CONTINUOUS MERCURY EMISSION MONITORING

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CONTINUOUS MERCURY EMISSION MONITORING

AGENDA

- SICK AG – Sensor Intelligence
- Global Challenge
- Legislation & Mercury Limit Values
- Continuous Mercury Monitoring
  - Classical measurement approaches
  - New measurement principle
- Certified Monitoring Systems
- Outlook
SICK – worldwide one of the leading manufacturers of sensors and sensor solutions for industrial applications

- 70 Years of experience. Founded 1946.
- 7,417 Employees worldwide
- 88 Countries with SICK presence: More than 50 subsidiaries and participations as well as numerous specialized agencies
- 1,267 Million euros Group sales in the fiscal year 2015
- 40,000 Products and thus widest product and technology portfolio in the sensor industry
- 3,000 Patents and thus leading in developing innovative sensor solutions
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GLOBAL CHALLENGE

- Mercury & its organic compounds are extremely toxic to humans & can cause health problems
- Mercury can enter food chain (esp. fish & shellfish) & be ingested by humans
  - Global mercury emissions are increasing (esp. due to coal combustion & mining)

The three phases of historical mercury emissions

Source: Streets (2011)
CONTINUOUS MERCURY EMISSION MONITORING
GLOBAL CHALLENGE

- Global anthropogenic Hg-emissions – relevant industries and countries

Source: Streets (2011)
Worldwide legislation refers to mercury limit values as **total mercury**

- the sum of elemental mercury ($\text{Hg}_0$) and the mercury compounds ($\text{Hg}^+$)
- emission monitoring systems have to monitor **total mercury** ($\text{Hg}_{\text{total}}$)

Mercury can only be detected in its elemental form ($\text{Hg}_0$)

- Each mercury analyzer needs a ‘converter step‘ to convert all mercury compounds into elemental mercury
- Due to the required converter, all total mercury analyzers are **extractive systems**

Mercury has to be monitored in the $\mu$g/Nm$^3$ range

- Each analyzer needs a possibility to eliminate or compensate cross sensitivity components in the flue gas such as $\text{SO}_2$
CONTINUOUS MERCURY EMISSION MONITORING WORLDWIDE LEGISLATION & LIMIT VALUES

- **Europe**
  - 50 µg/m³ daily average value for waste incineration plants (IED 2010)
  - Currently no requirement for continuous measurement of Hg
  - BREFs* for Large Combustion Plants – final draft is in preparation

- **Germany**
  - Waste incinerators/Power plants/Cement plants
    - 30 µg/Nm³ daily average value
    - 50 µg/Nm³ half hour average value
    - 10 µg/Nm³ yearly average value (2019)

- **USA**
  - Cement plants:
    - ≈ 12 µg/m³ Thirty day average value for existing plants
    - ≈ 4,5 µg/m³ Thirty day average value for new plants
  - Coal fired power plants:
    - ≈ 1,5 µg/m³ Thirty day average value for new plants

*Best available techniques reference document*
CONTINUOUS MERCURY EMISSION MONITORING
MERCURY MONITORING – CLASSICAL MEASUREMENT APPROACHES
- Available continuous mercury emission monitoring systems

Available continuous mercury emission monitoring systems

<table>
<thead>
<tr>
<th>Hg reduction</th>
<th>Hg- accumulation-separation</th>
<th>Measurement method</th>
</tr>
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<tbody>
<tr>
<td>Heated probe</td>
<td>Wet – chemical conversion</td>
<td>Atomic absorption spectroscopy (AAS)</td>
</tr>
<tr>
<td>Sampling filter</td>
<td>Thermal catal. conversion</td>
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- Cross sensitivity correction

Available continuous mercury emission monitoring systems

- Atomic absorption spectroscopy (AAS)
- Atomic fluorescence spectroscopy (AFS)
- Atomic emission spectroscopy (AES)
- Differential optical absorption spectroscopy (DOAS)
CONTINUOUS MERCURY EMISSION MONITORING
MERCURY MONITORING – CLASSICAL MEASUREMENT

APPROACHES

▪ Advantages and disadvantages of the conversion approaches

▪ **Wet chemical conversion**
  - 😊 Applied to all reference methods
  - 😊 Continuous exchange of reduction material
  - 😔 Handling of chemicals e.g. hydrochloric acid dilution
  - 😔 Disposal of chemical waste

▪ **Thermal catalytic converter**
  - 😊 Simple handling (exchange) of converter material
  - 😔 Gas components like SO₂, HCl reduce life-time of converter
  - 😔 Unperceived contamination of converter material

▪ **High temperature (Thermal conversion)**
  - 😊 No consumables
  - 😊 Reliable conversion method
  - 😊 Long-term stability
CONTINUOUS MERCURY EMISSION MONITORING
MERCURY MONITORING – CLASSICAL MEASUREMENT APPROACHES

- Available continuous mercury emission monitoring systems

### Measurement method

- Atomic absorption spectroscopy (AAS)
- Atomic fluorescence spectroscopy (AFS)
- Atomic emission spectroscopy (AES)
- Differential optical absorption spectroscopy (DOAS)

### Amalgamation:
Longer T90/reaction time of the analyzer, not really continuous monitoring

### Reference gas:
Additional costs for system owner

- **Heated probe**
- **Sampling filter**
- **Dilution**

#### Hg reduction

- Wet – chemical conversion
- Thermal catal. conversion
- Thermal conversion

#### Hg accumulation-separation

- Amalgamation
- Gold Trap
- Reference gas

#### Cross sensitivity correction

- Atomic absorption spectroscopy (AAS)
- Atomic fluorescence spectroscopy (AFS)
- Atomic emission spectroscopy (AES)
- Differential optical absorption spectroscopy (DOAS)
CONTINUOUS MERCURY EMISSION MONITORING
MERCURY MONITORING – CLASSICAL MEASUREMENT APPROACHES

- Available continuous mercury emission monitoring systems

Heated probe → Sampling filter → Dilution → Hg reduction → Hg- accumulation-separation → Measurement method

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Cross sensitivity correction

Atomic fluorescence spectroscopy (AFS)

Atomic emission spectroscopy (AES)

Differential optical absorption spectroscopy (DOAS)
CONTINUOUS MERCURY EMISSION MONITORING
MERCURY MONITORING – NEW MEASUREMENT PRINCIPLES

- Optimized approach

Heated probe

Sampling filter

Hg reduction

Measurement method

Optimized approach

Heated probe

Thermal catal. conversion

Hg reduction

Atomic absorption spectroscopy (AAS) with integrated Zeeman cross sensitivity correction
CONTINUOUS MERCURY EMISSION MONITORING
MERCURY MONITORING – NEW MEASUREMENT

PRINCIPLES

▪ **Patented direct measurement**
  ▸ Zeeman atomic absorption spectroscopy within high temperature cell

▪ **Advantages**
  ▸ No moving parts
  ▸ No Hg recombination
  ▸ No memory effects
  ▸ Continuous monitoring of total Hg
  ▸ Best possible cross sensitivity correction

▪ **Benefits**
  ▸ Reliable measuring results at any time for all target industries: waste incinerators, power plants and cement plants!
  ▸ One system setup for emission and process gas monitoring
CONTINUOUS MERCURY EMISSION MONITORING
MERCURY MONITORING – NEW MEASUREMENT PRINCIPLES

- System design

- High temperature cell
- Ejector
- Optical unit (analyzer)
- Electronics
- CALSIC300

System design
CONTINUOUS MERCURY EMISSION MONITORING
MERCURY MONITORING – NEW MEASUREMENT PRINCIPLES

- MERCEM300Z is type approved according to EN15267

  - Approved measuring ranges: 0 – 10/45/100/1000 µg/m³
  - Lowest approved measuring range for mercury analyzer: 0 – 10 µg/m³
    — Only two linearization functions required
  - Highest approved measuring range for mercury analyzer: 0 – 1000 µg/m³

  - Unique maintenance interval: 3/6 months!
    — Test gas is required only 2 times a year

  - First type approved system which is certified to monitor mercury at all plant types (waste incineration, power plants and cement plants)

  - Designed for harsh environmental conditions: -20°C up to + 50°C.
CONTINUOUS MERCURY EMISSION MONITORING
MERCURY MONITORING

- Alternative:
  - PS 12B, sorbent trap monitoring → discontinuous
  - Collection of mercury via activated carbon tube over specific period of time
  - Afterwards Hg-analysis in laboratory
    - Purchasing costs ↓
    - Running costs ↑
    - Limit value exceedances are not recognized (too late)
    - Performance of sorbent traps are depending on dust load
    - Paired trap agreement: What happens if mercury concentrations of both Hg-traps are too far off?
    - EU: availability >95 %
    - Results are strongly depending on analysis laboratory
- Why is continuous mercury monitoring important?

Hourly Hg concentration trend
Because the real concentration can change rapidly!

Hourly Hg concentration trend
Comparison between discontinuous and continuous mercury monitoring

**Mercury Concentration**

- **Stack Trap**
- **Stack CMM**
- **Load**

**Graph Details:**
- X-axis: Time (8/28/12 0:00 to 9/17/12 0:00)
- Y-axis: Mercury Concentration (ug/scm)
- Data points for specific dates:
  - 8/28/12 0:00
  - 9/2/12 0:00
  - 9/7/12 0:00
  - 9/12/12 0:00
  - 9/17/12 0:00
Continuous monitoring - Mercury cycle in cement plant

Source: Scheuch (2016)
Certification according to **EN15267**:

- **EN15267 – 1: General remarks**
  - EN15267 – 2: Initial assessment of the manufacturer’s quality management system and post certification surveillance of the manufacturing process
    - All technical changes to the device have to be monitored and will be reviewed by the testing institute

- **EN15267 – 3: Performance criteria und test procedures**
  - Laboratory test (cross sensitivity, linearity, measuring uncertainty, …)
  - Field test (availability, calibration function, reproducibility, maintenance interval, etc.)
  - For overall certification: Field test at 3 types of plants necessary!
    (waste incinerator, power plant, cement plant)

Quality assurance of the AMS according to **EN14181**

- **QAL1**: Type approval for general applicability
- **QAL2**: Function control and initial calibration at plant
- **QAL3**: Ongoing quality assurance control within maintenance interval
- **AST**: Annual surveillance test
CONTINUOUS MERCURY EMISSION MONITORING
CERTIFIED MONITORING SYSTEMS

- A CEM's type approval process comparable to EN15267 is not implemented
- Acceptance test during commissioning (plant operator bears all costs)
- Performance Specifications 12A must be fulfilled
  - Specification and test procedures for total vapor phase mercury continuous emission monitoring systems
  - „Certification“/function control during commissioning process on site:
    - (Linearity check, 7 day calibration error test, 3-Level system integrity check)
    - **RATA**: Relative Accuracy Test Audit, comparison measurements to reference method

- Ongoing Quality assurance/Quality control
  - Calibration error test, 1-Level system integrity check, Linearity check or 3-level system integrity check with elemental or oxidized mercury test gas
  - **RATA**: Comparison measurements have to be repeated on a yearly basis
  - „NIST traceable“ test gases (Hg0/Hg+) have to be used, or Elemental gas generators certified to NIST prime
  - Daily calibration required
## Continuous Mercury Emission Monitoring

### Certified Monitoring Systems

<table>
<thead>
<tr>
<th>Product Name</th>
<th>Manufacturer</th>
<th>Measuring Principle</th>
<th>Mercury Conversion</th>
<th>Field tests</th>
</tr>
</thead>
<tbody>
<tr>
<td>Supplier 1</td>
<td>CVAAS</td>
<td>- Dilution 1/50</td>
<td>SWIP</td>
<td>17. BImSchV</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Cat. reduction</td>
<td>Brown coal</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Amalgamation</td>
<td>Cement</td>
<td>13. BImSchV</td>
</tr>
<tr>
<td>Supplier 2</td>
<td>UV - DOAS</td>
<td>- Cat. reduction</td>
<td>WIP</td>
<td>17. BImSchV</td>
</tr>
<tr>
<td>MERCEM300Z</td>
<td>SICK MAIHAK</td>
<td>Zeeman AAS</td>
<td>WIP</td>
<td>17. BImSchV</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Reduction at 1.000 °C</td>
<td>Bitum. coal</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cement</td>
<td>13. BImSchV</td>
</tr>
<tr>
<td>Supplier 3</td>
<td>2-Way UV CVAAS</td>
<td>- Cat. reduction</td>
<td>WIP</td>
<td>17. BImSchV</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Gas cooler</td>
<td>Coal</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cement</td>
<td>13. BImSchV</td>
</tr>
</tbody>
</table>

**Abbreviations:**
- **SWIP:** Special waste incineration plant
- **WIP:** Waste incineration plant
- **AAS:** Atomic absorption spectroscopy
- **DOAS:** Differential, optic absorption spectroscopy
- **CVAAS:** Cold vapour atomic absorption spectroscopy
## Continuous Mercury Emission Monitoring

### Certified Monitoring Systems

<table>
<thead>
<tr>
<th>Name</th>
<th>Manufact.</th>
<th>Meas. range [µg / m³]</th>
<th>DL</th>
<th>MU</th>
<th>MI</th>
<th>Limitation</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Supplier 1</td>
<td></td>
<td>0 – 20/45/100</td>
<td>&lt; 0,01</td>
<td>10,2</td>
<td>3</td>
<td>System did not pass T90 time</td>
<td>15 m measuring gas line</td>
</tr>
<tr>
<td>Supplier 2</td>
<td></td>
<td>0 – 45 / 100</td>
<td>k.A.</td>
<td>10,7</td>
<td>2</td>
<td>System did not pass T90 time</td>
<td>10 m measuring gas line</td>
</tr>
<tr>
<td>MERCEM300Z</td>
<td>SICK</td>
<td>0 – 10 / 45&lt;br&gt;0 – 100 / 1.000</td>
<td>&lt; 0,05</td>
<td>2,3</td>
<td>6 *</td>
<td>none</td>
<td>35 m measuring gas line</td>
</tr>
<tr>
<td>Supplier 3</td>
<td></td>
<td>0 – 45 / 75</td>
<td>&lt; 1,0</td>
<td>8,4</td>
<td>3</td>
<td>none</td>
<td>10 m measuring gas line</td>
</tr>
</tbody>
</table>

**DL:** Detection limit in µg/m³ acc. to manufacturer or type approval  
**MU:** Measuring uncertainty in % relating to limit value 30 µg/m³  
**MI:** Maintenance interval in months  
* for measuring range 0-10 µg/m³, the maintenance interval is 3 months!
Continuous mercury measurement in a range below 10 µg/Nm³ is possible!
- In the US as well as in Europe
- Regulations in Europe (EN15267-3) are more pretentious

Mercury measurement in process gases is a reasonable/necessary supplement to meet future emission limits and to save costs.

2012: Performance test of MERCEM300Z for all relevant industries completed
- Today: more than 120 installed systems in the world
- Successful calibration on sites where no other system was possible to
MANY THANKS FOR YOUR ATTENTION.

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Technical Industry Manager
Process Automation

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APPENDIX
MERCEM300Z – OVERALL SYSTEM

- Our solution – high temperature
Ejector principle

- Exhaust gas
- Instrument air
- Cell 1000°C
- Optics
- Test gas generator
- Measuring gas line
- Filter
- Nozzle generator
- sampling system
Hg-monitoring in the raw gas of a waste incineration plant
Analyzer set-up unchanged to emission monitoring system
Parallel monitoring with 3 MERCEM300Z at different stages of plant process

Tasks:
- Mercury monitoring at more difficult flue gas conditions (higher dust load, higher concentration of cross sensitivity components)
- Fast response time necessary
- Monitoring of Hg-peaks up to the mg/Nm³ range

Benefits
- Control of Hg-deposition in scrubber
  → Possibility of fast reaction on changes in the plant process
- Dosing of coagulants
APPENDIX
MERCURY PROCESS MEASUREMENT

- Dynamic Hg process monitoring is possible
- Fast response times can be achieved
- High dynamics of monitoring system enables the detection of Hg peaks
- Dosing of coagulants/activated carbon can be controlled
- Hg-process monitoring is necessary to meet future Hg limit values and to save costs with dosing of coagulants and activated carbon