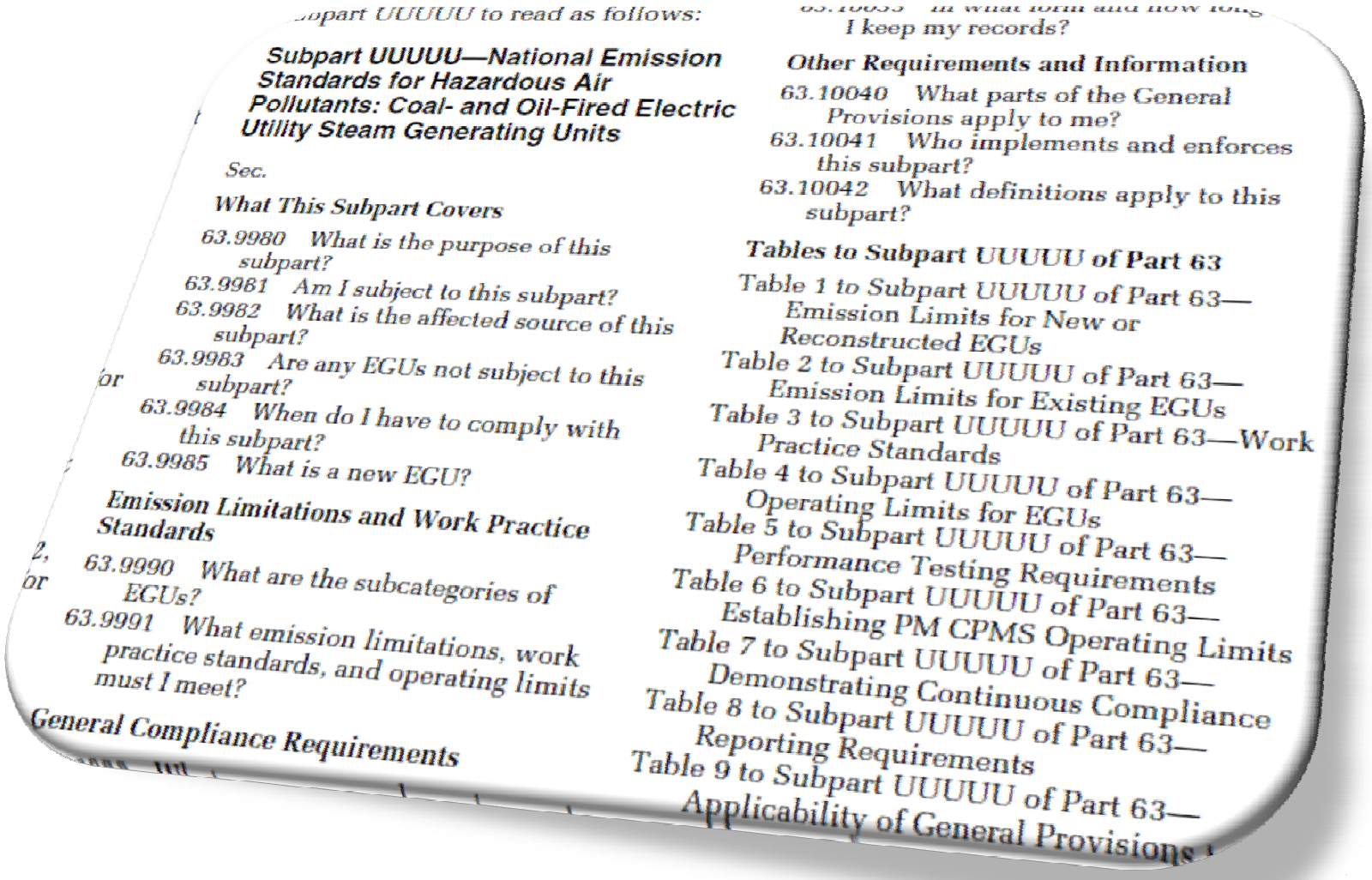
Quality Assurance



- Section 2 Breakthrough
- Section 3 Spike Recovery
- Paired sorbent trap agreement (%RD)

$$RD = \frac{|C_a - C_b|}{C_a + C_b} \, x\,100$$ (Equation 12B-7)

MATS



...bpart UUUUU to read as follows:

Subpart UUUUU—National Emission Standards for Hazardous Air Pollutants: Coal- and Oil-Fired Electric Utility Steam Generating Units

Sec.

What This Subpart Covers

63.9980 What is the purpose of this subpart?
63.9981 Am I subject to this subpart?
63.9982 What is the affected source of this subpart?
63.9983 Are any EGUs not subject to this subpart?
63.9984 When do I have to comply with this subpart?
63.9985 What is a new EGU?

Emission Limitations and Work Practice Standards

63.9990 What are the subcategories of EGUs?
63.9991 What emission limitations, work practice standards, and operating limits must I meet?

General Compliance Requirements

...63.10033 In what form and how long I keep my records?

Other Requirements and Information

63.10040 What parts of the General Provisions apply to me?
63.10041 Who implements and enforces this subpart?
63.10042 What definitions apply to this subpart?

Tables to Subpart UUUUU of Part 63

Table 1 to Subpart UUUUU of Part 63—Emission Limits for New or Reconstructed EGUs
Table 2 to Subpart UUUUU of Part 63—Emission Limits for Existing EGUs
Table 3 to Subpart UUUUU of Part 63—Work Practice Standards
Table 4 to Subpart UUUUU of Part 63—Operating Limits for EGUs
Table 5 to Subpart UUUUU of Part 63—Performance Testing Requirements
Table 6 to Subpart UUUUU of Part 63—Establishing PM CPMS Operating Limits
Table 7 to Subpart UUUUU of Part 63—Demonstrating Continuous Compliance
Table 8 to Subpart UUUUU of Part 63—Reporting Requirements
Table 9 to Subpart UUUUU of Part 63—Applicability of General Provisions

MATS Requirements

New and existing coal, IGCC and petcoke EGU's will have to monitor mercury

- Measure total vapor-phase Hg
- Report units of standard (lb/TBtu and/or lb/GWh)

Nuances

- No missing data procedures
- No bias adjustment factor
- Startup and Shutdown
- Possible LEE exemption

LEE Exemption

- Mercury, Avg < 10% of limit or PTE <29 lb/yr

  0.12 lb/Tbtu (0.0013 lb/GWh) for existing units, not low-rank coal

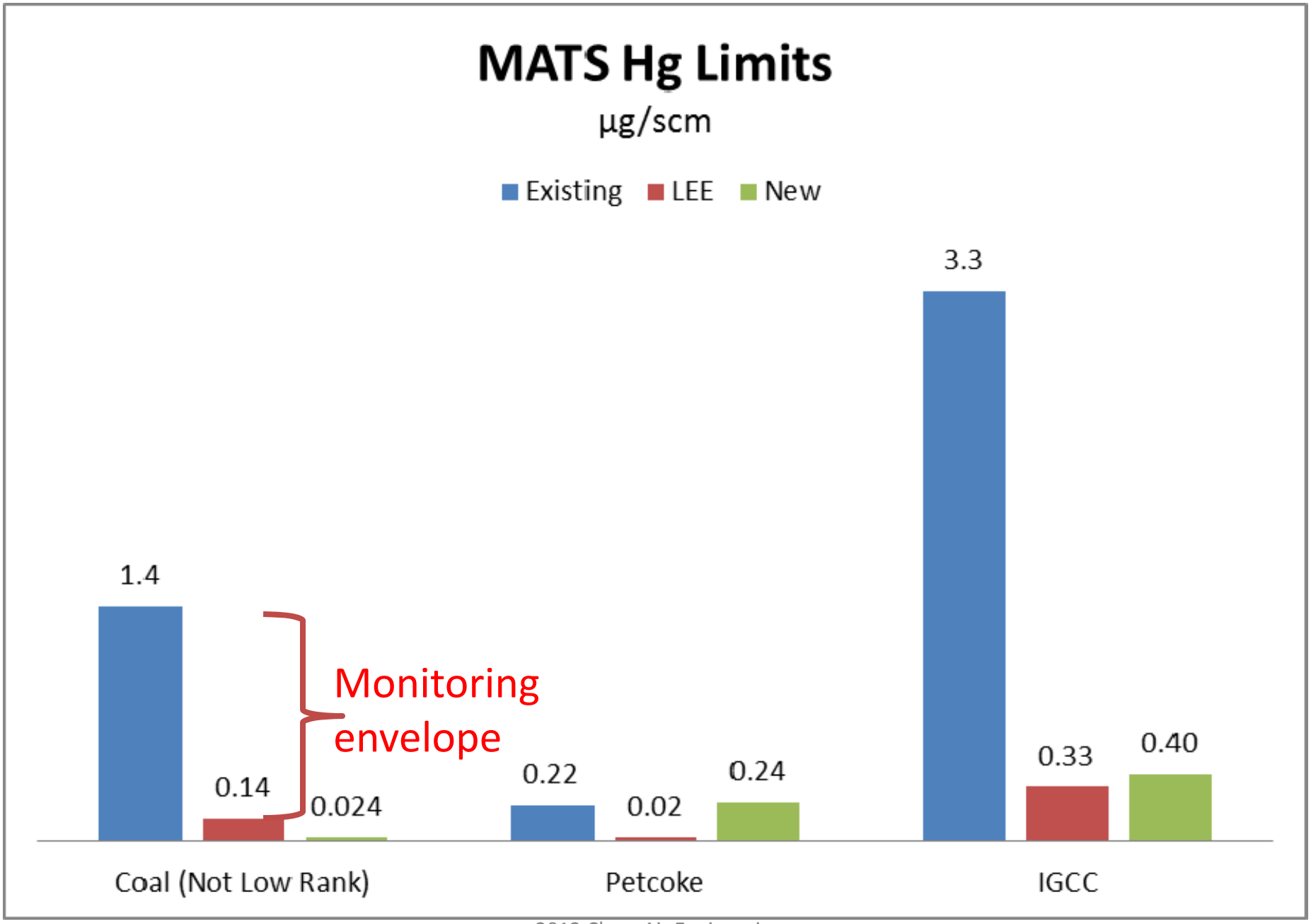
- 30-day stack test annually

Cannot claim LEE if:

- Scrubber with bypass, or
- New Unit

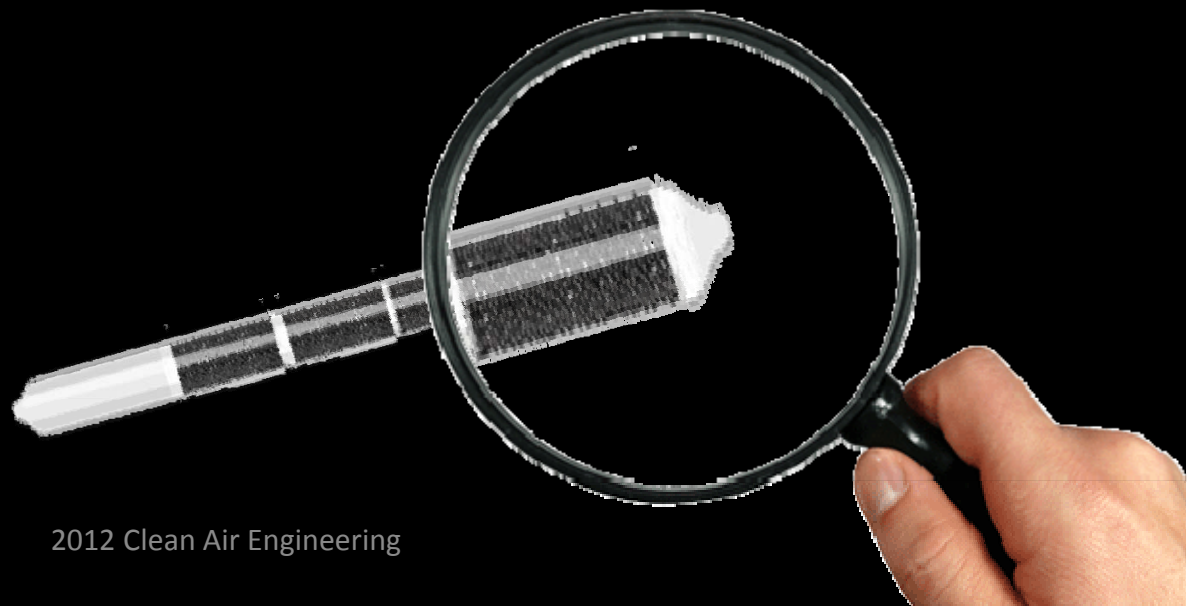
LEE Testing

- EPA Method 30B for 30 operating days
- Single point (10% centroidal area)
- Equal-length runs (minimum of three)
- 10-day maximum run length
- Hourly electrical load (MW) if calculating lb/GWh
- Also may need CO_2/O_2, H_2O, Q_{stack}
  - Certified CEMS
  - Daily Reference Methods


MATS Hg Limits
µg/scm
Existing
LEE
New
1.4
0.14
0.024
0.22
0.02
0.24
3.3
0.33
0.40
Monitoring envelope
Coal (Not Low Rank)
Petcoke
IGCC

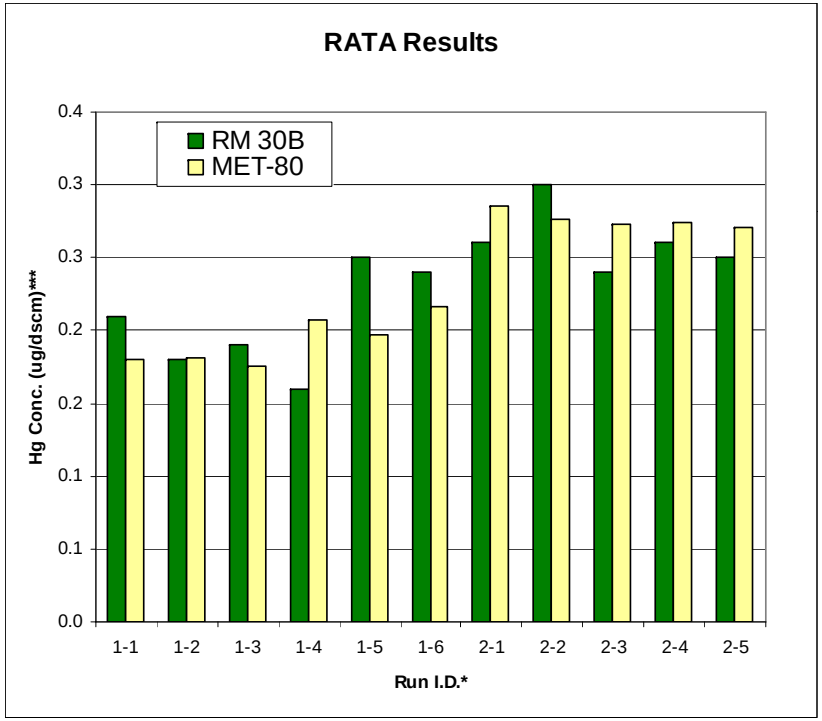
Sorbent trap monitoring at ridiculously low levels…

- How accurate is it?
- How reproducible is it?
- How reliable is it?
- How low can we go?



Accuracy

	Hg conc. (µg/dscm)			
	RM	MET80		
Run*	$C_{RM - Avg}$	$C_{CMMS-AVG}$	DIFF	%DIFF
1-1	**0.21**	**0.18**	0.03	14.3%
1-2	**0.18**	**0.18**	0.00	-0.6%
1-3	**0.19**	**0.18**	0.01	7.4%
1-4	**0.16**	**0.21**	-0.05	-29.4%
1-5	**0.25**	**0.20**	0.05	21.2%
1-6	**0.24**	**0.22**	0.02	10.0%
2-1	**0.26**	**0.29**	-0.03	-9.6%
2-2	**0.30**	**0.28**	0.02	8.0%
2-3	**0.24**	**0.27**	-0.03	-13.8%
2-4	**0.26**	**0.27**	-0.01	-5.4%
2-5	**0.25**	**0.27**	-0.02	-8.4%
All data (n=11)	**0.231**	**0.231**	0.0004 0.021 9.2%	

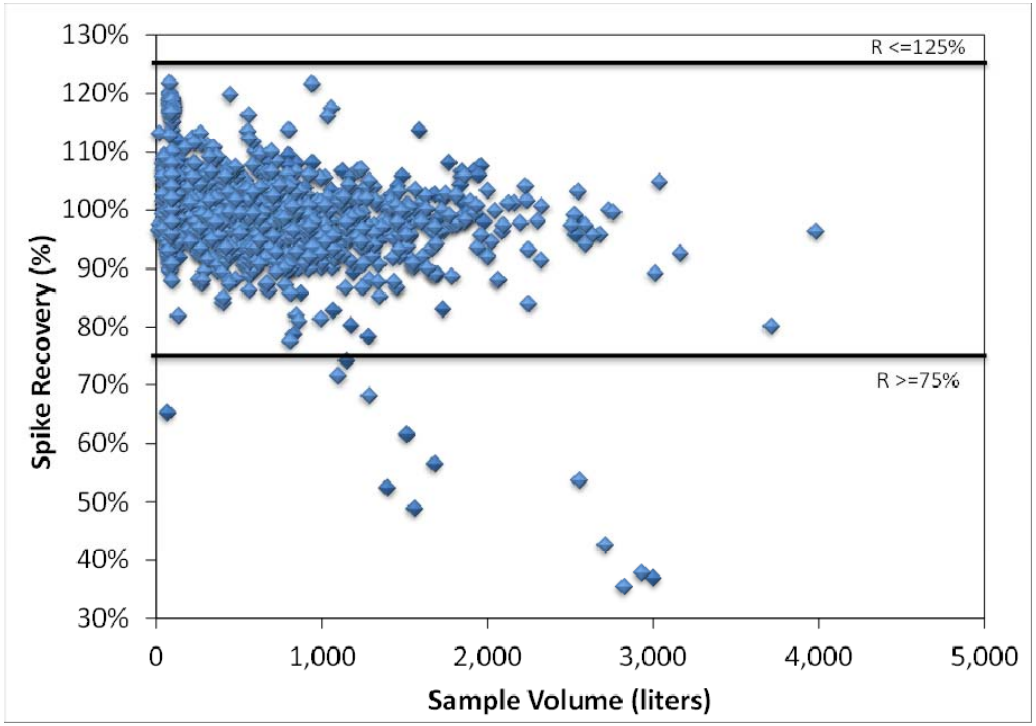


Traceability

- NIST-traceable standards
- Analyte spiking

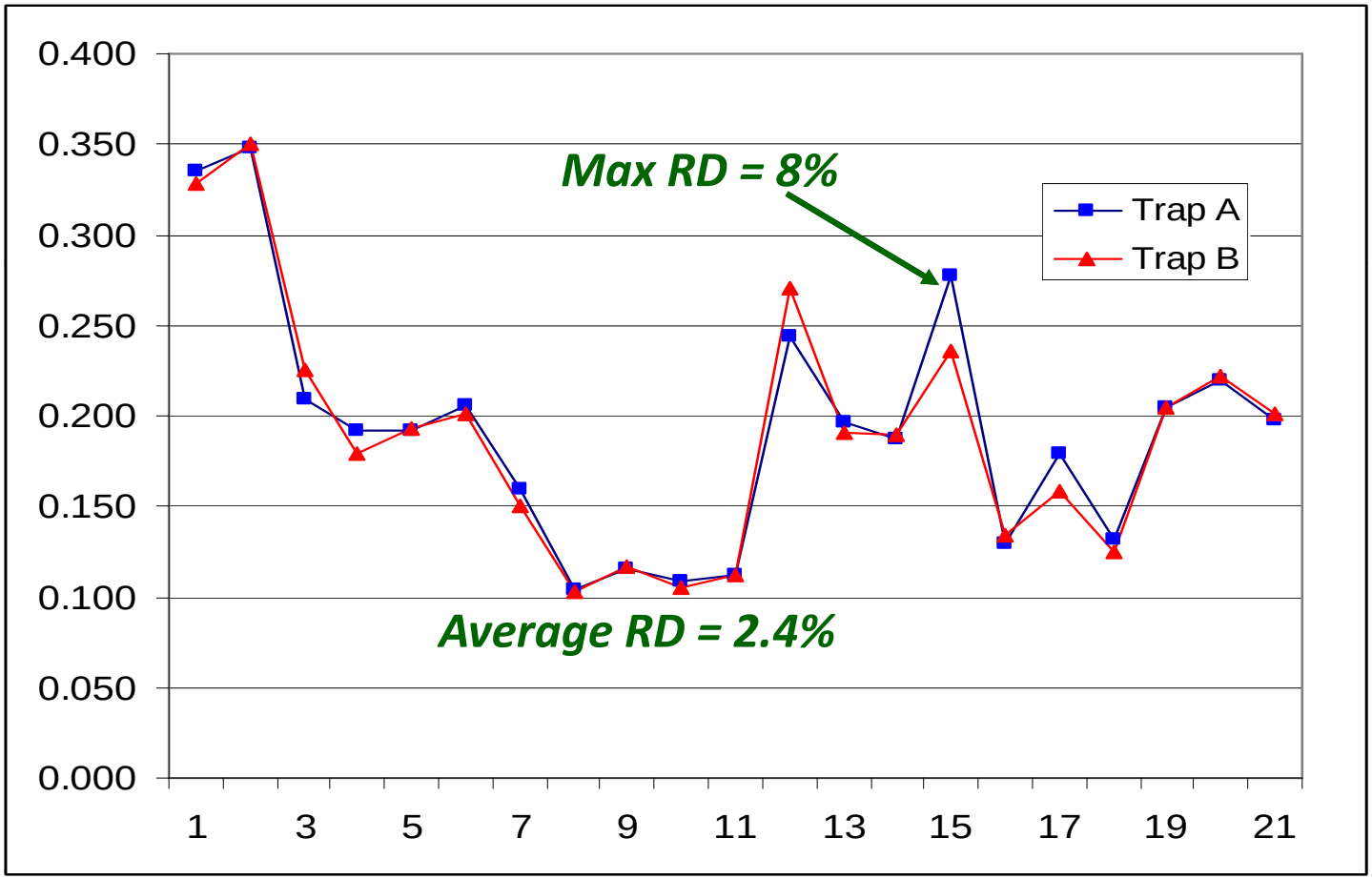
500 traps

3 years



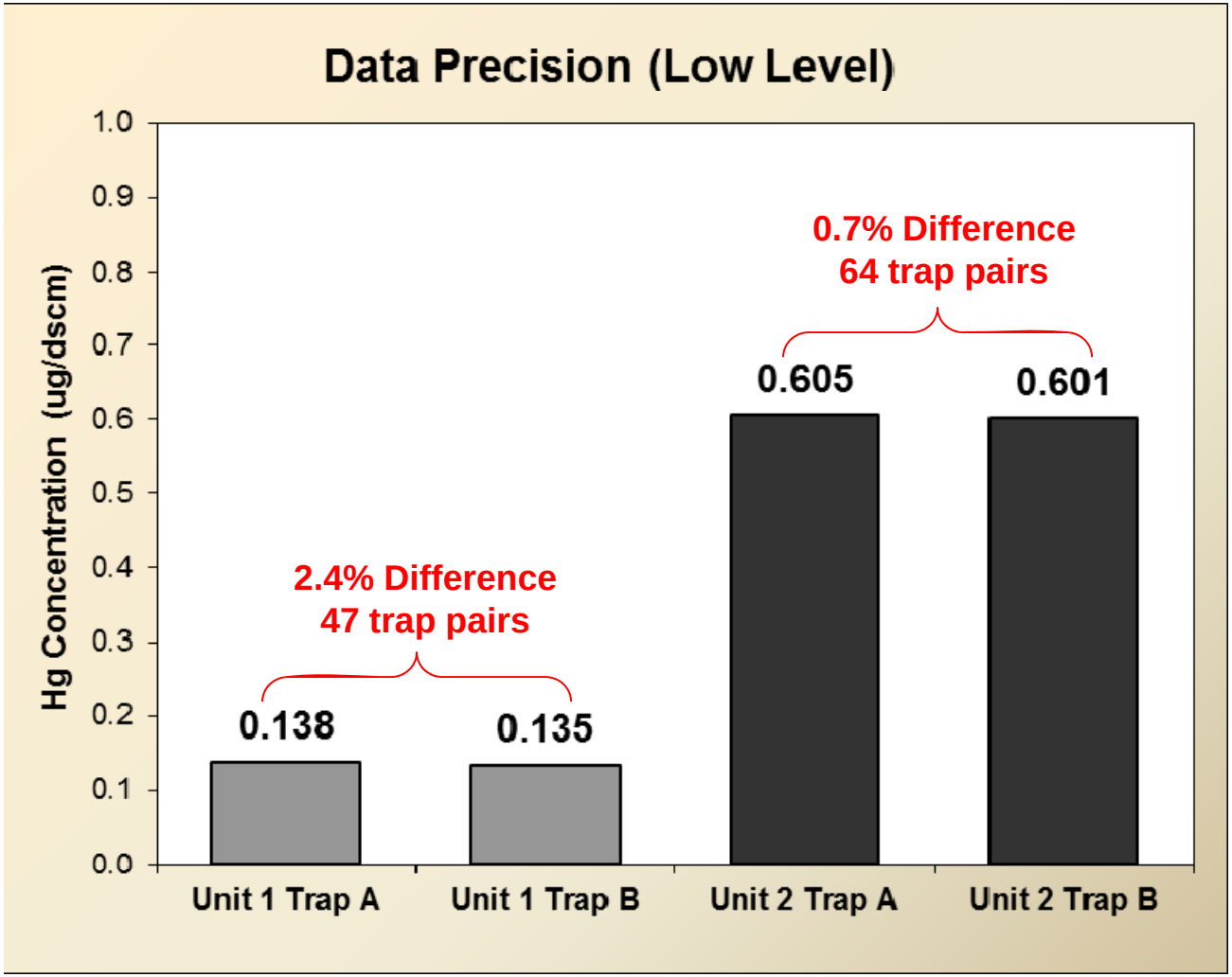
Mean spike recovery: 98.5%

Reproducibility

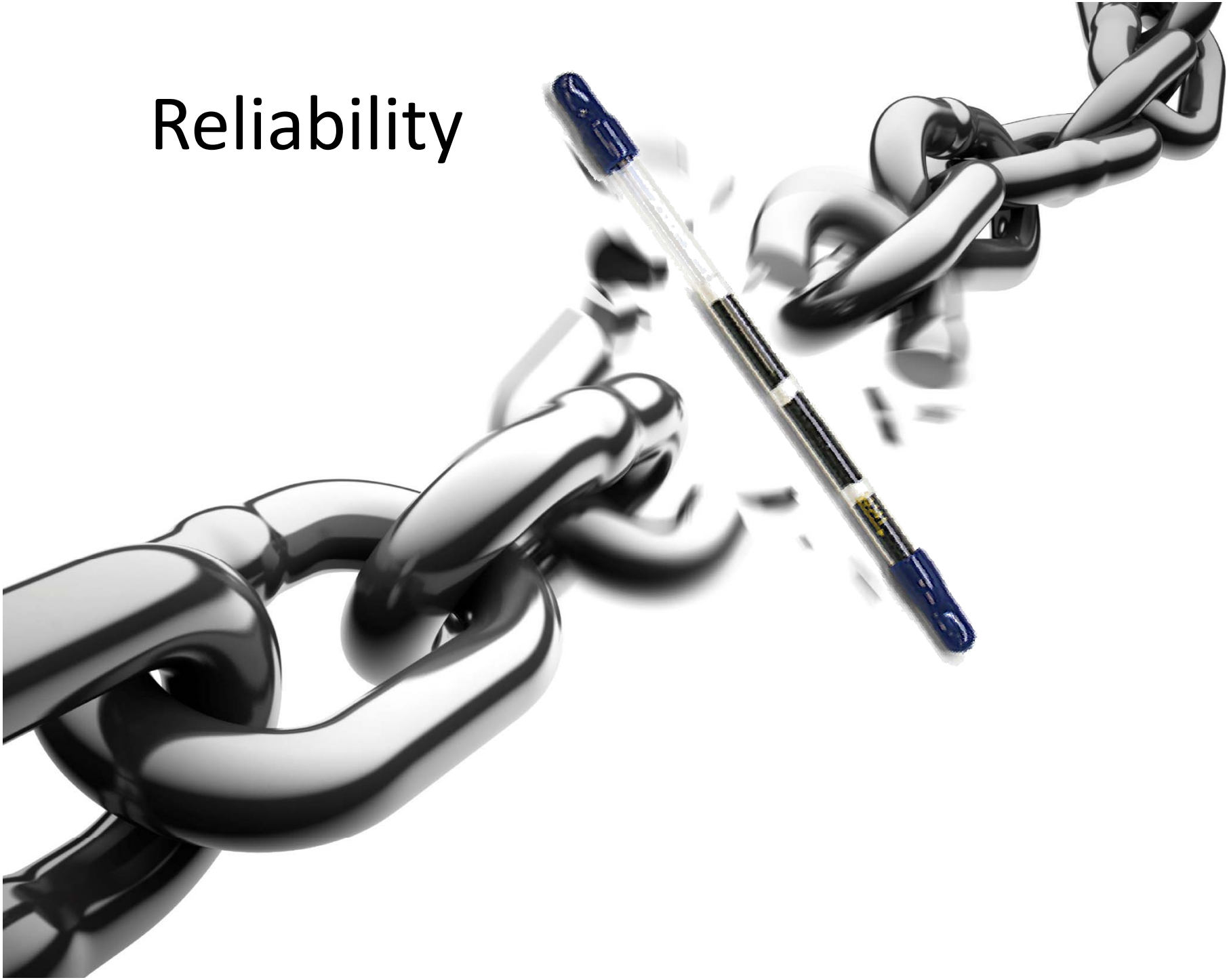


$RD=|C_A-C_B|/(C_A+C_A) \times 100\%$

Reproducibility



Reliability

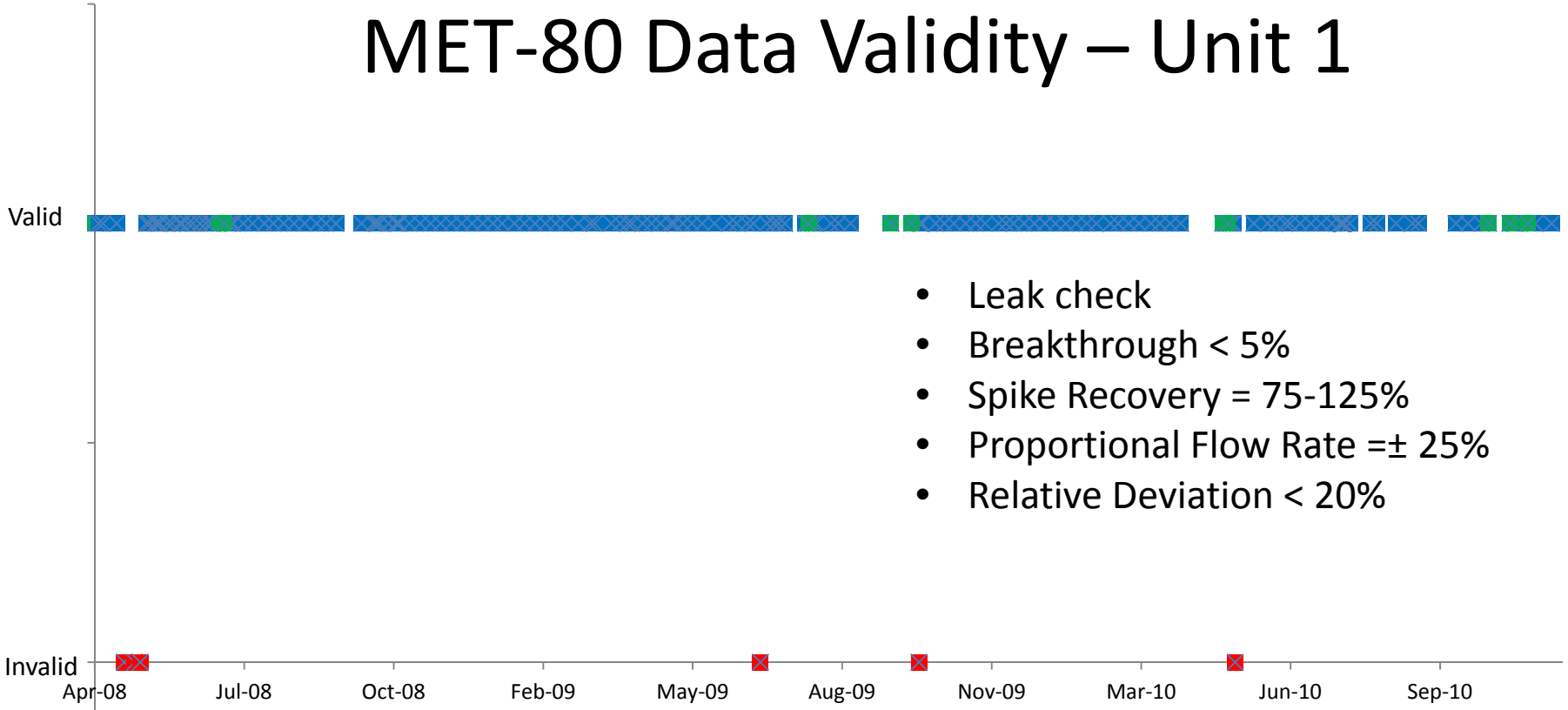


Reliability

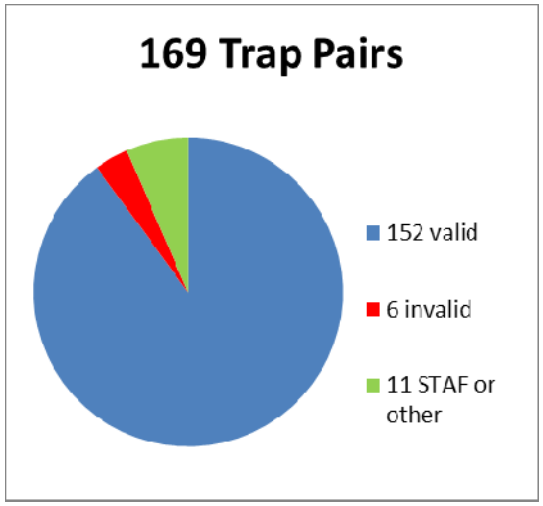
Case study

- Dominion Salem Harbor
- Compliance monitoring since 2008
- Three MET-80 systems

MET-80 Data Validity – Unit 1

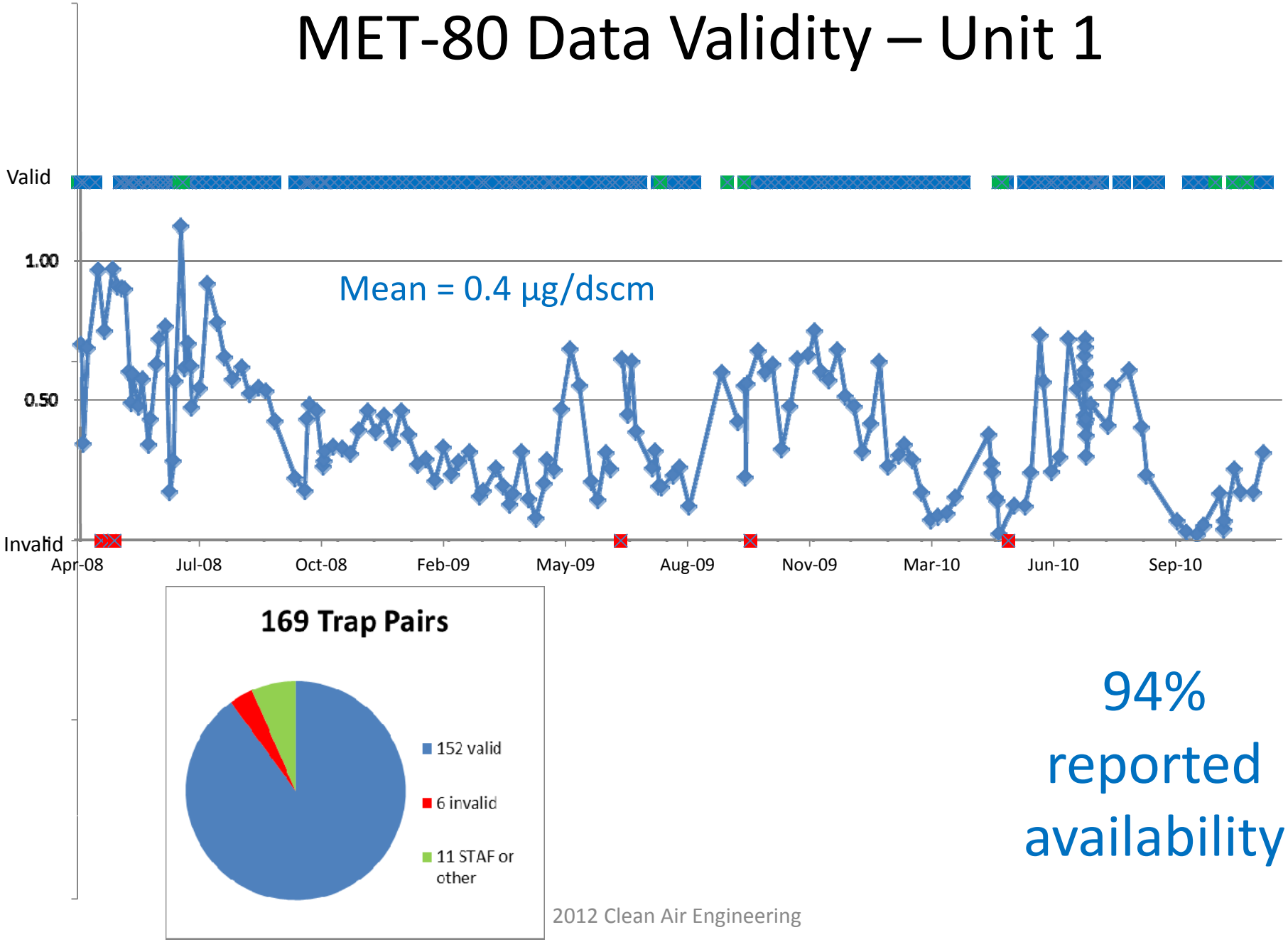


- Leak check
- Breakthrough < 5%
- Spike Recovery = 75-125%
- Proportional Flow Rate =± 25%
- Relative Deviation < 20%



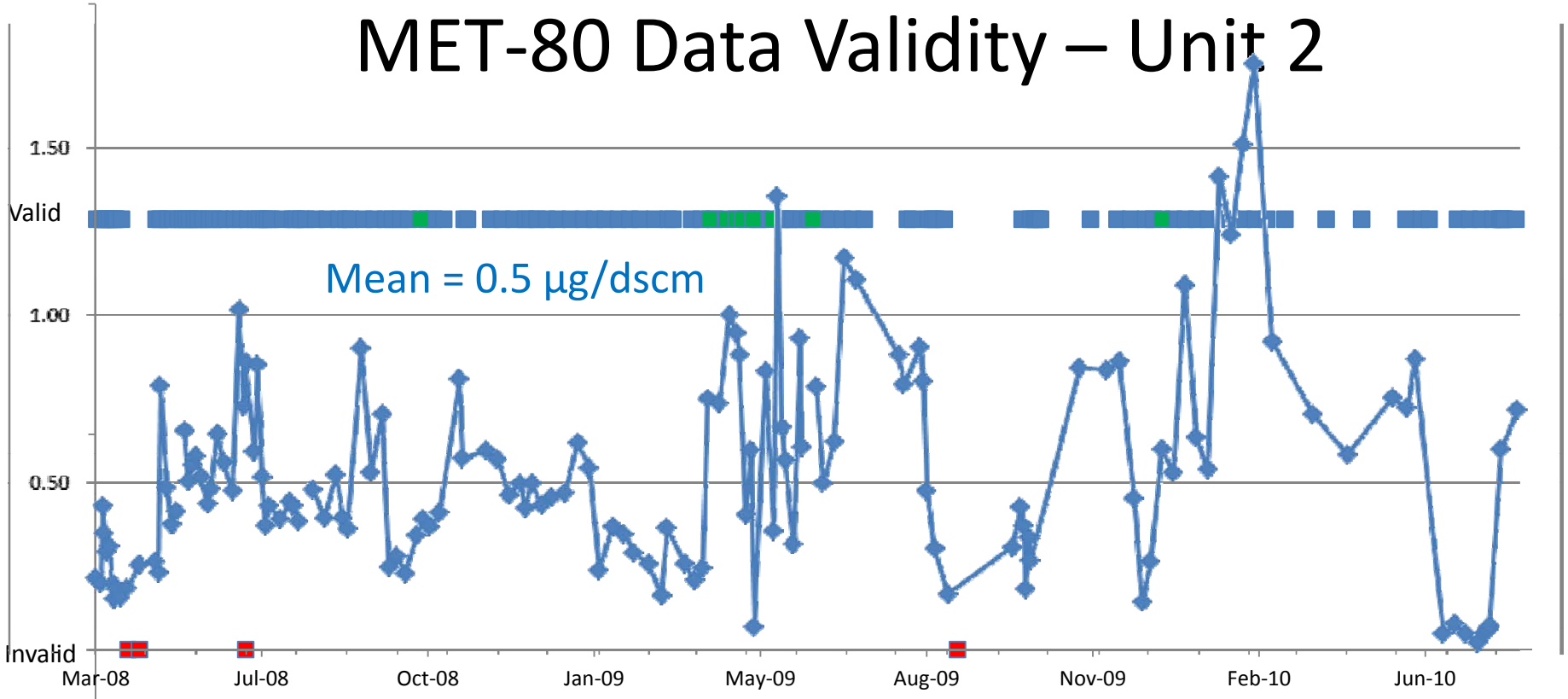
94% reported availability

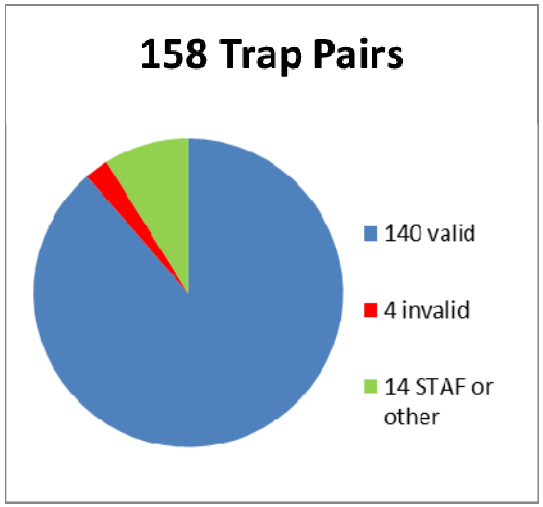
MET-80 Data Validity – Unit 1



94% reported availability

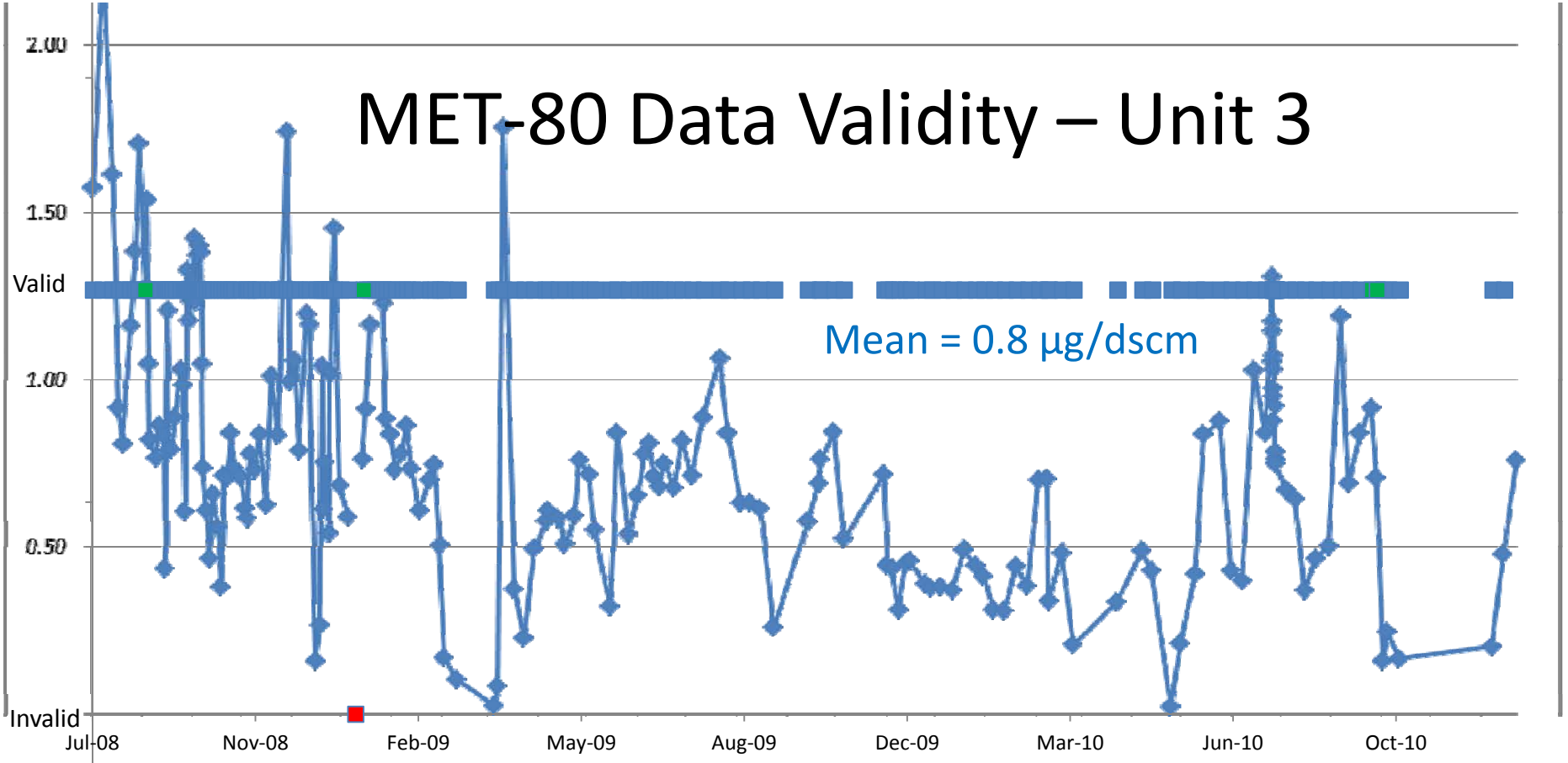
MET-80 Data Validity – Unit 2

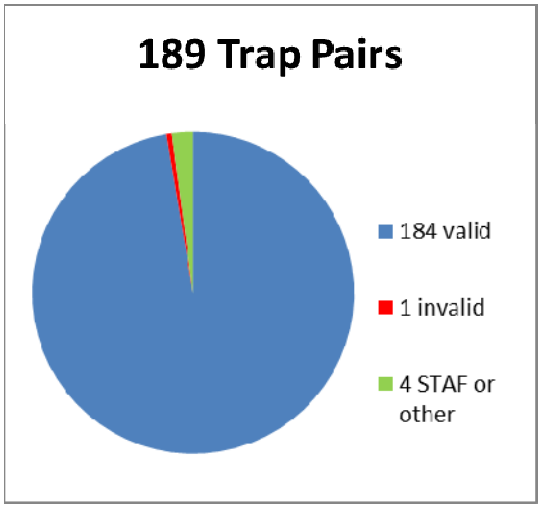




91% reported availability

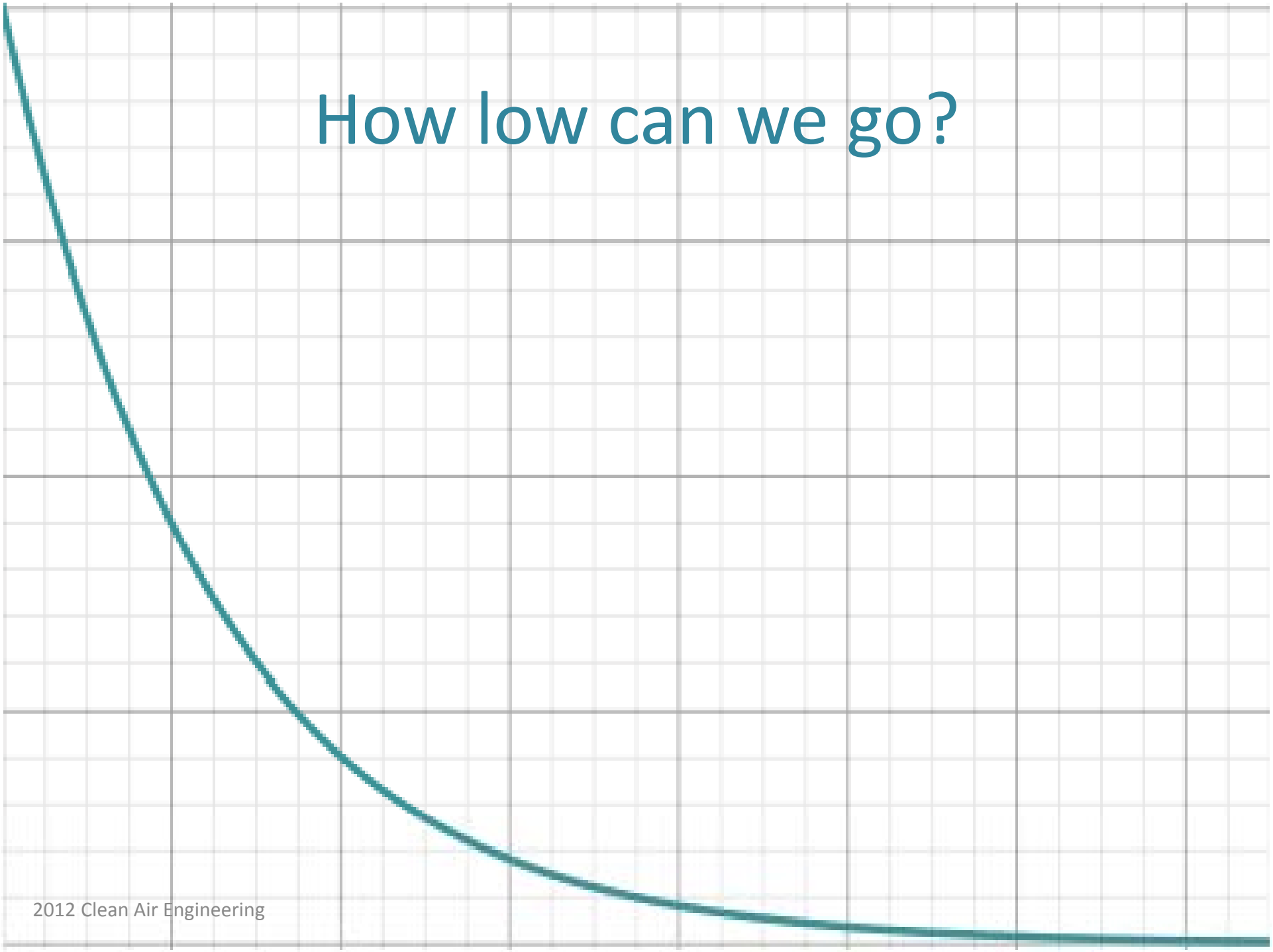
MET-80 Data Validity – Unit 3

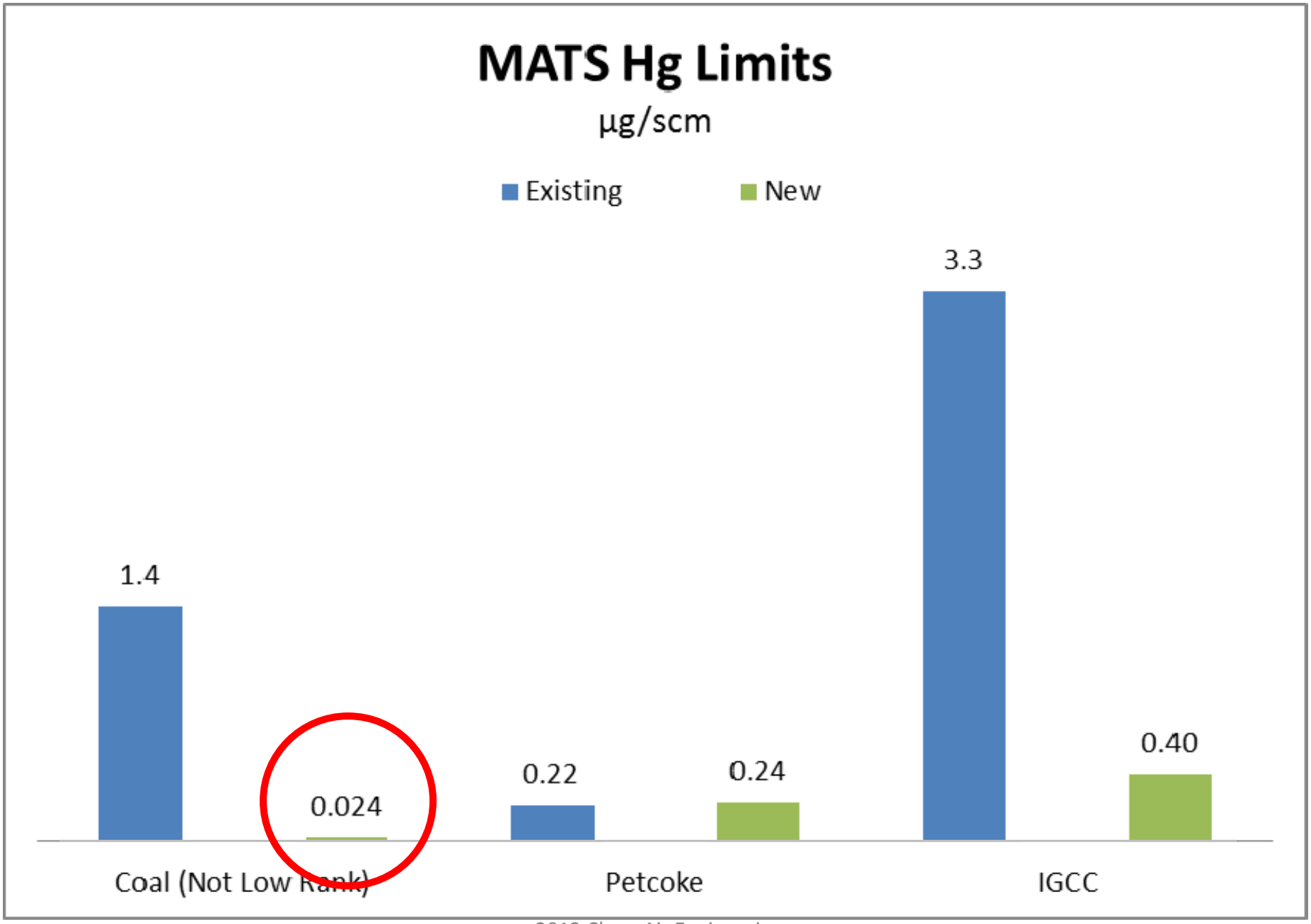


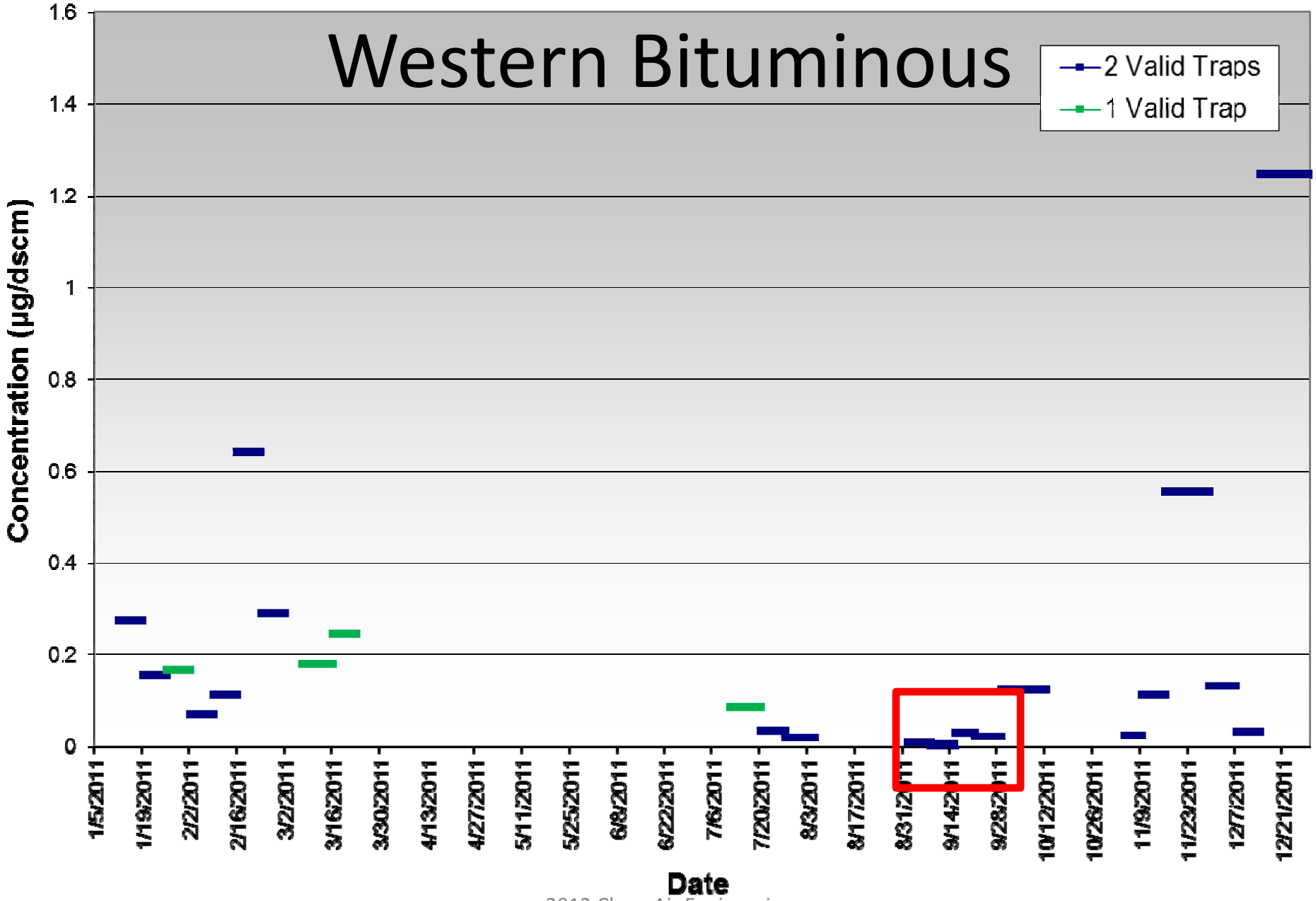


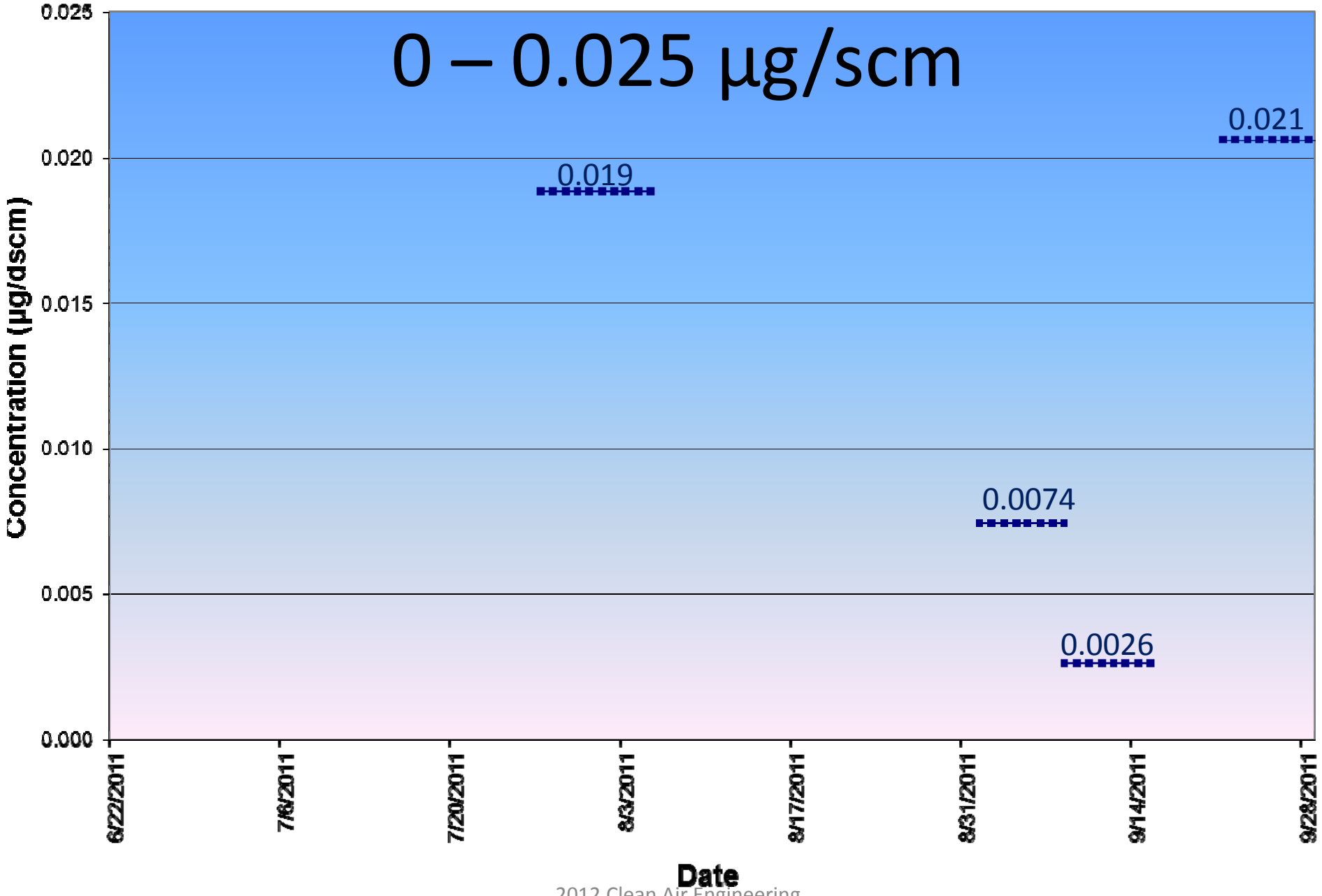
96% reported availability

How low can we go?




MATS Hg Limits
µg/scm
Existing
New
1.4
0.024
0.22
0.24
3.3
0.40
Coal (Not Low Rank)
Petcoke
IGCC

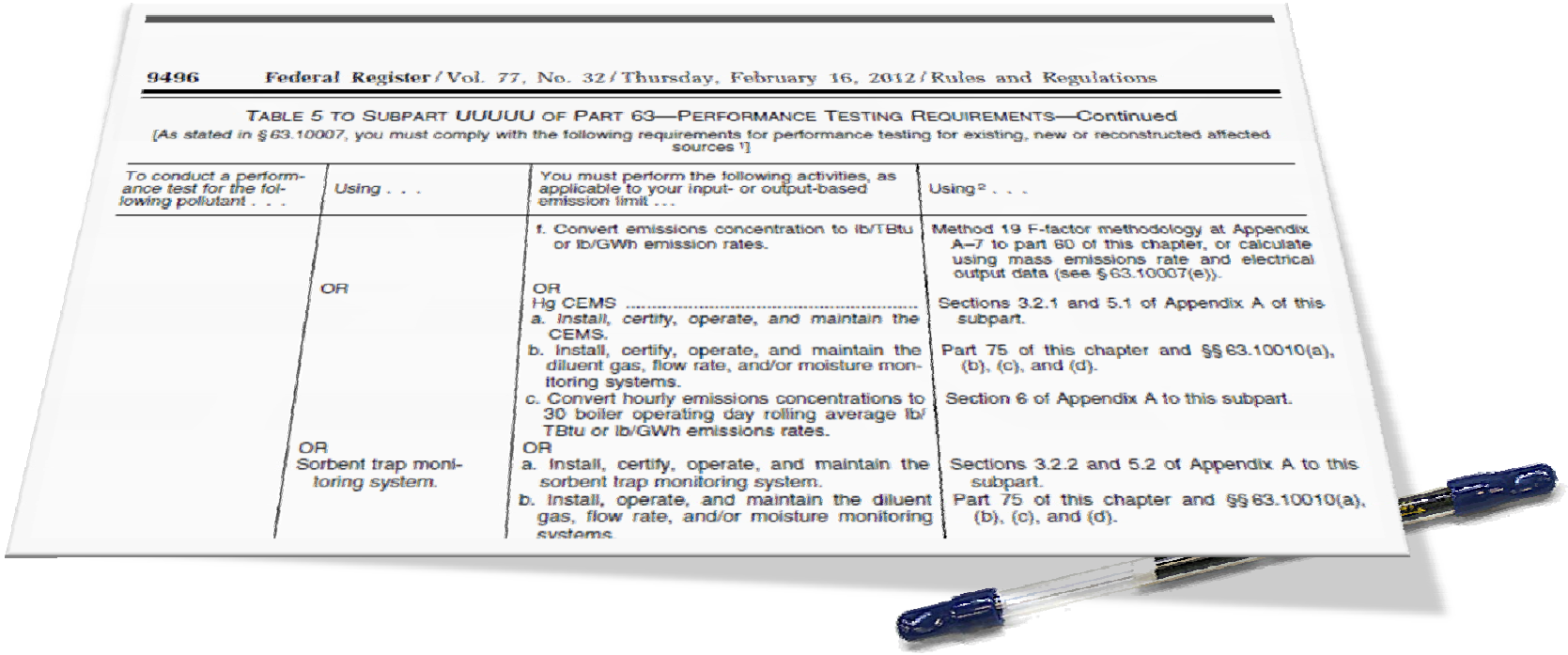

Western Bituminous
2 Valid Traps
1 Valid Trap
Concentration (µg/dscm)
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
1/5/2011
1/19/2011
2/2/2011
2/16/2011
3/2/2011
3/16/2011
3/30/2011
4/13/2011
4/27/2011
5/11/2011
5/25/2011
6/8/2011
6/22/2011
7/6/2011
7/20/2011
8/3/2011
8/17/2011
8/31/2011
9/14/2011
9/28/2011
10/12/2011
10/26/2011
11/9/2011
11/23/2011
12/7/2011
12/21/2011
Date


0 – 0.025 µg/scm
0.025
0.020
0.015
0.010
0.005
0.000
Concentration (µg/dscm)
0.019
0.021
0.0074
0.0026
6/22/2011
7/6/2011
7/20/2011
8/3/2011
8/17/2011
8/31/2011
9/14/2011
9/28/2011
Date

Take away

- MATS will require mercury measurements well below 1 µg/scm
- These levels can be measured
- Existing units: sorbent trap monitoring or CEMS
- New units: sorbent trap monitoring

Questions?



9496 Federal Register / Vol. 77, No. 32 / Thursday, February 16, 2012 / Rules and Regulations

TABLE 5 TO SUBPART UUUUU OF PART 63—PERFORMANCE TESTING REQUIREMENTS—Continued

[As stated in § 63.10007, you must comply with the following requirements for performance testing for existing, new or reconstructed affected sources [1]]

To conduct a performance test for the following pollutant . . .	Using . . .	You must perform the following activities, as applicable to your input- or output-based emission limit . . .	Using [2] . . .
		f. Convert emissions concentration to lb/TBtu or lb/GWh emission rates.	Method 19 F-factor methodology at Appendix A–7 to part 60 of this chapter, or calculate using mass emissions rate and electrical output data (see § 63.10007(e)).
	OR	OR	
		Hg CEMS	
		a. Install, certify, operate, and maintain the CEMS.	Sections 3.2.1 and 5.1 of Appendix A of this subpart.
		b. Install, certify, operate, and maintain the diluent gas, flow rate, and/or moisture monitoring systems.	Part 75 of this chapter and §§ 63.10010(a), (b), (c), and (d).
		c. Convert hourly emissions concentrations to 30 boiler operating day rolling average lb/TBtu or lb/GWh emissions rates.	Section 6 of Appendix A to this subpart.
	OR	OR	
	Sorbent trap monitoring system.	a. Install, certify, operate, and maintain the sorbent trap monitoring system.	Sections 3.2.2 and 5.2 of Appendix A to this subpart.
		b. Install, operate, and maintain the diluent gas, flow rate, and/or moisture monitoring systems.	Part 75 of this chapter and §§ 63.10010(a), (b), (c), and (d).

cleanair.com

contact@cleanair.com

800-632-1619