

Online, Direct Measurement of Volatile Siloxanes in Anaerobic Digester and Landfill Gases by Gas Chromatography with Mass Spectrometric Detection

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Presented at
2012 AWMA Air Quality Measurement Methods and Technology Symposium
Durham, North Carolina
April 26, 2012

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INTRODUCTION

Many of the methylated polysiloxanes found in digester and landfill gases have boiling points well above most of the target compounds in EPA Method TO-15. Even so, they have sufficient vapor pressures at ambient conditions to yield sufficient concentrations in the biogas fuel stream to befoul cogeneration engines and other related hardware (see Figure 1) due to combustion processes yielding silicon dioxide, and to coatings on catalyst media, thus reducing their effectiveness in controlling emissions. Many engine manufacturers are now specifying total siloxane upper limits in biogas in the range of 0.3 to 1.9 ppmV to minimize degrading effects on their gas-powered piston engines. Gas turbine manufacturers often set even tighter upper limits, typically in the total range of 2 to 7 ppbV (Table 1). If the biogas is to be processed and distributed through utility natural gas pipelines, these polysiloxanes in the gas must be removed to prevent downstream gas customers - both residential and commercial - from experiencing silica build-up at their gas burners. New approaches to filtering out siloxanes include a multi-layer carbon bed installed in-line with the feed gas to downstream outlets.¹ Continuous monitoring is mandated to sense when this filter bed suffers break-through and must be recharged.



Photo courtesy of County Sanitation Districts of Los Angeles County

Figure 1. White Silicon Dioxide Deposits on Heat Recovery Steam Generators result in loss of 20% heating value and damage at \$400K/yr.

Table 1. Warranty Limits for Total Siloxanes from Selected Engine Manufacturers (as of 1/31/2009).²

Engine Manufacturer	Total Siloxane Limit (mg/m³)	Total Siloxane Limit (ppmV) - based on D5	Total Siloxane Limit (g Si/MSCF)
Caterpillar	28	1.85	65.3
Jenbacher	10	0.66	23.3
Waukesha	25	1.65	58.3
Deutz	5	0.33	11.7
Solar Turbines	0.1	0.0066	0.23
IR Microturbines	0.06	0.004	0.14
Capstone Microturbines	0.03	0.002	0.07

Both digesters and landfills have widely variable concentrations for these polysiloxanes due to the dynamic processes taking place inside the biomass and in the associated headspace. It is not uncommon to see concentrations range from low ppbV and into mid ppmV levels. Continual monitoring of the gas stream can provide a better evaluation of the actual concentrations being generated and potential effects on downstream hardware. After processing bulk biogas to remove these siloxanes, measurements must be capable of accurately assessing concentrations into the very low ppbV range before releasing fuel for use, in order to satisfy warranty provisions of many engine manufacturers.

Several methodologies have been reported for analyzing biogas for polysiloxanes, including deployment of cold methanol impingers for liquid adsorption of the analytes, sorbent tubes with subsequent offline thermal desorption, and whole gas sampling into evacuated canisters or Tedlar[®] or Kynar[®] bags. All of these approaches have inherent limitations and each suffers from selective losses of various analytes.^{3,4} None is conducive to an online direct measure of siloxanes in a gas stream.

This report discusses a novel approach for measuring polysiloxanes online at regular time intervals with a fully automated gas chromatographic system with mass spectrometric detection. Minimal operator interactions are required during routine operations. Samples are directed to the analytical setup with a short length of heated transfer line from the gas source. This direct connection avoids potential loss of analytes that occurs with impingers, sorbent tubes, canisters or Tedlar bags, and to assure that ambient air does not enter in this stream to dilute analyte concentrations inappropriately. Sample points before and after the bulk cleanup process can be alternately monitored to verify effectiveness of siloxane removal. Calibration standards, blank checks and control samples are interwoven into the sampling sequence to validate performance of the analytical system. Results are shown for siloxanes, with concurrent measurement of target compounds listed in EPA Method TO-15 and calculations of energy (BTU) in the associated fuel gas.

EXPERIMENTAL

Analytical measurements are performed with a Bruker 451 Gas Chromatograph (GC) and Bruker SCION SQ Mass Spectrometer (MS) (Bruker CAM, Fremont, CA). Results are computed and reported using Bruker MS Workstation Version 8. This GC/MS system is modified by Lotus Consulting (Long Beach, CA) to perform automated, online measurements of a digester gas stream, with provisions for sampling from canisters and Tedlar bags. The system design in service is illustrated in Figure 2. Operating parameters are listed in Table 1. A multi-position stream selector valve is included to provide automated, unattended switching between sample, blank and standard streams. To prevent possible condensation of analytes in the interconnecting lines after the sample, all lines are heated to a minimum of 90 °C. The instrument includes a 400 mL glass sample loop, maintained at a constant 220 °C, to correctly apportion a fixed volume sample, independent of incoming sample and standard temperatures and pressures. Then this volume is directed into a hydrophobic mixed-bed

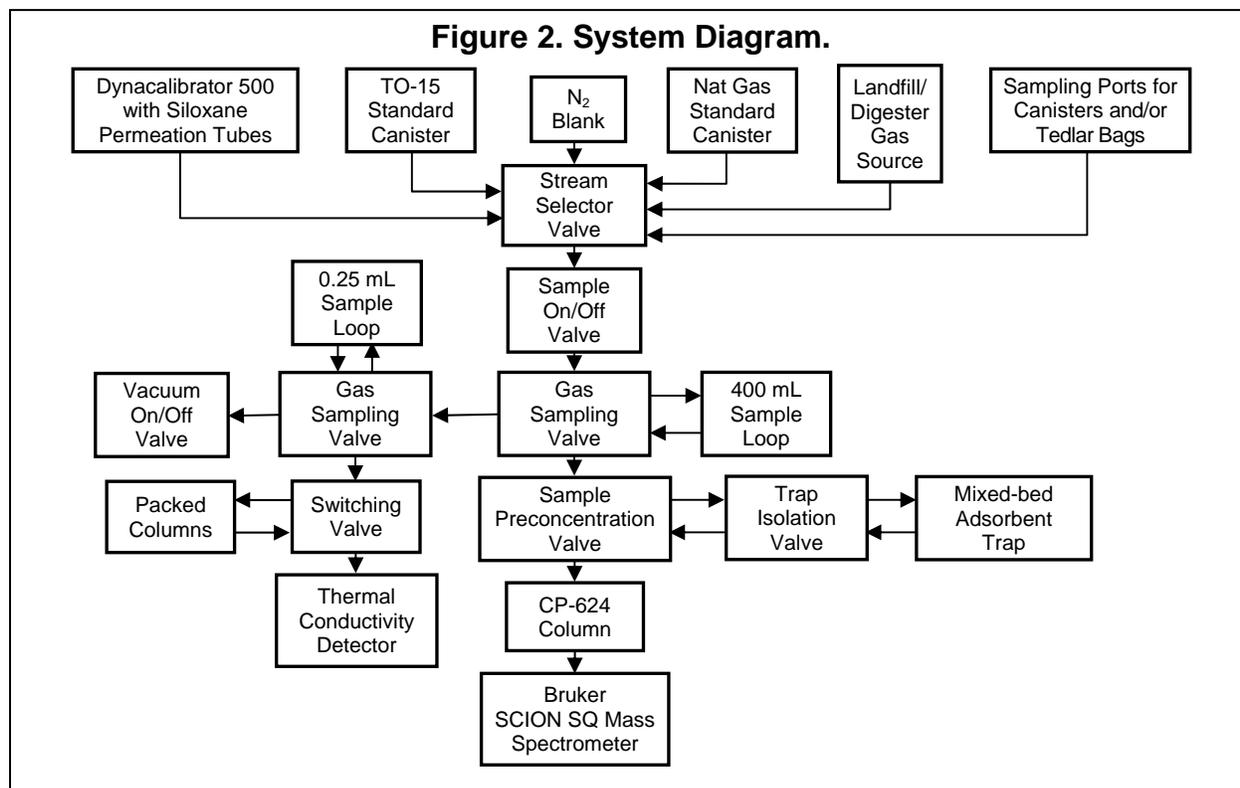


Table 1. Chromatographic and Spectrometric Parameters for Siloxane/TO-15 Analysis.

Inlet Sample Lines Temperature:	90 °C
Injection Loop Volume:	400 mL glass, 20 ml glass for LOD measurements
Loop Temperature:	220 °C
Adsorbent Trap:	Mixed-bed with glass beads and selected carbon packings
Valve Temperatures:	220 °C
Trap Temperature:	35 °C, hold for 7.1 min, ramp at 200 °C/min to 230 °C
Trap Coolant:	Compressed air at ~120 psiG
Column:	Agilent CP-624, 0.25 mm ID, 60 meters, df=1.40μ
Column Temperature Program:	35 °C, hold for 14 minutes, ramp to 230 °C at 5 °C/min.
Column Flow Rate:	2 mL/min, Helium
Typical Column Split Ratio:	49:1
Detector:	Bruker SCION SQ Mass Spectrometer
Mass Range:	40-500 m/z
Extended Dynamic Range:	On
Filament Temperature:	175 °C
Source Temperature:	150 °C
Electron Energy:	-70 eV
Manifold Temperature:	40 °C
Source Temperature:	150 °C
Transfer Line Temperature:	175 °C
Filament Emission Current:	80 μA
Total Cycle Time:	~58 minutes

adsorbent trap maintained with compressed air just above ambient temperature, to preclude use of cryogen for trapping. Water, methane, oxygen and carbon dioxide then pass on through to vent. After the sample is fully loaded onto the trap and flushed with nitrogen to vent, an appropriate valve is switched to isolate the trap during its heating, and then the trap is brought back in line and the isolation valve opened to inject the sample into the column. Valve operations make certain that the sample loop achieves consistent pressure prior to every injection, to correct for varying sample pressures, be it pressurized canisters, or bags and permeation oven flow at atmospheric pressure. All valving is accomplished with Valco series C_WE valves with microelectric actuators (Valco Instruments, Houston, TX). The installed column is a CP-624 0.25mm ID, 60m, $\text{df}=1.40\mu\text{m}$ capillary (Agilent, Santa Clara, CA).

Ten siloxane evaluated are listed in Table 2. Their standards are generated on demand with Dynacal[®] permeation tubes (VICI Metronics, Poughkeepsie, NY) and a Dynacalibrator[®] 500 Calibration Gas Generator (VICI Metronics, Poughkeepsie, NY) with dual chambers set at 50.00 °C.⁴ Nitrogen is the dilution gas, and its flow is controlled by calibrated rotameters in the Dynacalibrator. TO-15 standard is generated from a 65 component mix (1 ppm in nitrogen, Restek, Bellefonte, PA). Ten-component natural gas standard is obtained from Restek (Bellefonte, PA) and used as supplied.

Table 2. Mass Spectrometer Analyte Parameters.

Target Compound	Abbr.	CAS No.	Typical Ret.Time (min)	Reference Spectrum Ions	Quant Ion
1,1,3,3-Tetramethyldisiloxane	TMDS	3277-26-7	16.834	119,133	119
Hexamethyldisiloxane	L2	107-46-0	20.797	147,148,149	147
Hexamethylcyclotrisiloxane	D3	541-05-9	26.797	207,208,96,209	207
Octamethyltrisiloxane	L3	107-51-7	29.004	221,73,222	221
Octamethylcyclotetradisiloxane	D4	556-67-2	33.208	281,282,283,207	281
1,3-Dimethyltetra vinyl disiloxane	DMTVDS	16045-78-6	34.846	97,71,129,141,59	97
Decamethyltetrasiloxane	L4	141-62-8	35.680	207,73,295	207
Decamethylcyclopentasiloxane	D5	541-02-6	38.613	267,73	267
Dodecamethylpentasiloxane	L5	141-63-9	41.204	281,147,73,282	281
Dodecamethylcyclohexasiloxane	D6	540-97-6	43.925	73,147,74	73

Natural gas measurements are performed simultaneously with an on-board thermal conductivity detector (TCD). Gas components are separated on an 0.5 meter x 1/8" OD packed column with 30% DC200/500 on 80/100 mesh Chromosorb P NAW, plumbed with a 10 meter x 1/8" OD packed column with 30% DC 200/500 on 80/100 mesh Chromosorb P NAW (Supelco, Bellefonte, PA). These columns are configured with appropriate valving to yield the hexane+ portion first as a single peak, followed by full separation of methane through pentane. Chromatographic conditions for this measurement are listed in Table 3. Columns are mounted inside an independent isothermal oven to allow the conventional column oven to perform temperature programming for the siloxanes measurement and not affecting chromatography for these components. Gross heating values (BTU/ft³) are computed following protocols from the Gas Processors Association.⁵

Table 3. Chromatographic Conditions for Natural Gas Analysis.

Injection Loop Volume:	1.0 mL
Loop Temperature:	80 °C
Column:	30% DC 200/500 Chromosorb P NAW, 80/100 mesh, 0.5 meter x 1/8", plumbed in backflush-to-detector, and 10 meter x 1/8" stainless steel columns
Column Flow Rate:	20 mL/min, Helium
Column Temperature:	80 °C Isothermal
Detector:	Thermal Conductivity
Detector Temperature:	120 °C
Filament Temperature:	180 °C
Reference Flow:	20 mL/min, Helium
Detector Range:	0.5
Data Collection Rate:	3 Hz

RESULTS AND DISCUSSION

Reporting Units for Siloxanes

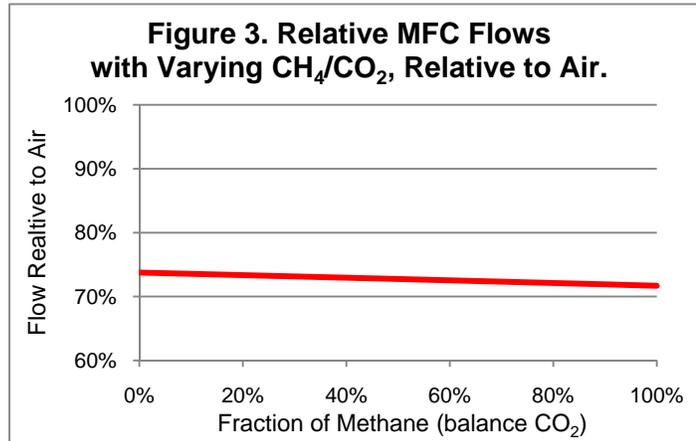
Most analytical results for siloxanes are routinely reported as ppmV for each analyte, the concentration unit for EPA TO15, or as $\mu\text{g}/\text{m}^3$, which is often employed for ambient air concentrations. The silicon atom is what produces silica to disrupt the efficacy of engines and emission controls. Although the weight percentage of silicon in most polysiloxanes is relative consistent, the reported value in units of W/V does not represent the potential of silica mass generated from combustion. An alternate reporting unit is "grams of silicon per 1000 standard cubic feet or grams Si per MSCF" of fuel. This anticipates the actual amount of silica build up, independent of the siloxane species. The calculation process is shown in Table 4. The multiplying factor for conversion from ppmV to grams Si/MSCF is provided in the last column for each siloxane.

Table 4. Details in generation of factor for conversion of concentrations from ppmV to g Si/MSCF.

Silicone Analyte	Molecular Weight	# of Silicons per Molecule	Atomic Weight of Silicon	Portion of Si by weight	Rel wt of Si	mg/m ³ Siloxanes for 1 ppmV ⁶	cubic meter to scf	mg/scf	g Si/MSCF for 1 ppmV
TMDS	134.32	2	28.09	56.17	0.418	5.49	35.31	193.9	81.08
L2	162.38	2	28.09	56.17	0.346	6.64	35.31	234.5	81.12
D3	222.46	3	28.09	84.26	0.379	9.10	35.31	321.3	121.69
L3	236.53	3	28.09	84.26	0.356	9.67	35.31	341.5	121.65
D4	296.62	4	28.09	112.3	0.379	12.13	35.31	428.4	162.24
DMTVDS	210.42	2	28.09	56.17	0.267	8.61	35.31	304.1	81.17
L4	310.68	4	28.09	112.3	0.362	12.71	35.31	448.9	162.30
D5	370.77	5	28.09	140.4	0.379	15.16	35.31	535.4	202.77
L5	384.84	5	28.09	140.4	0.365	15.74	35.31	555.85	202.83
D6	444.92	6	28.09	168.5	0.379	18.2	35.31	642.73	243.43

Systematic Errors with Mass Flow Controllers

A fixed volume sample loop is selected over the commonly employed mass flow controller to ensure that introduced volumes with standards in nitrogen are precisely equivalent to sample volumes from digester and landfill gases with high, variable levels of methane and carbon dioxide. Mass flow controllers are sometimes deployed in this type of measurement to gauge the amount of sample or standard that is loaded into concentrator traps. They are normally calibrated for a specific bulk gas, typically nitrogen or air. Their accuracy can vary significantly with changing bulk gas concentrations in the sample matrix due to changes in gases' thermodynamic properties.^{7,8}



Possible methane/carbon dioxide concentration ratios in digester gas can range from 61/38 to 63/35 volume%, with oxygen and nitrogen levels well below 1 volume%.⁹ Landfill gases can have methane/carbon dioxide ratios from 35/50 to 60/30 volume%.¹⁰ Figure 3 illustrates the computed change in flow rate for various concentration of methane and carbon dioxide, relative to flows with air. For example, a sample mixture of 62% methane and 38% carbon dioxide yields a controlled flow 28% lower than that with air, and results will be reported as 28% lower than their actual concentrations. Volume from a fixed loop is always a quantitative measure of the sample volume, independent of the bulk gas composition.

Systematic Flow Miscalculations with Rotameters

Rotameters are commonly used to measure sample flow into impingers and thermal desorption tubes to derive the total volume by multiplying with the sampling time interval. Since the composition of digester or landfill gas is not consistent due to the heterogeneous nature of the source and a change in bulk gas (methane and carbon dioxide) from the usual calibration gas (nitrogen), significant errors in the accuracy of the rotameter can be realized. Change in rotameter flow is inversely proportional to the square root of the change in average gas molecular weight.¹¹

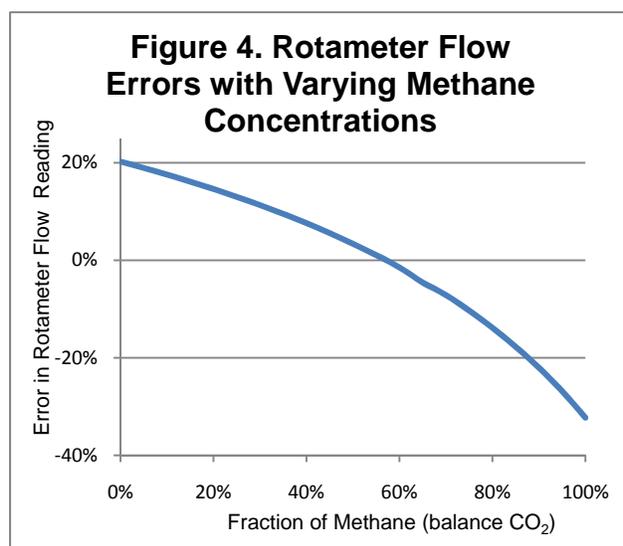


Figure 4 shows calculated errors in rotameter readings relative to nitrogen with varying amount of methane and balance carbon dioxide. At 57% methane and 43% carbon dioxide, this error is negligible, as this split matches the effective molecular weight of nitrogen. For methane levels above this, siloxane concentrations will be biased low, and less than 57% methane, this positive systematic error results from flows that will be too high. For example, if a rotameter calibrated for nitrogen is set to read 100 ml/min, an actual flow becomes 84 ml/min, or -14% error, for 80% methane and 20% carbon dioxide; siloxane concentrations will be reported as 14% lower than their real values. This systematic error does not appear with control samples, as they are typically standards in nitrogen and do not match up with the matrix of the sample. Mathematical corrections are not practical as the relative concentrations of the bulk gas typically can vary over any sampling interval. The measured volume from a sample loop is fully independent of the bulk gas composition.

Effects of Temperature and Pressure on Sample Loadings

Accurate sample loadings with fixed volume sample loops are very reliant on both Charles-Gay-Lussac (temperature) and Boyle-Mariotte Gas Laws (pressure).¹² To assure that the effects from changes in operating temperatures do not impact the injected sample volume, the sample loop is maintained at $220\text{ }^{\circ}\text{C} \pm 0.1\text{ }^{\circ}\text{C}$ inside a thermally isolated and controlled zone. This calculates from Charles-Gay-Lussac Law to be a contribution of only $\pm 0.02\%$ to the reproducibility of the measurement. This elevated temperature insures that water and all siloxanes in samples remain volatile through here.

Sample pressure at the time of injection has an inverse relationship to the effective volume, from Boyle-Mariotte Gas Law. The siloxane standards from the permeation oven are at atmospheric pressure. If the incoming sample has native pressures from 48 to 80 psiG,⁹ then the effective sample volume under these pressures will increase by ~400% to ~650% from its correlation with standards, and final concentrations for siloxanes will be significantly in error. Control of the impact from changing sample inlet pressures is accomplished by first loading the sample loop by opening up flow from the sample source and activating a sample vacuum pump to flush the loop with a new sample. Then vacuum is turned off so the sample loop attains the same pressure as the incoming sample, be it atmospheric from bags or permeation oven, or above atmospheric from sample gas source or canisters. Any excess pressure above ambient is then released to atmosphere just before injection to the absorbent trap to achieve consistent loop pressures, no matter the sample source. Although the atmospheric pressure varies over the day, especially with an approaching or clearing storm front, this effect is typically less than 0.5% on the volume.¹² Sample streams and canisters below atmospheric pressure will induce a new vacuum in the loop and cause room air to enter when the loop is opened to ambient air to equalize pressure. Pressures in these vessels must be brought above ambient to load correctly.

Difficulties with Internal Standards

Internal standards are an effective mechanism to correct for changes in the measurement of target analytes, especially for potential losses from extractions or through purging processes, such as EPA Method 8260B.^{13,14} By adding known amounts of unique compounds, their responses can be used to compensate for these changes. Internal standards have been employed to mathematically correct for changes in sample handling, chromatography and detection. Internal standards must:

- Be chemically and physically similar to associated analytes
- Be pure and not present naturally in unknown sample
- Perform similar chromatography to related analytes
- Be chromatographically separated from target compounds
- Not interfere in or not be interfered with mass ions generated by any analyte or matrix component, especially the quant ion(s)
- Interact with the entire sample process, as if they were an analyte

All three internal standards used in Method TO-15 fail to satisfy all of these requirements. Of the three internal standards specified (bromochlorobenzene, chlorobenzene-d5 and 1,4-difluorobenzene), only 1,4-difluorobenzene elutes in the chromatographic region of siloxanes, but comes out before most of the siloxanes commonly found in digester and landfill gases. The eight internal standards listed by S. Mathison, et alii,¹⁵ also have only 1,4-difluorobenzene coming anywhere close to siloxanes, eluting between L3 and D4. Both sets of internal standards mixes do not provide any monitoring for potential system loss of L5 and D6, the least volatile of the target set. These two analytes are very susceptible to underperformance on cool surfaces in the sample pathway where internal standards are not exposed. Thus the internal standards are not accurately monitoring system losses for all siloxanes.

Full recovery of all siloxanes, especially L5 and D6, is assured here with all transfer lines and valving maintained above 90 °C, and interconnecting lines made from very inert, internally-smooth electroformed nickel tubing (Valco Instruments, Houston, TX). Fortunately, performance of the mass spectrometer used in these experiments is very stable and not prone to change enough to require corrections with internal standards. Table 4 illustrates reproducibilities for retention times and raw area counts for siloxane standard runs. Internal standards are not deployed in any of these measurements.

Performance Summary for Siloxane Analyzer

Performance of this system is reported separately in a companion paper⁴ and is summarized in Table 4. These levels are well within requirements mandated for warranty coverage by many power generation suppliers. A 400 ml sample loop is purposefully selected to allow some flexibility in achieving low detection of siloxanes, and installation of an on-column splitter, set at 49:1, permits some adjustment of the injection volume onto the analytical column. If reported concentrations need to be elevated, the splitter ratio can be increased from the employed value of 49:1 to 999:1 to decrease peak sizes by approximately twenty fold. Or a lower split value will enhance detection at lower concentrations by allowing more analytes to be injected on column.

Table 4. Measured Performance for Various Siloxanes.⁴

Target Compound Abbr.	Linear Range (ppmV)	Detection Limit (ppbV)	Detection Limit (g Si/MSCF)	Area Precision for ~1 ppmV Standard	Retention Time Precision (min.)
TMDS	0.002 → 3.87	1.5	0.12	± 5%	±0.007
L2	0.001 → 2.92	1.7	0.14	± 13%	±0.005
D3	0.001(est.)* → 3.16	- *	- *	± 3%	±0.005
L3	0.0006 → 0.99	0.6	0.07	± 8%	±0.002
D4	0.001(est.)* →0.83	- *	- *	± 8%	±0.002
DMTVDS	0.001 → 0.83	0.03	0.002	± 6%	±0.003
L4	0.0001 → 0.78	0.03	0.005	± 8%	±0.002
D5	0.0001 → 0.67	0.08	0.016	± 9%	±0.001
L5	0.0001 → 0.61	0.04	0.008	± 6%	±0.002
D6	0.0005 → 2.57	0.5	0.12	± 6%	±0.002

*Tubes for these analytes depleted prior to these measurements being completed.

Chromatography of Siloxanes in Gas Sample in Tedlar[®] Bag from a Sanitation District Landfill

Numerous volatile chemicals found in landfills can readily be volatilized into the extracted vapor phase pumped out of a landfill mass. Sorting out siloxanes in the mix is simplified with the mass spectrometric detection as silicon compounds have distinctive masses to differentiate them from the multiple of possible compounds. Figure 4 illustrates a typical chromatogram of volatile siloxanes in a landfill gas sample. Although a reconstructed ion chromatogram limited to the target ions for siloxanes, extra peaks are generated, but they are readily eliminated as spectral matches by NIST library searches. Siloxane concentrations represented in Figure 5 are listed in Table 5.

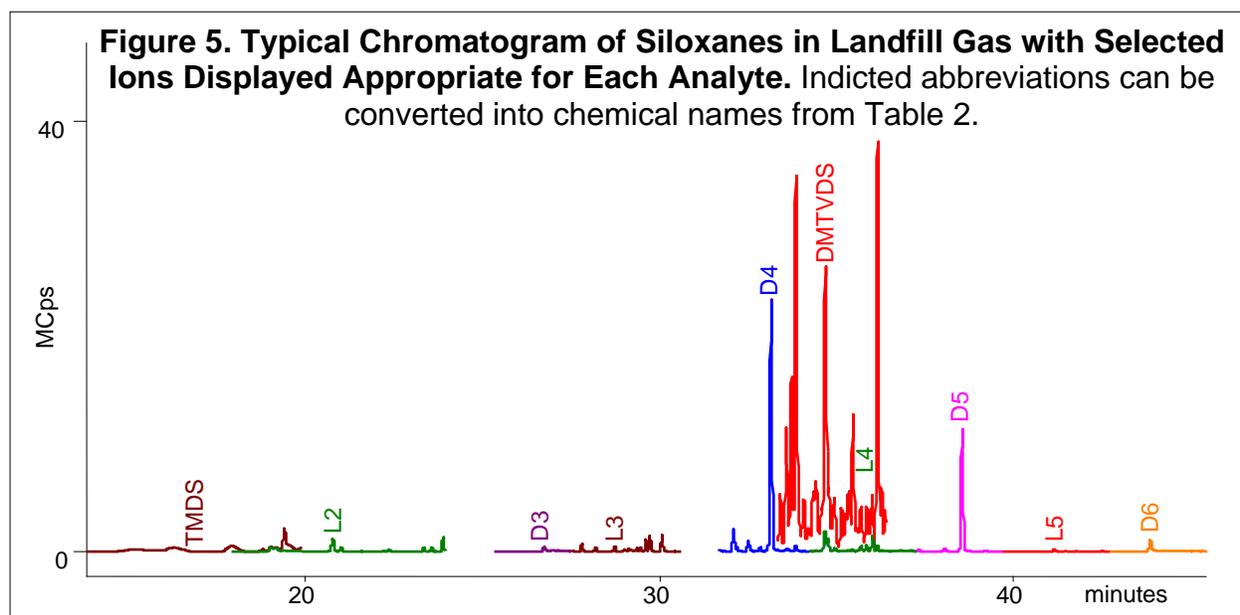


Table 5. Typical siloxane concentrations detected in landfill gas sample.

Target Compound Abbr.	Concentration (ppmV)	Concentration (g Si/MSCF)
TMDS	Not Detected	--
L2	0.060	4.87
D3	0.021	2.56
L3	0.008	0.97
D4	4.636	752.14
DMTVDS	0.609	49.43
L4	0.002	0.32
D5	0.189	38.32
L5	0.001	0.20
D6	0.006	1.46
Total		850.27 g Si/MSCF

Chromatography of Siloxanes in Fuel Sample at High Pressure Digester Gas Line, Prior to Cleaning Filter System

Most of the target siloxanes were detected in the raw digester gas sample. As might be anticipated from the prominence of the polycyclosiloxanes in commercial products that end up in urban sludge, these dominated in the reported concentrations. Typical results are shown in Figure 6 and Table 6. Decamethylcyclopentasiloxane (D5) and octamethylcyclotetradisiloxane (D4) dominate, as might be expected due to their common commercial use in personal products. The rest of the siloxanes contribute about 2% to the total.

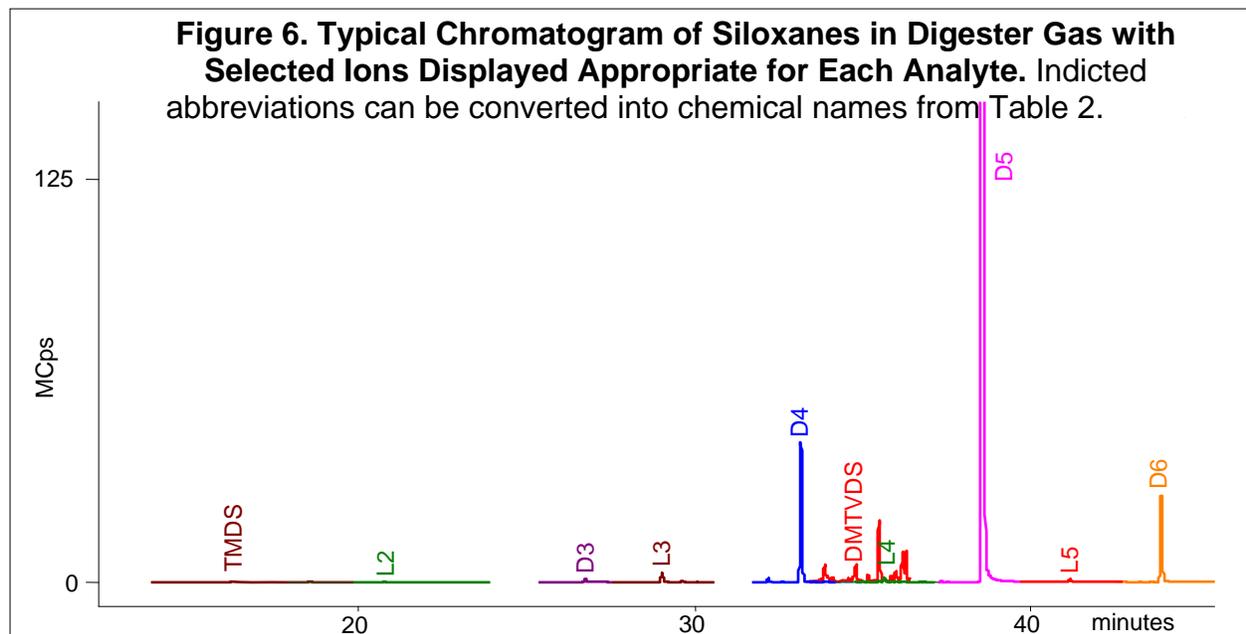


Table 6. Typical siloxane concentrations found in an unfiltered digester gas sample.

Target Compound Abbr.	Concentration (ppmV)	Concentration (g Si/MSCF)
TMDS	Not Detected	--
L2	0.004	0.32
D3	0.042	5.11
L3	0.122	14.84
D4	8.413	878.20
DMTVDS	0.107	8.68
L4	0.007	1.14
D5	11.446	2,320.89
L5	0.005	1.01
D6	0.111	27.02
Total		3,257 g Si/MSCF

Concentration Trends for Siloxanes in Digester Gas, Sampled after Cleaning System

Concentrations of siloxanes are very dependent on the composition of the sample at the time of sampling. The mixture can change over time as the location of the sampling is a dynamic process that is reliant on the sample at hand. It can change over time as siloxanes can be dumped into the sewer at random times, likely to be higher when people brush their teeth in the morning and evening, and take showers in the morning with additional use of hair shampoos and deodorant - major sources of siloxanes in sludge. Typical concentrations found in digester gas after the carbon filter are listed in Table 7, including values in units of g Si/MSCF. Results show that the filter reduces siloxane concentrations by a factor of about 135. Figures 7 and 8 summarize silicon concentrations detected in a digester gas stream monitored hourly over 16 days.

Table 7. Typical siloxane concentrations after carbon filter.

Target Compound Abbr.	Concentration (ppmV)	Concentration (g Si/MSCF)
TMDS	Not Detected	--
L2	0.004	0.35
D3	0.001	0.10
L3	Not Detected	--
D4	0.144	23.36
DMTVDS	0.02	0.02
L4	Not Detected	--
D5	0.0003	0.08
L5	0.0001	0.02
D6	0.0003	0.08
Total		24.01 g Si/MSCF

Figure 7. Concentration Trend for Total Siloxanes in Fuel Gas.

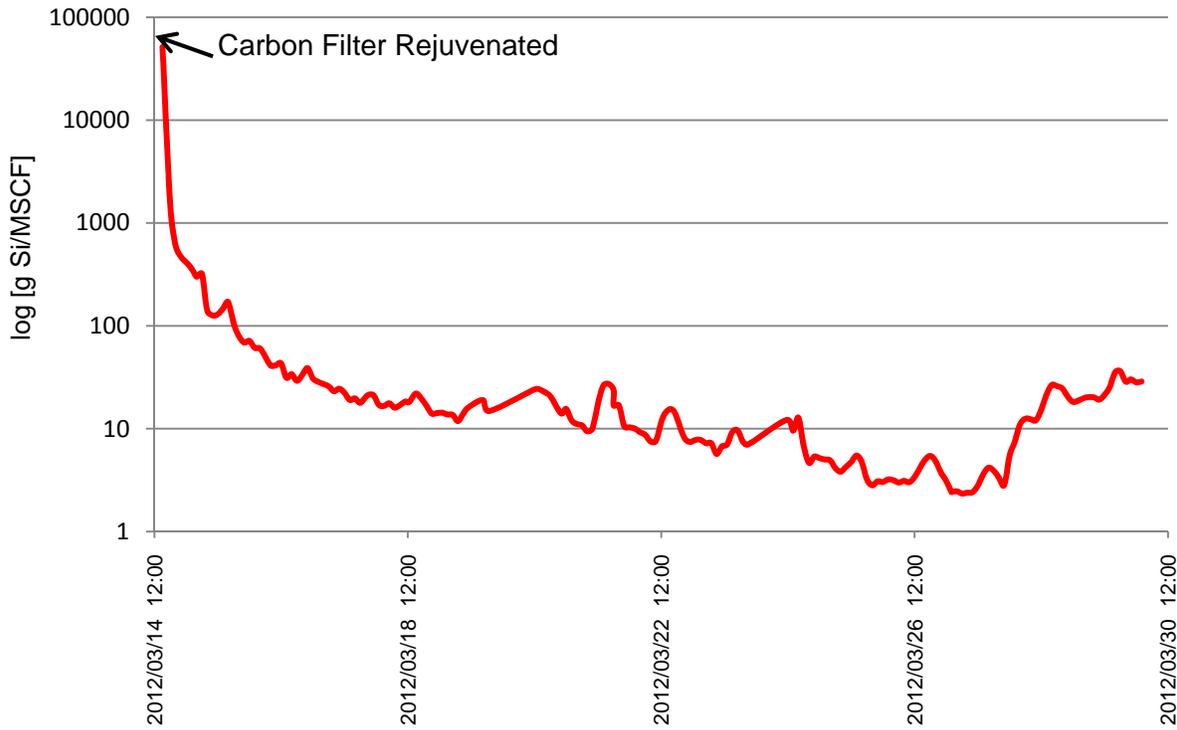
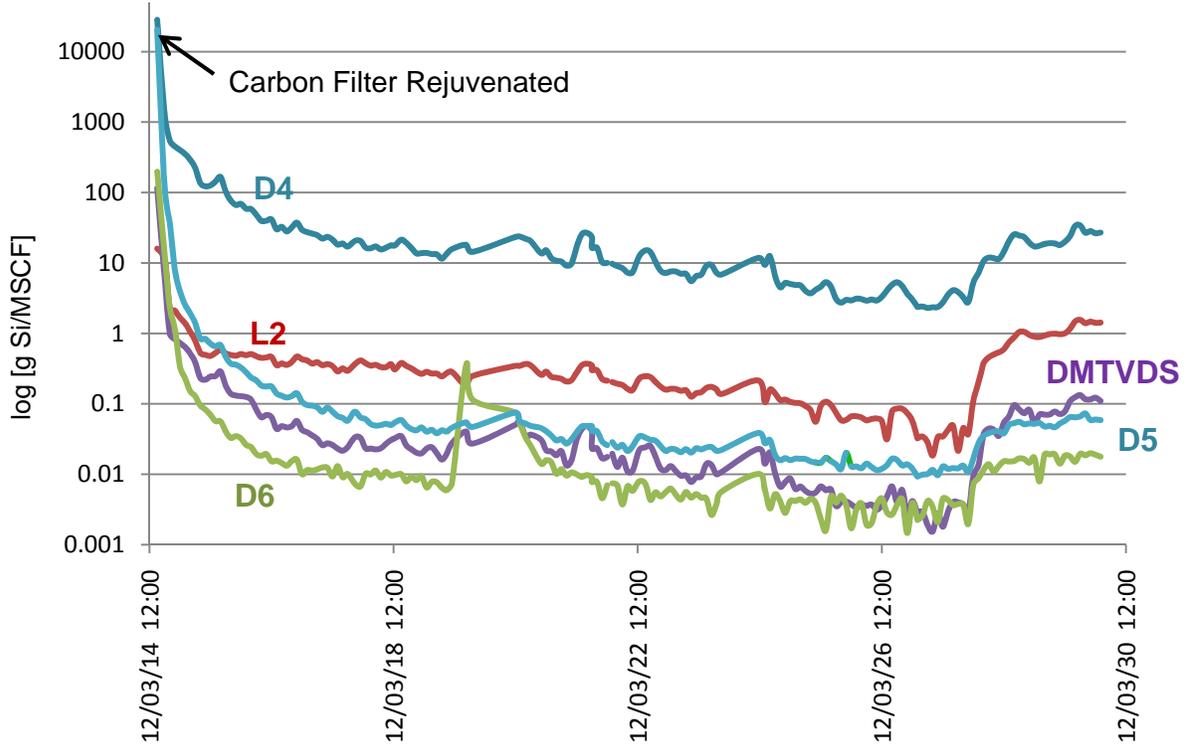
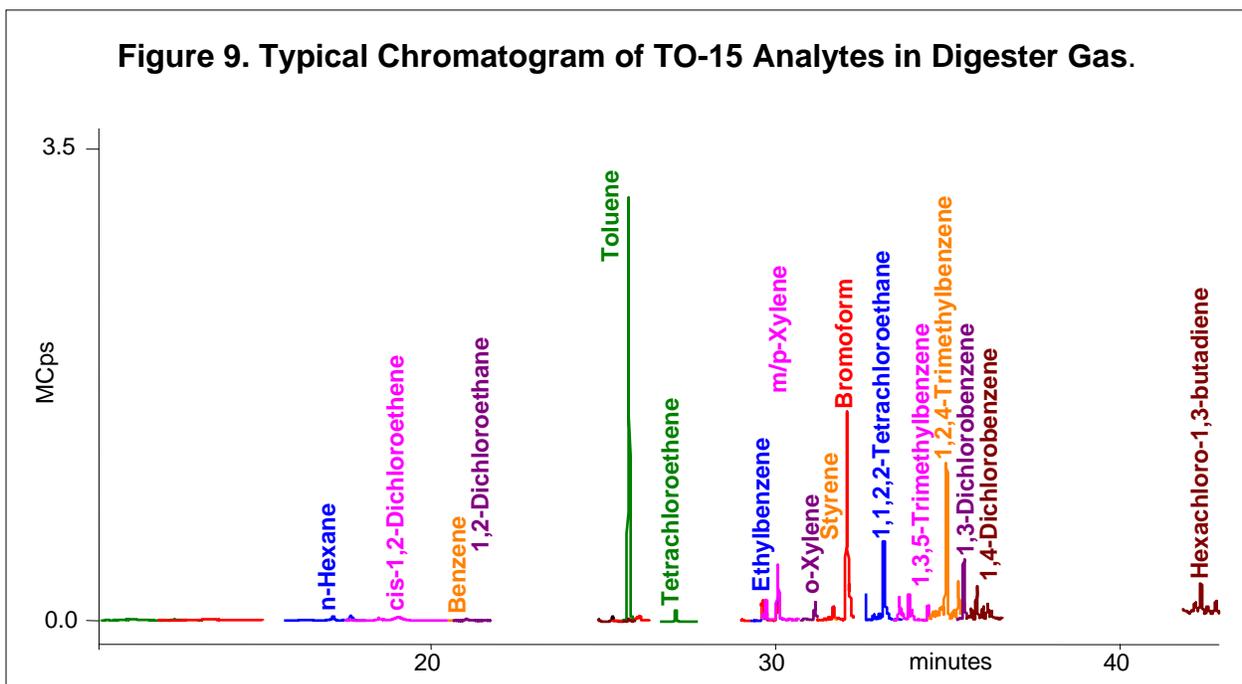


Figure 8. Concentration Trends for Selected Siloxanes



Chromatography for TO-15 Analytes in Digester Gas

Instrument design permits the full range of TO-15 analytes to be measured concurrently with siloxanes without hardware changes. As expected, most detected analytes are in the higher elution times, especially the benzene/toluene/ethyl benzene/xylenes (BTEX) collection. Most of the very volatile ones, such as Freons, are likely to have evaporated out from the surface of the sewage flow well prior to digestion and gas collection. Peak shapes for these early eluters in the chromatogram are distorted since they are not refocused with a cryogenically-cooled trap, and the column is not cooled below ambient that would aid in sharpening peaks by on-column trapping. A typical chromatogram showing selected ions used for analyte identification is displayed in Figure 9.



Selected TO-15 Analyte Concentration Trends for Digester Gas, Sampled after Cleaning System

As expected, the concentrations for most of the TO15 analytes follows trends observed with siloxanes, especially with a drop just after the carbon filter had been replaced. Figures 10 and 11 show typical levels for selected analytes detected over a 4 day span. The wide range of concentrations found in digester gas require a high performance mass spectrometer with a wide dynamic range to allow values to be reported with confidence and without intervention of the operator. Toluene is the dominate component measured, initially found above 2 ppmV, then leveling off at about 10 ppbV after the carbon filter had been rejuvenated. Many other analytes in the low and sub ppbV levels are easily monitored without hardware changes.

Figure 9. Selected Aromatic Analytes Detected in Digester Gas after Carbon Filter Over 4 Days.

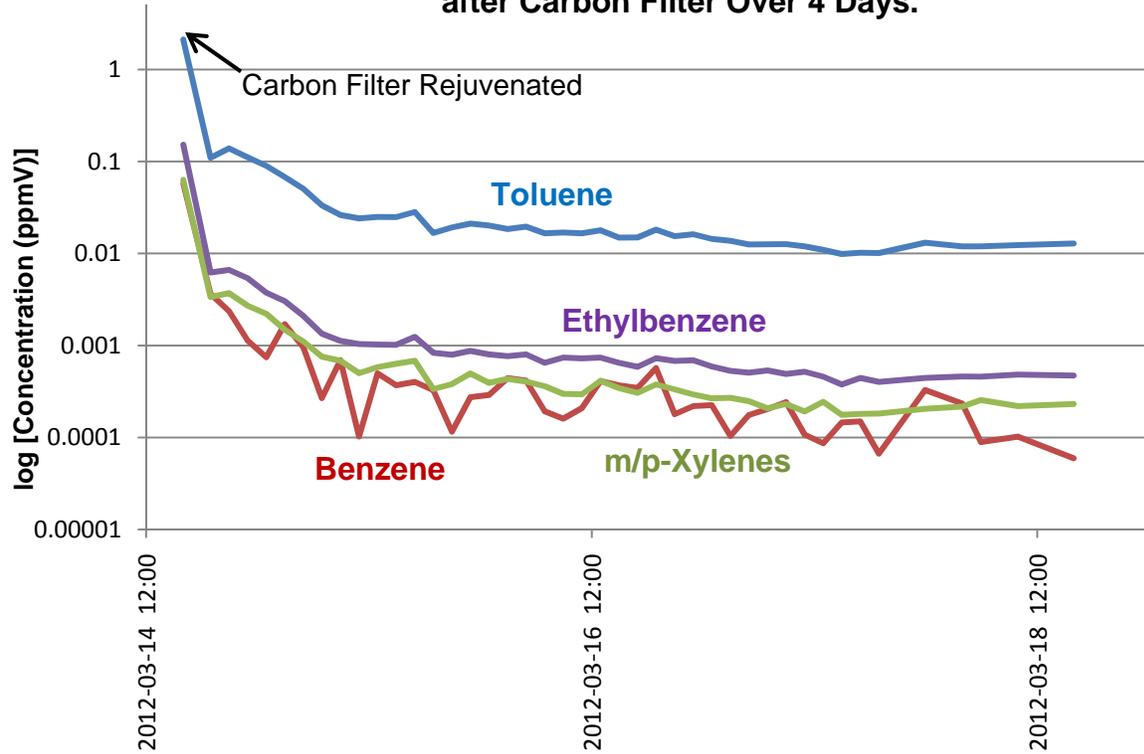
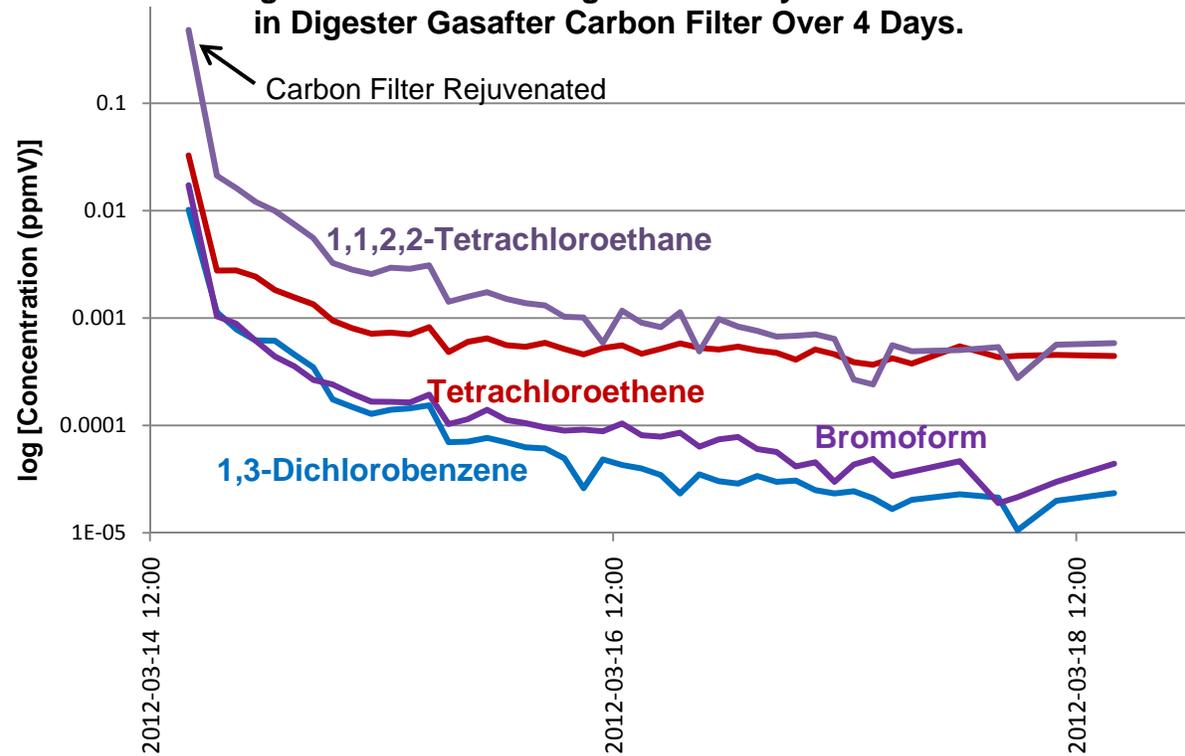
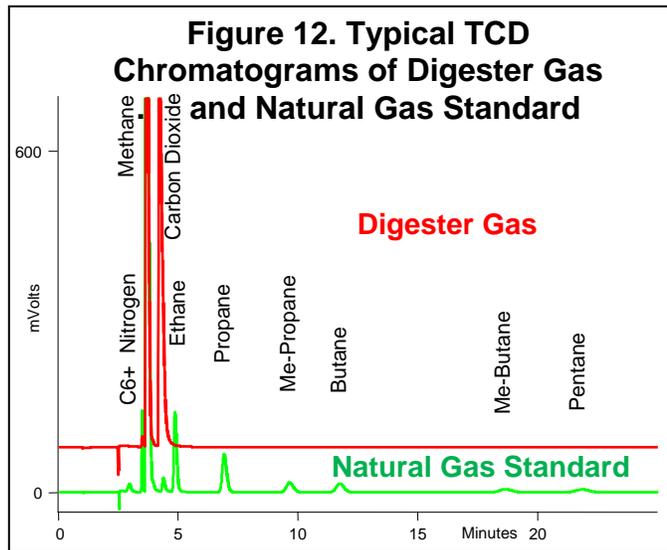


Figure 9. Selected Halogenated Analytes Detected in Digester Gas after Carbon Filter Over 4 Days.



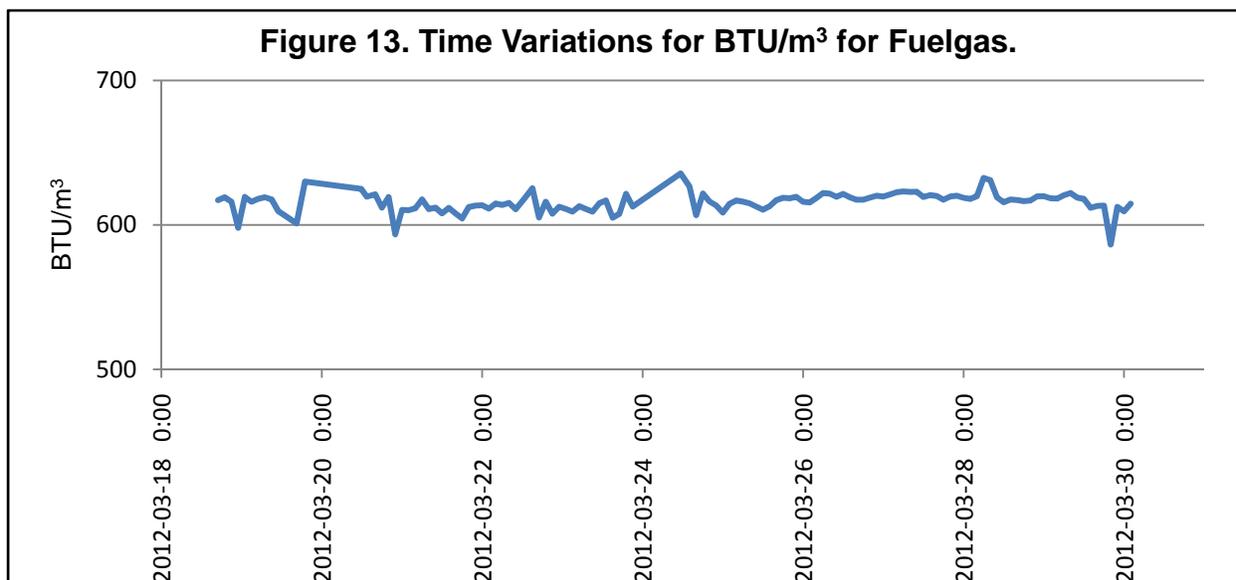
Chromatography for Natural Gas Measurements

Natural gas components are readily separated isothermally and monitored by thermal conductivity detection, as shown in Figure 12, with the hexane+ component eluting as a single peak before nitrogen. A typical digester gas sample exhibited no hydrocarbons, other than methane, due to filtering through a digester gas cleaning system. Any detection of non-methane hydrocarbons is likely to be an early indication of breakthrough for the carbon filter bed. These component levels down to 500 ppmV are easily monitored with this arrangement.



Trends in Gross Heating Values for Digester Gas, Sampled after Cleaning System

Hydrocarbon concentrations in digester gas stream are measured every hour and converted to BTU/ft^3 by first computing mole% values for all detected gases and then multiplying each hydrocarbon by its corresponding heating value.⁵ The total BTU/ft^3 then becomes the simple sum of these values. Variations in this heating value can then be reported and plotted for better visualization of changes over time. Figure 13 is an illustration of data collected over 12 days from a feed line to an on-line generating system. The average value over the interval is $616 \text{ BTU}/\text{ft}^3$ with a range from 586 to 636. This real-time information aids in ensuring that fuel fed to a generator remains known and predictable for the burners' optimum performance.



SUMMARY

Direct on-line measurements of siloxanes in digester and landfill gases offer near real-time assessment of concentrations in a dynamic process. This approach can sense a carbon filter breakthrough sooner than all off-line collection protocols involving solely snapshots, sometimes with only monthly sampling and testing. Breach of siloxanes in fuel carbon filter can rapidly degrade performance of emission control catalysts and other hardware, sometimes within several days.¹⁶ Direct connection to the analytical equipment reduces sample collection errors when ambient air could be mistakenly collected into a sample container, thereby affecting the accuracy of the final results. US Department of Energy “recommends that all digester and landfill operators collecting fuel gas either install a carbon filter to combat any potential siloxanes in fuels or at least regularly inspect the gas for these chemicals.”¹⁰ The system described here provides that assessment hourly to permit rapid response to a filter breakthrough.

Simultaneously with the measure of siloxanes, toxic compounds in the TO15 list are also determined. Gross heating values (BTU/ft³) are computed and reported concurrently.

ACKNOWLEDGMENTS

The authors express gratitude to Kim Christensen, Don von Voost and Thomas Nguyen of Orange County Sanitation District, Fountain Valley, Ca, for their generous assistance in producing raw data from an operating biogas generator system included in this report; to Colin D’Silva of Bruker CAM for the gracious loan of the Bruker 451 Gas Chromatograph and Bruker SCION SQ Mass Spectrometer engaged in these measurements; and to Santos Puente of VICI Metronics for providing siloxane permeation tubes employed for calibrations. Jace Jones of Jones Environment is respectfully acknowledged for loan of a VICI Metronics Dynacalibrator 500 for these siloxane tests. Will McCully of County Sanitation Districts of Los Angeles County kindly provided sample of landfill gas.

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KEYWORDS

siloxanes, linear methylated polysiloxanes, cyclic methylated polysiloxanes, TO-15, natural gas, calibration standards, permeation tube, landfill gas, digester gas, biofuel, cogeneration, linear range, dynamic range, mass spectrum of 1,3-dimethyltetra vinyl disiloxane, carryover, background, column bleed, gas chromatography, mass spectrometry, rotameter, mass flow controller,

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