Recent Developments and Techniques for Sampling Mercury

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Acknowledgements

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  - Mike Nemergut
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  - Jeff Socha
- ADA-ES
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Mercury Measurement Options

- Continuous (semi-continuous) Emissions Monitors
- Time Averaging with M324 (QuickSEM™)

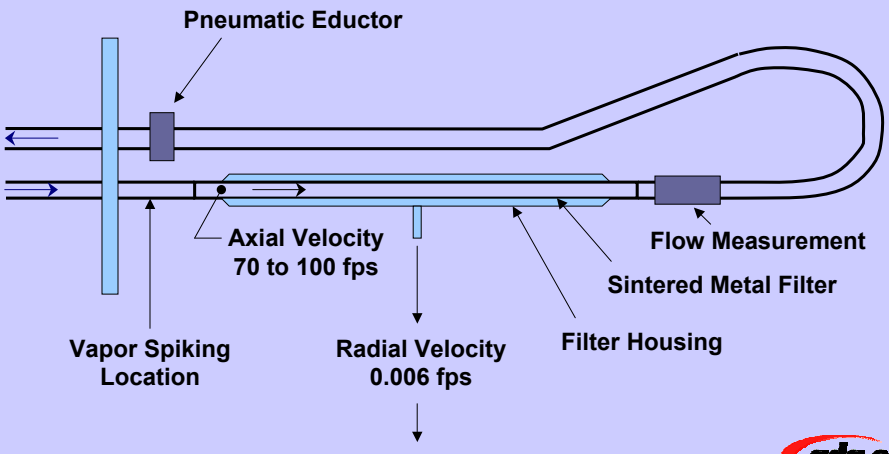
Key Components of Mercury CEMs

- Sample Extraction
- Sample Pretreatment System
- Sample Transport
- Mercury Analyzer
- Mercury Analyzer Calibration System

Key Components of Mercury CEMs

- Sample Extraction
  - Ash can remove and oxidize mercury
  - Inertial separation probes minimize ash artifacts
    - Probe material can oxidize mercury (stainless)
    - Probe may remove some oxidized Hg
    - High activity particulate can deposit on probe and remove Hg

Inertial Separation Probe



Inertial Probe – Thermo Electron (EPM)

- **Material: Stainless Steel**
- **Filter Diameter: 1/4 inch**
- **Design Flow Rate (acfm): 1.5 to 2**
- **Heated Filter Blowback**
- **Dilution Probe**

Results from Probe Performance Tests

- Good recovery of elemental and oxidized calibration gas when dynamically introduced upstream of filter
- Thermo probe did not oxidize mercury
  Some stainless steel probes display potential to oxidize mercury
- Thermo probe appeared to minimize effect of active particulate matter depositing in probe on vapor-phase mercury measurements

Key Components of Mercury CEM

- Sample Extraction
- Sample Pretreatment System
  - Conversion/Speciation
    - Most analyzers measure elemental mercury
      Oxidized mercury must be converted to elemental for measurement
  - Sample must be dry

Pretreatment Systems - Status

Conversion/speciation

1. Wet Chemistry - successfully used by researchers at several sites
2. Dry Converter – available commercially, evaluation and development continuing, some initial successes

Systems can be affected by flue gas chemistry

Dry Sample

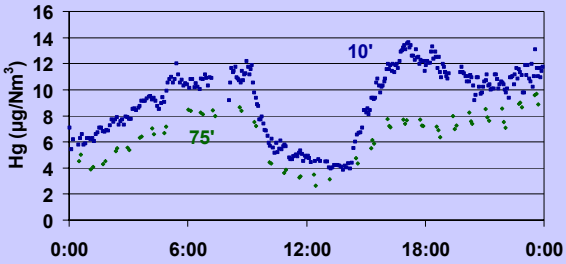
1. Measure hot gas
2. Cool gas and remove condensate
3. Lower moisture by dilution with dry air

Key Components of Mercury CEM

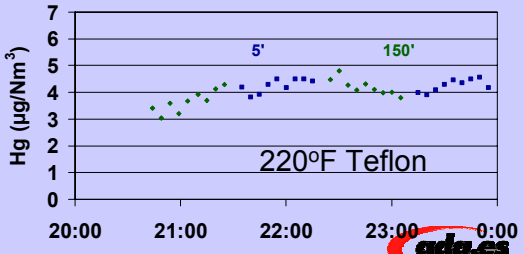
- Sample Extraction
- Sample Pretreatment System
- Sample Transport
  - Elemental Mercury
    - Sample must be dry
    - Fewer problems when heated (>200°F) or diluted with dry air
  - Oxidized Mercury
    - Can be transported in flue gas at T>400°F or diluted with dry air

  Recommended Options
  1. Conversion to elemental at extraction location
  2. Dilute sample with dry air to minimize reactions

Sample Transport – Elemental Hg, Raw Gas



Unheated Teflon



Key Components of Mercury CEM

- Sample Extraction
- Sample Pretreatment System
- Sample Transport
- Mercury Analyzer
  - Several options available
    - Most are cold vapor atomic absorption (CVAA) or atomic fluorescence (CVAF)

Mercury CEMs Technology Summary

- 12 Commercially Offered Monitors Identified
  - CVAA / UV Absorption (direct and Au) (9)
  - Au-CVAF (2)
  - DOAS (1)
- Under Development
  - Direct CVAF (1)
  - X-ray Fluorescence (1)
  - Plasma Emission Spectroscopy (1)
  - Cavity Ringdown Spectroscopy (1)

Range of Estimated System costs: $52,000-$180,000

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Average Adjusted Capital Cost: $87,000

Types of Commercial CMMs

Au-CVAA	Uses gold to concentrate Hg and remove SO_2 effects
Dual Beam CVAA	Direct measurement. Measures gas with and without Hg. Many scrub SO_2
Zeeman Shift CVAA	Direct measurement. Zeeman shift removes SO_2 interference for low to mid concentrations
Au-CVAF	Uses gold to concentrate Hg and remove O_2 and N_2
Filter tape with XRF	Total Hg (vapor + particulate)

How do you know if a monitor works? Performance Specification 12A

TEST

- Calibration Drift
- Zero Drift
- Response Time
- Calibration Error
- Calibration Precision
- Relative Accuracy

PERFORMANCE CRITERIA

- <10% OF STANDARD
- <5% OF THE STANDARD
- $\leq$ 2 min to 95%of final value
- +/- 15% ref method
- +/- 5% of Mean
- <20% of mean or 10% of standard

EPA-EMC CMM Results

Equipment Supplier	Bituminous Coal ESP RA (%)	PRB Coal SDA/FF RA (%)
A	30	NA
B	94	131
C	52	2
D	321	NA
E	84	12
F	37	12
G	NA	4

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Problems Encountered

- Unreliable Conversion Systems
  - Flue gas/converter chemistry
- Transporting and measuring raw gas (no dilution)
  - Losses in lines
  - Moisture and acids in analyzer
- Measurement
  - Amalgamation systems: reduced effectiveness of gold
  - Direct measurement AA: removing SO_2

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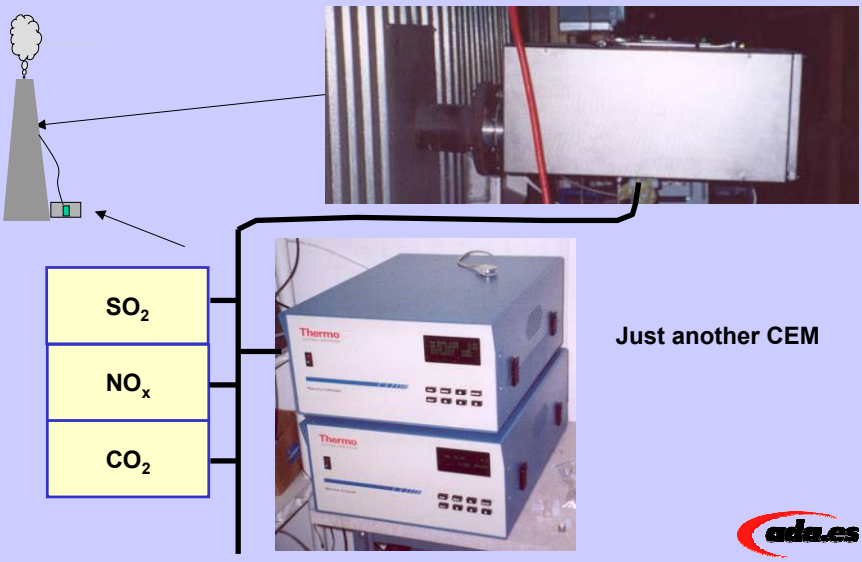
What does industry say they want for a Mercury CEM?

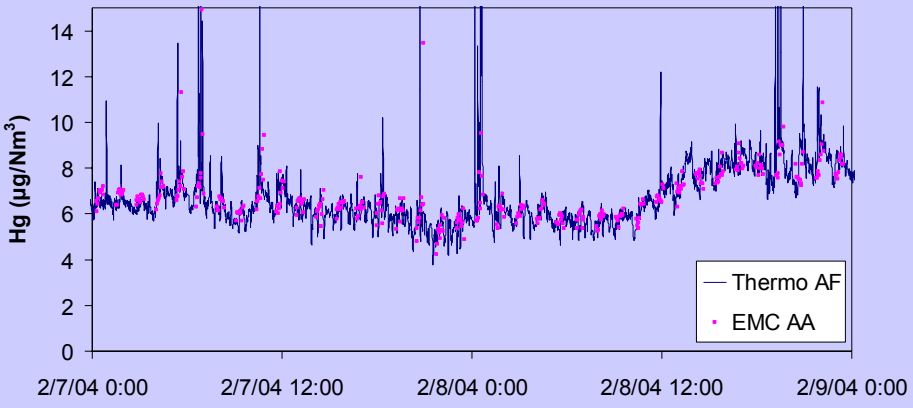


Just another CEM

Current Thermo CEM Operation

- Direct Measurement
- Diluted Sample
  - Lower moisture, less reactive
- Speciating
    - Conversion systems under evaluation
- Analyzer Detection Limit:
  Currently 5 ng/m^3
- No cross interference with SO_2

Analyzer Performance Comparison



Key Components of Mercury CEM

- Sample Extraction
- Sample Pretreatment System
- Sample Transport
- Mercury Analyzer
- Mercury Analyzer Calibration System
  1. Bottled Gas
  2. Vapor Generator

Calibration Options

1. Bottled Gas
   - Calibrate directly to analyzer
   - Check dilution ratio
   - Standardize vapor generator
2. Vapor Generator
   - Calibrate directly to analyzer
   - Check dilution ratio
   - Dynamic spiking upstream of filter

Thermo CEM Development Plans

- May ’04: Testing at low sulfur eastern bituminous site
- May ’04: Install 3 CEMS on PRB site
- June ’04: Install analyzer measuring Hg from plant CEM dilution gas. Conduct RATAs
- Summer ’04: Testing at high sulfur eastern bituminous site
- Fall ’04: Continue field testing with RATAs
- Spring ’05: Commercial units available

Mercury Measurement Methods: EPRI QuickSEM™

- Dry sorbent tube method obtains total mercury at low dust stack conditions
- Flexible sample duration: time-averaged samples from 30 minutes to a week in length
  (Relative accuracy and compliance periods)
- Proposed in MACT rule as EPA Method 324