# Mercury Speciation in Coal Combustion Flue Gas: Flue Gas Adsorbent Mercury Speciation (FAMS) Method

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DOE/NETL

Hg Measurements Workshop

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# Frontier Flue Gas Adsorbent Mercury Speciation Topics Covered

- History Of FAMS Method
- Total & Speciation Hg Methods
- Sampling Equipment
- Analytical Technique
- US EPA PBMS Validation – FAMS Vs OH
- DOE/NETL – Frontier CRADA – FAMS Vs OH
- Frontier vs OH Advantages
- Method Applications
- Conclusions

# Flue Gas Adsorbent Mercury Speciation (FAMS) Historical Studies Of Interest

- 1993 - Bloom develops/publishes solid sorbent and wet impinger flue gas Hg speciation method
- 1993-1994 –Method Intercomparison (EPRI)
  - > US EPA Method 29
  - > US EPA Method 101 A (Total Hg Only)
  - > Ontario Hydro
  - > MIT Method
  - > Frontier Method
- 1996 EERC (Pilot & Bench Scale) Evaluation

# Flue Gas Adsorbent Mercury Speciation (FAMS) Historical Studies Of Interest

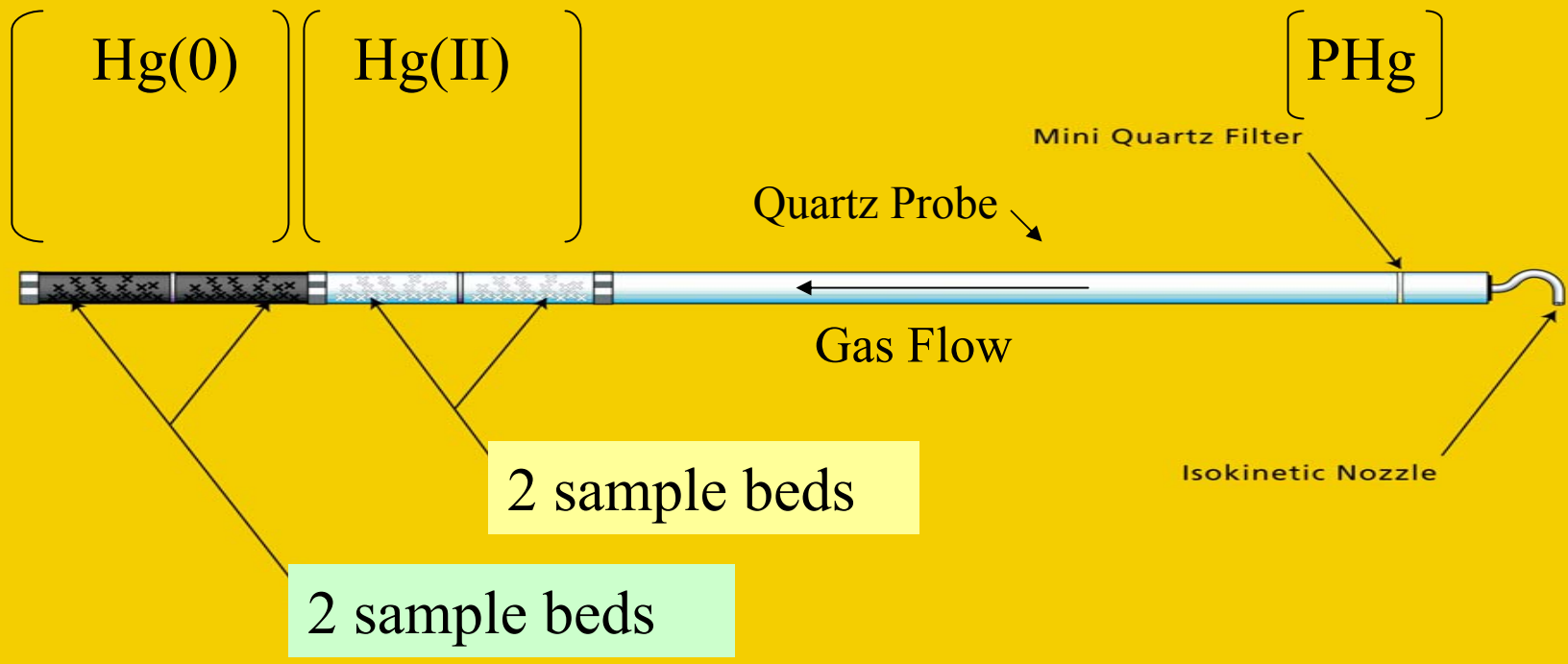
- 1997 – Frontier Internal Funded Evaluation
- 1997 – EERC Evaluation (Pilot System)
- 1998 – 1998 ADA Evaluation (Full Scale)
- 2000 – EERC Hosted US EPA PBMS Validation
- 2001 – DOE/Frontier CRADA 00-F038
- 2004 – DOE/Frontier Method Intercomparison

FAMS Now Fully Validated

# Flue Gas Adsorbent Mercury Speciation (FAMS) Method Hg Measurements

- Particulate Hg (PHg) - semi-isokinetic and/or incident particulate Quartz Fiber Filter
- Gaseous Oxidized Hg (Hg(II)) – KCl Solid Sorbent Trap
- Gaseous Elemental Hg (Hg(0)) – Chemically Impregnated Carbon Solid Sorbent Trap
- Total Hg = PHg + Hg(II) + Hg(0)

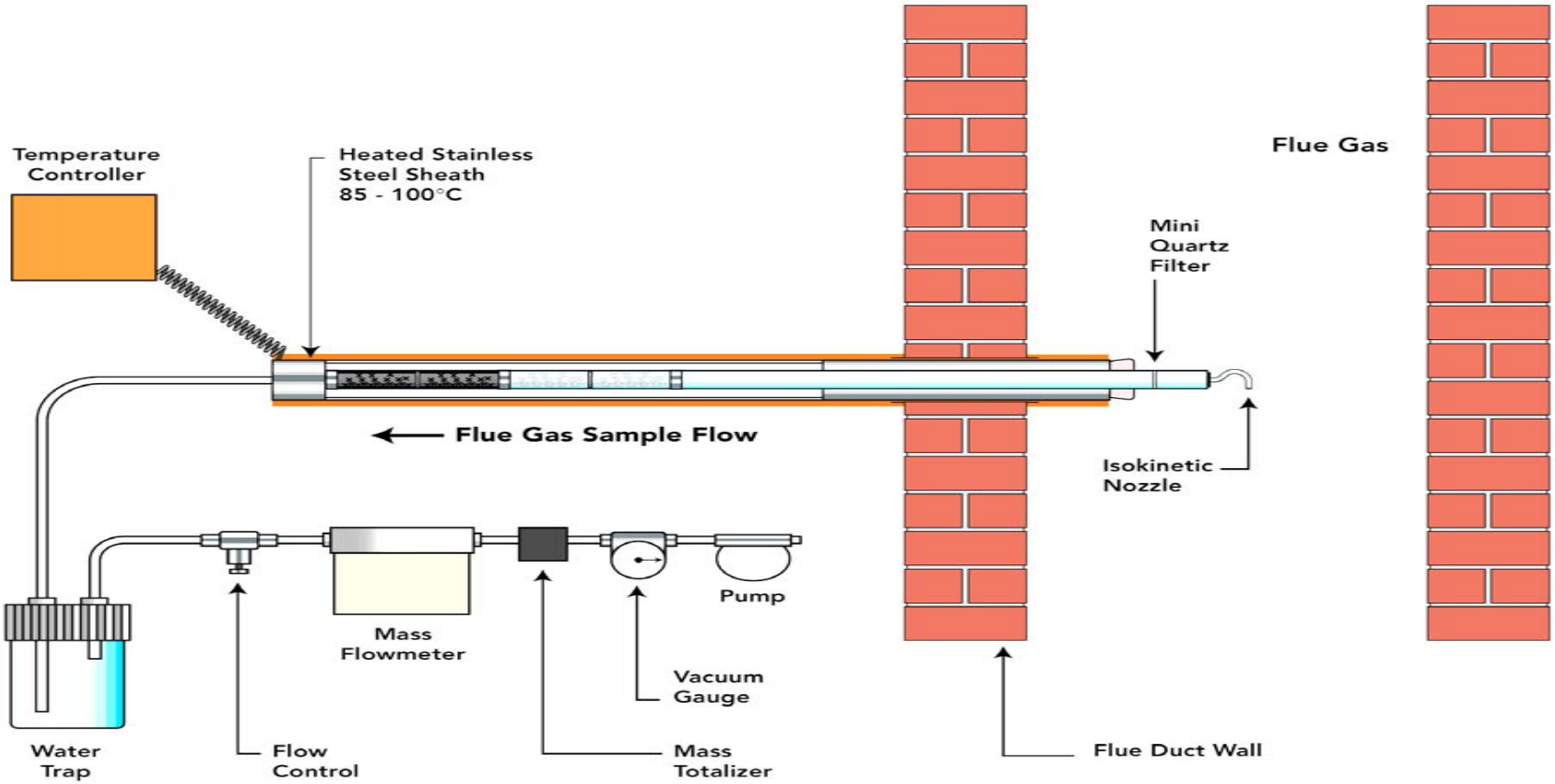
# Flue Gas Adsorbent Mercury Speciation (FAMS) Sample Trap View



# Flue Gas Adsorbent Mercury Speciation (FAMS) Principles of Operations

- Sequential Selective Adsorption Of Hg(II) and Hg(0)
- High Purity Solid Adsorbent Material
- Hg(II) Physi-sorbed onto KCl
- Hg(0) Chemi-sorbed and Physi-sorbed CIC
- 0.5 +/- 0.1 SLPM Flow Rate
- 95C +/- 5C Controlled Trap Temperature
- Sample Volume Range (15L to 5000L)
- Trap Hg Capacity - 5% (of the mass of the trap)
  Hg(0) = 1.5mg/trap  Hg(II) = 1mg/trap

# Flue Gas Adsorbent Mercury Speciation (FMSS) Sample Trap & Sampling System



# Key Components Of Frontier FAMS (Speciation) and FSTM (Total) Method

1. Analytical Method (CVAFS - US EPA Method 1631)
   - > Highly Sensitive/Accurate
   - > Low analytical MDL (pg/L)
   - > Fully Validated
2. Sample Media (FAMS & FSTM Trap) Low Hg Blanks
   - > PHg 0.03ng Hg/Filter
   - > Hg(0) 0.50ng Hg/trap
   - > Hg(II) 0.05ng Hg/trap
   - > Digestion Reagents - < 0.5 ng Hg/digest
3. Basic Field Sampling Clean Techniques
4. Highly Precise Sample Volume Measurement

# Overall FAMS Method Detection Limits

- PHg - 0.006 ug Hg/m^3
- Hg(0) - 0.0027 ug Hg/m^3
- Hg(II) - 0.0025 ug Hg/m^3
- THg - 0.0045 ug Hg/m^3

# FAMS and FSTM Blank to Signal Ratio

> Coal Flue Gas Hg Conc. (2-10 ug/m^3 or 2-10 ng/L)

> Trap Blank 1ng/Trap

> Flow Rate = 0.5 slpm

> 15L Sample Volume @ 2 ng Hg/L = 30 ng/trap (Blank To Signal = 1:30)

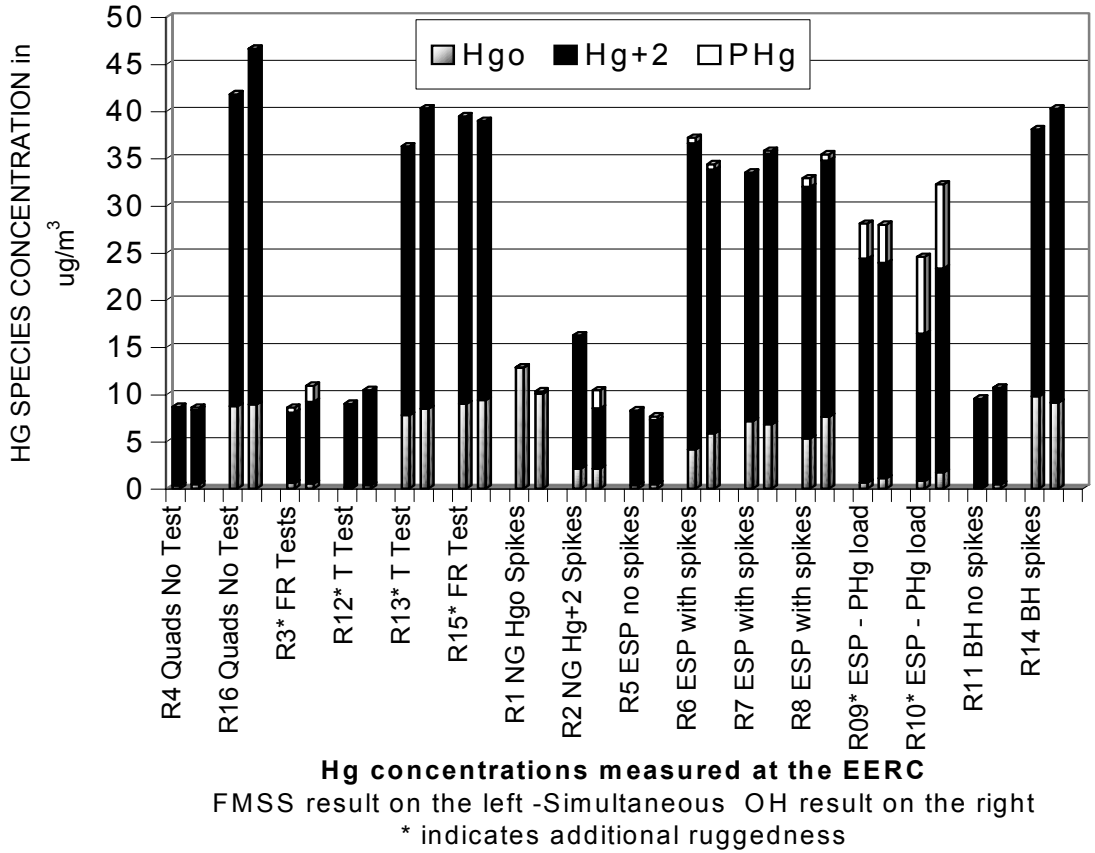
> 15L Sample Volume @ 10ng Hg/L = 150 ng/trap (Blank To Signal = 1:150)

> Accomplished in ~ 30 minute sample

# US EPA Performance Based Measurement Standard Validation Study @ EERC

1. Quality Control Requirement
2. Matrix Suitability
3. Laboratory Reproducibility
4. Method Detection Limit
5. Ruggedness
6. Accuracy
7. Precision
8. Bias
9. Interference

# PBMS Validation – Overall Summary Frontier FAMS v.s.Ontario Hydro




**Hg concentrations measured at the EERC**

FMSS result on the left -Simultaneous OH result on the right

* indicates additional ruggedness

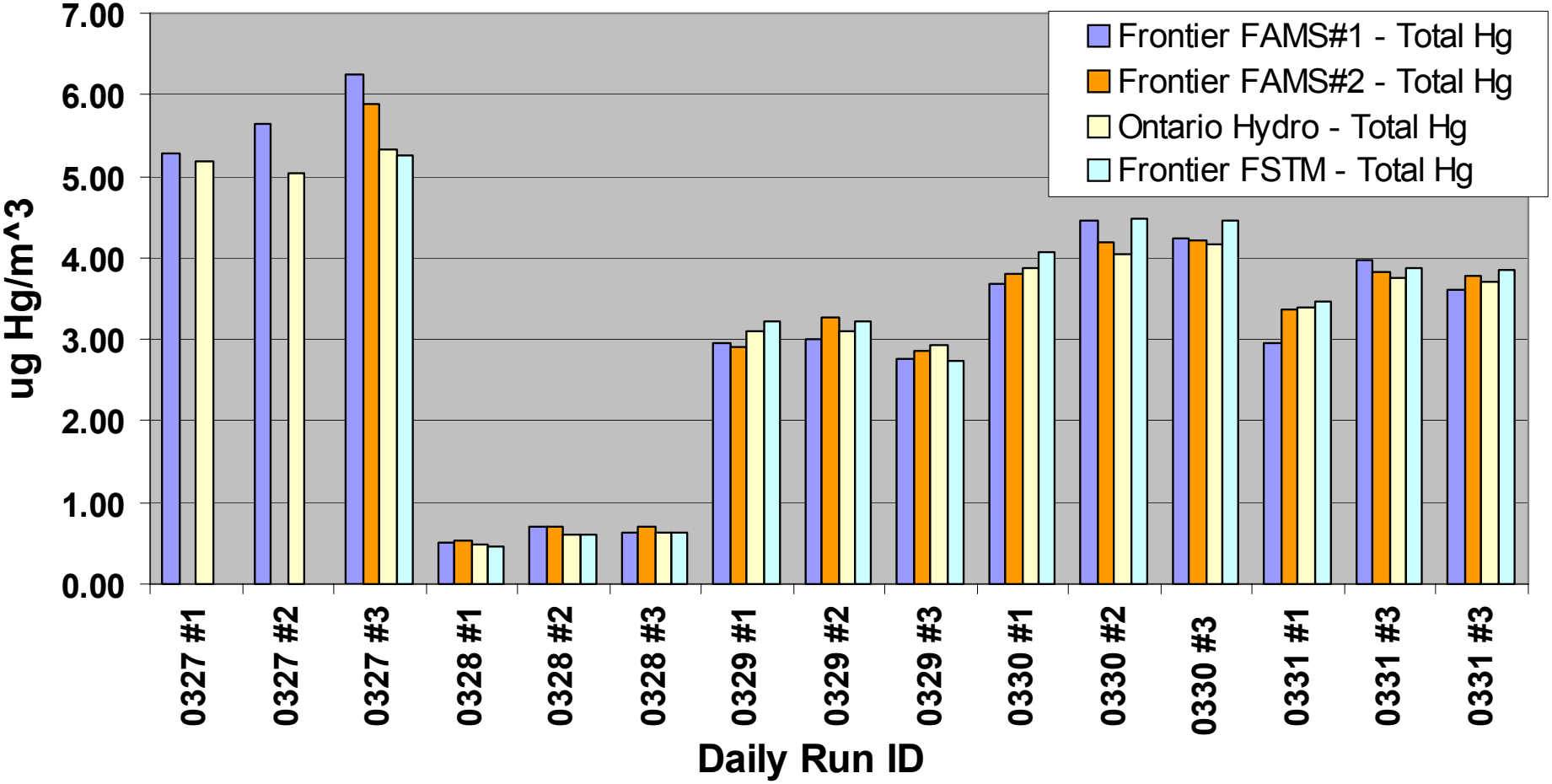
# FAMS PBMS Summary

- Mean of Frontier FAMS v.s OH for all species: 100 +/- 20%
- Passed All Rigorous PBMS Interference/Ruggedness Tests
- All Method Materials Are Routine and Commercially Available
- Method Passed Validation Rigors
- Method Currently Employed By Industry

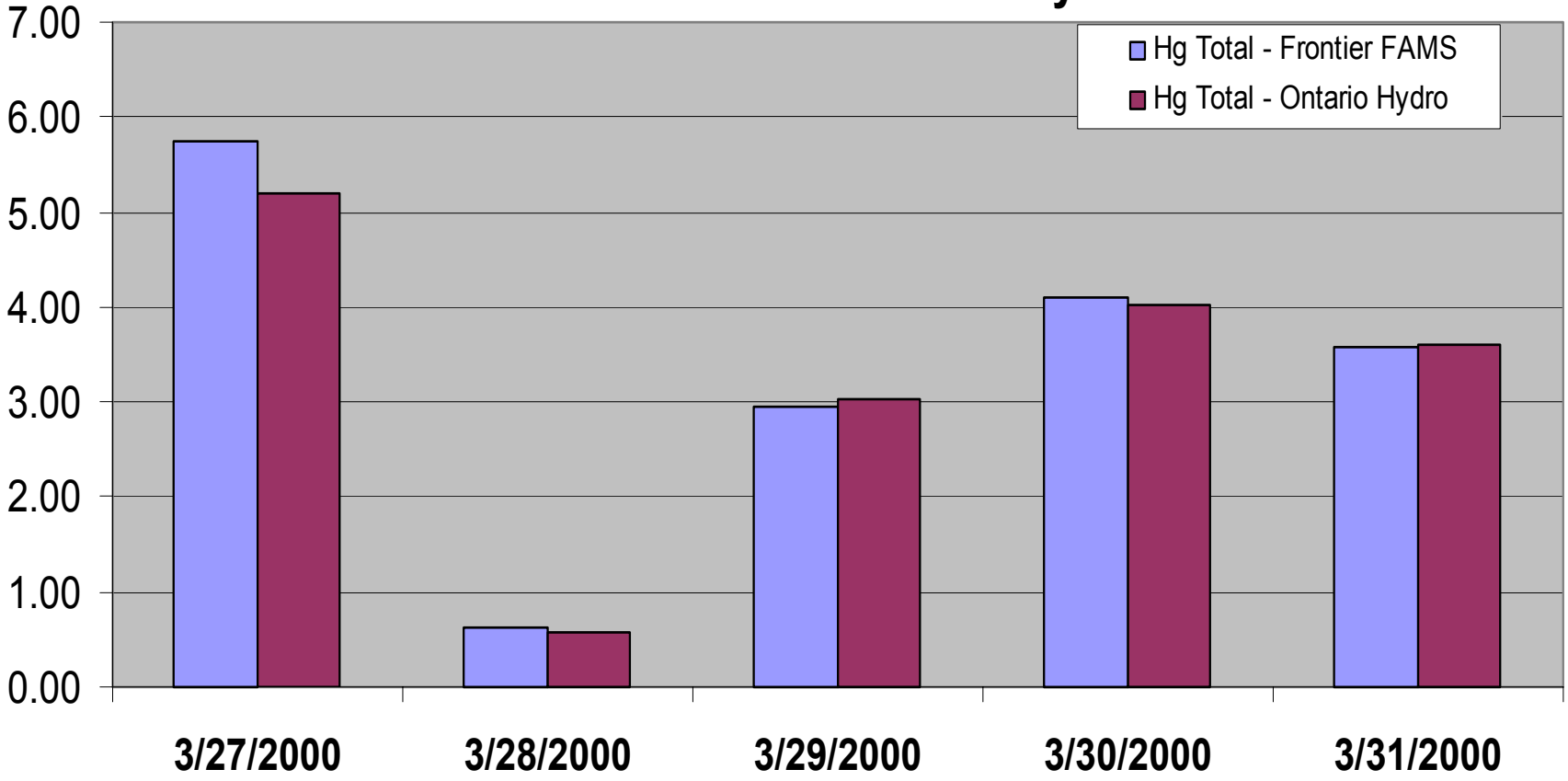
# 2001 Method Intercomparison @ DOE (Frontier (FAMS & FSTM) vs Ontario Hydro)

- Hosted at Department of Energy – FETC
- 5 Day Method Intercomparison
  - > Flue Gas Sorbent Total Mercury (FSTM)
  - > Flue Gas Adsorbent Mercury Speciation (FAMS)
  - > Ontario Hydro (Draft ASTM 1998)
- 2 Hour Training of DOE Sampling Personnel
- All samples were taken by DOE Personnel
- DOE FETL analyzed OH samples

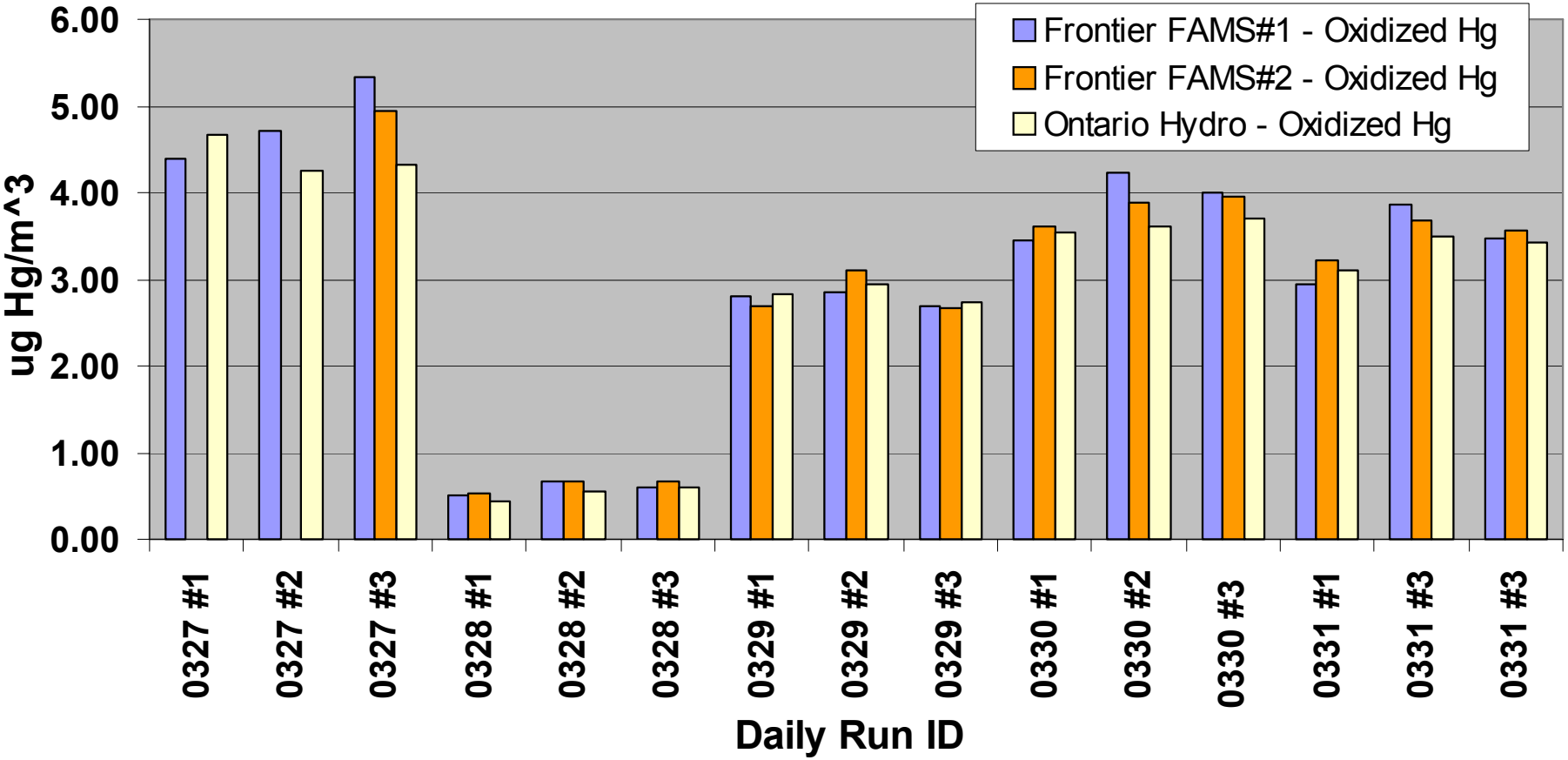
# DOE FETC - Intercomparison
## Total Hg By Run
## Frontier FAMS#1 vs FAMS#2 vs FSTM vs Ontario



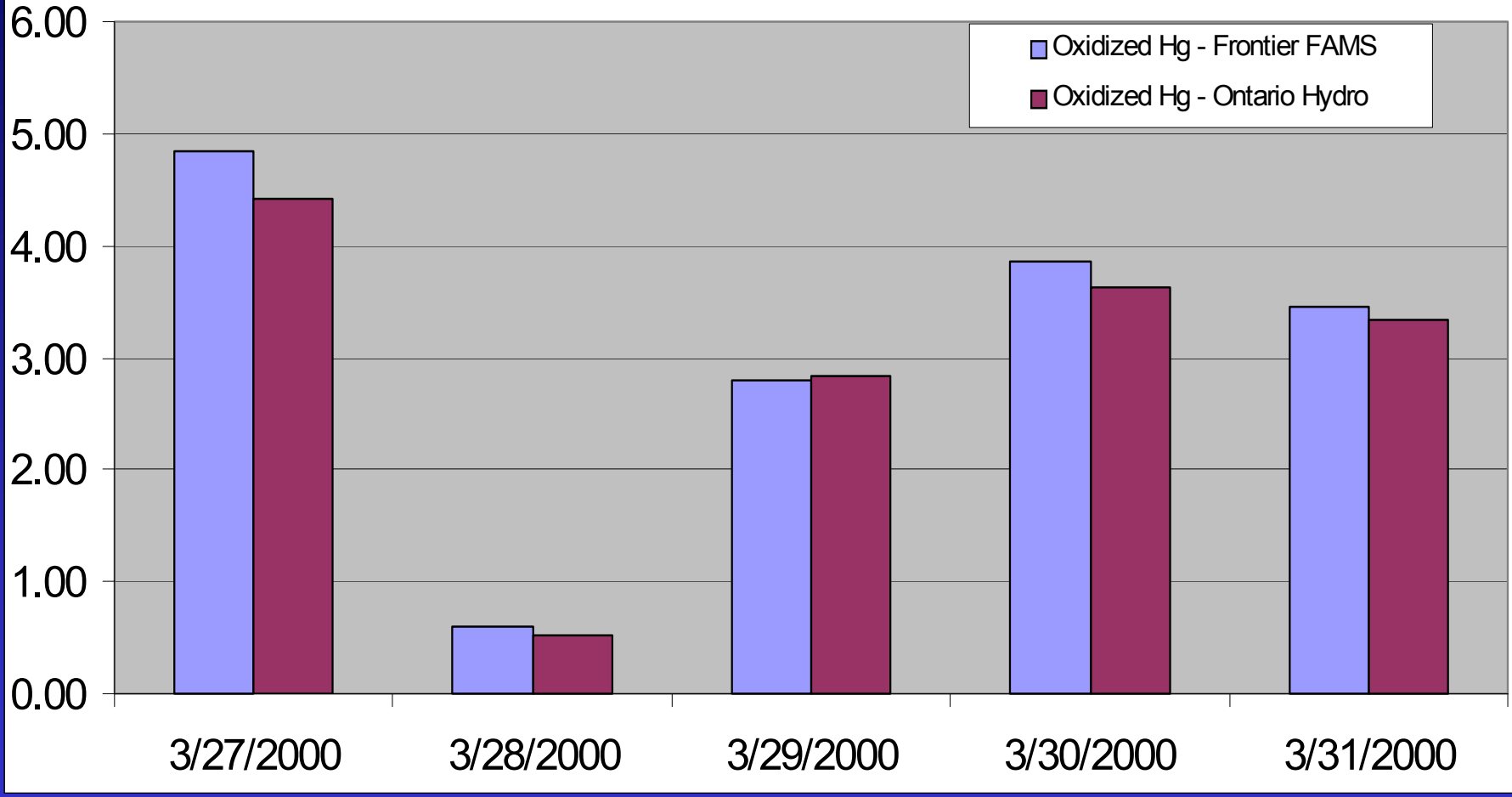
# DOE FETC Intercomparison - Daily Average Total Hg Frontier FAMS vs Ontario Hydro



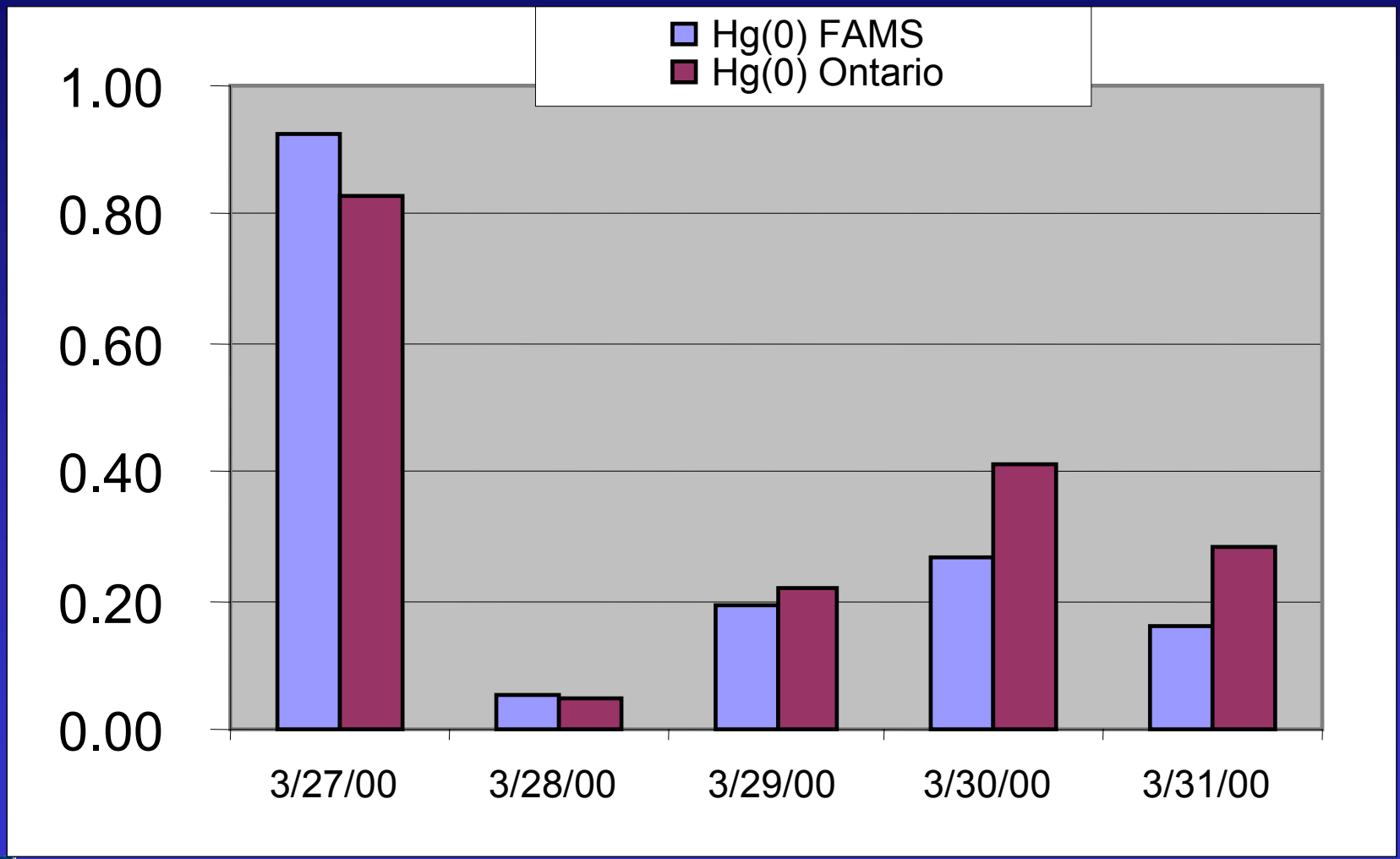
# DOE FETC - Intercomparison
## Oxidized Hg By Run
## Frontier FAMS#1 vs FAMS#2 vs Ontario



# DOE FETC Intercomparison - Daily Average Oxidized Hg (Hg(II)) Frontier FAMS vs Ontario Hydro



# DOE FETC Intercomparison
# Daily Average Elemental Hg – FAMS vs OH



# Frontier FAMS v.s. OH
# Summary Of Results @ DOE

- RPD Between Methods For Any Day

  Total Hg < 10% RPD

  Hg (II) < 13 % RPD

- Low Hg(0) Due To Carbon Injection (< 1 ug/m^3)

  Hg (0) < 19% RPD (First Three Days)

  Hg (0) = 63% RPD (03/31/00)

# Ontario Hydro Method Disadvantages

- Hazardous Chemicals (costly and difficult to ship)
- Antiquated Analytical Method (ASTM CVAA Method) (High MDL – 25 year old method)
- High Hg Blank Of Impinger Solutions (High blank requires large sample volumes)
- Large Sample Volume = Longer Sample Time/Sample
- Longer Sample Time = Less Data
- Large Sample Train Surface Area (Hg Wall Loss)
- Potential S02 Interferences
- High Method Overall Cost vs. Data Generation Ratio
- Poor Field QA Capability (No true field duplicates)

# FAMS and FSTM Method 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 S02/NOX/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

# FAMS (Speciated Hg) and FSTM (Total Hg) Applications

Sources:

- Coal Fired Power
- Municipal Solid Waste Incinerators
- Hg Retort Facilities
- Zn and Au Smelters
- Natural Gas Fired Power

Mission:

- Hg Compliance Testing
- Hg CEM Verification
- US EPA Method 324 – Emission Monitoring
- Hg Emission Control System Testing & Research

# FAMS (Speciation Hg) & FSTM (Total Hg) Conclusions

- Method Validated
- 2004 DOE Intercomparison – March 04
- Smelter Intercomparison – May 04
- Accurate and Precise Measurement Of Hg
- Easy Sampling Application
- Cost Effective
- More Data Points Generated
- Excellent R&D Tool For Hg Emission Control
- US EPA 324 – Manual Hg Emission Monitoring

# Flue Gas Adsorbent Mercury Speciation (FAMS) Studies Available Upon Request

- 2000 - US EPA PBMS Validation Study @ EERC
- 2001 – DOE/Frontier CRADA 00-F038
  "Comparison Of Sampling Methods To Determine Total and Speciated Hg in Flue Gas"
- 2001 – DOE/Frontier FAMS Vs. Ontario - Analysis
- 2004 – DOE/Frontier CFADA FAMS Vs. Ontario

# Analytical Method: CVAFS LOD v.s. LOQ

Limit Of Detection (LOD): (3 x Sigma)

"The point at which a measured value becomes larger than the uncertainty associated with it"

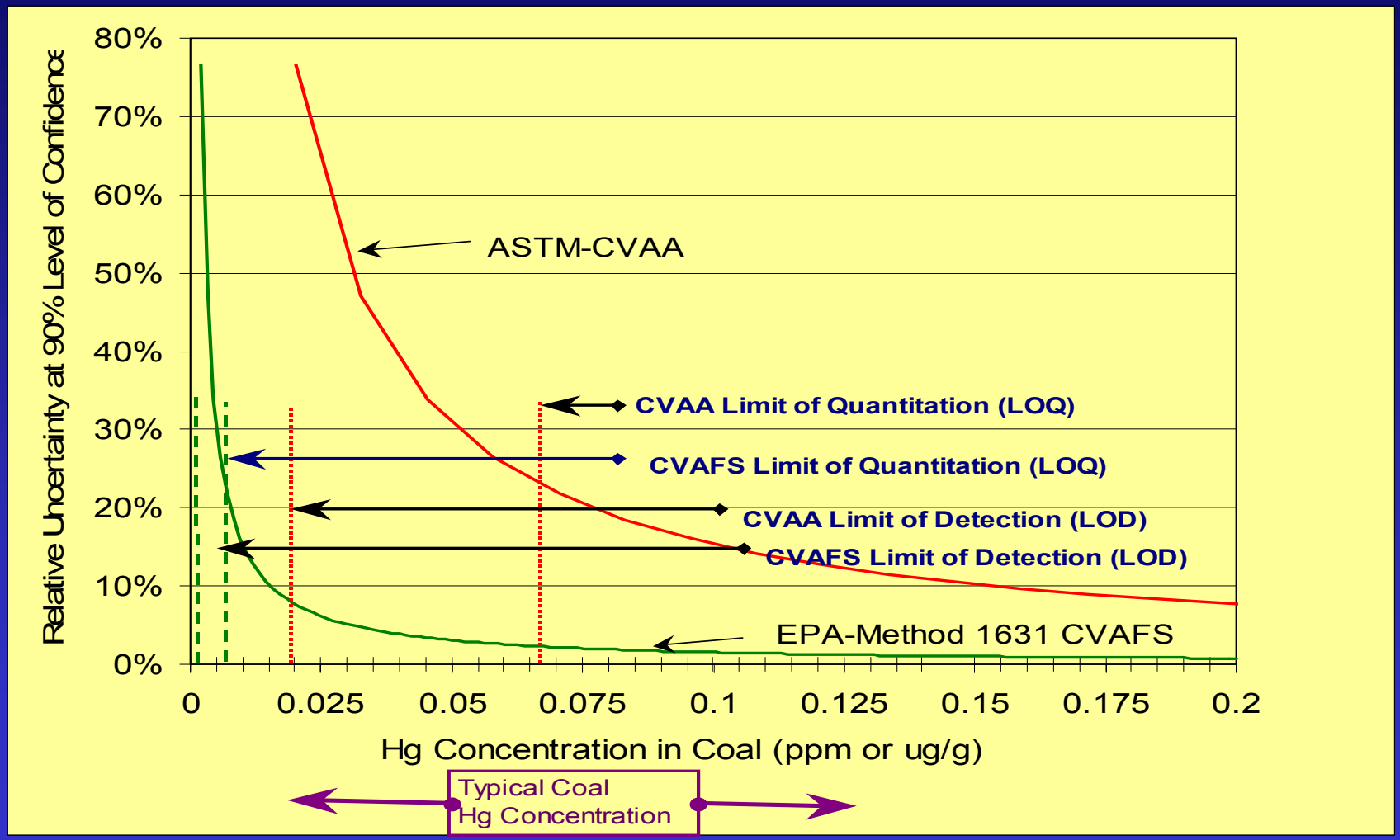
Limit Of Quantitation (LOQ): (> 10 x Sigma)

"The lower level where measurements become quantitatively meaningful" or

"The point where confidence in the measured value is at the 95% probability level (95% probable the results is accurate and reproducible)"

- Taylor 1987 - "Quality Assurance Of Chemical Measurements

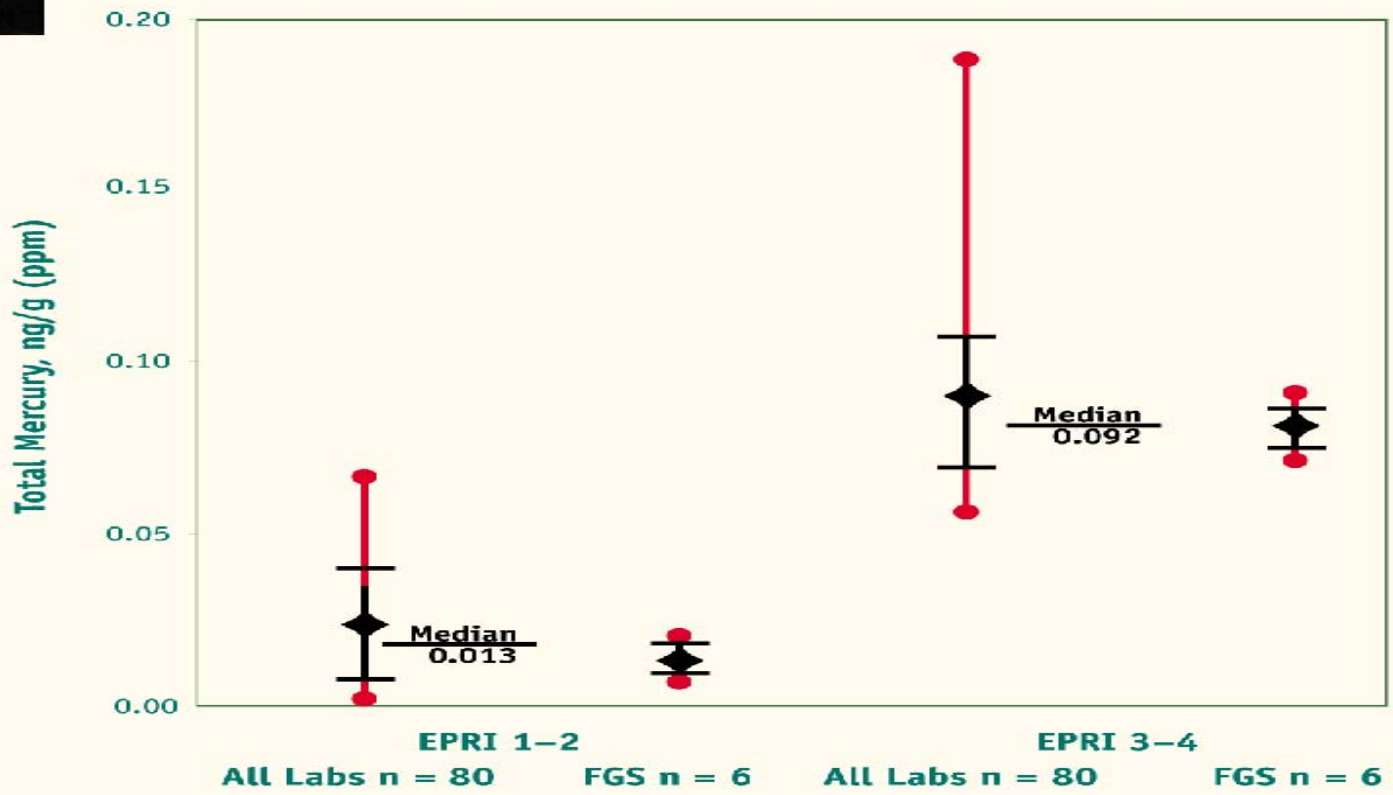
# Analytical Method: ASTM CVAA v.s. US EPA CVAFS



# Coal Mercury Measurements
# Variation Between Laboratories and Methods

## Figure 4

Between-lab (i.e., between-method) variability for total Hg in coal is too high.



# Blind Methods Intercomparison
# Coal Analysis Measurements

| FGS DRY Ash % | Lab X DRY Ash % | RPD | FGS DRY BTU/lb (HHV) | Lab X DRY BTU/lb (HHV) | RPD | FGS DRY Sulfur % | Lab X DRY Sulfur % | RPD |
|---|---|---|---|---|---|---|---|---|
| 9.06 | | | 12282 | | | 56.7% | | |
| 9.95 | | | 12175 | | | 50.8% | | |
| 10.70 | | | 12027 | | | 55.9% | | |
| 35.67 | 33.84 | 5.3% | 8090 | 8479 | 4.7% | 60.0% | 53.0% | 12.4% |
| 36.29 | 34.03 | 6.4% | 8042 | 8496 | 5.5% | 47.6% | 43.0% | 10.2% |
| 34.55 | 35.55 | 2.8% | 8340 | 8153 | 2.3% | 80.8% | 79.0% | 2.2% |
| 9.85 | 9.24 | 6.4% | 12183 | 12325 | 1.2% | 62.8% | 53.0% | 17.0% |
| 8.41 | 8.32 | 1.0% | 12374 | 12496 | 1.0% | 60.6% | 52.0% | 15.2% |
| 8.17 | 8.03 | 1.7% | 12430 | 13494 | 8.2% | 57.5% | 52.0% | 10.0% |
| 8.09 | | | 12423 | | | 56.4% | | |

| FGS DRY Chlorine ppm | Lab X DRY Chlorine ppm | RPD | FGS Dry Mercury ppm | Lab X Dry Mercury ppm | RPD |
|---|---|---|---|---|---|
| <100 | | | | | |
| <100 | | | | | |
| <100 | | | | | |
| 2300 | 1882 | 20.0% | 0.046 | 0.06 | 26.0% |
| 3000 | 2035 | 38.3% | 0.043 | 0.04 | 6.4% |
| 2800 | 2920 | 4.2% | 0.038 | 0.02 | 63.1% |
| <100 | <100 | | 0.030 | 0.03 | 0.9% |
| <100 | <100 | | 0.018 | 0.05 | 96.1% |
| <100 | <100 | | 0.017 | 0.05 | 97.7% |
| <100 | | | | | |

# CVAFS V.S. CVAAS
# AT High End Coal Hg Concentrations

| Sample | | | Laboratory X | | Frontier (FGS) |
|---|---|---|---|---|---|
| Date | Description | Sample ID | Initial Hg | Resubmit Hg | Hg |
| | | | ppm | ppm | ppm |
| 3/22/00 | Daily Coal Composite | 965-974 | 0.13 | N/A | 0.0695 |
| 3/23/00 | Daily Coal Composite | 978-985 | 0.12 | N/A | 0.0663 |
| 3/24/00 | Daily Coal Composite | 989-999 | 0.13 | N/A | 0.0673 |
| 3/28/00 | Daily Coal Composite | 1041-1054 | 0.10 | 0.09 | 0.0610 |
| 3/30/00 | Daily Coal Composite | 1071-1082 | 0.13 | 0.08 | 0.0559 |
| 3/31/00 | Daily Coal Composite | 1087-1098 | 0.11 | 0.08 | 0.0530 |
| 3/22/00 | BH flyash-day | 975-A BH | 0.31 | N/A | 0.260 |
| 3/23/00 | BH flyash-day | 986-A BH | 0.08 | N/A | 0.027 |
| 3/24/00 | BH flyash-day | 1000-A BH | 0.19 | N/A | 0.144 |
| 3/28/00 | BH flyash-day | 1055-A BH | 1.10 | N/A | 1.035 |
| 3/30/00 | BH flyash-day | 1083-A BH | 0.14 | N/A | 0.099 |
| 3/30/00 | BH flyash- sootblow | 1085-A BH | 0.09 | N/A | 0.047 |

# Cold Aqua Regia – CVAFS Method
# Low Analytical Variability