Measurement of Toxic Organic Compounds in Biogas and Biomethane by GCMS

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INTRODUCTION

California recently enacted legislation to mandate monitoring of toxic and carcinogenic compounds in biogas from landfills, publicly owned treatment works (POTW or sewage treatment plants) and dairies prior to allowing this gas to enter the public pipeline for natural gas within California. The California Public Utilities Commission, in conjunction with the California Air Resources Board and Office of Environmental Health Hazard Assessment, has adopted criteria for acceptance of biogas for public use (Table I).[1,2] Implementation of these new requirements is set to start at the end of 2013. These include measurement of a list of Constituents of Concern and proposed reference methods. The action levels are based on risk assessments for human health and require adjustments to the suggested protocols to make accurate appraisals of these analytes. Six of the constituents can be assessed by gas chromatography with mass spectrometric detection.

Lotus Consulting has configured a Bruker SCION/456 GCMS to measure these six compounds, and has adapted the reference measurement procedures to handle the specified action levels. A flame ionization detector (FID) was used to provide a rapid screen of concentrations for organics. Based on this result, an appropriate GCMS method is automatically selected to perform the measurement. Final results are compared to the mandated trigger and action levels, and a flag is generated for compounds exceeding these levels.

Table I. California Public Utilities Commission Target Levels for Toxics in Biomethane.

Constituent of Concern	Trigger Level (µmol/mol)	Lower Action Level (µmol/mol)	Upper Action Level (µmol/mol)	Reference Method
Vinyl Chloride	0.33	3.3	8.3	EPA TO-15
Methacrolein	0.37	3.7	18	EPA TO-11 (HPLC)
Toluene	240	2,400	12,000 [sic]	EPA TO-15
Ethylbenzene	6.0	60	150	EPA TO-15
total Dichlorobenzenes (as 1,4-Dichlorobenzene)	0.95	9.5	24	EPA TO-15
n-Nitroso-di-n-propylamine	0.0061	0.061	0.15	EPA 8270 (solvent extraction)

The referenced EPA TO-15 test method is specifically designed for ambient air measurements.[3] It is not set up to handle the significantly higher concentration ranges specified by the new regulations, and a different bulk gas of methane, instead of ambient air. This analyzer modifies these approaches by using fixed volume loops to inject samples directly into the column sets, without requiring tedious serial dilutions to get sample concentrations within range of the reference methods.

EXPERIMENTAL

Analytical measurements were performed with a Bruker 456 Gas Chromatograph (GC) equipped with a flame ionization detector and a Bruker SCION SQ Prime Mass Spectrometer (MS) (Bruker CAM, Fremont, CA). Results were computed and reported using Bruker MS Workstation Version 8. This GC/MS system was modified by Lotus Consulting (Long Beach, CA) into Air SCION to perform conventional canister sampling, and automated, online measurements of ambient air, landfill gas and digester gas streams, with provisions for sampling from Tedlar bags. A multi-position stream selector valve was 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 attachment, all lines were heated to a minimum of 90 ºC. All valving was accomplished with Valco series C_WE valves with microelectric actuators (Valco Instruments, Houston, TX). A sample pathway was set for analyte concentrations above the range of a direct injection. Here a fixed volume sample was directed through a gas sample valve.

Prescreen with Flame Ionization Detector

The dynamic range mandated for these measurements require a prescreen assessment of the expected concentration range of the sample. Then a suitable method can be selected to accurately report results. The operator can prepare a judgment based on results from a quick run with an flame ionization detector. Once the sample is run with this prescreen, the MS Workstation is then automatically activate the appropriate method to select the accepatble sample loading to be within range of the mass spectrometer. The criteria is preselected by the operator based on virtually any result in the prescreen report, using Boolean logic expressions for the decision.

Chromatographic Conditions for FID Prescreen Measurements

Column: BR-1, 30 m., 0.032 mm ID, 1 µm df (Bruker, Fremont, Ca)
Injection Volume: 10 ml
Injection: Automated Gas Sampling Valve
Injection Split: 1:49
Column Temperature Program:
    Initial Temperature: 40 ^{o}C, hold 0.00 minutes
    Temperature Ramp: 20 ^{o}C/min
    Final Temperature: 240 ^{o}C, hold 2.00 minutes
Detector Range: 10^{-12} amps/mv, autoranging from 100 µV to 1,000 V

Chromatographic Conditions for TO-15 Related Measurements

Concentrator Parameters
Adsorbent Trap: multi-layer hydrophobic mixed bed
    Initial Temperature: +55 ^{o}C, hold 9.10 minutes
    Temperature Ramp: +200 ^{o}C/min

Temperature: +202 °C, hold 51.30 minutes
Cryofocus Trap: 90 µl empty trapping
Initial Temperature: +79 °C, hold 2.60 minutes
Temperature Ramp: -200 °C/min
Temperature: -146 °C, hold 8.10 minutes
Temperature Ramp: +200 °C/min
Temperature: +202 °C, hold 48.40 minutes
Fixed Volume Loops: 300 µL and 400 ml
Water (150 µL) was added to all evacuated canisters to generate a final relative humidity level inside of about 50%, to preserve target analytes, especially polar ones.

Column Conditions
Column: BR-624ms, 60 m., 0.25mm ID, 1.4 µm df (Bruker, Fremont, Ca)
Column Flow: 2.0 ml/min with EFC Type 23
Column Temperature Program:
Initial Temperature: +50 °C, hold 6.00 minutes
Temperature Ramp: -100 °C/min
Temperature: +20 °C, hold 9.70 minutes
Temperature Ramp: 3 °C/min
Temperature: +100 °C, hold 0.00 minutes
Temperature Ramp: +9 °C/min
Final Temperature: 250 °C, hold 0.67 minutes

Mass Spectrometer
Source: EI
Filament Emission Current: 80 µA
Electron Energy: -70 eV
Source Temperature: 200 °C
Transfer Line Temperature: 170 °C
Manifold Temperature: 40 C
Full Scan (for peak locating) and Selected Ion Monitoring (for monitoring)
Extended Dynamic Range (EDR™) activated

Table II lists the operating parameters for the mass spectral identification of target analytes.

Table II. Operating Parameters for Target Analytes

Analyte	Retention Time (minutes)	Selected Ions	Quant Ion(s)
Chloroethene	16.198	62,64	62
Methacrolein	25.400	70, 41, 39	70
Toluene	38.885	91, 92	91
Ethyl Benzene	45.103	106, 91, 65	106
Dichlorobenzenes (as 1,4 Dichlorobenzene)	51.013	146, 148, 111, 75	146
n-Nitroso-di-n-propylamine	62.080	70, 80, 130	70 + 80

Calibration Standards

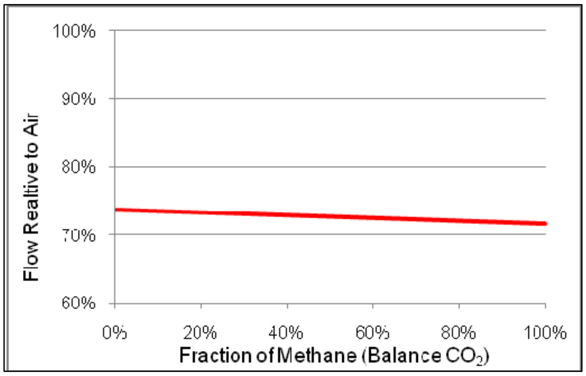
Standards for biogas and biomethane measurements were generated from Dynacal® permeation tubes supplied by VICI Metronics, with their Dynacalibrator® Model 505 (VICI Metronics, Poulsbo, Wa). Calibration data are presented elsewhere.[4]

RESULTS AND DISCUSSION

Concentration Units

The California Public Utilities Commission lists the target and action levels in units of µg/m^3. To permit more direct comparison to concentration units in EPA Method TO-15, these values are converted to molar concentrations[5] by analytes' molecular weights and the molar gas volume at 25 °C of 24.465 moles/L, as listed in Table I. The unit of "µmol/mol" conforms to the IUPAC protocol,[6] as it emphasizes chemical relationships, eliminates artificial variability associated with mass changes due to chemical reactions, and clarifies the labeling difficulties between the short (American) and long number (European) scales.

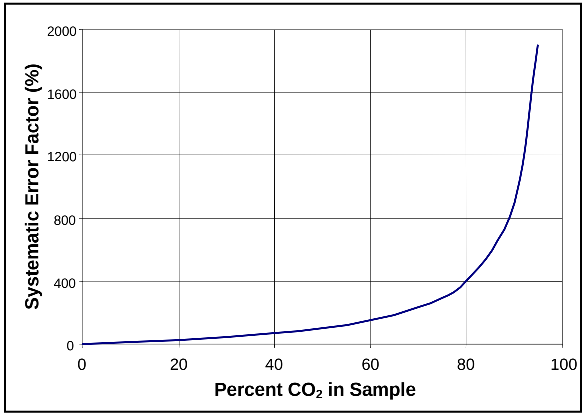
Figure 1. Relative MFC Flows with Varying CH4/CO2, Relative to Air.



Change in Bulk Gas and Effects on Measurements

Method TO-15 is solely intended to measure ambient air samples, as denoted in its title. For digester gas samples, possible methane/carbon dioxide concentration ratios can range from 61/38 to 63/35 volume%, with oxygen and nitrogen levels well below one volume%.[7] Landfill gases can have methane/carbon dioxide ratios from 35/50 to 60/30 volume%.[8] And biomethane is typically around 97% methane, with a balance of carbon dioxide and other hydrocarbons. Figure 1 illustrates the computed errors in flow rate for mass flow controllers with various concentrations 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.

Figure 2. Systematic Volume Errors with Mass Flow Controllers Located after Trapping of Carbon Dioxide.



In addition, if the trapping system is cold enough to ensnare carbon dioxide (below -78 °C), then the sample volume set with the mass flow controller will be enhanced by the loss of this major constituent. The amplitude of this error is shown in Figure 2. This issue is not apparent when comparing results against standards in nitrogen or air, as it is a systematic error and is not corrected with standards prepared in a different matrix. The proper procedure to measure these sample types is to use fixed volume samples loops. This process generates an accurate sample volume independent of the matrix composition. Sample loop volumes can range from 10 microliters to 400 ml or more, with multiple loops of varying volumes installed within a system to handle a large dynamic range of concentrations. For the results presented here, loops of 300 µL and 400 ml were used.

Chromatography Considerations for Target Analytes

Methacrolein – The specified method for this constituent is EPA Method TO-11A, which uses adsorbent cartridges for sample collection and analysis by liquid chromatography.[9] This process cannot be employed in an on-line measurement scheme. Instead, this analyte has been included in the compound list for measurement by gas chromatography/mass spectrometry.

n-Nitroso-di-n-propylamine – This analyte is to be measured by solvent extraction and then gas chromatography/mass spectrometry with EPA Method 8270.[10] This procedure does not lend to being automated. Even though it has a heavier mass then the others, it does elute off of a capillary column in a gas chromatograph with conditions amenable to the others. Thus, it is included in this measurement. With a very low target concentration, detection of this analyte requires a large sample loading and use of selected ion monitoring in the spectrometer to enable it to be picked out from other compounds eluting in the area.

Separation of all target compounds plus others in TO-15 List – Although only six analytes in biogas/biomethane are measured, chromatographic conditions were selected to allow inclusion of other compounds, such as benzene, xylenes, and di-methyl/trimethyl benzenes. If only these six are targeted, the column temperature program can be altered to ramp faster and generate a short chromatogram.

Results for a Typical Raw, Unfiltered Biogas Sample from a Sewage Treatment Plant

Chloroethene (Vinyl chloride) - This analyte elutes very early in the chromatogram, but is readily picked out from other eluters by selecting to monitor only its unique ions of 62 and 64 in the area (Figure 3). Sample volume is 400 ml.

Methacrolein - Methacrolein is readily detected by this technique, and yields a nice response with 400 ml sample loading (Figure 4).

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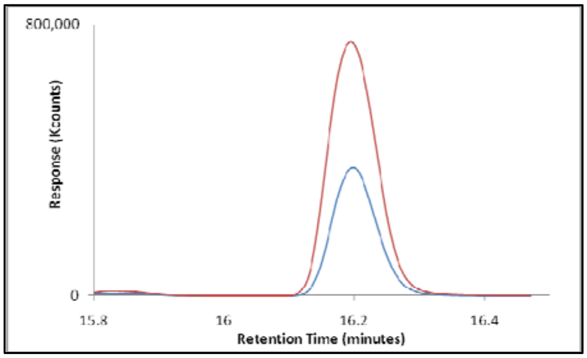
Figure 3. Chromatogram of Chloroethene - 0.19 µmol/mol standard in red, biogas in blue.



Toluene - As expected, the target levels for toluene are huge and can readily overload the column system and distort the chromatography, including a shift in expected retention times (Figure 5). Throttling down the load volume to 0.30 ml allows this component to be properly measured (Figure 6)

Ethyl Benzene - This compound is easily picked out from adjacent peaks due to unique identifying ions of 106, 91 and 65. It's target levels require use of the smaller 0.30 ml sample loop.

Dichlorobenzenes - Fortunately, these three analytes elute very close to each other and can be monitored with the same ions. The results for the three compounds are summed together to yield a total Dichlorobenzenes. Figure 8 shows a typical chromatogram. Sample volume is 0.30 ml

Figure 4. Chromatogram of Methacrolein – 1.1 µmol/mol standard in red, biogas in blue.

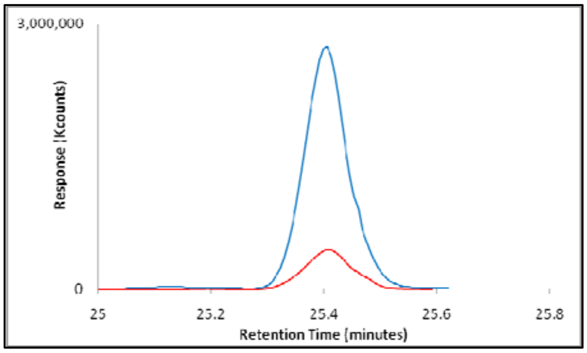
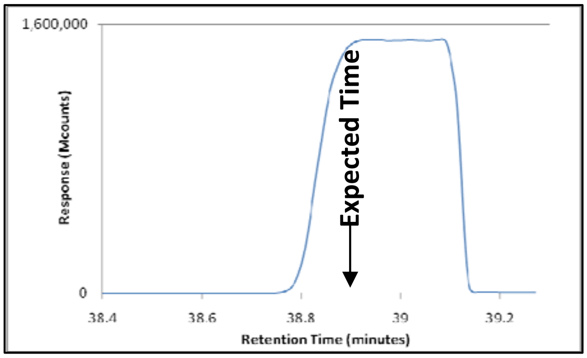


Figure 5. Chromatogram of 9.0 µml/mol Toluene in biogas with 400 ml sample.



n-Nitroso-di-n-propylamine - Although this analyte is usually considered as a semivolatile compound, it can be measured along with volatile organics, eluting late in the chromatogram. The target levels in the low nmol/mol range mandate use of the larger 400 ml sample loop. Figure 9 provides an example of its chromatography.

Figure 6. Chromatogram of Toluene with 0.30 ml loop – 9.0 µmol/mol standard in red, biogas in blue.

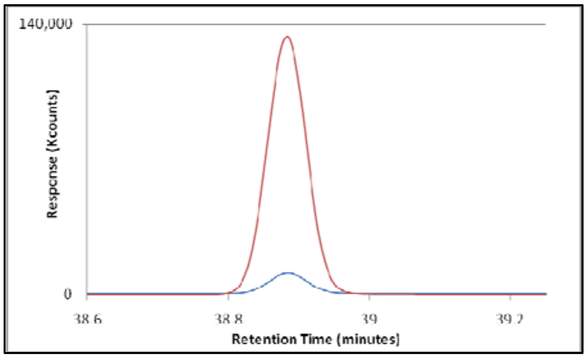


Figure 7. Chromatogram of Ethyl Benzene – 1.8 µmol/mol standard in red, biogas in blue.

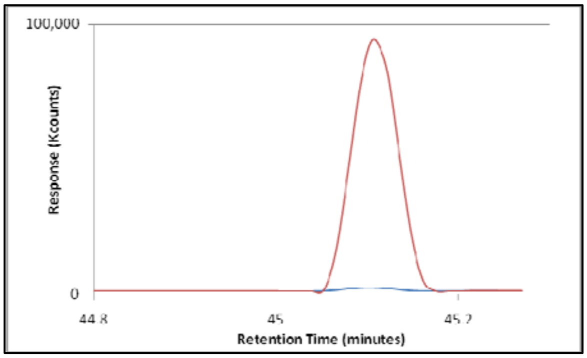


Figure 8. Chromatogram of 1,4-Dichlorobenzene – 0.6 µmol/mol standard in red, biogas in blue.

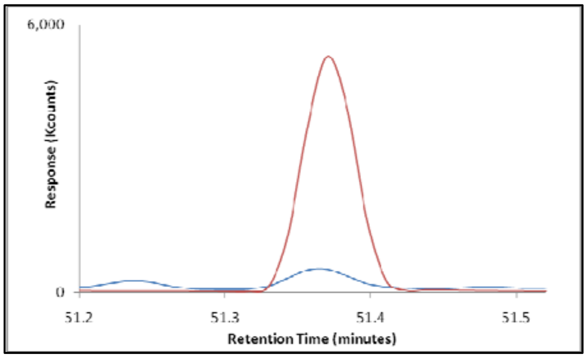
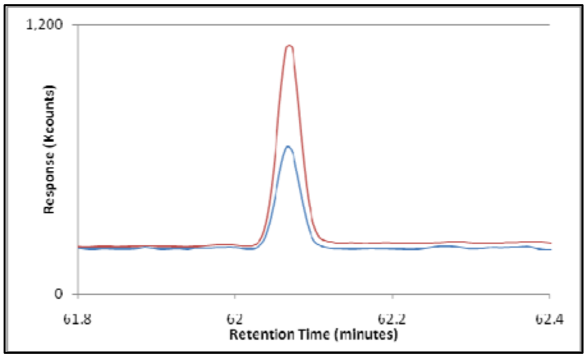


Figure 9. Chromatogram of n-Nitroso-di-n-propylamine – 0.014 µmol/mol standard in red, biogas in blue.



Concentrations Found in a Raw, Unfiltered Biogas Sample - An undiluted sample was introduced into the analytical system and generated results listed in Table III. Appropriate ample loops were selected for the expected concentration ranges of the analytes.

Table III. Results for an Diluted Raw, Unfiltered Biogas Sample

Analyte	Concentrations Found in Untreated Biogas (µmol/mol)	Sample Volume (ml)
Chloroethene	0.089	400
Methacrolein	0.28	400
Toluene	0.72	0.30
Ethyl Benzene	0.024	0.30
Dichlorobenzenes (as 1,4 Dichlorobenzene)	0.013	0.30
n-Nitroso-di-n-propylamine	0.007	400

SUMMARY

Gas chromatography/mass spectrometry is demonstrated to be sensitive enough and capable of handling the wide concentration ranges expected to be monitored for six of the constituents of concern listed by the California Public Utilities Commission, especially when measuring these in an on-line automated process. These compounds can be measured simultaneously with other TO-15 analytes and volatile siloxanes. Fixed volume sample loading for biogas/biomethane samples is mandatory to properly measure the sample volume loaded into the system. A rapid prescreen with an included flame ionization detector assesses the contamination level of the sample and can automatically set the appropriate instrument conditions for accurate measurements. Addition of a thermal conductivity detector to the system can then measure hydrocarbon concentrations needed for calculation of energy in the biogas/biomethane (BTU), and the specific gravity of the gas sample.

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