Mercury Monitoring Technologies and Detection Principles

a technical solution to meet every need...

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Regulations, where do we stand?

- Since vacating the Clean Air Mercury Rule (CAMR), the implementation of mercury monitoring has primarily fallen on the state and local regulators.
- The EPA often uses Consent Decrees to mandate mercury monitoring.
- Cement MACT requires plants to monitor mercury emissions in kiln exhaust.
- More industry monitoring on the horizon.
  - Industrial Boiler MACT
  - Utility Boiler MACT
Detection Technologies

- **Continuous Monitoring**
  Cold Vapor Atomic Fluorescence
  Example: Thermo Freedom Mercury Series

- **Continuous Batch Measurement**
  Pre-Concentration on Gold Filter, Thermal Desorption, Atomic Fluorescence
  Example: Tekran Series 3300

- **Long Term Batch Measurement**
  Sorbent Trap or Appendix K
  Example: Apex Instruments
Continuous Monitoring

The Mercury Freedom System

- Dilution based measurement
- Inertial Filter Sample Conditioning
  - Conversion at the Stack
  - Direct Measurement CVAF
    - High sensitivity
    - True real-time monitoring
    - Modular design
    - i/Series platform
Continuous Monitoring

Model 80i Hg Analyzer

- Direct Measurement CVAF
  - Continuous measurement
  - No additional gasses required
- Diluted Sample
  - Lower moisture, less reactive
- Speciating
  - Measures either Hg\textsuperscript{T} or Hg\textsuperscript{0}
- Analyzer Detection Limit:
  Currently ~1 ng/m\textsuperscript{3} (~0.1 ppt)
- No cross interference with SO\textsubscript{2}
Hg Fluorescence

\[
\text{Hg} + h\nu (254 \text{ nm}) \xrightarrow{I_a} \text{Hg}^* \\
\text{Hg}^* \xrightarrow{K_f} \text{Hg} + h\nu (254 \text{ nm})
\]

\[
I_a = I_o[1-e^{-ax(Hg)}]
\]

\[
I_f ; I_o ax(Hg) \text{ or } K (Hg)
\]

High Intensity Hg Lamp
Reflective Filtering
Enhanced Light Baffling
Bandpass Filter
Thermo has used 2 versions of Hg probes.
- GC & Fast loop.
- GC no longer sold. Too many problems.
- Fast loop still being offered.
- M&C developed Hg probe based on SP2006 Dilution probe
- Cemtek recommends M&C Hg probes for new installations & replacements.
- Less maint., easier to pass integrity tests
Thermo sold several hundred Hg systems.
Most were installed, only some operational.
Utilities deciding whether to restart Hg or replace with Sorbent Trap systems.
Restarts might include replacing Thermo probe with M&C.
Some using Thermo Hg for Hg control & Sorbent trap for compliance.
Lessons Learned

- Thermo has lowered sample bundle temp requirements due to premature heater failures.
- Long sample line lengths might require separate heating zones.
- Initial certification can be tricky. Need to understand process, carbon injection, controls & operations.
- Remote access by integrator important to assist with troubleshooting.
- Get additional training. Consider maintenance contracts.
- Verify Hg levels with sorbent traps prior to certification testing if possible.
Continuous Batch Measurement

Series 3300 CMMS Components

Model 3330 Inertial Probe

Model 3320 Sample Conditioner

Model 2537A AF Analyzer

Model 3310 Calibration Unit
Continuous Batch Measurement

Principles of Operation

- Mercury in sample gas is pre-concentrated onto (pat’d) pure gold cartridge

- Adsorbed mercury is thermally desorbed

- Detected by atomic fluorescence detector

- Two cartridges are used to alternately sample and desorb allowing continuous operation
  - No gaps in data stream
Continuous Batch Measurement

Flow Diagram of Mercury Analyzer (Pat’d)
Continuous Batch Measurement

Valve Assembly

- Downstream A/B Valve
- CARTRIDGE A
- Heater A
- Thermal Cutoff Reset Switch
- Upstream A/B Valve
- COOLING FAN
- Bypass Valve
- Exit Line (To Detector)
- CARTRIDGE B
- Heater B
- Teflon Nut (1 of 4)
- Upstream Valve Bracket
- Sample Inlet Fitting
- Continuous Batch Measurement
Tekran Probe

- Tekran adopted the M&C Hg probe early on and that’s the only probe Tekran offers.
- Reduced probe issues, higher accuracy, improved performance.
- Requires own 19” rack for all components. High temp sample line required.
HGP Dual Trap Sampling Probe

Configuration:
- Heated Sample Probe – Dual Probe Heaters
  - Length (4, 6, 9, 12 ft Standard)
  - Material – C276 Hastelloy or 316 SS
- Enclosure – Insulated SS Junction Box
- Trap Sizes – 10mm Large Standard
- Optional 6mm Small Trap Adapter
  - Paired trap holders
- Pitot Tube – Optional S Type Pitot
Long Term Batch Measurement

Apex

- Heated Sample Probe
- Packing Gland
- Sorbent Traps
- Cabinet
- MercSampler™ Console
- Stirling Gas Conditioner
- Heated Umbilical/Sample Line
- A/C

Reliable and Easy To Use

Laptop

Pedestal (Optional)
Long Term Batch Measurement

XC-6000EPC Flow Diagram
Long Term Batch Measurement

M&C Products

Inside Probe Box

STS Probe

Sample Control System

Cam Lever

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Sorbent Trap

Configuration:
- Section 1: Sample Collection Section
- Section 2: Breakthrough Indicator Section
- Section 3: Vapor-Spike Section to Measure Recovery

Long Term Batch Measurement
Gaining popularity over Instrumental Method.
- Lower initial cost. Higher labor but lower maintenance, service & parts.
- Multiple Manufacturers: Apex, Environmental Supply, M&C, Clean Air Eng. & more
- Systems becoming more automated & easier to use.
- Some include data logging & remote access.
- Stacks without elevators or easy access can be problematic.
# Method Comparison: Detection Levels

<table>
<thead>
<tr>
<th>Detection Method</th>
<th>Range</th>
<th>Detection Limit</th>
<th>Sample Cycle Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Continuous Monitoring</td>
<td>0-50 μg/m³</td>
<td>2 ng/m³</td>
<td>Continuous (60 - 300 sec Rolling Average Time)</td>
</tr>
<tr>
<td>Continuous Batch Measurement</td>
<td>0.1 - 10,000 ng/m³</td>
<td>&lt; 0.1 ng/m³</td>
<td>2 ½ - 60 minutes</td>
</tr>
<tr>
<td>Long Term Batch Measurement</td>
<td>N/A</td>
<td>Dependent upon analysis technique</td>
<td>Several hours - several weeks (Dependent upon concentration present in process)</td>
</tr>
</tbody>
</table>
## Method Comparison

<table>
<thead>
<tr>
<th>Detection Method</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Continuous Monitoring</strong></td>
<td>▪ True real time feedback for process control.</td>
<td>▪ Large upfront investment costs&lt;br&gt;▪ Maintenance intensive system&lt;br&gt;▪ NIST traceable calibration gases/sources issue&lt;br&gt;▪ Consumable chlorine gas for mercuric chloride generator</td>
</tr>
<tr>
<td><strong>Continuous Batch Measurement</strong></td>
<td>▪ Lower detection levels possible due to time integration of sample.</td>
<td>▪ Large upfront investment costs&lt;br&gt;▪ Maintenance intensive system&lt;br&gt;▪ NIST traceable calibration gases/sources issue</td>
</tr>
<tr>
<td><strong>Long Term Batch Measurement</strong></td>
<td>▪ Lesser initial investment for system startup.</td>
<td>▪ Labor intensive process requiring post installation maintenance and analysis costs&lt;br&gt;▪ Must climb stack on daily/weekly basis for sample collection&lt;br&gt;▪ Glass trap breakage - loss of data&lt;br&gt;▪ Sample breakthrough - loss of data&lt;br&gt;▪ Chain of custody sample issues</td>
</tr>
</tbody>
</table>
# Method Comparison: System Costs

<table>
<thead>
<tr>
<th>Detection Method</th>
<th>Budgetary System Cost</th>
<th>Budgetary Maintenance</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Continuous Monitoring</strong></td>
<td>$200,000</td>
<td>▪ Quarterly Maintenance Contract: $10,000*</td>
</tr>
<tr>
<td></td>
<td>▪ NEMA 12 Rack Mounted</td>
<td>▪ Spare Parts: $25,000 (Consumable &amp; Recommended)</td>
</tr>
<tr>
<td></td>
<td>▪ 250 feet Umbilical</td>
<td>▪ Installation Services Incl</td>
</tr>
<tr>
<td></td>
<td>▪ DAHS Integration Not Incl</td>
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<td></td>
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<tr>
<td><strong>Long Term Batch Measurement</strong></td>
<td>$125,000</td>
<td>▪ Site Labor: TBD**</td>
</tr>
<tr>
<td></td>
<td>▪ NEMA 12 Rack Mounted</td>
<td>▪ Ohio Lumex Analysis System: $75,000***</td>
</tr>
<tr>
<td></td>
<td>▪ 250 feet Umbilical</td>
<td>▪ Spare Parts: $5,000 (Consumable &amp; Recommended)</td>
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<tr>
<td></td>
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<td></td>
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</table>

*Cost for a third party quarterly maintenance contract. Additionally, a site technician will be required to perform daily/weekly/monthly system checks according to the Quality Assurance Program.

**Site technician will be required to climb the stack to the sampling point on a daily/weekly basis to change the sorbent traps as well as perform daily/weekly/monthly system checks according to the Quality Assurance Program.

***Sorbent traps may be sent to offsite laboratory for analysis in lieu of purchasing a site dedicated analysis system.
## Sorbent Trap System Comparison

<table>
<thead>
<tr>
<th>System Feature</th>
<th>Apex Instruments</th>
<th>M&amp;C Products</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>User Interface</strong></td>
<td>▪ Laptop interface with console used to initiate flow checks after trap replacement</td>
<td>▪ Integrated touchscreen on NEMA 4X enclosure for initiation of trap replacement post leak checks</td>
</tr>
<tr>
<td></td>
<td>▪ Ethernet and Modbus TCP/IP communication</td>
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</tr>
<tr>
<td><strong>Probe</strong></td>
<td>▪ Standard probe offering in hastelloy for corrosive stack environments</td>
<td>▪ Standard probe offering in stainless steel</td>
</tr>
<tr>
<td></td>
<td>▪ Optional hastelloy probe available</td>
<td>▪ Optional hastelloy probe available</td>
</tr>
<tr>
<td><strong>Moisture Removal/Collection System</strong></td>
<td>▪ Stirling cooler with condensate collected in graduated bottles for moisture correction</td>
<td>▪ Peltier chiller with NIST traceable mass flow sensors for measurement of moisture removal</td>
</tr>
<tr>
<td><strong>Housing</strong></td>
<td>▪ Rack mount system in self contained 19” rack with HVAC</td>
<td>▪ Wall mount NEMA 4X enclosure</td>
</tr>
</tbody>
</table>

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