Mercury Sampling: A Comparison of Common Test Methods

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Air and Acoustic Monitoring Conference

October 26, 2016

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Presentation Overview

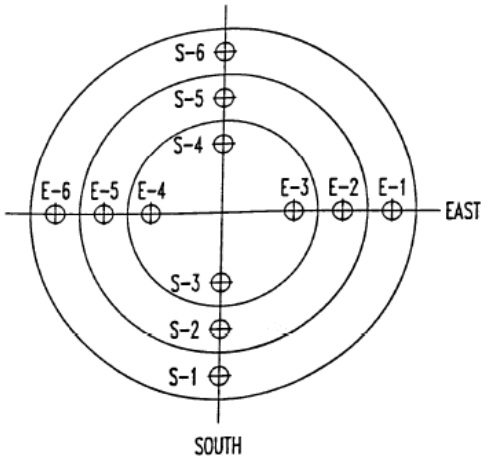
- A review of common manual mercury sampling methods
- The advantages and disadvantages of each test method
- A summary of things to consider when choosing a test method
- A comparison of paired train sampling data

Mercury Sampling Methods

- There are three commonly used sampling methods for total mercury and a fourth sampling method used for mercury speciation.
- These sampling methods can be characterized as either isokinetic or non-isokinetic sampling.
  - Isokinetic Sampling Methods
    - US EPA Method 101A
    - US EPA Method 29
    - Ontario Hydro Mercury Speciation Method/ASTM D6784-02
  - Non-Isokinetic Sampling Method
    - US EPA Method 30B

Isokinetic vs. Non-Isokinetic Sampling

- Isokinetic Sampling:
  - Sampling at multiple points across several traverses of the stack or duct
  - Purpose is to capture particles that pass through a defined area without disturbing their path
  - the velocity of gas entering the sampling nozzle is equal to the velocity of the undisturbed gas stream at each point



- Non-Isokinetic Sampling:
  - Typically single point sampling at a constant flowrate for a specified period of time

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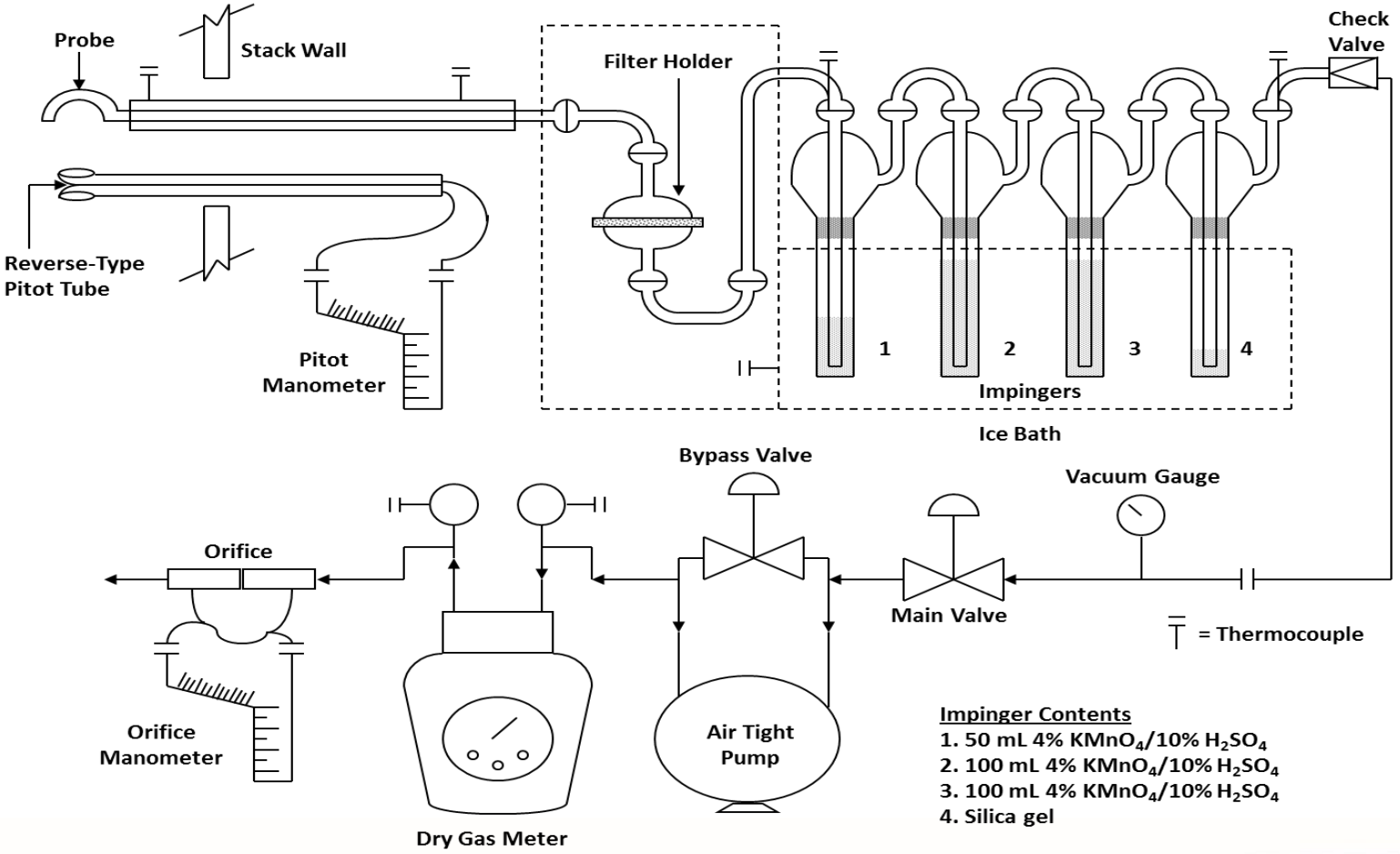
US EPA Method 101A



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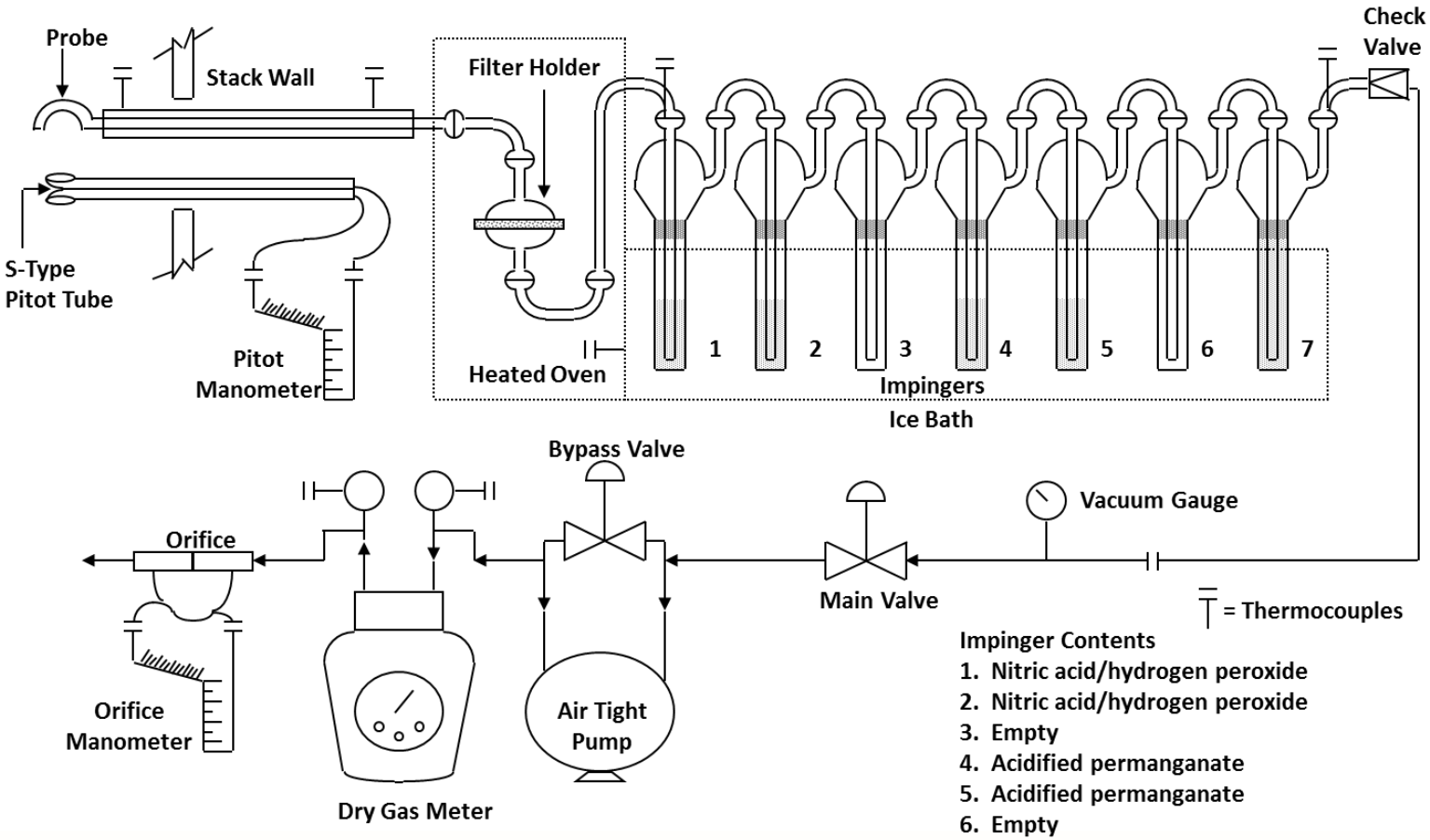
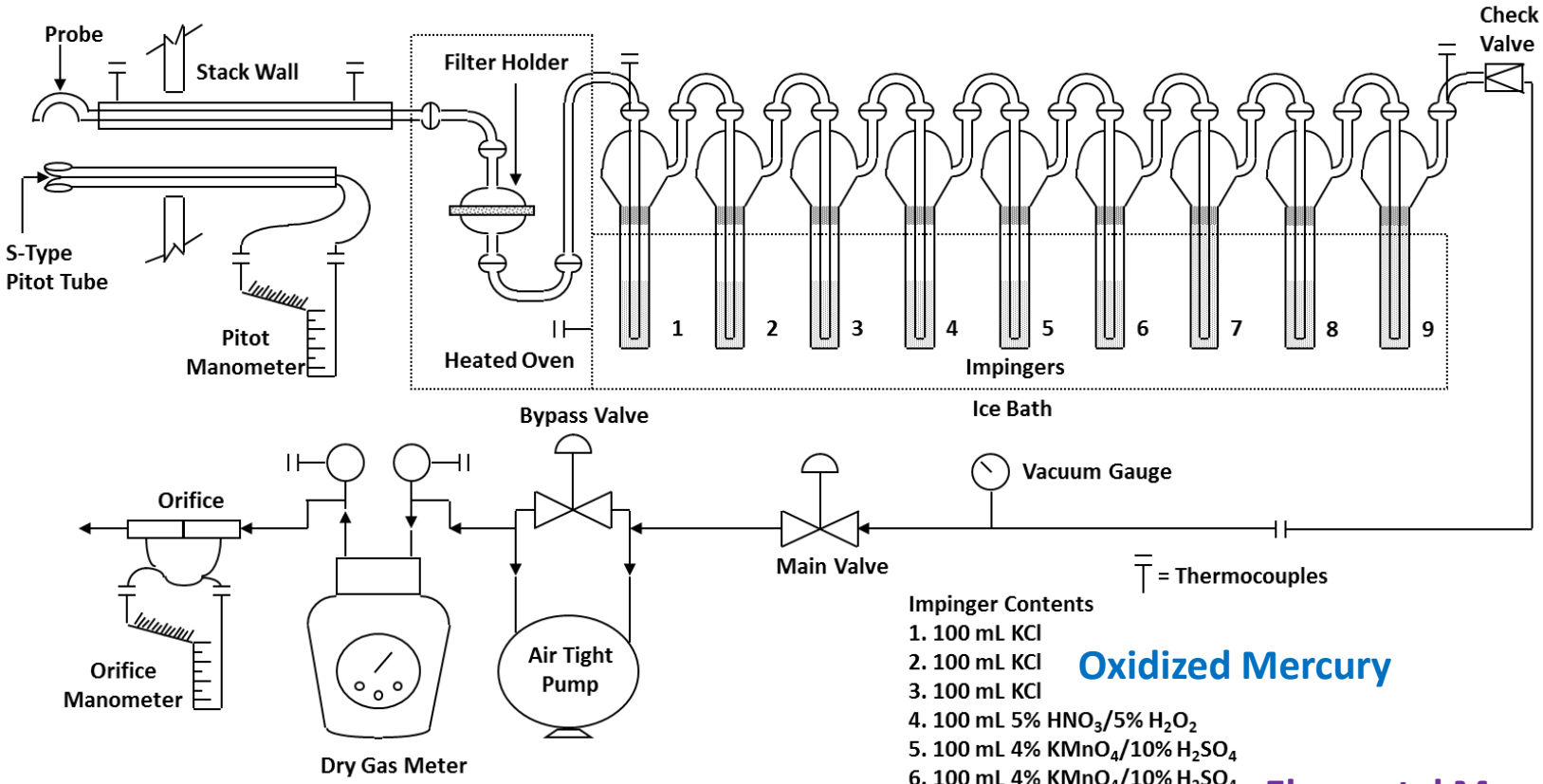
US EPA Method 29



Ontario Hydro Method



Impinger Contents

1. 100 mL KCl
2. 100 mL KCl
3. 100 mL KCl
4. 100 mL 5% HNO_3/5% H_2O_2
5. 100 mL 4% $KMnO_4$/10% H_2SO_4
6. 100 mL 4% $KMnO_4$/10% H_2SO_4
7. 100 mL 4% KMnO4/10% H_2SO_4
8. 100 mL 4% KMnO4/10% H_2SO_4
9. Silica Gel

Oxidized Mercury

Elemental Mercury

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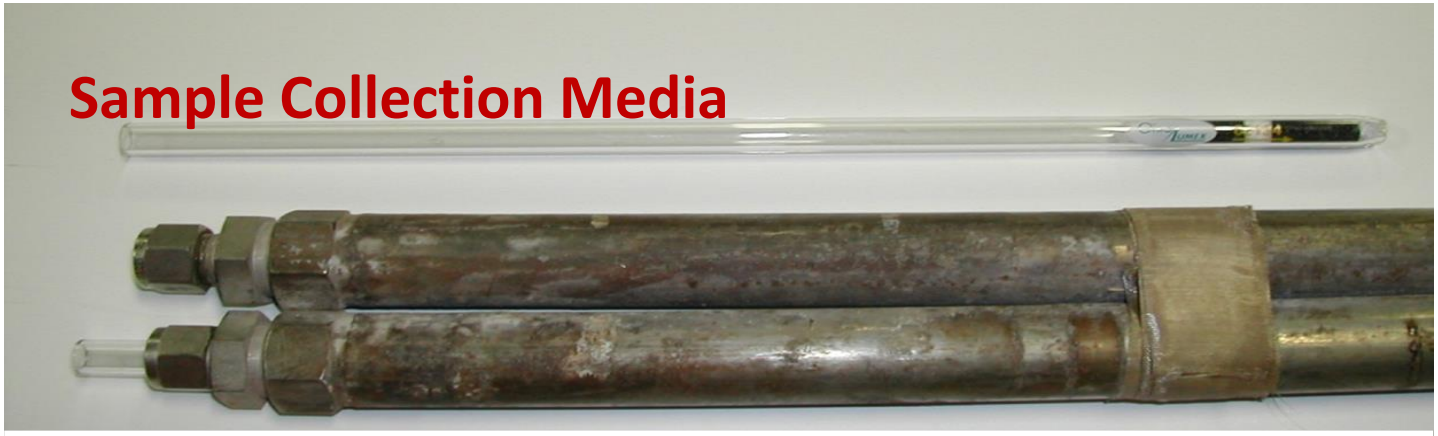
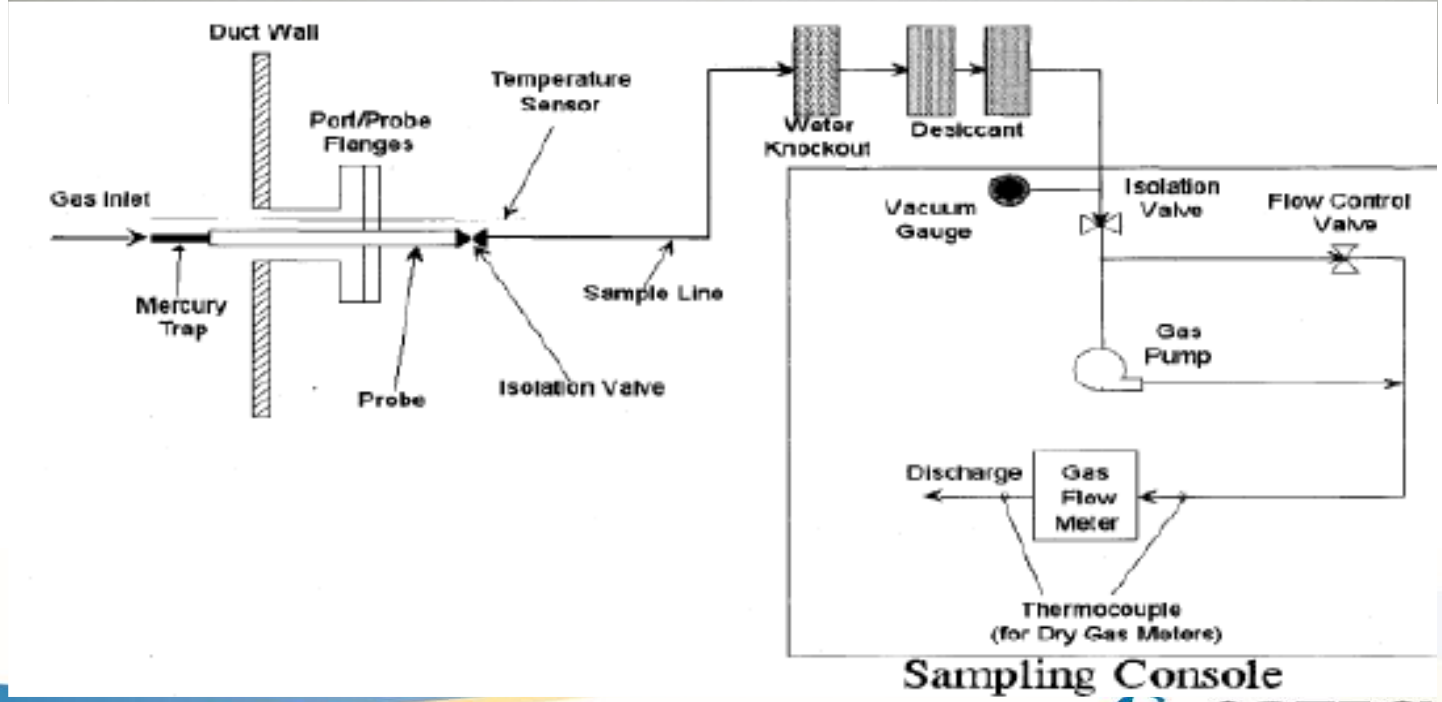
US EPA Method 30B





Method Comparison

Test Method	Sample Duration	Approximate Recovery Time	Number of Samples/Test	Cost
Ontario Hydro Method	~ 3 hours	~ 1.5 hours	10	$$$$
ASTM D6784-02	~ 3 hours	~ 1 hour	6	$$$
US EPA Method 29	Typically 2 – 4 hours	~ 1 hour	7	$$$
US EPA Method 101A	Typically 2 – 4 hours	~ ½ hour	1 – 3	$$
US EPA Method 30B	Typically 1 hour (up to 30 days)	< ½ hour	2 (Paired Tubes)	$

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Comparison of Test Analytes

Test Method	Total Hg	Particulate Hg	Gaseous Hg	Hg (0)	Hg(II)	Other Metals
Ontario Hydro Method	Yes	Yes	Yes	Yes	Yes	
ASTM D6784-02	Yes	Yes	Yes	Yes	Yes	
US EPA Method 29	Yes	Yes	Yes			Yes
US EPA Method 101A	Possible	Possible	Yes			
US EPA Method 30B			Yes	Possible	Possible	

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What Method to Use?

- Depends on what you are looking for
- Depends on the purpose of the testing
  - Compliance
  - Engineering Tests
  - RATA
- Depends on the nature of the gas stream
  - Particulate matter
  - Moisture content
  - Acid gases

M30B QA/QC Requirements

While US EPA Method 30B may look like the easiest and cheapest option there are minimum QA/QC requirements that must be met in order to validate the tests.

- US EPA M30B minimum QA/QC requirements:
  - Spike Recovery
  - Paired Trap Agreement
  - Breakthrough

US EPA M30B – Spike Recovery

- Mercury traps must be pre-spiked with known quantities of mercury prior to sampling
- The recovery spike must be within 50 to 150% of the **expected** mass collected in the traps during sampling
- Spike recovery must be between 85% and 115%

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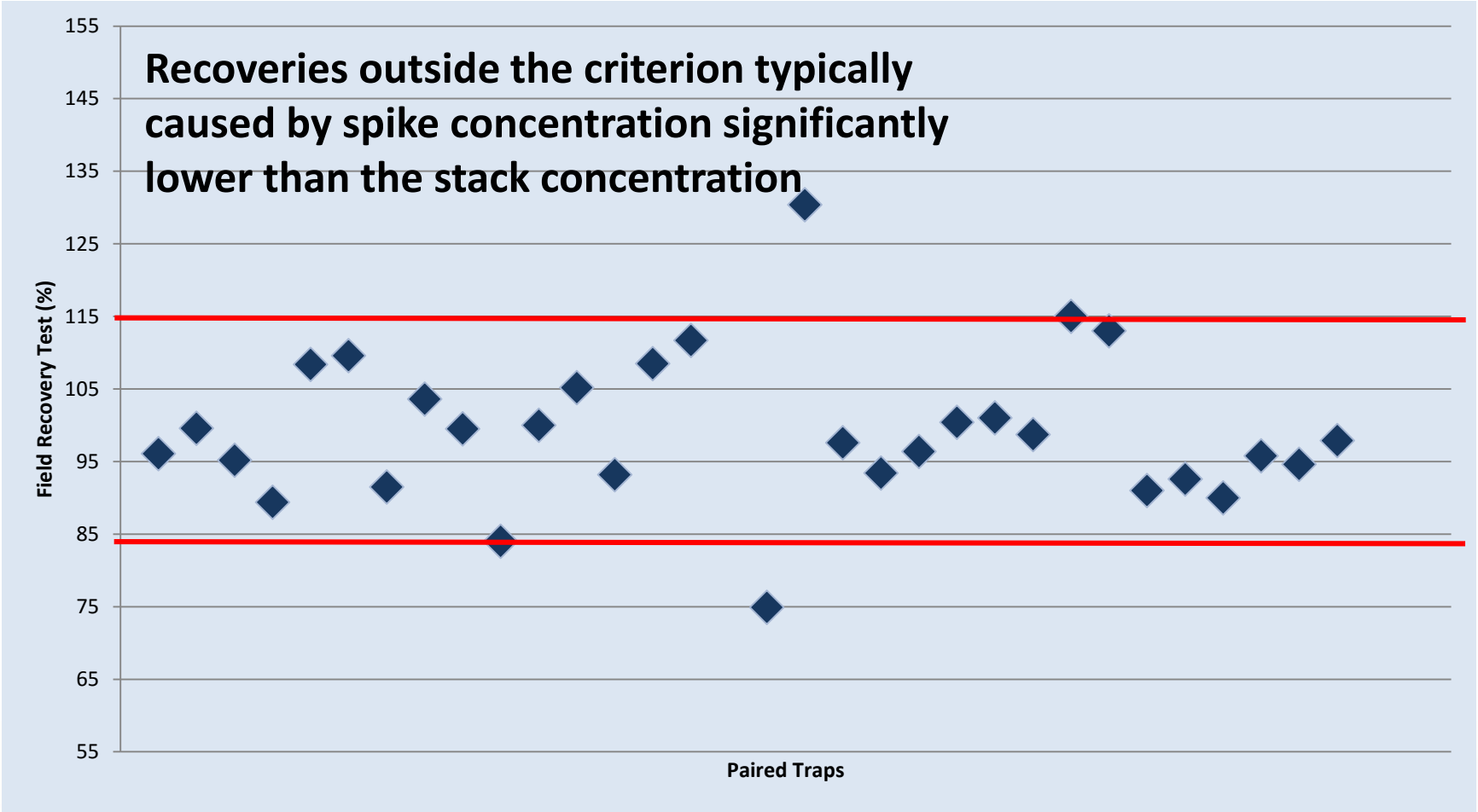
Spike Recovery Results from Source Testing Programs



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US EPA M30B – Paired Trap Agreement

- The method requires the paired sorbent trap agreement to be:
  - ≤10% relative deviation for mercury conc. greater than 1 µg/Rm^3; or
  - ≤20% relative deviation for mercury conc. less than 1 µg/Rm^3
- If the paired trap agreement is greater than the above stated limits the run is not valid
- You need 3 valid runs for a compliance quality test program

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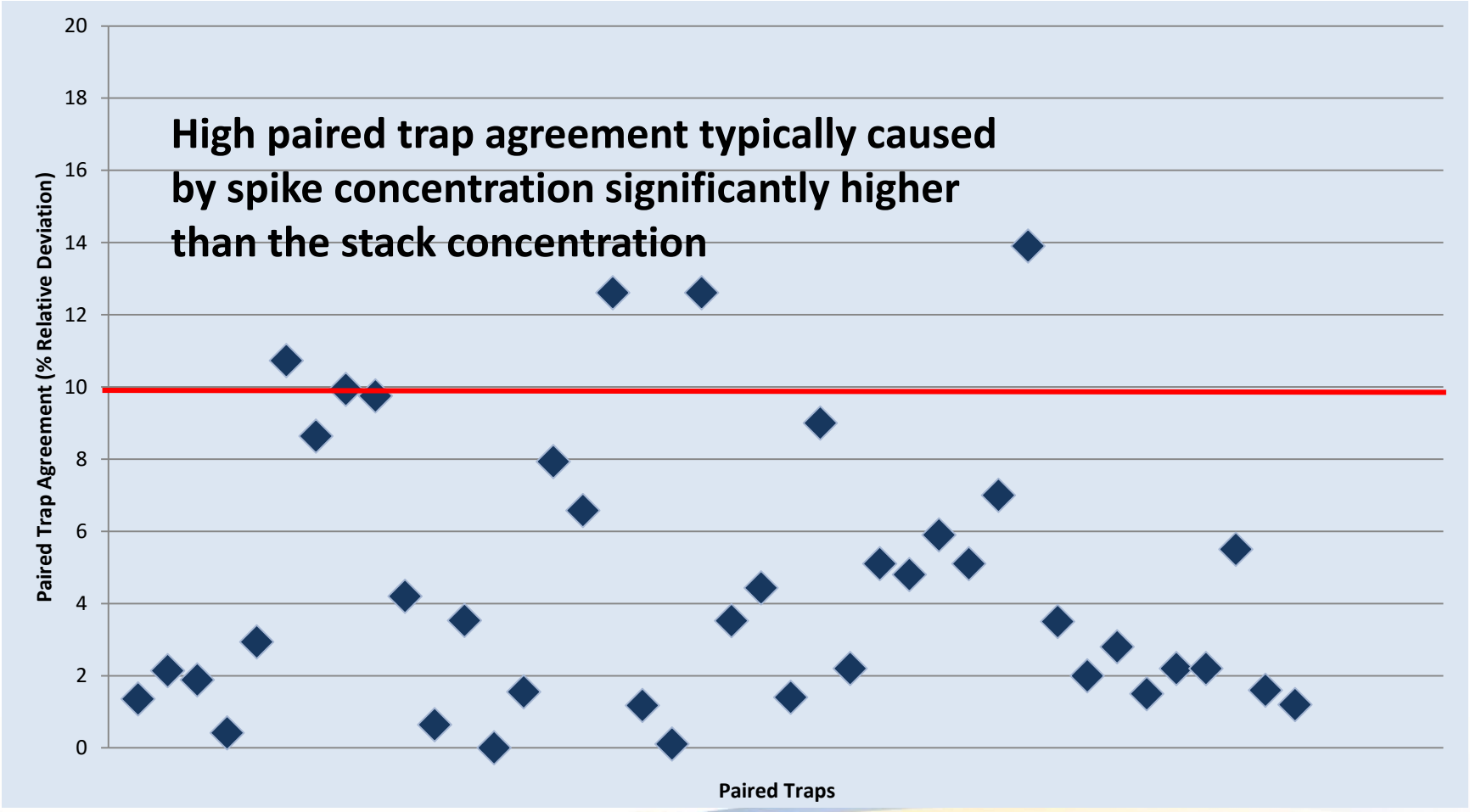
Paired Trap Agreement from Source Testing Programs



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US EPA M30B – Breakthrough

- The method requires the Section 2 breakthrough to be:
  - ≤10% of the Section 1 mercury mass for mercury conc. greater than 1 µg/Rm^3; or
  - ≤20% of the Section 1 mercury mass for mercury conc. less than 1 µg/Rm^3
- If the breakthrough is greater than the above stated limits the run is not valid as there is the potential for mercury loss

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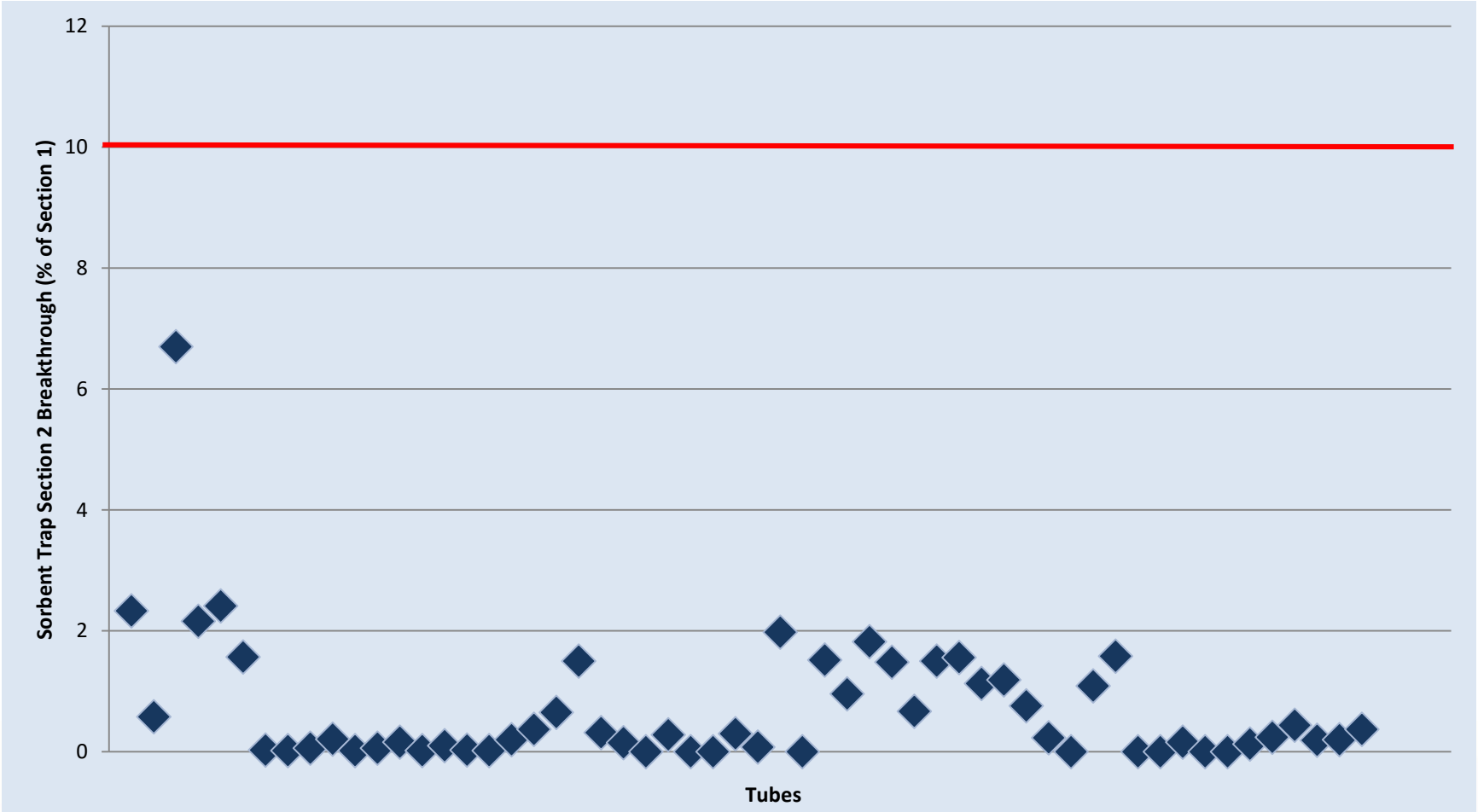
Section 2 Breakthrough from Source Testing Programs



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What does this mean?

You may need to do more than three test runs and/or more than one spike recovery to ensure QA/QC requirements are met.

Otherwise the MOECC may reject the results if testing is being used to determine compliance with ECA limits or to meet site specific periodic testing requirements (i.e. quarterly sampling)

Mercury Comparison Data

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US EPA Method 101A

Paired Train Results

Test No.	Mercury Conc. µg/Rm³	% Difference
1A 1B	119.6 114.8	2.0
2A 2B	86.5 86.8	0.2
3A 3B	54.4 56.6	2.0
4A 4B	117.3 117.8	0.2
5A 5B	100.8 101.5	0.4
6A 6B	105.9 101.7	2.0
7A 7B	95.0 99.6	2.4

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US EPA Method 29 vs. Ontario Hydro Method Paired Train Results

Test Series	Sample Method	Mercury Conc. µg/Rm^3	% Difference
1	M29 Ontario Hydro	4.66 4.38	6.0
2	M29 Ontario Hydro	1.29 1.27	1.6
3	M29 Ontario Hydro	10.4 10.0	4.0

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US EPA Method 30B vs. Isokinetic Sampling

- Sampling notes:
  - Isokinetic Sampling Trains
    - Sampling period ranged from 3-5 hours
    - Multi-point sampling
  - Method 30B Sampling Trains
    - Sampling period was 60 minutes
    - Single point sampling
    - Average results of paired traps

US EPA Method 30B vs. Isokinetic Sampling

- Analysis and emission calculation notes:
  - Isokinetic sampling train data includes mercury captured on the filter
  - Method 30B data is the average of the paired traps
  - Fractions <RDL were assigned a value of zero when calculating emission data

Comparison testing was conducted with the assistance of Ohio Lumex who contributed the M30B sampling media and analysis for the program.

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Industry	Sampling Method	Stack Temp. (°C)	Stack Moisture (%)	Mercury Conc. (µg/Rm³)
Coal Fired Power Plant	101A 30B	60	13	0.77 0.75
Medical Waste Incinerator*	29 30B	45	6	3.03 4.64
Municipal Waste Incinerator*	29 30B	230	17	4.12 6.01
Electric Arc Furnace*	29 30B	60	2	8.17 7.08
Hazardous Waste Incinerator I	29 30B	190	40	22.5 23.0
Bio-Solids Incinerator	101A 30B	25	3	26.9 27.6
Hazardous Waste Incinerator II	29 30B	240	48	443 505

* Indicates a batch process with the potential for inconsistent feed material

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Questions?

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