Calibration Standards for Measurement of Toxic Organics in Biogas and Biomethane Using Permeation Tubes

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INTRODUCTION

The California Public Utilities Commission has mandated recently that biomethane for public consumption must be assayed for a list of "constituents of concern" and has set action levels based solely on risk assessments for human health (Table I).[1,2] Most of the action levels for organics are in the medium to high µmol/mol (ppmV) levels, but one - n-Nitroso-di-n-propylamine - has its trigger level in a low nmol/mol (ppbV) value . Accurate and stable gas standards are required for proper quantitation of these compounds.

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)	Indicated 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)

Gas standards in cylinders for these levels of analytes suffer from loss due to the very low volatility of some of the target analytes, from the extremely high required concentration action levels, and from interactions with cylinder interior surfaces and regulator innards. One analyte – n-Nitroso-di-n-propylamine – has a low vapor pressure and cannot remain stable in high pressures of cylinders or canisters. And Toluene at 1.2%V is well above any reasonable effort to keep it volatile in any sample container at reasonable temperatures.

This paper reports on the creation of standards for these target toxic organics from permeation tubes. Advantages for this approach include:

- Permeation rates NIST traceable with weight loss over time.
- Fresh standards on demand.
- Gas standards available for low vapor pressure components.
- Selectable concentration levels by simple adjustment of dilution flows.
- Positive identification of peaks by selection of permeation tubes being analyzed.
- Standard introduction into analyzer matching process for samples.
- Minimal operator interactions.
- Easy addition of new "constituents of concern" into mix.

Results using permeation tubes containing pertinent volatile organics are presented with creation of multi-level calibration curves over a wide dynamic range and computation of detection limits.

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 automated, online measurements of ambient air, landfill gas and digester gas streams, with provisions conventional sampling canisters and Tedlar® bags. A multi-position stream selector valve was included to provide automated, unattended switching between multiple 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). Two sample pathways were set for analyte concentrations above the range of direct injection into the spectrometer. Here, two fixed volume sample loops were directed through gas sample valves to ensure that correct injection volumes are independent of gas composition.

Chromatographic Conditions for TO-15 Related Measurements

Concentrator Parameters

Adsorbent Trap: multi-layer hydrophobic mixed bed
    Initial Temperature: +55 °C, hold 9.10 minutes
    Temperature Ramp: +200 °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 ^{o}C/min
Temperature: +100 ^{o}C, hold 0.00 minutes
Temperature Ramp: +9 ^{o}C/min
Final Temperature: 330 ^{o}C, hold 0.67 minutes

Mass Spectrometer

Source: EI
Filament Emission Current: 80 µA
Electron Energy: -70 eV
Source Temperature: 200 ^{o}C
Transfer Line Temperature: 170 ^{o}C
Manifold Temperature: 40 ^{o}C
Operating Modes - Full Scan (for initial peak locating) and Selected Ion Monitoring (for monitoring)
Extended Dynamic Range activated

Calibration Standards

High level standards for biogas and biomethane measurements were generated from permeation tubes supplied by VICI Metronics, with their Dynacalibrator Model 505 (VICI Metronics, Poulsbo, Wa). Multi-point calibration points with these devices were generated by altering the dilution gas flow passing the tubes. Both Dynacal (with Teflon® membranes) and G-Cal (with silicone membranes) permeation tubes from VICI Metronics were used to generate gas standards at various concentration levels by simply altering dilution flows.

RESULTS AND DISCUSSION

Concentrations of these contaminates can impact approval for injection of biogas into the pipeline and therefore must be accurate. Detection limits must be well below these action levels. The status of biomethane injection into the public gas line is directly impacted by these analytical results. A major obstacle to the measurement is the huge dynamic range of these analytes. This puts added pressure on the instrument design and quality of calibration standards to allow them to be measured properly. Tthe upper action level for toluene is 2,000,000 times the trigger level for n-Nitroso-di-n-propylamine. Then imposing a requirement to achieve detection well below its action levels extends the dynamic range by at least another decade.

To handle this wide range of concentrations, the instrumentation is set up with two sample injection loops, one at 0.30 ml for the high concentrations analytes and a second at 400 ml for Chloroethene, Methacrolein and n-Nitroso-di-n-propylamine. A flame ionization detector is included to perform a quick assessment of concentrations found and then is programmed automatically to select the appropriate loop size.

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, as listed in Table II, by analytes' molecular weights and the molar gas volume of 24.465 moles/L at 25 ^{o}C. [5] 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.

Table II. Translation of Units to Proper Molar Concentrations

Ratio of Analyte to Total	Invalid Reporting Units	Molar Units for Gases
1:100	%	cmol/mol
1:10^6	ppm	µmol/mol
1:10^9	ppb	nmol/mol
1:10^{12}	ppt	pmol/mol
1:10^{15}	ppq	fmol/mol
1:10^{18}	---	amol/mol

Creation of Gas Standard for n-Nitroso-di-n-propylamine

Vapor pressure for this analyte (0.86 mm Hg at 25 ^{o}C[3]) is too low to allow reasonable concentrations in pressurized cylinders. A more reliable approach is with a permeation tube that generates a fresh standard on demand from pure liquid. Results for the calibration sequence for this compound are presented below.

Creation of Gas Standard for Toluene at 12,000 µmol/mol (1.2 cmol/mol – 1.2 %V)

This level is strictly based on human health risks and is not possible to produce as a calibration standard under normal operating conditions for the chromatographic system. Even creation of a standard from pure liquid inside a diffusion vial at 50 ^{o}C and exposing the vapors directly to a flowing inert gas stream only yields a maximum concentration of 283 µmol/mol. All results reported below are based on a Toluene permeation tube with a maximum concentration of 9 µmol/mol, as a higher level overloads the analytical system. Concentrations in raw, unfiltered biogas are expected to be well below the value of this available standard,[4] and even lower with processed biomethane.

Creation of Gas Standard for Chloroethene

The permeation device for this standard is a G-Cal steel chamber with a silicone membrane to provide an emission rate compatible with the levels needed for the measurement. An added benefit of this device is that it is light-tight to prevent polymerization of chloroethene with exposure to light.

Linearity

Linearity measurements are performed by setting up the Dynacalibrator with sequentially different flows to generate multiple levels, as shown in Table III. Typical results for two of the target analytes are presented in Figure 1 for Toluene, with its high action limits, and Figure 2 for n-Nitroso-di-n-propylamine, with the lowest. Linearity studies were performed for all six target analytes, and results are summarized in Table IV.

Table III. Calibration Levels for Linearity Measurements of Toluene and n-Nitroso-di-n-propylamine

Rotameter Setting	Total Purge Flow (ml/minute)	Concentrations for Toluene (µmol/mol)	Concentrations for n-Nitroso-di-n-propylamine (µmol/mol)
0	339	9.02	0.028
1	986	3.10	0.0048
2	1,778	1.72	0.0026
4	3,380	0.90	0.0014
8	6,650	0.46	0.00071
15	12,069	0.25	0.00039

Figure 1. Calibration Curve for Toluene, 0.30 ml Loop

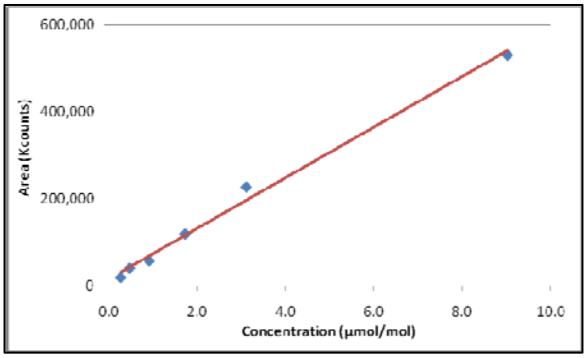

Figure 2. Calibration Curve for n-Nitroso-di-n-propylamine, 400 ml Loop

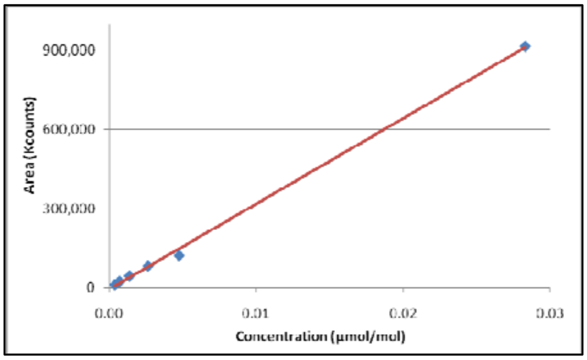

Table IV. Summary of Calibration Results

Analyte	Sample Volume (ml)	Calibration Range (µmol/mol)	Average Response Factor (Kcounts/µmol/mol)
Chloroethene	400	0.0055 – 0.396	82,575,777
Methacrolein	400	0.032 – 1.14	55,875,506
Toluene	0.30	0.25 – 9.0	72,546
Ethyl Benzene	0.30	0.050 – 1.77	63,883
1,4-Dichlorobenzene	0.30	0.016 – 0.56	149,700
n-Nitroso-di-n-propylamine	400	0.00039 – 0.028	31,824,145

Detection Limits

Computing limits for this system is difficult, as the target concentrations are all very high, compared with those typically found in ambient air. Table 5 lists computed detection limits based on seven runs and three times the standard deviation of a series of runs at the lowest operating condition of the system. With the 0.30 ml sample loop and dilution flow of 12,069 ml/minute being the lowest concentration level achievable with the Dynacalibrator, and with permeation tubes set up for the target concentrations, these limits are more than adequate to accurately measure component concentrations against the target levels.

Table V. Computed Detection Limits for Target Analytes

Analyte	Measured Concentration Level (µmol/mol)	Computed Detection Limit (µmol/mol)	PUC Trigger Level (µmol/mol)
Chloroethene	0.0055	**0.0027**	0.33
Methacrolein	0.032	**0.005**	0.37
Toluene	0.25	**0.047**	240
Ethyl Benzene	0.050	**0.015**	6.0
1,4-Dichlorobenzene	0.016	**0.0067**	0.95
n-Nitroso-di-n-propylamine	0.00039	**0.00005**	0.0061

SUMMARY

The described analytical system is very capable of measuring concentrations of six of the organic constituents of concern specified in new California regulation for acceptance of biomethane into the common carrier pipelines. Even though concentrations can range from low nmol/mol to high µmol/mol levels, the system can report accurately these levels. Standards for calibration of the system are freshly generated with proper use of permeation devices at many of the target concentrations. However, action levels for Toluene are so high that any attempt at creating a standard at this level will cause fallout in a liquid during the process.

Even though the indicated reference methods are listed as EPA Method TO-11 for Methacrolein and EPA Method 8270 for n-Nitroso-di-n-propylamine, the gas chromatography and mass spectrometry technique discussed here is very appropriate for both analytes and allows real-time, on-line measurements to be performed together with the other analytes.

California Office of Health Hazard Assessment (OEHHA) will continue to evaluate additions and deletions to their list of Constituents of Concern. This analytical system is well suited to adapt to these changes by simply altering the mass spectrometer's scan parameters to the new compounds. Standards for the new analytes can be added by easy addition of new permeation tubes for the new compounds into the mix.

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