Mercury Speciation in Flue Gas from Coal-fired Power Stations

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Overview

• Hg in stack gas measurements
  – Why?
  – Offline analysis
• Continuous Emission Monitors
  – Sample collection
  – Sample transport
  – Sample pre-treatment
  – Analysis
  – Calibration
• Typical Data
• Summary
Why Measure Power Station Hg Emissions?

• Public concern about Hg emissions
  – Environmental accumulation of toxic metals
• Major sources of emissions:
  – coal fired power plants
  – waste incinerators
• Transport strongly dependent on speciation
• Regulatory compliance
  – US EPA Clean Air Mercury Rule (March 2005)
Offline Analysis

Reference methods

**EPA Methods 29 and 101a** *(Total Mercury)*
Impinger based – HNO$_3$/H$_2$O$_2$ or H$_2$SO$_4$/KMnO$_4$

**Ontario Hydro Method** *(Speciation)*
ASTM Method D6784-02
Impingers with KCl & H$_2$SO$_4$/KMnO$_4$

Monitoring methods

**QuickSEM™** *(Total Mercury)*
40 CFR Part 75 Appendix K
Carbon trap based
Offline Analysis

Reference methods
- Average data over 1+ hours
- Labour intensive
- Delay for results from lab.

Monitoring methods
- Average data over hours or days
- Delay for results from lab.
Online Analysis
Continuous Emissions Monitor (CEM)

Sample collection
Sample transport
Sample pre-treatment
Analysis
Calibration

Stack

Heated Sample Line

PROBE

Speciation Module

Hg_0
Hg_T

Computer
Sir Galahad
Stream Selector
Calibration Device
Sample Collection - The Probe

- Sample Collection - The Probe
- Stack
- PROBE
- Speciation Module
- Hg^0
- Hg^T
- Computer
- Sir Galahad
- Stream Selector
- Calibration Device
Inertial Probe Schematic

- Eductor
- Venturi
- Flange
- Pump
- Cal Gas Port
- Gas Sample to Analyser
- Gas Outlet
- Gas Inlet
Sample Transport – Heated Lines

- Sample Transport
- Heated Lines
- Stack
- Probe
- Heated Sample Line
- Speciation Module
  - Hg⁰
  - Hg⁹
- Sir Galahad
- Stream Selector
- Calibration Device
- Computer
Sample transport

- **Inert materials**
  - Durinert (glass) coatings
  - PFA/PTFE components

- **Temperature**
  - Raw sample
  - Ash-free sample
Sample Pre-treatment – The Speciation Module

Stack

Heated Sample Line

Speciation Module

HgT

Hg0

PROBE

Computer

Sir Galahad

Stream Selector

Calibration Device
The Speciation Module

- Hot Flue Gas
- Primary Vent
- Thermolytic convertor
- HgCl₂ adsorbent
- Optional Reagent Feed
- Heated Oven
- Drain Pump
- Peltier Cooler
- Hg_{Total}
- Hg^0
Typical Data Using Bench Scale Apparatus

Dry Base Speciation Unit, Hg\(^{\text{T}}\) channel
Effect of different flue gas components

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- Air
- Water, HCl
- Water, HCl, SO\(_2\), NO\(_2\)
- Water, HCl, SO\(_2\), NO\(_2\), NO
Analysis – The Sir Galahad

PROBE

Heated Sample Line

Stack

Speciation Module

Hg0

HgT

Sir Galahad

Stream Selector

Calibration Device

Computer
Sir Galahad
Amalgamation – Atomic Fluorescence Spectroscopy

- Why AFS?
  Sensitivity
  Selectivity
  Simplicity

- Why amalgamation?
  Sample pre-treatment – selectivity
  Sample preconcentration
Schematic Flow Diagram of the Sir Galahad

PSA

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Calibration

Stack

- PROBE
- Heated Sample Line
- Speciation Module
- Hg^0
- HgT
- Sir Galahad
- Stream Selector
- Computer
- Calibration Device

PSA
On-Line Calibration System

Air

MFC 1

MFC 2

Hg Reservoir

Blank

Oven

Span
A Power Station in Kentucky

- 120MW unit
- Fuel: bituminous coal
  - Kentuckian
- Environmental controls
  - Electrostatic Precipitator (ESP)
  - *No* Flue Gas Desulphurisation (FGD)
  - *No* DeNO$_x$
    - (low NO$_x$ burners)
A Power station in Kentucky
Stack monitoring
Inertial probe & wet/dry speciation

- Wet and Dry Hg^T show good agreement
A Power Station in SE England

- 500MW unit
- Fuel: bituminous coal
  - Russian
  - Colombian
  - South African
  - ≤10% biomass (cereal pellets)
- Environmental controls
  - Electrostatic Precipitator (ESP)
  - No Flue Gas Desulfurisation (FGD)
  - No DeNO$_x$
A Power station in SE England
Stack monitoring
Heated filter blowback probe & dry speciation
Unattended operation

- Hg levels trend with unit load
A Power station in SE England
Stack monitoring
Heated filter blowback probe & dry speciation
Unattended operation

- SO₂ trending – shows variation in fuel

![Graph showing SO₂ and Hg concentrations over time.]

- Hg in coal:
  - A: 30 ppb
  - B: 100 ppb
Conclusion

CEM developed to measure mercury in power station stack gases

Difficult sampling, transport and pretreatment issues have been addressed

Successfully operated unattended on numerous power station stacks