

Lotus Consulting presents:

Toxic Organics in Biomethane Analyzer (TOBA)

California recently enacted legislation, AB 1900 Gatto (leginfo.legislature.ca.gov/faces/billTextClient.xhtml?sessionId=a19a71582eb992268a71325116db?bill_id=201120120AB1900) to mandate monitoring of toxic and carcinogenic compounds in biomethane from landfills, publicly owned treatment works (POTW or sewage treatment plants) and dairies prior to allowing this gas to enter the natural gas pipeline within California. The California Public Utilities Commission, in conjunction with the California Air Resources Board and Office of Environmental Health Hazard Assessment, is to adopt criteria for acceptance of biomethane for public use (www.arb.ca.gov/energy/biogas/biogas.htm).

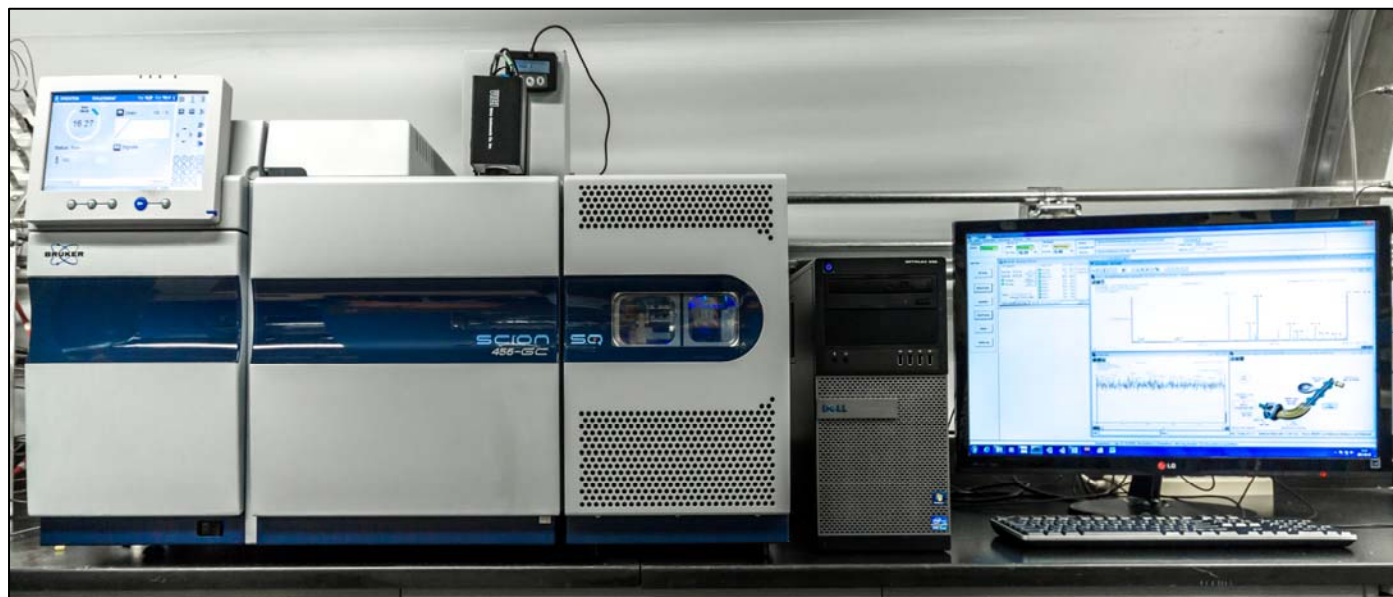
Implementation of these new requirements is set for the end of 2013. These include measurement of a list of Constituents of Concern and proposed test methods. The action levels are based on risk assessment for human health. Eight of the constituents can be assessed by gas chromatography with mass spectrometry and sulfur detectors.

The new regulations require biomethane sources to be tested twice (over 2-4 weeks) upon initial operations and then quarterly or annually depending on measured levels against trigger and action levels. If levels exceed the any Upper Action Level, that source is then shut out of the pipeline.

Although filtered biogas is expected to be well below these levels, filter breakthrough or bypassing the filter can allow levels to exceed these action levels. Regular monitoring of the biomethane product gas provides assurances that toxic or carcinogenic concentrations are not released into the pipeline.

The referenced methods are specifically designed for ambient air measurements and are not set up to handle the significantly higher concentration ranges specified by the new regulations, and the different bulk gas of methane. This analyzer modifies these approaches by using fixed volume loops to directly inject samples into the column sets, without requiring serial dilutions to get the sample concentrations within range of the reference methods

Lotus Consulting has configured a Bruker SCION/456-GC GCMS with a Pulsed Flame Photometric Detector (PFPD) to measure eight of the compounds, and has adapted the reference measurement protocols to handle the specified action levels. A Flame Ionization Detector (FID) is used to provide a rapid screen of concentrations for organics. Based on this result, an appropriate GCMS and PFPD method is automatically selected to perform the measurement. Results are compared to the trigger and action levels, and a flag is generated for compounds exceeding these levels.



Bruker SCION-456 GCMS configured for Toxic Organics in Biomethane Analyzer.

California List of Organic Constituents of Concern in Biomethane.

Constituent of Concern	CAS Number	Trigger Level (ppmV)	Lower Action Level (ppmV)	Upper Action Level (ppmV)	Reference Method
total Dichlorobenzenes (as 1,4-Dichlorobenzene)	106-46-7	0.95	9.5	24	EPA TO-15
Ethylbenzene	100-41-4	6.0	60	150	EPA TO-15
n-Nitroso- di-n-propylamine	621-64-7	0.0061	0.061	.15	EPA 8270
Vinyl Chloride	75-10-4	0.33	3.3	8.3	EPA TO-15
Hydrogen Sulfide	7783-06-4	22	216	1,080	ASTM D6228
Methacrolein	78-85-3	0.37	3.7	18	EPA TO-11
Alkyl Sulfides	-	12	120	610	ASTM D6228
Toluene	108-88-3	240	2,400	12,000 [sic]	EPA TO-15

The system is designed to operate without cryogen so that the instrument can be readily deployed in a mobile laboratory or in an on-site shed to conduct measurement at the biomethane injection point, or in a land-based laboratory with samples brought to the system either in Tedlar bags or canisters.

COMMENTS ON ACTION LEVELS

These levels are solely based on risk assessments, and may not be attainable under expected pipeline pressures and temperatures. For example, the upper action level for toluene is 1.2%V is only realized with a pipeline pressure below 100 psiG and temperatures above 85 °F, based on its vapor pressures. All other conditions will cause toluene to drop out of the vapor phase into a liquid at the upper action level. Similarly, the dichlorobenzene vapors will drop out as liquid at temperatures below 77 °F and above 900 psiG, at concentrations near its upper action level. Sample containers used for collection must be maintained at sufficient temperatures and pressures to avoid loss of analytes from the vapor state during transport to the laboratory for analysis.

PRESCREEN BY FLAME IONIZATION DETECTOR

Target concentrations for analytes measured by TO-15 range from 0.33 ppmV to 12,000 ppmV, and the instrument must be capable of measuring well below the lowest level to get an accurate assessment of the vinyl chloride trigger level. A single mass spectrometer method cannot handle this dynamic range of $>3.6 \times 10^5$. A rapid prescreen of target values are assessed with a short run to a flame ionization detector. If concentrations are high, a low sensitivity method is automatically selected; if no large peaks are detected, then a more sensitive method is activated and the sample is run automatically.

HYDROGEN SULFIDE AND ALKYL SULFIDES

The sulfur detector of choice for a mobile lab is the pulsed flame photometric detector, as it is very rugged and can be started up without much delay. Its linear range can be adapted to the mandated target values with choice of injection volume into the capillary column. The final report includes all of the alkyl sulfides grouped as a single concentration.

n-NITROSO-DI-n-PROPYLAMINE BY TO-15

This amine is labeled as a semi-volatile compound and is normally measured with EPA 8270, but the process to prepare a gas sample is extensive and tedious. Since this compound has a vapor pressure (0.08 mm Hg) similar to other TO-15 analytes, it can be included with this easier method, especially when performing on-line assays.

METHACROLEIN BY TO-15

The reference method for this analyte is EPA TO-11, where the sample is loaded into a DNPH cartridge at the sampling site and returned to the laboratory for analysis by liquid chromatography. This approach cannot be performed on-line and usually requires a several day turnaround for results. With other related aldehydes included in the TO-15 list, methacrolein can be measured along with the other organics by on-line mass spectrometry.

VOLATILE SILOXANES MEASUREMENT

Although siloxanes are not directly listed in the new regulations for biomethane, they are frequently included in the target list by gas utilities to insure that elevated concentrations will not befoul burners, turbines, flame sensors and pollution control devices. These are measured by concentrating an aliquot with an in-line absorbent trap and mass spectrometer.

CALIBRATION STANDARDS AND CONTROLS

Since these action levels can have major impacts on operations of the biomethane processing plant, results must be as accurate as possible, with standards at each of the three levels. Some of the analytes are either not stable in compressed gas cylinders or can drop out on the tank's interior surface, affecting their accuracy.

Standards for the toxic and carcinogenic analytes are freshly produced from pure component liquids with permeation tubes housed in a constant temperature oven made by VICI Metronics. Standards to match each action level are generated by simply altering the dilution flow past the tubes.



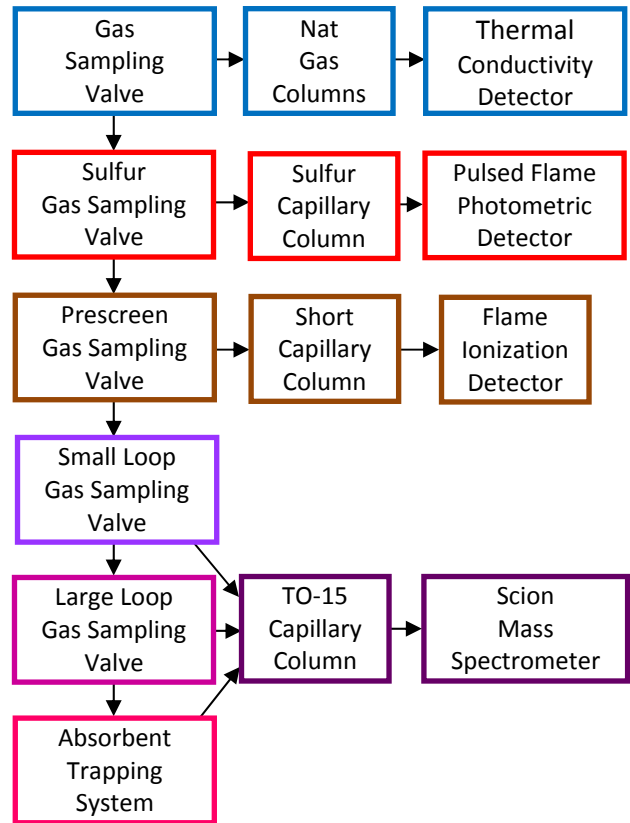
VICI Metronics Dynacalibrator 500.

NATURAL GAS CALCULATIONS

To complete chromatographic measurements for biomethane, separation of the gaseous hydrocarbons and computations for BTU and specific gravity are performed with required columns, an in-board thermal conductivity detector and system workstation. The on-line system can report hourly values for these results.

HARDWARE CONFIGURATION

- Bruker 456-GC Gas Chromatograph
- Bruker SCION Mass Spectrometer
- Required valving with micro-electric actuation
- Heated valve ovens for all valves
- Heated sample/standard lines
- Multi-position automated gas sampler
- Pulsed Flame Photometric Detector
- Flame Ionization Detector
- Thermal Conductivity Detector
- VICI Metronics Dynacalibrator 500
- Bruker MS Workstation
- Split Capillary Injector for syringe injection



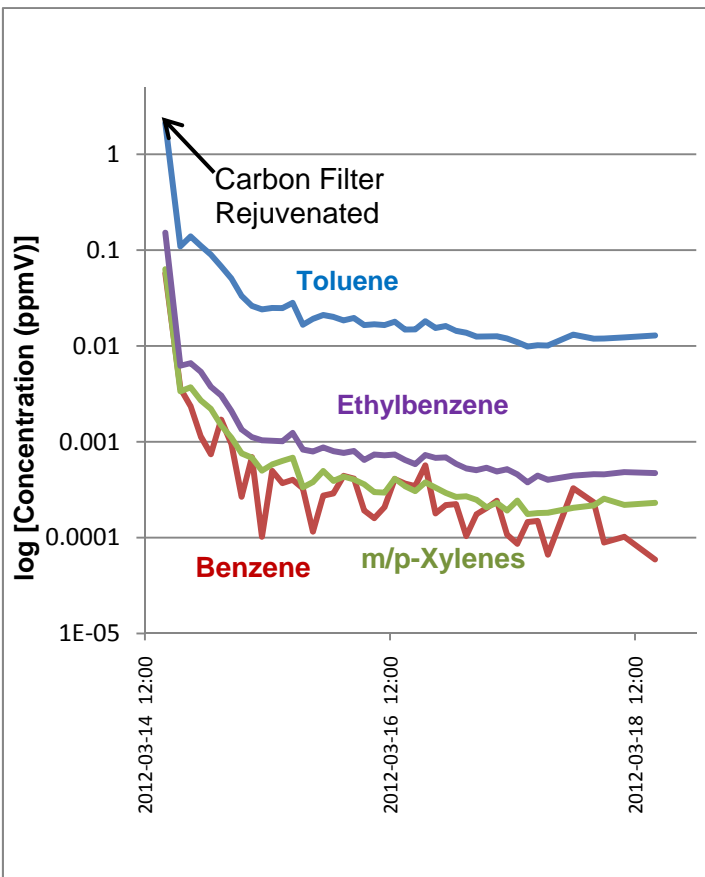
On-line Toxic Organics/Siloxanes in Biomethane Analyzer at an active sewage treatment plant.

ON-LINE TOXIC ORGANICS IN BIOMETHANE ANALYZER (TOBA)

By attaching the analyzer to the sampling point for assaying, hourly measurements of target analytes can monitor performance of the filtering process, especially for possible breakthrough. Included a software package includes alarms and signals to shut down gas flows to the pipeline with results exceeding action levels.

EXPLOSION-PROOF TESTING

Both the Bruker 456-GC and SCION MS have been tested and certified for use in potentially explosive atmospheres by an independent testing laboratory, following provisions of the ATAX Directive 94/9/EC.



Selected Aromatic Analytes in Digester Gas detected hourly over 4 days.



On-Line Toxic Organics/Siloxanes in Biomethane Analyzer at an active landfill.

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