Siloxane Sampling, Analysis and Data Reporting
Recommendations on Standardization for the
Biogas Utilization Industry

Jeffrey L. Pierce, P.E.
Senior Vice President
SCS Energy

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Siloxanes – What and Why?

- Siloxanes are volatile organic silicon compounds (VOSCs)
- Widely used in personal health and beauty products and in commercial applications
- Found in the ppmv level in landfill gas and WWTP digester gas
- When burned as a fuel, the silicon (Si) in siloxane oxidizes to silica (SiO$_2$)
- Silica deposits cause performance and maintenance problems with LFGE equipment
Silanes and Silanols

• Silanes and silanols are also increasingly useful VOSCs
• Silanes and silanols are also present in landfill gas and WWTP digester gas
• Trimethylsilanol is frequently found in biogas and in large quantities
• If lab is not reporting at least some silanes and silanols, you are not capturing a large portion of the VOSCs in your test program
# Common VOSCs in Landfill Gas

<table>
<thead>
<tr>
<th>Formal Name</th>
<th>AKA</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexamethyldicyclotrisiloxane</td>
<td>$D_3$</td>
<td>Si$_3$-$O_3$-(CH$_3$)$_6$</td>
</tr>
<tr>
<td>Octamethyldicyclotetrasiloxane</td>
<td>$D_4$</td>
<td>Si$_4$-$O_4$-(CH$_3$)$_8$</td>
</tr>
<tr>
<td>Decamethyldicyclopentasiloxane</td>
<td>$D_5$</td>
<td>Si$_5$-$O_5$-(CH$<em>3$)$</em>{10}$</td>
</tr>
<tr>
<td>Hexamethyldisiloxane</td>
<td>$L_2$</td>
<td>Si$_2$-$O$-(CH$_3$)$_6$</td>
</tr>
<tr>
<td>Octamethyltrisiloxane</td>
<td>$L_3$</td>
<td>Si$_3$-$O_2$-(CH$_3$)$_8$</td>
</tr>
<tr>
<td>Trimethylsilanol</td>
<td>MOH</td>
<td>Si-(CH$_3$)$_3$-OH</td>
</tr>
</tbody>
</table>
## Properties of Selected VOSCs

<table>
<thead>
<tr>
<th>Compound</th>
<th>MW</th>
<th>% Silicon</th>
<th>Vapor Pressure (mmHg)</th>
<th>Boiling Point (°F)</th>
<th>Water Solubility (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D₃</td>
<td>222</td>
<td>.380</td>
<td>10</td>
<td>273</td>
<td>1.56</td>
</tr>
<tr>
<td>D₄</td>
<td>297</td>
<td>.378</td>
<td>1.3</td>
<td>347</td>
<td>0.06</td>
</tr>
<tr>
<td>D₅</td>
<td>371</td>
<td>.379</td>
<td>0.4</td>
<td>410</td>
<td>0.02</td>
</tr>
<tr>
<td>L₃</td>
<td>236</td>
<td>.357</td>
<td>3.9</td>
<td>306</td>
<td>0.04</td>
</tr>
<tr>
<td>MOH</td>
<td>90</td>
<td>.312</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Reporting on a speciated basis is important since all VOSCs are not equal in silicon content and properties.
Units of Reporting for VOSCs

| **Mass as Total Compound (at Actual CH₄)** | mg/m³ |
| **Mass as Silicon Only (at Actual CH₄)** | mg Si/m³ |
| **Mass as Total Compound (at 100% CH₄)** | mg/m³ |
| **Mass as Silicon Only (at 100% CH₄)** | mg Si/m³ |
| **Volumetric as Total Compound** | ppmv |
| **Mass Silicon per Energy Content** | lbs Si/mmBtu |

Can be reported as a total value or on a speciated basis
VOSCs in Landfill Gas per SCS Database

• VOSCs varied from 4.5 mg/m$^3$ (0.41 ppmv) to 161 mg/m$^3$ (13.9 ppmv)
• Most common VOSCs are D$_4$ (found 90% of the time); D$_5$ (found 83% of time); and MOH (found 77% of the time)
• Next most frequently found VOSCs are L$_2$ (found 45% of the time) and D$_3$ (found 20% of the time)
• Ten other VOSCs were seen (each found no more than 7% of the time)
Methods of Sampling and Analyzing for Siloxanes and/or VOSCs

- Air Toxics method
- Jet Care method
- OSB method
- AtmAA method
- AnSol method
- Deutz method
- Jenbacher method
Air Toxics Method

- Methanol impinger method
- Sample gas is bubbled through two midget impingers in series
- VOSCs are absorbed into the methanol
- Three hour sample run
- Determine concentration and mass of five siloxane compounds \((D_4, D_5, D_6, L_2\) and \(L_3\)) in methanol by GC/MS (gas chromatograph/mass spectrometer)
- Back calculate concentration of siloxanes in gas based on gas volume processed
- Reported as mg/m\(^3\) or ppmv
Methanol Impinger Sample Train
Air Toxics Method

- Widely used in the biogas industry for over a decade
- A composite sample rather than a grab sample
- Method detection limit is relatively high, but can ask for “J” values
- Does not include silanes and silanols. Includes $D_6$ (which is not often present)
- Labor intensive and sample train is subject to upsets
- Do the impingers actually capture all of the VOSCs in the biogas?
### Air Toxics Method
Three Impinger Test Runs

<table>
<thead>
<tr>
<th></th>
<th>Landfill A</th>
<th>Landfill B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Impinger No. 1 Capture</td>
<td>59.23 mg/m³</td>
<td>21.73 mg/m³</td>
</tr>
<tr>
<td>Impinger No. 2 Capture</td>
<td>2.68 mg/m³</td>
<td>1.23 mg/m³</td>
</tr>
<tr>
<td>Impinger No. 3 Capture</td>
<td>0.57 mg/m³</td>
<td>0.37 mg/m³</td>
</tr>
<tr>
<td>Total Capture</td>
<td>62.48 mg/m³</td>
<td>23.33 mg/m³</td>
</tr>
</tbody>
</table>

Landfill A: VOSCs in first two impingers = 99.1%
Landfill B: VOSCs in first two impingers = 98.4%
Jet Care Method

- Oil sampling method
- Sample is bubbled through three oil bottles in series
- VOSCs are absorbed into the oil
- One hour sample run
- Analyze total silicon in oil by GC/ICP (inductively coupled plasma). Do not differentiate if the silicon is from VOSCs or from particulates
- Back calculate concentration of silicon in gas based on gas volume processed
- Reported as mg Si/m³ at 100% methane equivalent
Jet Care Sample Train
Jet Care Method

- Limited use in biogas industry, but gaining traction due to Solar Turbine’s identification of Jet Care as preferred test method
- Mineral oil may not capture 100% of the VOSCs
- Composite sample rather than a grab sample
- Detection limits are similar to Air Toxics
- Captures all silicon, including that which is already silica. Silica may be a less problematic compound than VOSCs
- Results are not speciated
OSB Method

- Grab samples in bags
- Twenty-two VOSCs are analyzed for using GC/MS
- Direct determination of concentration of VOSCs in gas
- Results reported in mg/m$^3$, mg Si/m$^3$ and ppmv on a speciated basis
OSB Method

• Widest application has been testing for ultra-low VOSC levels in high-Btu plant product gas. Otherwise, not in wide use
• Very low limits of detection. OSB insists on use of bags with non-silicon based valve lubricants
• Broad VOSC scan includes a few VOSCs not tested for by any other lab, which are present in significant quantities
Deutz Method

- Not a method per se, but Deutz requires that gas be tested by Umweltanalytik RUK in Germany for warranty purposes
- Samples drawn in bags and shipped to Germany
- RUK tests for eight VOSCs – L₂, L₃, L₄, D₃, D₄, D₅, MOH and tetramethylsilane
- Low limits of detection
- Results reported in mg/m³ and mg Si/m³ at methane content collected and at 100% methane content equivalent
Deutz Method

- Use is limited to Deutz sites – limited body of data available
- Samples must be shipped overseas
- Has extended list of VOSCs
- Low limits of detection
- Units are conveniently expressed
Jenbacher Method

- Not a method per se. Jenbacher prefers, but does not insist, that VOSCs be tested by TUV Suddeutschland in Germany
- Gas is passed through a sample tube containing activated carbon, and the tube is shipped to the lab. The sample draw time is 30 minutes
- The mass of VOSCs on the activated carbon is determined by GC/MS and the concentration of VOSCs in the gas is back calculated
- The lab tests for eleven VOSCs – L₂, L₃, L₄, D₃, D₄, D₅, MOH and four silanes
- Results are reported as mg/m³, mg Si/m³ and ppmv (as Si equivalent)
Jenbacher Method

- Generally only applicable to Jenbacher sites. Jenbacher will rent the sample train out
- Very limited comparative database available
- Samples must be shipped overseas
- Activated carbon may not capture 100 percent of the VOSCs, but it probably does
- Units are conveniently expressed
- Low limits of detection
AtmAA Method

- Moderate use in LFGE industry -- not affiliated with or required by an equipment supplier
- Gas sampled by bag or canister. Lab analysis by GC/MS
- Now target -- L₂, L₃, L₄, D₃, D₄, and D₅. Prior to 2007, included MOH and tetramethysilane
- Prior to 2007, AtmAA did not use actual VOSC standards for GC/MS calibration, basing their response on toluene, with the lab results were noted as being “semi-quantitative”
- Reports are presented on a ppmv basis. Since the results are speciated, they are able to be converted to mg/m³
AtmAA Method

- Results after 2007 are quantitative. Prior to that date they are approximate. In aggregate, the old data was under-reporting the quantity of VOSCs in the vicinity of about 45%
- Moderately low limits of detection
- The need to convert from ppmv to mg/m³ is a nuisance
Ansol Method

- Bag samples or canisters
- Ten specific VOSCs plus “all others.” Uses GC/AED (atomic emission detector)
- Ten specific VOSCs are – L₂, L₃, L₄, L₅, D₃, D₄, D₅, D₆, MOH and tetramethylsilane. All others generally run less than 10% of total
- Reports VOSCs on a speciated basis as ppmv (as Si) and as mg Si/m³ in total
Ansol Method

• Moderate use in the LFGE industry – not affiliated with or recommended by an equipment supplier
• Low limits of detection
• Conversion of reported units to mg/m³ or mg Si/m³ on a speciated basis is complicated
Comparison of Laboratory Results
Search for the Rosetta Stone

<table>
<thead>
<tr>
<th></th>
<th>Air Toxics</th>
<th>Jet Care</th>
<th>OSB</th>
<th>Jenbacher</th>
<th>AtmAA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site A</td>
<td>18.83</td>
<td>57.21</td>
<td>34.85</td>
<td>49.32</td>
<td></td>
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<tr>
<td>Site B</td>
<td>13.84</td>
<td>51.10</td>
<td>88.97</td>
<td>32.10</td>
<td></td>
</tr>
<tr>
<td>Site C</td>
<td>11.31</td>
<td></td>
<td>26.10</td>
<td></td>
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</tr>
<tr>
<td>Site D</td>
<td>0.33</td>
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<td>2.78</td>
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<td>Site E</td>
<td>7.79</td>
<td>12.06</td>
<td></td>
<td>4.20</td>
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<tr>
<td>Site F</td>
<td>8.74</td>
<td>43.13</td>
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</tr>
<tr>
<td>Site G</td>
<td>81.63</td>
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<td>60.60</td>
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<tr>
<td>Site H</td>
<td>58.68</td>
<td></td>
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<td>32..2</td>
</tr>
<tr>
<td>Site I</td>
<td>6.58</td>
<td></td>
<td>21.55</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Summary of Sampling, Analysis and Data Reporting Problems

• List of target compounds analyzed varies from 5 to 22 between labs
• At least one lab historically reported of semi-quantitative results
• Different lab analytical methods – GC/MS, GC/AED
• Different sampling methods – methanol, oil, bag and activated carbon tubes
• Different limits of detection
• Data reported in different units
Recommendations

• Always express results on a mg Si/m$^3$ basis
• Always report results on a speciated basis
• The minimum VOSC target list should include: D$_3$, D$_4$, D$_5$, L$_2$, L$_3$ and MOH
• European laboratories offer no advantage over North American labs. Use North American labs unless required by equipment manufacturer