HCl CEM: “Best Practices” and Technology Overview
Name: Dan Kietzer – SICK Process Automation
Contents

- Experience
- Best Practices
- PS18 – Brief Overview
- Technology Overview
  - NDIR – Gas Filter Correlation
  - Tunable Diode Laser Spectroscopy – TDLS
  - Fourier Transform IR – FTIR
  - Cavity Ringdown
- Discussion / Questions
Experience

There is over 30 Years experience in measuring HCl in CEM applications
- Cement
- Power
- Waste Incineration
- Pharmaceutical

Typical spans are in the 0 - 5/10 ppm range
**Best Practice**

- Fast and correct measurement of HCl in ppm concentrations can only be made when you measure wet.
  - This prevents errors due to absorption, desorption effects from HCl on the wetted parts.

- Keep the entire sample train hot/insulated to prevent cold spots
  - System components should be kept at a minimum of 185° C to prevent cold spots
    - Swagelok fitting on inlet/outlet pump
    - Sample pump
    - Flange and tube at the sample probe
    - Ends of sample line extending from heated line (insulated)
    - Vent tube from photometer (avoid salt formation)
    - Sample probe tube (if flue gas below acid dewpoint)

- Sample at high temperature and high flow rate.
  - Shortens the time the sample is in contact with the system components, minimizing memory effects.
HCl is not CO. Calibration gas injection is the most troublesome part of HCl monitoring.

- Cylinder values can be effected by dirty pressure regulators, improper handling of the regulators or incompatible materials used in the sample system

- Cylinders < 100ppm need to be tested for long term stability
  - HCl/N2 mixtures down to 1 ppm show stability in passivated Luxfer aluminum cylinders
  - HCl/N2 mixtures down to 25 ppm show stability in nickel plated steel cylinders.

- Dry calibration gas injection at the probe leads to issues with absorption/desorption
  - Measurement stability time of the system can be very long (>35-40 min at <10ppm); if the measurement range is low, this uses a lot of expensive cal gas
  - This issue is not specific to any measurement technology (NDIR, TDLS, FTIR)

- Options
  - Automated wet calibrator can be integrated into the system.
    - NIST Tracable, easy to use
  - Humidification of dry gas increases response time.
Will be inclusive of all technologies; extractive, dilution, in-situ

Will include provisions for:
- Linearity
- Interference Tests
- Limit of Detection (LOD)
- Response Time
- Cal Error
- RATA and/or Dynamic Spiking
  - Reference methods may include EPA Method 320/321, ASTM D-6348-12.
  - EPA Method 26A may also be used, but not for Portland Cement kilns

- One of the major parameters to be addressed is the definition of standards (dry cylinders, wet gas generators)
  - Both will likely be allowed
NDIR Monitoring Technique

- Multi-component
- Undiluted Hot Wet Extractive
- Utilizes Gas Filter Correlation Technique for HCl
- Simple and reliable sample system
- Long path cell for low ranges
- > 3000 installations worldwide
### Relevant Measuring Ranges

<table>
<thead>
<tr>
<th>Gas</th>
<th>Lower Limit</th>
<th>Upper Limit</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>0</td>
<td>10</td>
<td>ppm</td>
</tr>
<tr>
<td>NH₃</td>
<td>0</td>
<td>15</td>
<td>ppm</td>
</tr>
<tr>
<td>SO₂</td>
<td>0</td>
<td>25</td>
<td>ppm</td>
</tr>
<tr>
<td>CO</td>
<td>0</td>
<td>40</td>
<td>ppm</td>
</tr>
<tr>
<td>NO</td>
<td>0</td>
<td>80</td>
<td>ppm</td>
</tr>
<tr>
<td>CO₂</td>
<td>0</td>
<td>25</td>
<td>Vol.-%</td>
</tr>
<tr>
<td>H₂O</td>
<td>0</td>
<td>40</td>
<td>Vol.-%</td>
</tr>
<tr>
<td>O₂</td>
<td>0</td>
<td>21</td>
<td>Vol.-%</td>
</tr>
<tr>
<td>NO₂</td>
<td>0</td>
<td>50</td>
<td>ppm</td>
</tr>
<tr>
<td>N₂O</td>
<td>0</td>
<td>50</td>
<td>ppm</td>
</tr>
<tr>
<td>CH₄</td>
<td>0</td>
<td>70</td>
<td>ppm</td>
</tr>
</tbody>
</table>

Smallest ranges @ standard conditions dry (H₂O, O₂: wet)
Tunable Diode Laser Spectroscopy uses a laser light scanning over a specific absorption wavelength area of desired measurement component.

Laser selectivity means high sensitivity and minimal cross-interference effects.

“Line locking” technique eliminates measurement drift.

Inline gas cell can be used for daily validation.

Available in in-situ and extractive configurations:
- In-situ: Cross stack and probe
- Extractive: Hot wet
TDLS Cross Stack Versions – Min Range: 0-10ppm

Cross stack version
- Daily validation via gas cell
- Spiking difficult
TDL Monitoring Technique

TDLS Probe Versions – Min Range: 0-10ppm

Filtered Probe

Open Path Probe
TDL Monitoring Technique

- A complete TDLS system in one housing

- Minimum Range: 0-5 ppm HCl

- Extractive „hot-wet“ measurement

- Heated, volume- and flow- optimized multi-pass gas cell, 290ml

- 19“-rack for control cabinet installation
FTIR Monitoring Technique

- Fourier Transform IR Technique utilizes a moving mirror in an interferometer to generate a “interferogram” of the sample absorption spectrum.

- Performing a mathematical Fourier transform on the “interferogram” generates an absorption spectrum of the entire used spectral range.

- FTIR can generate multi-component measurement results, including HCl.

- Hot wet sample system

- Typical minimum range of HCl: 0-10ppm
Cavity Ringdown

- Cavity ringdown measures by tuning light rays from a laser in the IR spectrum where the component to be measured is absorbed.

- Measuring the time it takes for the light to fade, or “ringdown” gives an accurate molecule count.

- Dilution extractive measurement technique

- Range: 0-5ppm (+/- 1 ppb)
Summary

- There are many, well known and used measurement techniques for monitoring of HCl
- Minimum range and detection limits meet current requirements
- NDIR and FTIR offer multi-component options
- TDLS and Cavity Ringdown offers single component option
- Sample handling is key
  - Keep Sample Hot
  - Move Sample fast
- Calibration is the difficult part
  - Accuracy and handling of dry gas cylinders
  - Absorption/Desorption for dry gases
  - Wet Calibration
Thank you for your attention.