An Overview of Mercury Monitoring Options

David Graham, Uniper Technologies Ltd.
Introduction

• What do we need to measure?
  • Total mercury $Hg^T = Hg^0 + Hg^{2+} + Hg^P$
  • $Hg^P << (Hg^0 + Hg^{2+})$
  • Vapour phase Hg sufficient for coal fired plant with modern control technology

• What is emitted?
  Depends on PM control technology
  • ESP only: $Hg^0$ and $Hg^{2+}$
    $Hg^{2+}$ is water soluble
  • ESP + FGD: mostly $Hg^0$
  • ESP + FGD + SCR: mostly $Hg^0$
    $Hg^0 \rightarrow Hg^{2+}$ enhanced by the SCR catalyst
Anticipated range of mercury concentration?

![Graph showing anticipated range of mercury concentration](image)

- ESP only (50%)
- ESP+FGD (75%)
- ESP+FGD+SCR (90%)
Options for mercury monitoring I

- Periodic measurement to EN 13211:2001
  - Industrial Emissions Directive ‘For combustion plants firing coal or lignite, the emissions of total mercury shall be measured at least once per year.’
  - Flue gas @ 20 to 30 l/min, for 1 to 2 h, >1Nm³
  - Probe/filter >120°C
  - Cooled impingers (KMnO₄/H₂SO₄) (Breakthrough<5%)
EN13211 ≡ Ontario-Hydro Method (OHM)

EVALUATION AND COMPARISON OF U.S. AND EU REFERENCE METHODS FOR MEASUREMENT OF MERCURY, HEAVY METALS, PM2.5 AND PM10 EMISSIONS FROM FOSSIL-FIRED POWER PLANTS

Dr. Nenad Sarunac, Energy Research Center, Lehigh University Feb 2007 (tested in July 2006 at Armstrong PP)
Options for mercury monitoring II

- Continuous measurement to EN 14884:2005
  - LCP BREF Continuous monitoring required unless it can be demonstrated by other means that the ELV will not be exceeded
Options for mercury monitoring II

- Continuous measurement to EN 14884
- Instrumental methods
- Primary measurement is Hg$^0$
- Convertor Hg$^{2+} \rightarrow$ Hg$^0 \rightarrow$ Hg$^T$
- Speciation by:
  - Converter switching in/out
    - Hg$^{2+} = Hg^T$ (in) $- Hg^0$ (out)

Courtesy Tekran Instrument Corporation
Continuous analysis - Approach 1A CVAFS

- Sample dilution with gold trap amalgamation
- Inertial probe to exclude particulate (M&C)
- Heated inert transfer lines
- Dilution ratios 40:1 (PSA); 30:1 (Tekran)
- Thermo-catalytic converter $\rightarrow$ $\text{Hg}^T$
- Dual gold traps - continuous sampling – 3min cycle - Ar
- CV Atomic Fluorescence Spectrometry
- Very linear and selective (no $\text{SO}_2$ interf.)
- Detection limits (PSA):
  - 0.1 pg (absolute mass)
  - 4 ng/m$^3$ (40:1, 1 dm$^3$ sample vol)
Continuous analysis - Approach 1B CVAFS

- Sample dilution without gold trap amalgamation
- Inertial probe to exclude particulate
- Heated inert transfer lines (Thermo – converter at stack – simplifies transport)
- Dilution ratios 40:1 (Thermo); 50:1 (Gasmet)
- Thermo-catalytic converter → HgT
- Thermo-Scientific and Gasmet direct reading CVAFS
- Diluted sample (no gold traps) Carrier N₂
Continuous analysis - Approach 2 AAS (no dilution)
Continuous analysis - Approach 3 DOAS

Courtesy Opsis
Continuous analysis - Approach 1A results

Power plant in the Netherlands (PS Analytical)

<table>
<thead>
<tr>
<th>CEM result /µg m⁻³</th>
<th>OHM result (RM) /µg m⁻³</th>
<th>Difference (d) /µg m⁻³</th>
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<tbody>
<tr>
<td>17.36</td>
<td>17.29</td>
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Continuous analysis - Approach 1B results

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<table>
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<tr>
<th>Test Run</th>
<th>Date</th>
<th>Start Time</th>
<th>End Time</th>
<th>Reference Method Hg</th>
<th>CEM Output Hg</th>
<th>(RM-CEM) Difference (di)</th>
<th>Difference^2 (di^2)</th>
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<tbody>
<tr>
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<td>1552</td>
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Meets specifications for annual RA

Courtesy Thermo Fisher Scientific
Continuous analysis - Approach 1B results
Continuous analysis – High temperature

Heated probe → Sampling filter → Thermal Conversion

Hg reduction

Measurement method

Atomic absorption spectroscopy (AAS) with integrated Zeeman cross sensitivity correction

Courtesy Sick Gmbh
European QA standards

Operator’s responsibilities:
- Installation of compliant equipment (QAL1)
- In-situ calibration of CEMs using an accredited test laboratory (QAL2) (audit)
- Annual check of the calibration (AST)
- Ongoing QA based on regular zero and span checks (QAL3)
- Submission of QAL2 & AST reports and ongoing maintenance of records
- Checking of hourly averages against the Valid Calibration Range (weekly)
## Certification of CEMs - MCERTS

<table>
<thead>
<tr>
<th>Certificate Holder</th>
<th>Model</th>
<th>Certified Range</th>
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<tbody>
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<td>Durag GmbH</td>
<td>HM 1400 TRX Mercury Analyser</td>
<td>0 to 45 µg/m³</td>
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<tr>
<td></td>
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<td>0 to 75 µg/m³</td>
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<td>Opsis AB</td>
<td>AR 602Z/Hg</td>
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<td>SICK MAIHAK GmbH</td>
<td>MERCEM300Z Mercury Monitoring System</td>
<td>0 to 10 µg/m³</td>
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<td>0 to 45 µg/m³</td>
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</table>
Options for mercury monitoring III

- Semi-Continuous measurement to prEN XXXX (ex US)
- LCP BREF Semi-Continuous monitoring allowed

Relative Deviation <= 10%

Laboratory analysis following …
Thermal desorption
Leaching or Digestion

Courtesy Ohio-Lumex
Options for mercury monitoring III

One week sampling intervals
Also used as an SRM in the US

Sorbent Sampler Systems

Clean Air Met-80
Environmental Supply HGK-PF
Altech Environment Amesa-M
Apex Instruments XC-6000

M&C STS

Courtesy Ohio-Lumex
Options for mercury monitoring III

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

Reliable and Easy To Use

Laptop
Pedestal (Optional)

Courtesy Apex Instruments
Sorbent Trap Method ≡ OHM ≡ EN13211
How much does it all cost?

HgCEMS v. Sorbent tubes
Ownership Costs

Cumulative Cost of Ownership

Year of Operation of HgCEMS

$800,000
$600,000
$400,000
$200,000
$

0 1 2 3 4 5 6

HgCEMS
Vavg

Courtesy Tekran Instrument Corporation
Concluding Remarks

- EU mercury monitoring requirements are increasing
- Concentration levels are low for coal fired plant
- Periodic measurement to EN 13211:2001
  - Annual test under IED (from 1 Jan 2016)
  - Accredited Test Laboratory (ISO 17025)
- Continuous measurement to EN 14884:2005
  - LCP BREF requires this unless alternative means of demonstrating compliance (2021?)
  - Various techniques available (Hg$^T$ as Hg$^0$)
- Certification is limited but UK, European & US instruments have the required sensitivity
- Capital outlay and running costs are high
- Semi-Continuous measurement to prEN XXX
  - Simple measurement with rigorous QA
- Capital outlay lower but analysis costs to consider