



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 VOCs in Landfill Gas

Formal Name	AKA	Formula
Hexamethylcyclotrisiloxane	D ₃	Si ₃ -O ₃ -(CH ₃) ₆
Octamethylcyclotetrasiloxane	D ₄	Si ₄ -O ₄ -(CH ₃) ₈
Decamethylcyclopentasiloxane	D ₅	Si ₅ -O ₅ -(CH ₃) ₁₀
Hexamethyldisiloxane	L ₂	Si ₂ -O-(CH ₃) ₆
Octamethyltrisiloxane	L ₃	Si ₃ -O ₂ -(CH ₃) ₈
Trimethylsilanol	MOH	Si-(CH ₃) ₃ -OH

Properties of Selected VOSCs

Compound	MW	% Silicon	Vapor Pressure mmHg	Boiling Point (°F)	Water Solubility (mg/l)
D ₃	222	.380	10	273	1.56
D ₄	297	.378	1.3	347	0.06
D ₅	371	.379	0.4	410	0.02
L ₃	236	.357	3.9	306	0.04
MOH	90	.312		210	

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 CH ₄)	mg/m ³
Mass as Silicon Only (at Actual CH ₄)	mg Si/m ³
Mass as Total Compound (at 100% CH ₄)	mg/m ³
Mass as Silicon Only (at 100% CH ₄)	mg Si/m ³
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/m³ (0.41 ppmv) to 161 mg/m³ (13.9 ppmv)
- Most common VOSCs are D₄ (found 90% of the time); D₅ (found 83% of time); and MOH (found 77% of the time)
- Next most frequently found VOSCs are L₂ (found 45% of the time) and D₃ (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 midjet 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 D₆ (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

	Landfill A	Landfill B
Impinger No. 1 Capture	59.23 mg/m ³	21.73 mg/m ³
Impinger No. 2 Capture	2.68 mg/m ³	1.23 mg/m ³
Impinger No. 3 Capture	0.57 mg/m ³	0.37 mg/m ³
Total Capture	62.48 mg/m³	23.33 mg/m³

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 VOCs are analyzed for using GC/MS
- Direct determination of concentration of VOCs in gas
- Results reported in mg/m^3 , $\text{mg Si}/\text{m}^3$ 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 TÜV SÜD 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 tetramethylsilane
- 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/m^3 or $\text{mg Si}/\text{m}^3$ on a speciated basis is complicated

Comparison of Laboratory Results Search for the Rosetta Stone

	Air Toxics	Jet Care	OSB	Jenbacher	AtmAA
Site A	18.83	57.21	34.85	49.32	
Site B	13.84	51.10	88.97	32.10	
Site C	11.31		26.10		
Site D	0.33		2.78		
Site E	7.79	12.06		4.20	
Site F	8.74	43.13			
Site G	81.63				60.60
Site H	58.68				32..2
Site I	6.58		21.55		

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-quantative 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/m³ basis
- Always report results on a speciated basis
- The minimum VOSC target list should include: D₃, D₄, D₅, L₂, L₃ and MOH
- European laboratories offer no advantage over North American labs. Use North American labs unless required by equipment manufacturer