Field Validation of an On-Line FTIR Analyzer for Measuring Total Siloxane Content in Landfill Gas

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Why Monitor Siloxanes in Biogas?

- Assess Biogas Fuel Quality
  - Quantify Methane and CO₂ content
  - Verify composition before gas enters pipeline
  - Verify impurity levels

- Siloxane Impurities
  - High temperature: SiO₂ powders form
  - Turbines - mechanical wear and tear
  - Boilers - particulate build up – increase in maintenance frequency
  - SCR Catalysts – plugged in minutes
  - Micro-turbines can be destroyed

- 2009 Engine MFG Siloxanes Limits in mg/m³
  - Caterpillar 28
  - Jenbacher 10
  - Waukesha 25
  - Deutz 5
  - Solar Turbines 0.1
  - IR Microturbines 0.06
  - Capstone Microturbines 0.03
Traditional Landfill Gas Siloxane Sampling and Analysis

- Process
  - Landfill gas sample collected at site
  - Sample sent to off site analytical lab
  - Analysis results generally take 1 week turn around time

- Traditional Sampling Methods
  - Extraction / Concentrators
    - Thermal Desorption tubes (Tenex)
    - Impingers (methanol)
    - JetCare (oil-based extraction)
    - Extra processing needed to release or determine Siloxane content
  - Direct Sampling Methods
    - Tedlar bags
    - Suma Canisters
      - Canisters must be coated with glass
Issues with Traditional Sampling Methods

- Difficultly in sending gas samples across borders
  - Interstate as well as national border issues
- Not representative
  - One shot analysis over 2 – 30 minutes
- Sample prep or conditioning required
  - Remove H₂O
  - Concentrate sample
  - Recover / extract from media - Some Siloxanes unrecoverable
- Inconsistencies in reported results for duplicates
  - Sample handling issues
  - Conversion of TMS and Siloxanes during transportation, due to media or H₂O content
FTIR as the Alternative Siloxane Sampling & Analysis Tool

- On Site continuous sampling and analysis
  - Pre- and Post-Scrubber analysis with same instrument

- No sample gas conditioning required
  - Sample gas pressure used to flow gas into FTIR
  - H₂O removal not required
  - Rapid Analysis
    - 20 seconds to 1 minute

- FTIR detects multiple species at same instance
  - Siloxanes have strong FTIR signal – ppb detection
  - CH₄, CO₂, H₂O – from ppb to percent level
  - Analyze for other components as well
    - NH₃, CO, COS, Hydrocarbons, etc.
MKS Patented Total Siloxane Method

- Does not provide speciated Siloxane numbers
  - Not needed – only useful for filter development
- Provides one number for all of the main straight chain (L2-L5) and cyclic (D3 – D6) siloxanes
- Reports Trimethylsilanol (TMS) as well as Total Si at current CH$_4$ content
  - Total Siloxanes as mg/m$^3$ and Si (mg/m$^3$)
  - Total TMS as mg/m$^3$ and Si (mg/m$^3$)
  - Total TMS and Siloxanes as Si (mg/m$^3$)
  - Scale reported values to the Laboratory value
- Calibrations based upon Permeation Devices
  - Permeation device mechanism NIST Traceable
FTIR Landfill Gas Siloxane Analysis

- **MKS AIRGARD® FTIR**
  - Transported to Landfill port via hand cart (75 lbs)
  - Setup < 15 minutes
  - Continuous analysis - 60 sec scan time
  - Total Siloxane method used
    - Conservative Detection Limit 0.2 mg/m³

- **Landfill Sites – 9 Total**
  - Three sites had Siloxane scrubber systems
    - Different filter media at each site
  - 7 sites collected Tenex adsorption tubes
  - 1 site collected Tedlar Bag
Total Siloxane Landfill Gas Analysis Validation Process

● Goal
  – Use lab analysis on gas sample to validate FTIR method in the field

● Field Collection Process
  – Collect FTIR Landfill gas data
    ▶ Gas Spectra for Raw and Processed Landfill gas
    ▶ Run continuously at 1 minute rate
  – Collect Landfill Gas Samples for Laboratory Analysis
    ▶ Collect duplicate samples
    ▶ Tenex spaced 30 minutes apart due to gas collection time
    ▶ Tedlar bag collections immediately after Tenex collection
  – Send gas samples to preselected labs

● Use Lab results to validate the FTIR field Data
  – Use FTIR Total Siloxane method
  – Scale the Total Siloxane value to the Lab reported results
FTIR Total Siloxane Analysis
East (2) and West (4) Sites

**RED**  Total Siloxane (Si mg/m³)
**WHITE** Total TMS (Si mg/m³)
### Example of Same Laboratory Different Landfill Discrepancies

<table>
<thead>
<tr>
<th>Site</th>
<th>Tenex TMS (Si mg/m³)</th>
<th>FTIR TMS (Si mg/m³)</th>
<th>Tenex Total Siloxane (Si mg/m³)</th>
<th>FTIR Total Siloxane (Si mg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>East #1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pre-scrubber</td>
<td>3.3</td>
<td>3.35</td>
<td>12.7</td>
<td>14.7</td>
</tr>
<tr>
<td>Post-scrubber</td>
<td>0.35</td>
<td>2.8</td>
<td>4.7</td>
<td>4.4</td>
</tr>
<tr>
<td>East #2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>No scrubber</td>
<td>3.9</td>
<td>4.1</td>
<td>8.1</td>
<td>9.4</td>
</tr>
<tr>
<td>West #1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pre-scrubber</td>
<td>7.9</td>
<td>2.7</td>
<td>3.1</td>
<td>9.4</td>
</tr>
<tr>
<td>Post-scrubber</td>
<td>0.11</td>
<td>0.8</td>
<td>2.2</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>Component</td>
<td>Tenex Inlet1</td>
<td>FTIR</td>
<td>Tenex Outlet1</td>
<td>FTIR</td>
</tr>
<tr>
<td>-----------</td>
<td>-------------</td>
<td>------</td>
<td>---------------</td>
<td>------</td>
</tr>
<tr>
<td>TMS</td>
<td>6.552</td>
<td>2.330</td>
<td>0.103</td>
<td>0.63</td>
</tr>
<tr>
<td>L2</td>
<td>0.619</td>
<td>0.600</td>
<td>0.019</td>
<td>0.001</td>
</tr>
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<td>0.346</td>
<td>1.670</td>
<td>0.407</td>
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PPM not Si (mg/m³)
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D4 Raw Landfill Pre-Scrubber

D4 (ppm)
### Example of Single Landfill Multiple Laboratory Discrepancies

<table>
<thead>
<tr>
<th></th>
<th>Scrubber Inlet WET / RAW (Si mg/m³)</th>
<th>Scrubber Inlet DRY (Post Chiller) (Si mg/m³)</th>
<th>Scrubber Outlet (Si mg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tedlar AnSol</td>
<td>Tedlar OSB</td>
<td>TENAX CAS</td>
</tr>
<tr>
<td>(2) Siloxane</td>
<td></td>
<td></td>
<td>3.407</td>
</tr>
</tbody>
</table>

* Reports Total Si which includes particulates as well as volatiles
Method Validation Issues

- Which Golden Standard do you use for comparison or scaling?

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</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tedlar AnSol</td>
</tr>
<tr>
<td>(1) Siloxane</td>
<td>0.838</td>
</tr>
<tr>
<td>(1) Siloxane+TMS</td>
<td>0.838</td>
</tr>
<tr>
<td>(2) Siloxane</td>
<td>0.563</td>
</tr>
<tr>
<td>(2) Siloxane+TMS</td>
<td>0.971</td>
</tr>
</tbody>
</table>

- Which Laboratory is correct?
  - Duplicate samples are inconsistent
  - One lab did not detect TMS all others did

- What sampling method is correct?
FTIR Field Validation Process Using Analyte Spiking

- Analyze the FTIR Response to the Spike Gas
  - Run the Landfill gas sample through the FTIR
  - Dilute 10% of landfill gas with “known” Siloxane mix (Spike)

- Validate the FTIR Response
  - Use the CO₂ response to determine the dilution amount
  - Calculate how much Siloxane should reach the FTIR in the diluted stream
  - Calculations
    - Determine Native Siloxane – run Landfill gas only
    - Determine Siloxane content of the undiluted Siloxane Gas Mixture
    - Determine Siloxane content during the 10% Spike
    - Calculate the % Recovery (Actual Spike / Expected Spike)
    - If within ± 30% Expected Value then this is “validated”
Analyte Spike
Experimental Setup

- Landfill Gas
- Rotameter
- "T" connector
- Heated Sample Line (For All Season Use)
- Siloxane Mixture in N2
- 3 Way valve
- Needle Valve
- Rotameter
- FT-IR Cell
- Vent
On Site Field Validation Study

- **GC/FID for External Validation**
  - Analytical trailer equipped with GC/FID transported to site
  - 12 min / full scan
  - Used to validate Siloxane Mixture and Spikes

- **FTIR**
  - MKS AIRGARD transported to site
  - 1 min / scan
Field GC / FID Issues

- GC/FID equipment available for only one day
- Requires daily field calibration
  - Calibration standards necessary for on-site analysis
- Permeation tubes used for Siloxane calibrations
  - >2 hours run time for stable permeation reading
  - Permeation Tubes bundled to shorten wait time
    - Bundled tubes produced incorrect concentrations
      - Results were reproduced later in the lab
    - Conversion of siloxanes in the permeation oven
    - Incomplete permeation of other siloxanes
  - Initial concentration of TMS in Tedlar bag unknown
- Unable to verify GC Peaks in the field
  - Concentrations measured by GC are unknown
  - Direct GC to FTIR comparison unable to be performed
  - Need better Field transportable Siloxane and TMS standards
Landfill Siloxane and TMS Spike Tests

![Graph showing the concentration of silicon (Si) over time in different stages of a scrubber system. The graph compares TMS as Si (mg/m³), Total Si (mg/m³), and Total Si (w TMS) (mg/m³).]
Other Issues Related to Siloxane Field Validation

● Sampling Methods
  – Shipping samples – Customs, DOT Hazard forms
  – Conversion of L2, D3, D4 and TMS to other compounds

● Field Calibration Methods
  – Permeation Device
    ‣ Only one tube in oven at any one time
    ‣ Time to equilibrium extremely long
    ‣ Higher concentrations not accurate
  – Syringe Pump
    ‣ Hard to vaporize
    ‣ Low concentrations only
    ‣ Mixtures can be made using Hexane solution
  – Cylinders
    ‣ Siloxanes stick to the walls
    ‣ Cylinders not readily available
    ‣ Not certified
    ‣ Not in high concentrations
**Field Validation Method**

Proposed Modifications *(Brown)*

- **Use Cylinder Gas Mixtures**
  - (A) Purchase from Gas Supplier
    - TMS needs its own cylinder
    - Siloxanes blended in a cylinder
  - (B) Or create own using siloxane blends using diffusion method
    - Yet to be tested
    - Must be in Summa Canisters
  - (C) Use Syringe Pump
    - Mix with Hexane to vaporize

- **Analyze Cylinder gases response on FTIR prior to shipping**
  - Send equipment and cylinders to site

- **Analyze the FTIR Response to the Spike Gas**
  - Run Cylinder gases response on FTIR at Site prior to Spike Test
  - Run the Landfill gas sample through the FTIR
  - Dilute 10% of landfill gas with “known” Siloxane mix (Spike)

- **Validate the FTIR Response**
  - Use MFCs for Landfill gas and Spike gas if possible
    - Or at least use MFC for Spike gas and CO₂ for dilution amount
  - Calculate how much Siloxane should reach the FTIR in the diluted stream
  - Calculations
    - Determine Native Siloxane – run Landfill gas only
    - Determine Siloxane content of the undiluted Siloxane Gas Mixture
    - Determine Siloxane content during the 10% Spike
    - Calculate the % Recovery (Actual Spike / Expected Spike)
    - If within ± 30% Expected Value then this is “validated”
Proposed ASTM Field Validation Method

- FTIR, Gas cylinders and field equipment ready
- Currently looking for site near Raleigh, NC
  - Prefer site with Siloxane Removal system and existing GC (or other analyzer) for Siloxanes comparison
- Multi-Analyzer Round Robin
  - Round Robin tests at Los Angeles County Sanitation District (LACSD)
  - Analyze samples in the field as well as in the lab at same time as GC-ICP, GC-MS
  - Send field collected samples to various labs for analysis:
    - Tenex
    - Methanol Impingers
    - Tedlar bag
    - Summa Canisters
- Create ASTM Test Methods
  - Lab GC-XX – Sally Mathison LACSD
  - FTIR Field Method – Barbara Marshik MKS Instruments
Summary

- **MKS AIRGARD® FTIR Technology**
  - Clearly capable of analyzing siloxanes and TMS to very low concentrations
  - At-line analysis in high level CH₄, CO₂ and H₂O
  - Fixed installations or transportable to site

- **Total Siloxane and Total Silicon Method**
  - Works well in raw or scrubbed biogas applications
  - TMS and Siloxane continuous monitoring at <0.2mg/m³

- **FTIR Field Validation**
  - Laboratory analysis varies so too much to determine which is correct
  - Better FTIR MDLs can be provided once field validation is completed