Evaluating Performance of Measurement Systems Configured for TO-15 Toxic Organics in Ambient Air and Other Bulk Gases

Randall Bramston-Cook and Edward Bramston-Cook
Lotus Consulting
5781 Campo Walk
Long Beach, California 90803

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INTRODUCTION

The primary approach to measuring trace volatile organics in ambient air remains the EPA Compendium Method TO-15 using gas chromatography and mass spectrometry.[1] This protocol was last updated in 1999 (later supplemented with a update in 2004 for extremely low level vapor intrusion studies[2]) with performance criteria purposefully limited to allow instruments of that era to meet all indicated requirements. Dramatic improvements in instrument capabilities have extended performance well beyond listed abilities in the method. With these enhancements, new procedures are needed to demonstrate performance accomplishments. Better detection capabilities put added pressure on blank checks to ensure that the analytical system is not contributing responses that match with target analytes, especially after repetitive cycling of adsorbent traps. Linear ranges can now extend over much wider span than the method listed range of 50, often widening to 10^4 or more. The conventional Cartesian plots of calibration data and associated least-squares fitting tend to skew the quality of the fit. A more useful display is a plot of response factor vs log[concentration] for each calibration level. With this extension to a wider range, carryover of high concentration analytes can severely impact subsequent runs. Procedures are presented to minimize this effect. Also discussed is the effect from sample canister pressures on the accuracy of results.

This EPA method is often referenced for measuring concentrations well outside the specified range, and with sample matrices radically different than ambient air. For example, California Human Health Screening Levels (CHHSL)[3] specifies TO-15 for vapor intrusion range in concentrations from 0.0095 nmol/mol[4] (carbon tetrachloride - indoor residential) to 511,000 nmol/mol (1,1,1-trichloroethane - soil gas commercial), as listed in Table I.

Table I. California Human Health Screening Levels for Vapor Intrusion.

Chemical	Indoor – Residential (nmol/mol)	Indoor – Commercial (nmol/mol)	Soil Gas – Residential (nmol/mol)	Soil Gas – Commercial (nmol/mol)
Benzene	0.026	0.044	11.4	38.5
Carbon Tetrachloride	0.0095	0.016	4	13.5
1,2-Dichloroethane	0.030	0.050	12.3	41.5
cis-1,3-Dichloroethene	9.2	13	4,000	11,200
trans-1,3-Dichloroethene	18	26	8,000	22,500
Methyl *tert*-butyl ether (MTBE)	2.6	4.4	1,100	3,800
Naphthalene	0.014	0.023	6.1	20.2
Tetrachloroethene (PCE)	0.060	0.10	28	89
Toluene	83	116	36,000	100,000
1,1,1-Trichloroethane (TCA)	420	588	182,000	511,000 [sic]
Trichloroethene (TCE)	0.230	0.380	222	745
Vinyl chloride	0.012	0.020	5.2	17.5
Xylenes (m&p)	168	235	73,000	200,000
Xylene (o)	168	235	73,000	200,000

In another new regulation, the California Public Utilities Commission with California AB 1900 (2012)[5,6] mandated measurements of toxics organics in biomethane, with action levels from 0.33 µmol/mol vinyl chloride to 12,000 µmol/mol Toluene [sic] in biomethane, and cite the reference method as TO-15 for four of the target analytes, shown in Table II.

Table II. 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
total Dichlorobenzenes (as 1,4-Dichlorobenzene)	0.95	9.5	24	EPA TO-15
Ethylbenzene	6.0	60	150	EPA TO-15
n-Nitroso-di-n-propylamine	0.0061	0.061	.15	EPA 8270
Vinyl Chloride	0.33	3.3	8.3	EPA TO-15
Hydrogen Sulfide	22	216	1,080	ASTM D6228
Methacrolein	0.37	3.7	18	EPA TO-11
Alkyl Sulfides	12	120	610	ASTM D6228
Toluene	240	2,400	12,000 [sic]	EPA TO-15

All of these levels are well outside the reference method calibration range. Special operations are presented to allow these samples to be properly reported, independent of the sample matrix and without severe sample manipulations to get concentrations within the operating range of the analyzer.

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).

Two pathways were configured for sample injection into columns. One corridor was set up set with mass flow controlled loading of typically 300 ml sample into a multi-bed adsorbent trap held at near ambient temperature. Water, methane and carbon were allowed to pass on through to vent. After the dose is loaded and flushed with nitrogen, the contents are passed onto a cryofocus trap to reduce the effective analyte concentration. The trap contents are isolated while the cryofocus trap heated up. Then the full trap contents are injected into the analytical column with a true flow controller.

A second pathway was set for analyte concentrations above the range of the direct injection. Here a fixed volume sample was directed through a gas sample valve to a column inlet splitter to allow further reduction in sample loading into the column. Simply by altering this split ratio in preset methods, extremely high levels were reduced into the working range of the mass spectrometer.

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 ^{o}C, hold 51.30 minutes
Cryofocus Trap: 90 µl empty trapping
  Initial Temperature: +79 ^{o}C, hold 2.60 minutes
  Temperature Ramp: -200 ^{o}C/min
  Temperature: -146 ^{o}C, hold 8.10 minutes
  Temperature Ramp: +200 ^{o}C/min
  Temperature: +202 ^{o}C, hold 48.40 minutes
Trapping variable as needed from 0.2 min. to 6 min.
Mass Flow Controller Flow Rate: 50 ml/min
Fixed Volume Loops: 300 µL and 3.0 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 ^{o}C, hold 6.00 minutes
  Temperature Ramp: -100 ^{o}C/min
  Temperature: +20 ^{o}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: 250 ^{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 C
Full Scan (for peak locating) and Selected Ion Monitoring (for monitoring)
Extended Dynamic Range (EDR™) activated

Sample Loading with Mass Flow Controller

The instrument included a mass flow controller for sample loading with low level analytes. A sample pressure regulator was installed just after the automated sampler to provide a consistent sample pressure for the mass flow controller. Sample is first allowed to flow into the pathway without trapping to flush all samples lines with the new sample. After a typical two minute delay, the sample was then directed into a hydrophobic mixed-bed adsorbent trap maintained just above ambient temperature. Water, methane, oxygen and carbon dioxide passed on through to vent. Sample volume loaded onto the trap became a product of mass flow controller flow rate and time allowed for trapping. This allowed loading volumes from 10 ml to over 300 ml by simply altering this time interval. After the sample was fully loaded onto the trap and flushed with nitrogen to vent, an appropriate valve was switched and the adsorbent trap heated to transfer the sample components to a cryofocus trap to reduce the effective volume to less than 90 microliters, Then the new trap was isolated during its heating, and brought back in-line. The isolation valve opened to inject the sample into the column.

Sample Loading with Fixed Volume Sample Loop

The system was also equipped with sample loops with various volumes ranging from 0.1 ml to 1 ml, maintained at a constant temperature. This addition allowed an extension of the concentration range of the mass spectrometer into much higher concentrations required by some methods. Valve operations with fixed volume loops made certain that the sample loop achieved consistent pressure prior to every injection, to correct for varying sample pressures, be it pressurized canisters, Tedlar bags or permeation tube flow at atmospheric pressure.

Calibration Standards

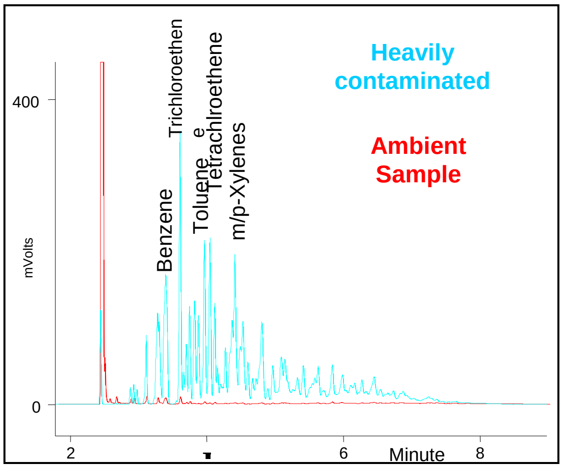
Working TO-15 standards were generated from a 1 µmol/mol (ppmV) standard from Restek (Bellefonte, Pa) and serially diluted into working standards ranging from 100 pmol/mol (pptV) to 100 nmol/mol (ppbV) with a Lotus Consulting Pressure Station Model PS-1 (Long Beach, Ca). High level standards for vapor intrusion and biomethane measurements were generated from Dynacal® 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.

RESULTS AND DISCUSSION

Prescreen with Flame Ionization Detector

A common dilemma with measurement of unknown environmental samples is what are their anticipated levels and what conditions are needed to accurately quantitate target analytes within the operating range of the analyzer. Possible concentrations can range from ambient levels of low pmoles/mole up into µmol/mol, and can be outside the range of the detector. A quick assessment of contamination can be accomplished with a quick prescreen with a flame ionization detector capable of measuring a very wide range of concentrations for every sample. With the huge dynamic range available with this detector, a judgment can be made to load a sample with a low-volume pathway, or to process a larger volume with an enhanced mode, with a special program StarRanger (Lotus Consulting, Long Beach). Figure 1 illustrates the ability of a flame ionization detector to prejudge concentration levels in samples

Figure 1. FID Chromatographs of prescreens of samples to rapidly assess contamination levels.



Extended Linear Range with Mass Spectrometer

Calibration Plots with Response Factor Versus log[Concentration] – With an extended dynamic calibration range over orders of magnitude now achievable, the classic Cartesian plots of detector response versus concentration does not allow proper visual assessment of linearity, as illustrated in Figure 2. The low concentrations end up tightly bunched at the lower scale levels and are virtually unreadable. A better approach for handling very wide concentration ranges is to plot response factors for each levels versus log[concentration], as depicted in Figure 3. This presentation permits concentrations over many orders of magnitude to be plotted along with an indication of linearity over the range, and how well the data fits into a target tolerance band. Typical linear ranges measured with the system exceed 10,000 – from <3 pmol/mol to >100 nmol/mol for 300 ml sample loading.

Figure 2. Typical Cartesion calibration plot of response versus concentration.

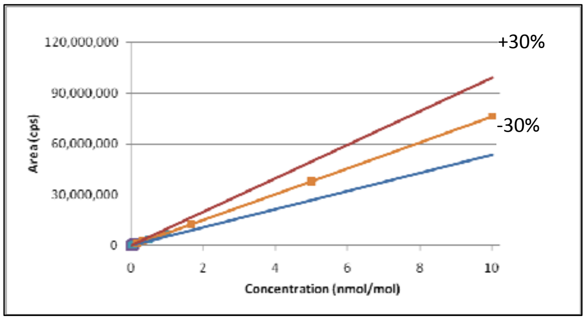
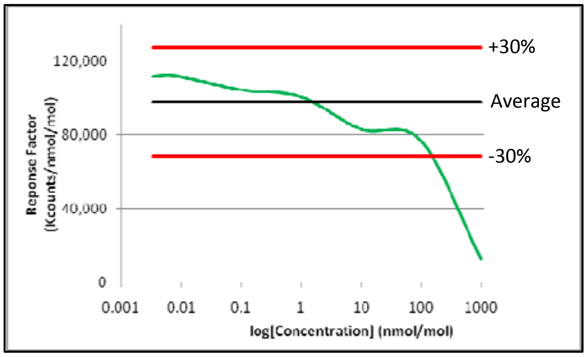


Figure 3. Plot of response factor versus log[concentration] for Propene over four orders of magnitude.



Sample Volumes Set with Mass Flow Controller – a very convenient facet with operation of these controllers is the easy generation of a multi-point calibration by setting the flow rate and then varying the tine interval that the sample flows into the first concentrator. This accomplishes a concentration range typically over a factor of 30. To extend the range further, a second level standard, typically a simple dilution of the higher standard is measured the same way, and then a third, and even a fourth and fifth. This sequence can establish the full range of modern spectrometers, often approaching five orders of magnitude.

Fixed Volume Sample Loops – Some target analytes in screening mandates greatly exceed the capabilities of all chromatographic systems, especially affecting column and detectors performances with severe overloading. One approach to allow these levels to be measured without the tedious process of diluting the sample into range is to use small fixed volume sample loops to produce an accurate aliquot of the sample and standards, and then use the same analytical process as performed with the mass flow controller. The FID prescreen can determine the anticipated level and an automatic judgment can be made on the proper path of fixed volume loop or mass flow controller.

Nitrogen Blank

Measurement of target analytes' concentrations must not include any contribution from the system, especially from impurities in supply gases and system contamination. Possible sources include the possible backflow of sample from rapid trap heating, especially with high level analytes, through the connecting tubing and the resulting contamination of upstream pneumatic components. Some small pencil filters should be inserted in these lines to collect the residue, but then they can become a source for constant bleed. However, at least it is easier to replace these inexpensive filters then to replace more costly pneumatic controls. Even then, polymers used in these controllers can outgas compounds that can interfere in the measurements. Small heat-activated gettering alloy purifiers are inserted to further clean up the carrier and purge gases. Figure 4 and Table III illustrate achievable system blanks. Typical results using Selected Ion Monitoring (SIM) are less than 0.3 pmol/mol.

Figure 4. Total Ion Chromatogram (TIC) of Nitrogen Blank.

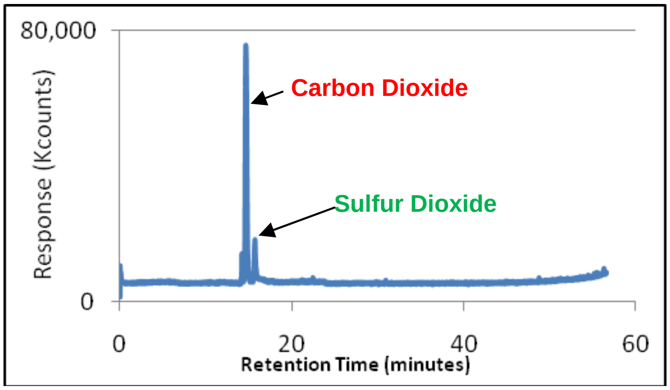


Table III. Typical Levels in N2 Blank

Analyte	Blank Levels pmol/mol
Propene	0.10
Ethanol	0.52
Benzene	0.15
Hexachlorobutadiene	0.14

Sample Carryover

Results reported for a specific sample must represent the true concentration for that sample and cannot have any contributions from analytes carried over from previous samples, especially ones with major hits for target analytes. A proper design for a TO-15 system minimizes this sample carryover by continuously purging all interconnecting lines between valves and traps when a sample is not being loaded. In addition, a new sample is allowed to flow without trapping for at least two minutes to flush out the incoming sample lines and multi-position automated sampler. Any unswept deadvolumes must be avoided, commonly generated by tees and crosses installed in the sample pathways, especially with insertion of pressure/leak monitoring of sample containers. Table IV lists performance of a typical system for selected analytes - one early in the chromatogram, one late, one easy, and one a bit tougher.

Table IV. Typical Carryover

Analyte	Carry-over after 1 µmol/mol
Propene	0.008%
Ethanol	0.112%
Benzene	0.015%
Hexachlorobutadiene	0.007%

Detection Limits

Ability to measure extremely low concentration levels is greatly impacted on cleanliness of the system, especially natural system background levels and sample carryover from previous high samples. With careful considerations of flushing all sample lines with both clean purge gas and the new sample, detection into the very low pmol/mol levels can be achieved. Figure 5 demonstrates typical chromatograms for a 3.3 pmol/mol concentration of selected analytes using Selected Ion Monitoring (SIM) and their associated nitrogen blanks. Table V lists detection limits for these analytes. Limits are computed by three times the standard deviation of seven consecutive runs at 3.3 pmol/mol.

Figure 5. SIM Chromatograms at 3.3 pmol/mol with N_2 blanks of Propene, Ethanol, Benzene and Hexachlorobutadiene.

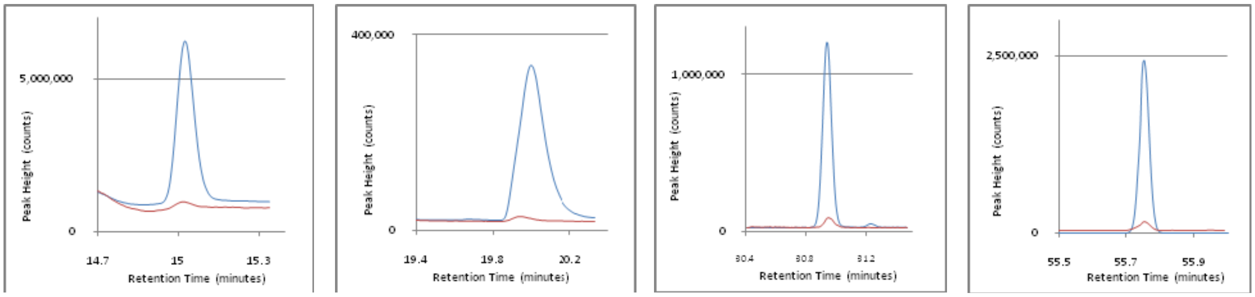


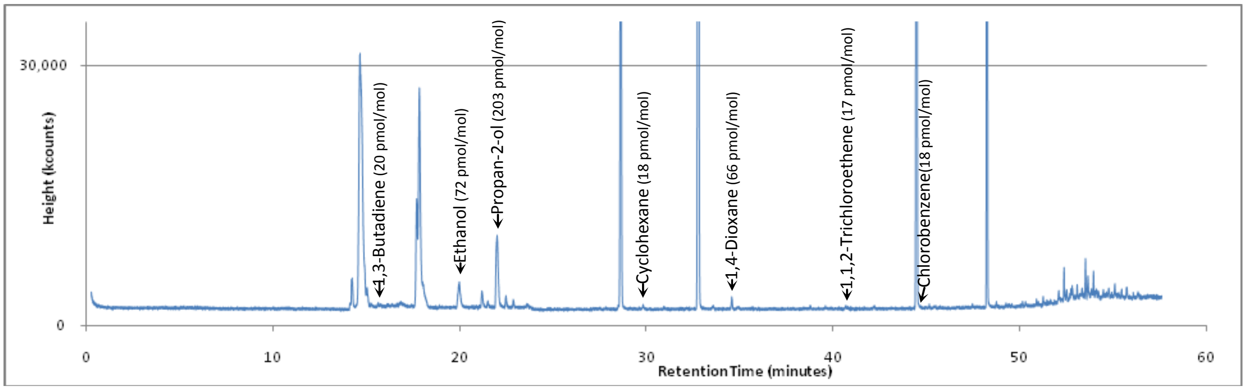
Table V. Typical Detection Limits

Analyte	**Detection Limit (pmol/mol)**
Propene	0.4
Ethanol	3.8
Benzene	0.9
Hexachlorobutadiene	2.5

Ineffective Use of Internal Standards

EPA Method TO-15 specifies use of specific addition of internal standards to ostensibly correct for sample-to-sample variations in system performance. Specific problems with this process have been discussed elsewhere.[7] One major issue relates to measurement of low level analytes when the normal concentration of internal standards are added. Inherent impurities in the internal standard are often target analytes and limit detection at low concentration levels (Figure 6). Modern instrumentation is normally very stable and reproducible, negating the requirement of internal standards with EPA Method TO-15.

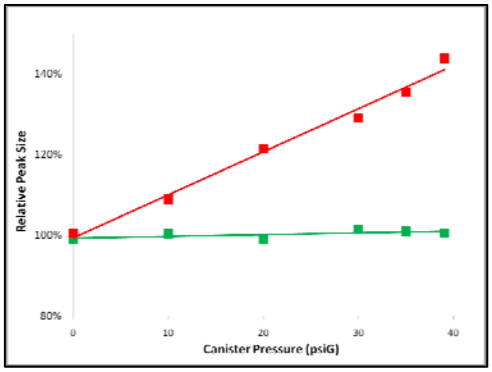
Figure 6. Detected Analytes in 10 nmol/mol Internal Standard Mix



Effects of Sample Pressure on Mass Flow Controllers

Mass flow controllers are calibrated for specific inlet and outlet pressures to maintain their accuracies. If the input path is allowed to have varying pressures, gas compression from Boyle-Mariotte's Law will increase the amount of sample loaded into the first concentrator trap as shown in red with Figure 7. To assure accurate performance of the flow controller with varying sample pressures, an inline low-volume pressure regulator set to 3 psiG to throttle down pressures. When a Tedlar bag or ambient air sample is attached, this regulator allows sample flow to be unimpeded.

Figure 7. Comparison of peak size without pressure regulator (red) and with regulator (green).

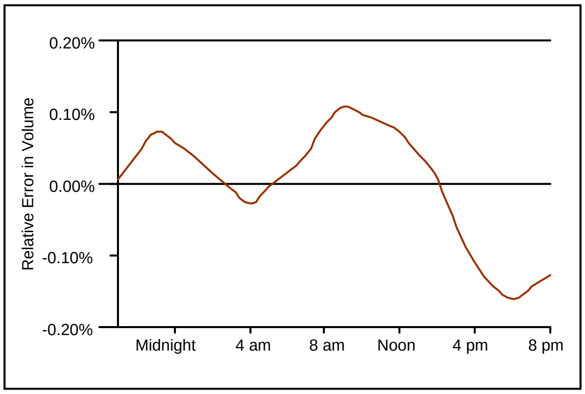


Effects of Sample Loop Pressure and Temperature with Fixed Volume Loops

When a sample is loaded into a sample loop, its pressure at injection must be made consistent from run to run, and from standard to sample, to yield consistent results from Boyle-Mariotte's Law. One mechanism is to always vent the sample loop to atmosphere just prior to injection into the chromatograph. This operation must be designed to handle pressurized samples, as well as samples naturally at atmospheric pressure, such as Tedlar® bags or ambient samples that are sucked in by vacuum. Obvious this approach does not work for samples below atmospheric pressure as once the sample loop is opened to atmosphere, room air will be sucked back into the void and significantly alter the sample composition. In this case, the loop must be evacuated first and then filled with sample, with the sample pressure in the loop upon injection being accurately measured without venting and then applied as a correction to results, or the sample can be pressurized above atmospheric with an inert gas diluent and a correction applied to the results to account for the dilution through the Lotus Consulting PS1 Pressure Station.

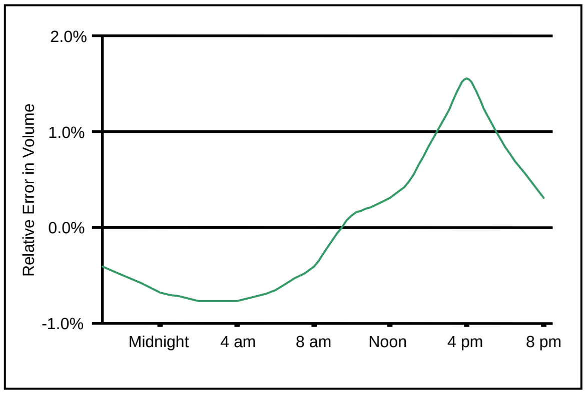
Interestingly, atmospheric pressure ***does*** change over a day. And when measurements are made over an extended time period, this deviation can impact the quality of results. Corrections become mandatory if this variation exceeds the required precision of the measurement, and if the measurement span for standards and samples is more than a few hours, especially if the barometer changes due to an approaching storm or post-storm clearing. Figure 8 provides an indication of atmospheric pressure effects on sample volume for a typical summer day in Long Beach, California. This magnitude can change with weather, with recorded extremes of 7% above average (1968, Agata, Siberia) and 14% below (1979, Western Pacific).[8,9]

Figure 8. Error in Sample Volume with Varying Atmospheric Pressure over One Day.



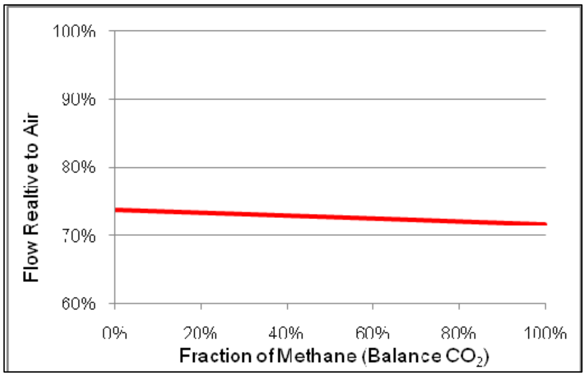
Temperature of the loop at injection remains as a variable in the Ideal Gas Law by Charles-Gay-Lussac's Law. If the measurement is not crucial, temperature at the loop can be allowed to vary somewhat. However, to achieve the ultimate performance, temperature of the loop must remain very constant, as any variation directly impacts the sample volume. A change in loop temperature, between the time when calibrating the system with a standard and then later running a sample, directly influences the consistency of the measurement. This variation is illustrated in Figure 9 for a typical summer day in Long Beach, California.

Figure 9. Errors in Sample Volume with Varying Ambient Temperature over One Day.



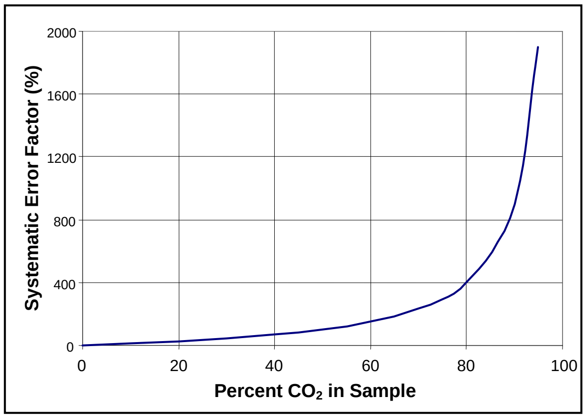
Change in Bulk Gas and Effects on Measurements - Method TO-15 is solely intended to measure ambient air samples, as denoted in its title. For digester gas samples, possible methane/carbon dioxide concentration ratios can range from 61/38 to 63/35 volume%, with oxygen and nitrogen levels well below one volume%.[10] Landfill gases can have methane/carbon dioxide ratios from 35/50 to 60/30 volume%.[11] And biomethane is typically around 97% methane, with a balance of carbon dioxide and other hydrocarbons. Figure 10 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 10. Relative MFC Flows with Varying CH4/CO2, Relative to Air.



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 11. 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.

Figure 11. Systematic Volume Errors with Mass Flow Controllers Located after Trapping of Carbon Dioxide[4]



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.

Table VI. Typical Retention Time Reproducibilities

Analyte	Retention Time Reproducibility
Propene	± 0.004 minutes
Ethanol	± 0.004 minutes
Benzene	± 0.006 minutes
Hexachlorobutadiene	± 0.005 minutes

Importance of Retention Time Reproducibility

Selected ion monitoring (SIM) aids in achievement of very wide dynamic concentration ranges by restricting ions only to the pertinent ones for the target analytes around their expected retention times. Reducing the assigned time windows yields longer scan times for the target ions and improves detectability of the analyte. However, if the peak retention moves outside the expected time window, all information related to that analyte peak is lost and can only be recovered by a sample rerun after times are adjusted. Retention time is critical in maintaining peak elutions within the expected windows. Typical results are presented in Table VI. All TO-15 analytes measured for this report gave reproducibilities less than ±0.030 minutes, with most being better than ±0.006 minutes. Huge concentrations of some analytes can generate column overloading and their retention times can shift as a result. Results for these peaks must be scrutinized to ensure that the shift did not cause distortions in results,

SUMMARY

A well-designed analytical system with an adaptable gas chromatograph and high performance mass spectrometer is capable of extending the dynamic range of measurements well beyond established protocols. Possible ranges exceed 10,000 for most analytes with detection down to single digit pmol/mol. Clean nitrogen blanks, necessary to properly measure very low concentration levels, can be achieved with careful setup of adequate flushing for interconnecting sample lines and valving, and proper filtering of the incoming supply gases. Also, internal standards can provide added contaminates of many of the target analytes, well above likely detection limits.

The sample composition can have a major impact on the quality of the measurement, especially with biogas and biomethane. These matrices must use fixed volume sample loops to properly set the sample loading. Selected ion monitoring can significantly enhance the performance of the system, but mandates very tight retention reproducibility to maintain the advantage. An included flame ionization detector can be set up to prescreen every sample prior to analysis and put the operating conditions for the chromatographic system appropriate for the expected level. This process helps avoid time-consuming sample reruns.

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4. Concentrations are reported in molar units, following recommendations of NIST and IUPAC. For example, “ppmV” becomes “µmol/mol”, “ppbV” is “nmol/mol”, and “pptV” translates to “pmol/mol.” See old.iupac.org/publications/books/gbook/green_book_2ed.pdf; physics.nist.gov/Pubs/SP811/sec07.html; and R Bramston-Cook, “Concentration Units in Gas Analysis, Lotus Consulting, Long Beach, CA.

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Lotus Consulting
310/569-0128 Fax 714/898-7461
Email: randy@lotusinstruments.com

5781 Campo Walk
Long Beach, California 90803
Website: lotus instruments.com