

16 Years Of Hg Measurements Via The Solid Sorbent Method

Draft US EPA Method 30B

Supported By

Wet Acid Digest / US EPA Method 1631 (CVAFS)

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**(1) Frontier Geosciences Inc. (2) TRC Environmental Corp
(3) Supelco (Sigma Aldrich)**



EPA 30B Hg RATA Team

Turn Key US EPA RATA Package



Equipment Manufacturing

- Field Equip. MFG
- Leasing Program
- Technical Support



Trap Distribution Packaging

- Trap Packing
- Worldwide Dist.
- US/Europe/East Asia



Traps & Analysis Technical Support

- Mfg Trap Material
- Analytical Lab
- Project Mgmt
- Technical Support



Field Testing Partners

- Field Sampling
- RATA Via EPA 30B
- Project Management



16 Years Of Hg Measurements Via The Sorbent Method

- Topics Covered -

- Hg RATA Methods Available To Industry
- History Of US EPA Draft 30B: 1991-2006
- Principles Of The Sorbent Trap Method
- Wet Acid Digestion/Analysis Via US EPA 1631
- RATA Protocol – Highest Probability Of Certification
- Recent Examples Of RATA Produced



Hg RATA Methods Available To Industry

- **Ontario Hydro Method:** The Ontario Hydro method is expensive, difficult to implement in the field, potential analytical issues (reported @ the US DOE 2005 Hg Measurements Workshop), potential difficulty to measure low Hg emission sources (less than 1 ug Hg/m³).
- **Instrument Reference Method (EPA Method 30A):** The instrument reference method (US EPA Method 30A) after several years of development, still considered in the R&D stage.....viable commercial method for performing Hg RATAs in 2008?
- **Sorbent Trap Method (US EPA Method 30B):** Frontier (with the critical support of EPRI), 16 years ago developed the principles of the sorbent method which are now embodied in US EPA Method 30B giving this method the advantage of 16 years of Hg measurements on coal fired power emissions. The method is backed by a highly sensitive, wet-acid digestion and analytical method (US EPA 1631-CVAFS) that enables the method to demonstrate on a routine basis, reliable precision, accuracy and very low detection limits (down to 0.1 ug Hg/m³). In experienced hands, US EPA Method 30B RATA samples can be analyzed via 24 hour turn-around analysis back in the lab or via on-site analysis.



Why Was US EPA 30B (Sorbent Method) Promulgated To Support The Hg RATA Effort?

- **Recognized Need For A Reliable Hg RATA Method**
- IRM Still In Development
- **1992-2006: Sorbent Trap Method Used Widely**
- **Ontario Hydro**
 - Issues With Ontario Hydro As RATA Method
 - OH Reliability: Reliability
 - OH Difficulty Implementing Method
 - OH Analytical Issues: (Reported @ 2005 DOE Hg Work Shop)
 - Decreasing # Of Labs Offering OH Analysis (Liability/Difficulty?)
 - Difficult To Ship Impinger Solutions To Lab (Hazardous)
 - Data Turn-Around = 15-28 Days To Know If RATA Failed
 - Cost



US EPA Method 30B

History Of Solid Sorbent Hg Method: 1991-2006

- 1991/4 Multiple Intercomparisons with EPA Method-29 (301h Validation Study)
- 1996 Mercury Speciation: A Comparison Between EPA Method 29 and Sorbet Trap Method
- 1997 Mercury Speciation Methods for Utility Flue Gas – Sorbet Total Hg Method and FAMS Methods
- 2000 US EPA PBMS Validation at EERC (USEPA/ EERC/Frontier Geosciences)
- 2001 DOE NETL Method Intercomparison (DOE, NETL)
- 2002 EPRI-Southern Company-TVA Bowen Hg Intrcomparison Study
- 2004 DOE-EPRI-WE Energies Pleasant Prairie Hg Intercomparison Study
- 2004 DOE NETL Method Intercomparison – (OH/Sorbent Method (Total and Speciation))
- 2003/4 Development of CAMR Appendix K Sorbet Trap Method (EPRI/EPA/ADA-ES/FGS)
- 2004 EPA-OAQPS RATA (CEM/AppK/OH)
- 2005 EPA-ORD RATA (CEM/Sorbent method/OH)
- 2006 DOE/EPRI/Reliant Sorbet Trap Method RATA Evaluation Of Sorbet Method
- 2006 European Union Methods Intercomparison (CEM/Sorbent Method/OH)
- 2006 US EPA ETV Program Intercomparison (CEM/Sorbent Methhod/OH)
- 2007/8 *Some Of The United States First Official RATAs (Hg CEM and App K)*



Sorbent Method Development and Measurements Supported Since 1991 by:

- EPRI (PISCES Project + Others) / EPRI-ES
- ADA-ES
- US-DOE FETC
- USEPA
- Frontier Geosciences Internal Research Funding
- European Union – MOE Project
- State Agencies
- Electric Utilities
- Industry – Alcoa, Noranda, Consol + others
- Research Institutions – EERC, MSE Technologies



Frontier Geosciences Inc

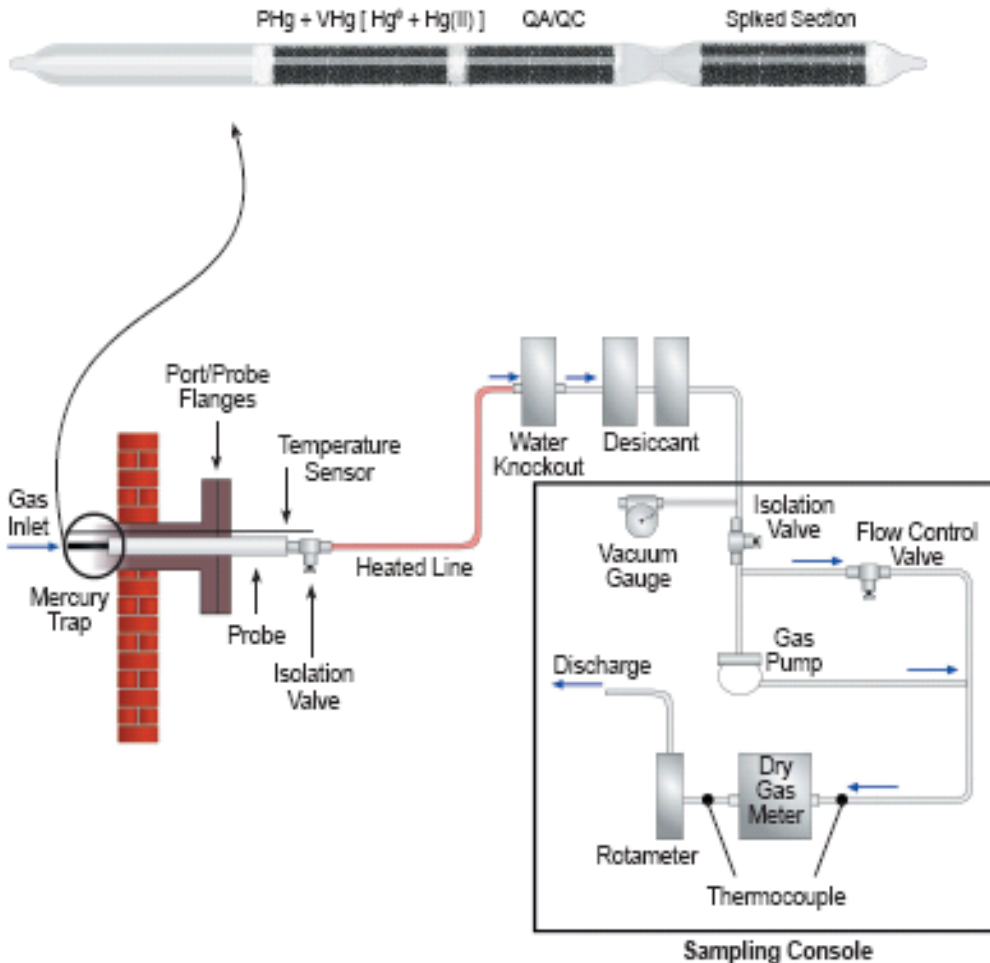
History Of Innovation Behind US EPA Method 30B

- **Frontier – EPRI Designed The Sorbent Trap Hg Method Back In 1991:**
Frontier with the critical support of EPRI, designed the original concept of the Hg sorbent trap, digest/analytical and field sampling method over 16 years ago, which is now embodied in both US EPA Method 30B and App K.
- **Frontier - Co-author Of Digest/Analytical Method US EPA 1631 (CVAFS):**
Frontier co-authored and served as the US EPA referee lab for the validation of the analytical method US EPA Method 1631 (CVAFS), the principles of which are embodied in the digest and analytical method used to support Hg sorbent trap analysis (US EPA Method 30B)
- **Frontier + Teaming Partners Supported Development Of App K**
Frontier, along with ADA-ES and the critical support of EPRI, helped validate the method now embodied in 40 CFR Part 75 Appendix K.
- **Frontier - Sorbent Trap Manufacturer For 16 Years:**
Frontier has been manufacturing, testing and analyzing Hg sorbent traps that are the principle traps used to support over 12 intercomparisons and validation studies of the Hg sorbent method as applied to coal combustion flue gas.



Appendix K Sampling Schematic

Appendix K Spiked Trap - Continuous Emission Monitoring (1-10 Day Sampling)



Sorbent Traps

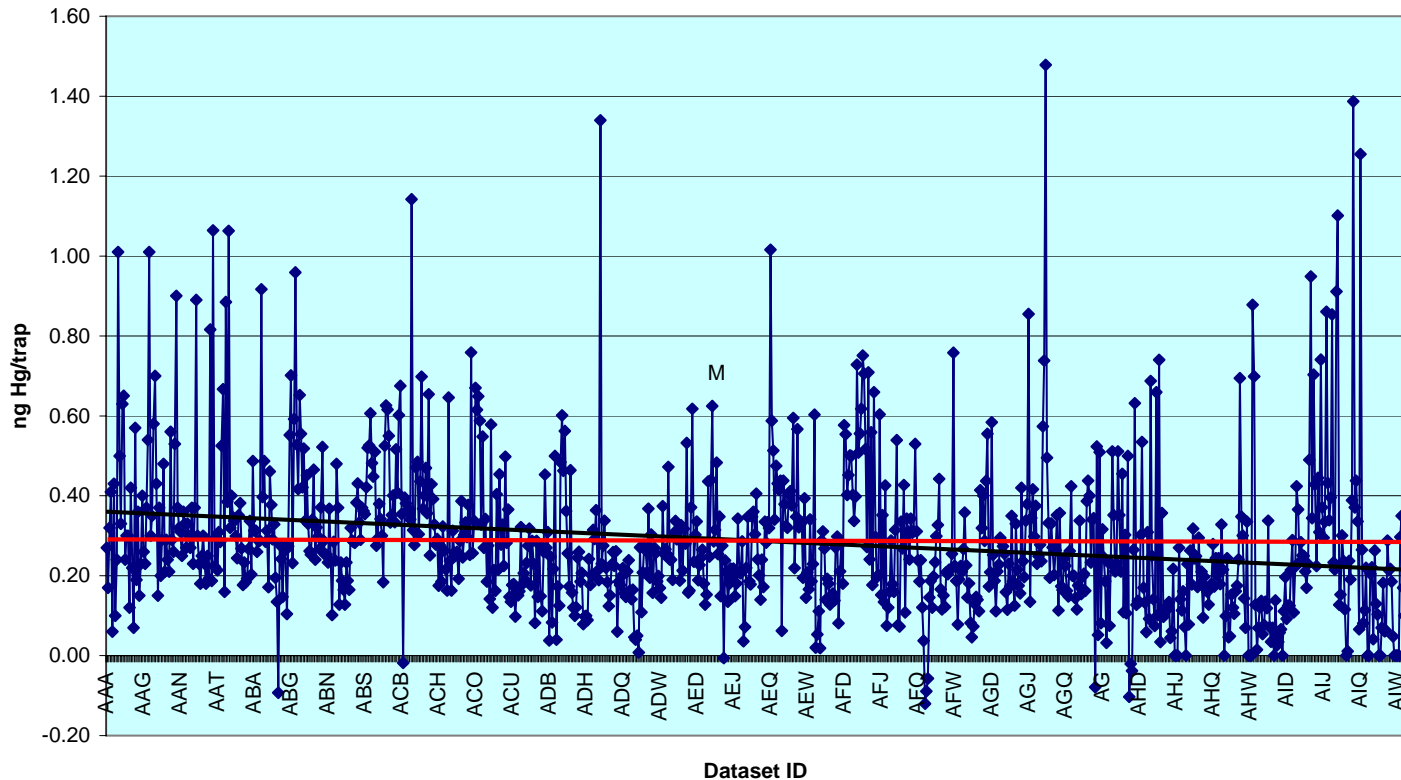
- Specialized Solid Sorbent Trap (FSTM™)
- Existing Sampling Equipment
- Easy To Implement
- 1/10th Cost Of Impinger Methods
- No Hazardous Materials
- Routine Field QA/QC includes simultaneous duplicates/trips

Frontier FSTM™ Trap – Hg Trap Blanks

Good Blank:Signal Ratio = Shorter Sample Time

Frontier FSTM Solid Sorbent Trap Hg Blank Results

n=916, mean=0.288, stdev = 0.196



Frontier Sorbent Trap Advantages

- No Hazardous Chemicals (No HAZMAT Shipping)
- Modern/Highly Sensitive/Routine/Fully Validated Analytical Method (US EPA 1631 CVAFS)
(MDL is 50 to 200 times lower than ASTM)
- Low Mercury Blank Of Trap (<1 ng/trap)
(Low Hg Blank Allows For 15L Sample Volume)
- Low Sample Volume Allows For Shorter Sample Times
- Shorter Sample Time = More Data
- Minimal Sample Train Surface Area (No Hg Wall Loss)
- No SO₂/NO_X/Ash Interferences For Coal Fired Fluegas
- Very Low Method Overall Cost (Labor and Analysis)
- Excellent Field QA Capability (simultaneous Field Dup)
- Smaller/Easier Equipment Package



Principles Of Analytical Method For Analysis Of US EPA 30B Solid Sorbent Traps

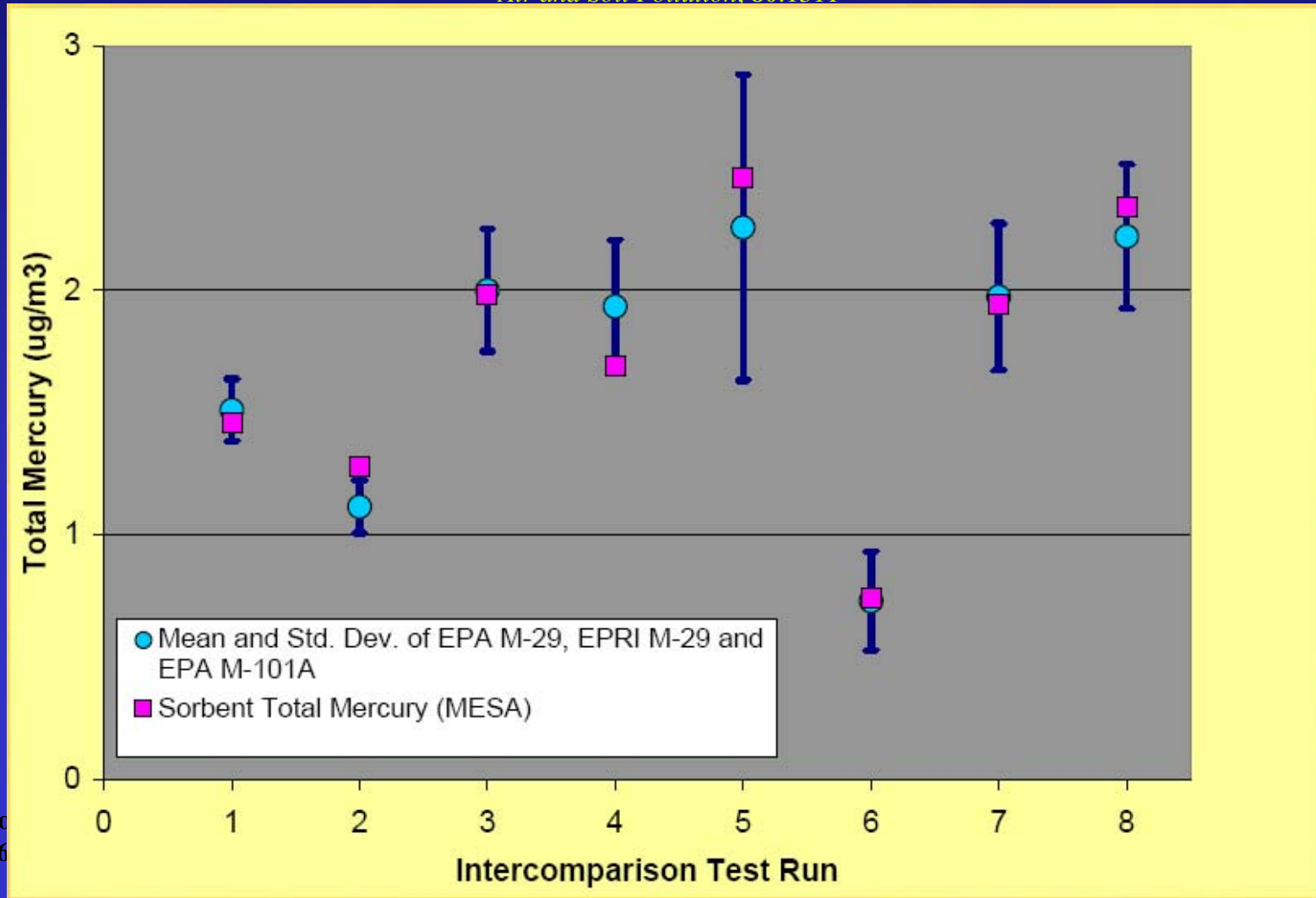
US EPA Method 1631, Revision E (Digestion II)

- Digest Trap or Solids via $\text{HN03}/\text{H2S04}$ Hot Acid Reflux
- Oxidize w/ BrCl converts Hg-org and Hg^0 to Hg (II)
- Pre-reduction with NH_2OH to destroy free BrCl
- Reduction with SnCl_2 to convert Hg (II) to Hg^0
- Purge and Dual Gold Amalgamation Preconcentration
- Thermal Desorption Into CVAFS Detector

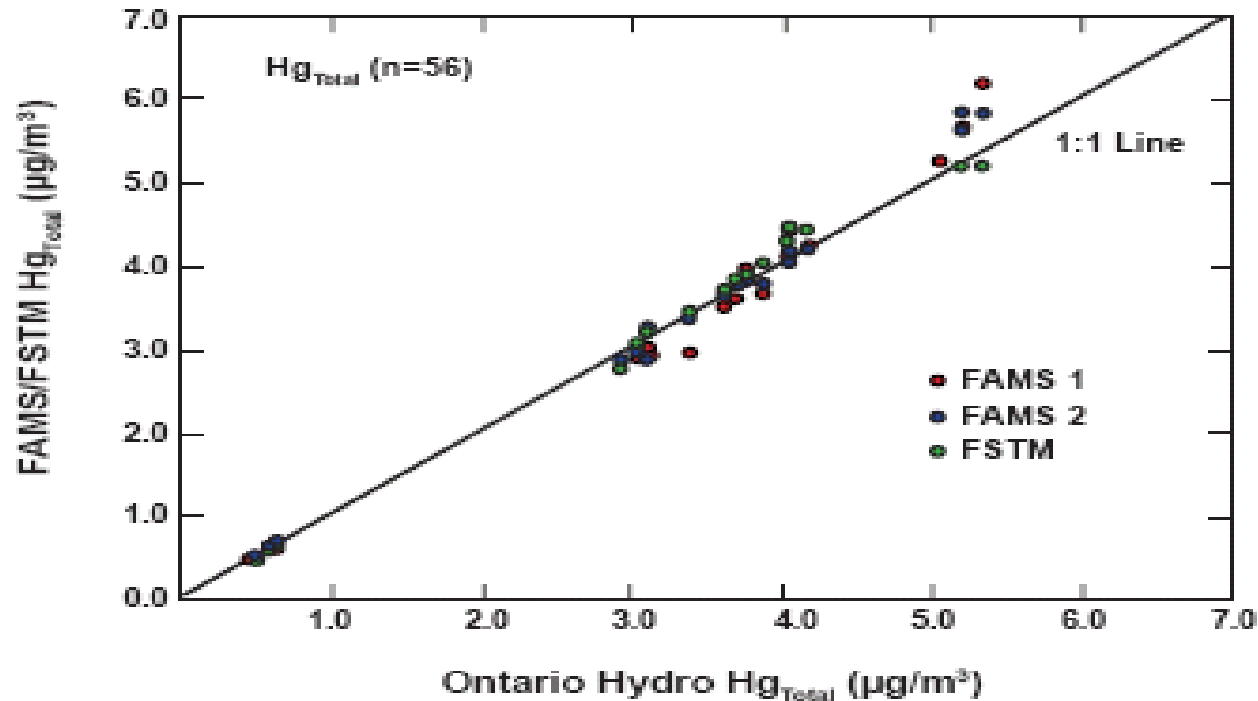


EPA and EPRI Fluegas Total Mercury Method 301 Validation (1993) Nott B.R., Huyck K.A.,

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. Nott B., (1995) "Intercomparison of Stack Gas Mercury Measurement Methods," *Water, Air and Soil Pollution*, **80**:1311



Results Of DOE FETC 2001 Intercomparison 15 Runs: Sorbent Method Vs Ontario Hydro



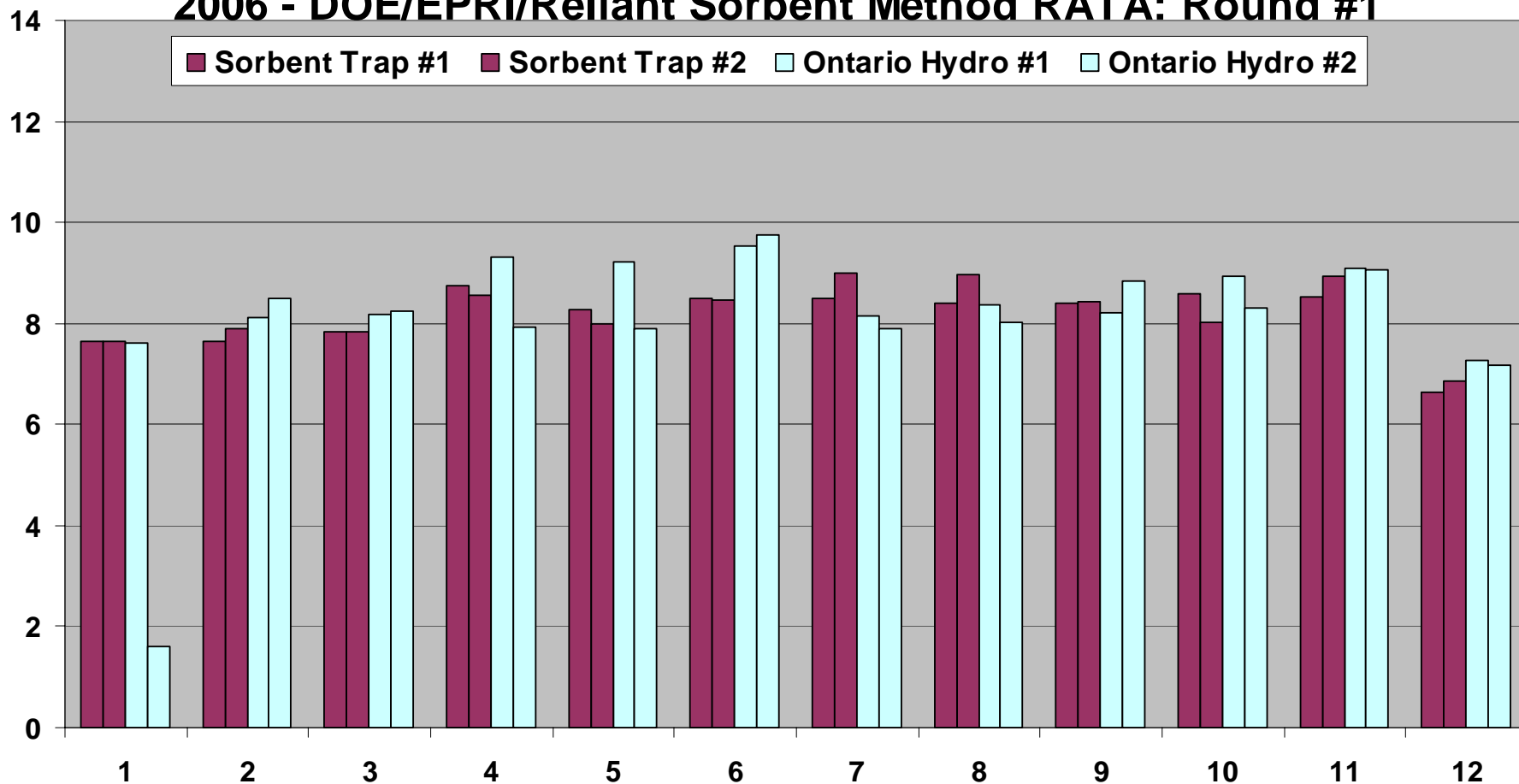
Trap	Intercept	Slope	R2
FAMS 1	-0.18	1.08	0.975
FAMS 2	-0.09	1.07	0.987
FSTM	0.00	1.03	0.992

2006 DOE/EPRI/Reliant Sorbent Method RATA Evaluation

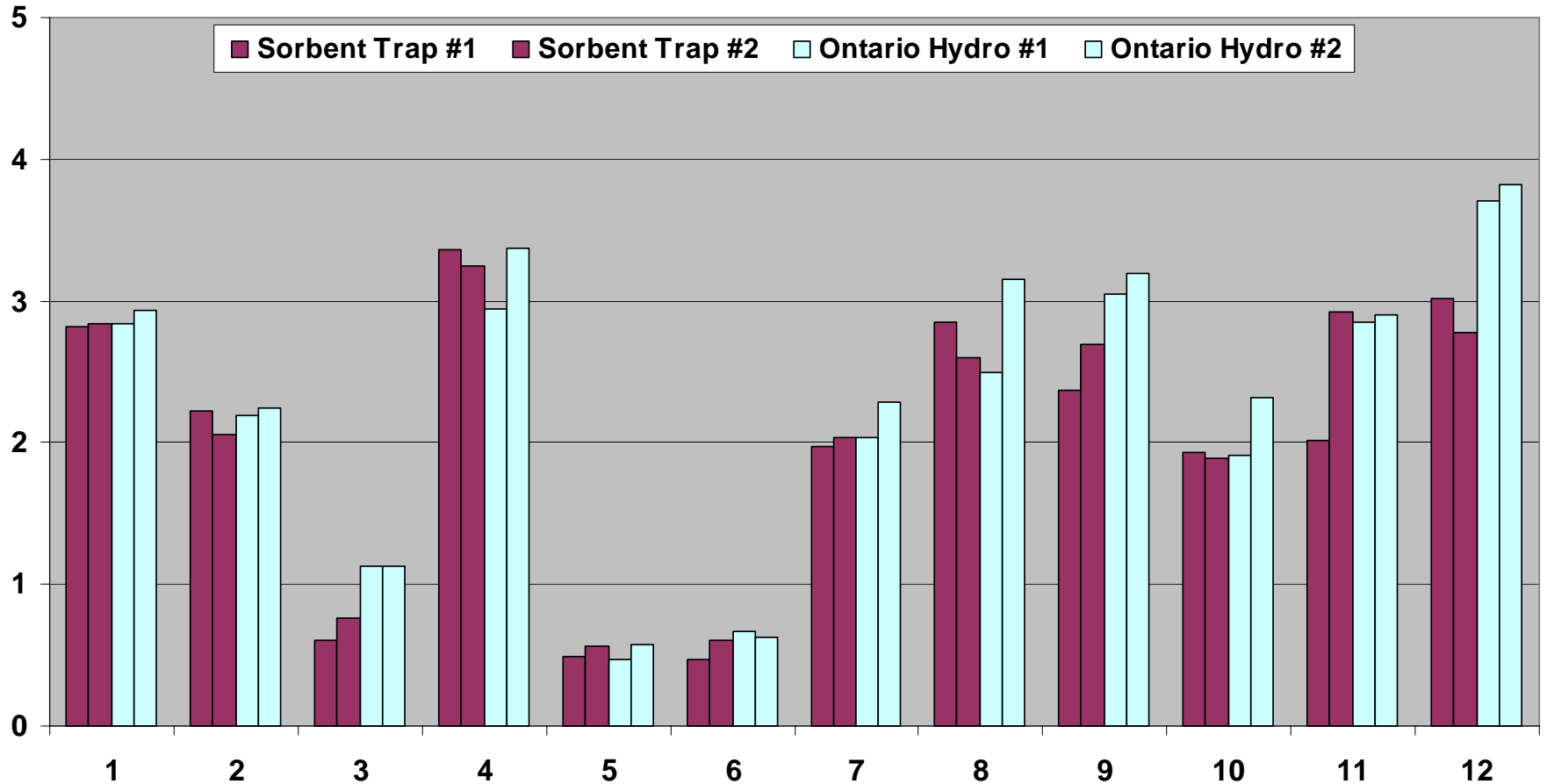
- **Three Test Site Locations**
 - 1) Normal Operations (No Hg Removal)
 - 2) Activated Carbon Injection ~ 80% Target Hg Removal
 - 3) Activated Carbon Injection ~ 90% Target Hg Removal
- **Ontario Hydro Method: EERC**
 - OH Method Co-Author (Good Confidence In OH Data)
 - On Site Analysis
- **Sorbent Trap Method Reliant / FGS**
 - Reliant Staff Trained On Sorbent Method and Took Samples
 - FGS Provided Equipment, Traps and Analysis
 - Reliant Sent Traps To Frontier For Analysis 10 Day TAT



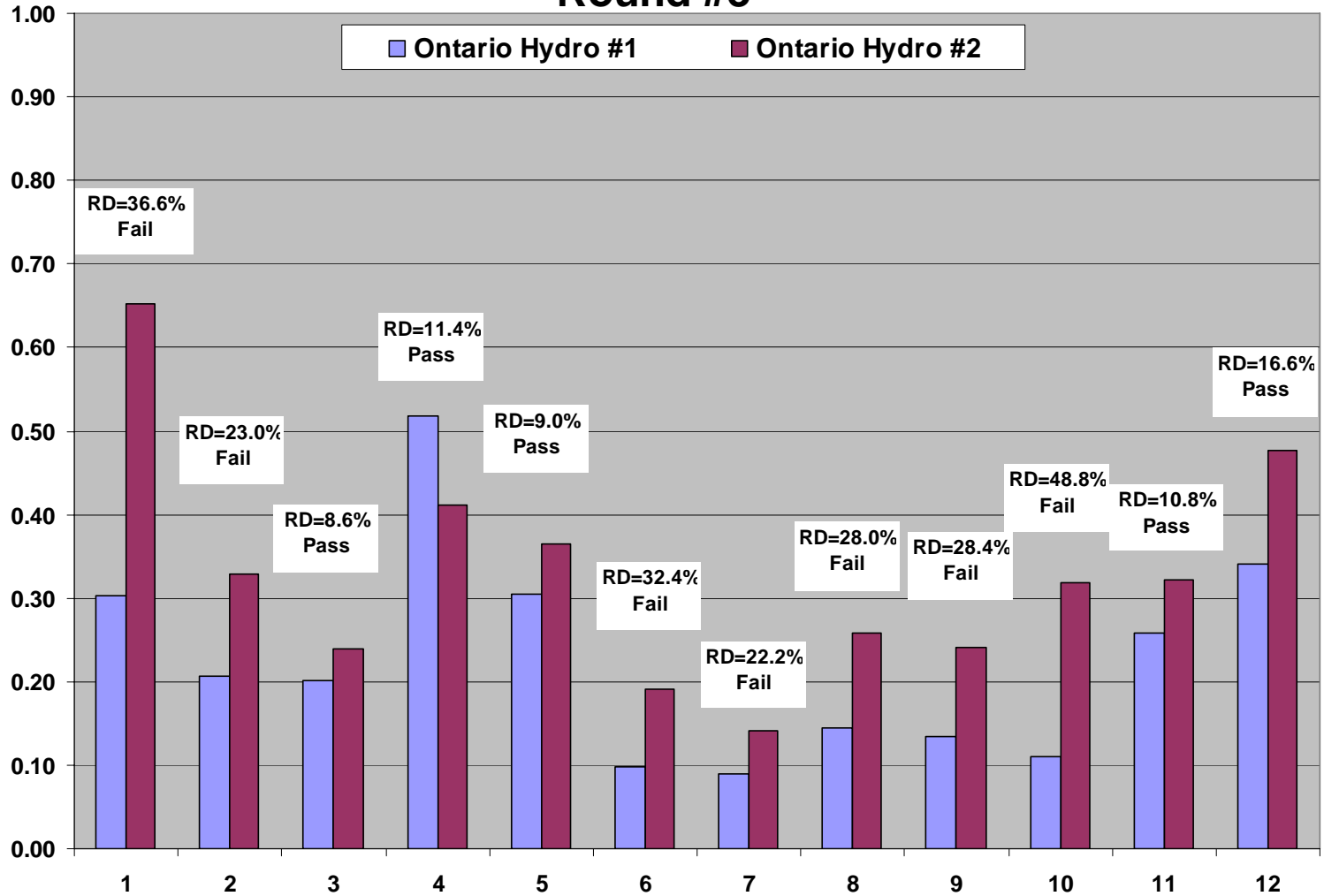
2006 - DOE/EPRI/Reliant Sorbent Method RATA: Round #1



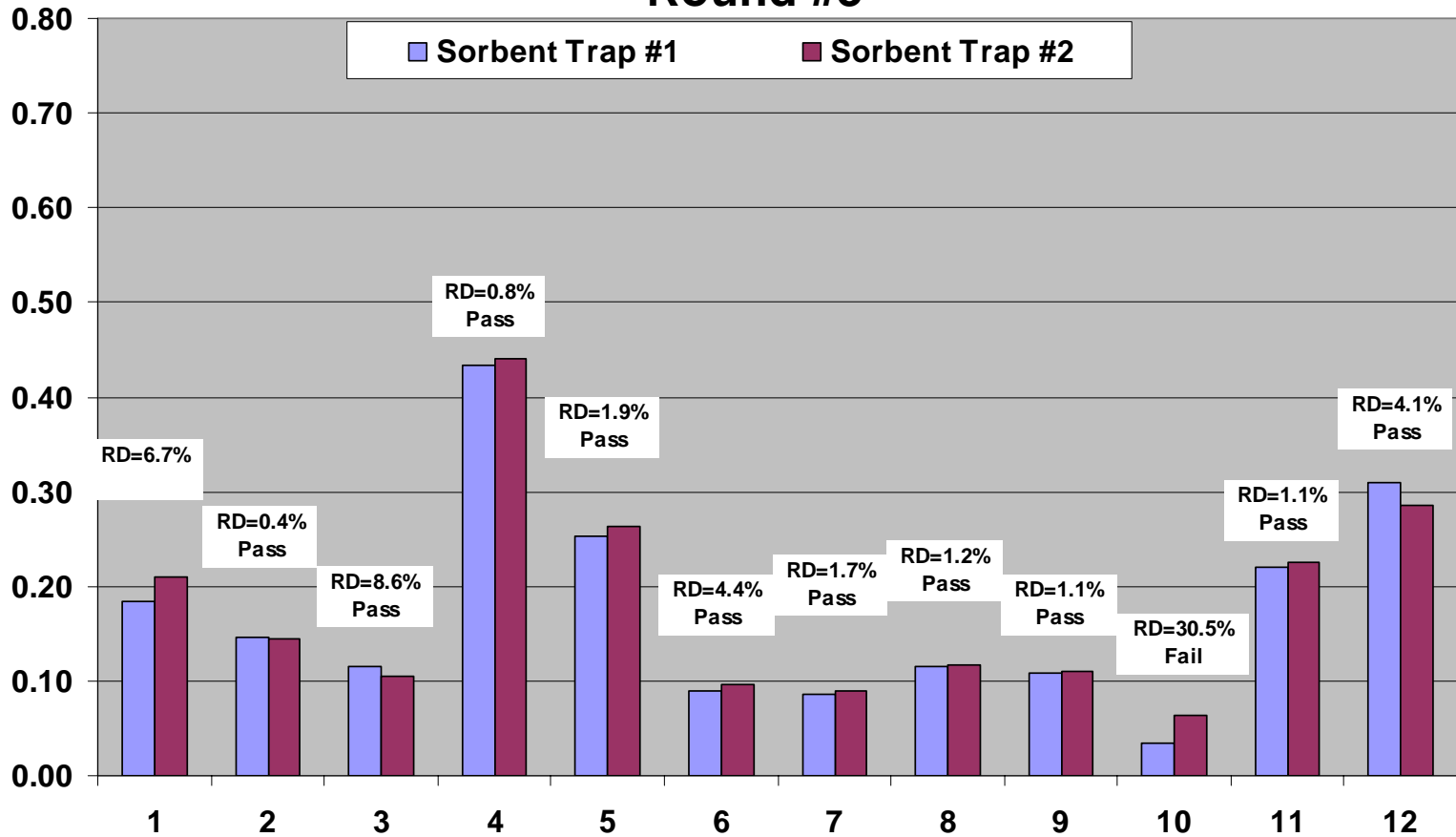
2006 - DOE/EPRI/Reliant Sorbent Method RATA: Round #2



DOE/EPRI/Reliant Sorbent Method RATA: Round #3



2006 - DOE/EPRI/Reliant Sorbent Method RATA: Round #3



Advantages: Draft EPA 30B Via Wet Acid Digestion / US EPA Method 1631 (CVAFS)

- 16 Years Of Proven Testing – Reliable Analysis Method
- Wet Digestion Method/ 1631 Considered Gold Standard 30B
- All EPA Method (US EPA Method 1631, Revision E, Digest II)
- 24 Hour TAT/On Site Analysis Available
- Wet Acid Digestion Allows Us To:
 - Re-Analyze/Confirm The RATA Results If Needed – Key To Tekran!
 - Frontier Archives All Wet Acid Digests For Potential Re-analysis
 - Rigorous QA package ensures high quality/compliance data package
 - Method Promulgated Back In 1997 (On US EPA Web Site)



Most Conservative RATA Approach For Analysis Thermal Desorption Method?

- **Thermal Desorption Is A Destructive Method** – Once Burned Into Detector Sample Spent – No Possibility Of Verifying Results Via Re-analysis (Example Of Recent Field Campaign)
- **Does Not Follow The Same Rigorous QA/QC** that US EPA Method 1631 CVAFS (Analytical Duplicates, Analytical Spikes, etc)
- **Instrument Drift?** – If Instrument Drifts At End Of Run (Below 90% CCV Recovery) Data Is Invalid – Can Not ReRun Samples. Have To Rerun The Entire RATA.



The Highest Probability Of Passing A Hg RATA

Approach For Highest Likelihood Of Passing A Hg RATA:

- **RATA Protocol:** An efficient, conservative field testing protocol (Not RATA until CEM is pre-certified that the CEM is ready for official RATA)
- **Experienced 30B Field Staff:** Experienced field sampling staff that have performed sorbent trap sampling for years
- **Proven/Reliable Sorbent Traps:** The most reliable Hg sorbent traps with 16 years of tested, proven experience
- **Proven/Reliable Analytical Method:** The most reliable Hg analysis available (US EPA Method 1631-CVAFS), performed by the laboratory that designed and perfected the principles of US EPA 30B over 16 years ago.



Recent Frontier/TRC RATA: US EPA 30B Vs Tekran

Selected Run Substitution Summary					
<i>d bar</i>	<i>Sd</i>	<i>t-value</i>	<i>cc</i>	<i>RM mean</i>	<i>RA</i>
-0.316	0.201	2.306	0.155	3.10	15.15
CEM mean = 3.42		*Difference between mean RM and CEMS		PASS	
Avg. Mw = 297.0		0.32			

# Of runs	30 Spiking Criteria	RATA Method
Pass/Fail	(Average = 85%-115%)	Pass/Fail?
12/12	101.0%	PASS

TABLE 1: Frontier/TRC RATA Results

Lab Data Set ID	Lab Run #	Sample ID	Sample Vol (Liters)	Total Hg (ug/m3)	RD	
THG16-071114-1	13	R1T1-FSTM A	26.71	3.44		
THG16-071114-1	14	R1T2-FSTM A	26.86	3.48	0.6%	PASS
THG16-071114-1	15	R2T1-FSTM A	27.18	3.31		
THG16-071114-1	16	R2T2-FSTM A	27.80	3.40	1.3%	PASS
THG16-071114-1	17	R3TSpike-FSTM A	27.52	3.75		
THG16-071114-1	20	R3T2-FSTM A	27.77	3.43	4.5%	PASS
THG16-071114-1	21	R4T1-FSTM A	26.23	3.10		
THG16-071114-1	22	R4T2-FSTM A	26.40	3.00	1.6%	PASS
THG16-071114-1	23	R5TSpike-FSTM A	25.52	3.16		
THG16-071114-1	24	R5T2-FSTM A	25.78	2.95	3.4%	PASS
THG8-071107-1	13	R6T1-FSTM A	24.40	3.22		
THG8-071107-1	14	R6T2-FSTM A	24.79	3.61	5.7%	PASS
THG8-071107-1	15	R7T1-FSTM A	27.21	3.21		
THG8-071107-1	16	R7T2-FSTM A	27.71	2.97	3.9%	PASS
THG8-071107-1	17	R8TSpike-FSTM A	24.45	2.90		
THG8-071107-1	20	R8T2-FSTM A	25.06	3.03	2.3%	PASS
THG8-071107-1	21	R9T1-FSTM A	24.86	2.83		
THG8-071107-1	22	R9T2-FSTM A	25.14	2.90	1.2%	PASS
THG8-071107-1	23	R10T1-FSTM A	24.99	3.04		
THG8-071107-1	24	R10T2-FSTM A	25.49	3.01	0.4%	PASS
THG17-071108-1	51	R11T1-FSTM A	25.69	2.42		
THG17-071108-1	52	R11T2-FSTM A	26.16	2.63	4.1%	PASS
THG10-071109-1	14517	R12T1-FSTM A	26.35	2.56		
THG10-071109-1	14518	R12T2-FSTM A	26.42	2.81	4.7%	PASS

US EPA 30B RATA Options:

Option 1: Take Samples and Send Back To FGS (5 Day TAT)

(Reliant Energy Takes Samples – Has Such High Confidence In Their Ability To Perform Sampling And Frontier's Ability To Analyze Traps – No Need For On-Site Analytical Or Fast TAT)

- 20 RATAs To Be Performed For Reliant In This Way

Option 2: Send Traps To FGS / 24 Hour Turn-Around Time

- > Take Samples – FedEx Overnight To Frontier
- > Frontier Produce Results By End Of Next Day
- > Get Results Same Time Frame As On-Site Analysis

Key Advantage #1: 30% Cheaper Than On-Site Analysis

Key Advantage #2: Samples Analyzed In Controlled Lab Setting

= **High Probability Of Higher Quality Analytical Results**



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- All EPA Method (US EPA Method 1631, Revision E, Digest II)
- 24 Hour TAT/On Site Analysis Available
- Lower Cost / Easier For Field Teams To Implement (Simple)
- Low Level Detection Limit – Allows Routine Measurement Of Low Sources
- Wet Acid Digestion Allows Us To:
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