Cautions with Sample Loadings for TO15 Analyzers

by:

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Sample presentations to an analytical instrument for measurement of toxic compounds in air can take several pathways. EPA Method TO15¹ is frequently cited as the designated approach for assessment of volatile toxic organics in samples from ambient air, vapor intrusion, landfill emissions, digestor gases, stack emissions, and perimeter monitoring of industrial sites Often the process involves collection the sample and loading it into a gas chromatograph/mass spectrometer equipped with a concentrator to bring the measured levels into the range of the instrument. To enhance the sample loading, a mass flow controller is regularly employed to accurately dose in a sample volume well above normally used for other analyses in a gas chromatograph/mass spectrometer. Selection of the method for loading samples depends on the purpose of the analysis.

A. On-site Sampling

A process that maintains sample integrity is to locate the instrument at the sampling site inside a mobile lab or instrument shed. No sample component degrades from processing into collection devices and is lost from long holding times before analysis. This allows on-line analysis of sample streams, such as biogas feedstock to a chemical process or power generation, perimeter assessments by running repetitive samples over an extended time span, or kinetic studies of reactions.

	Sample Name	Sample	Гуре	Cal. level	lnj.	Injection Notes	AutoLink	Ai.▲ (IS	Add
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Figure 1. Interval sampling is easily set up with displayed entries in the Scion MSWS SampleList. Interval is set up for 1 hour on the hour; other values can be used.

¹ Determination of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters And Analyzed By Gas Chromatography/ Mass Spectrometry (GC/MS) www3.epa.gov/ttnamti1/files/ ambient/airtox/to-15r.pdf

B. Tedlar Bags

Samples can be collected into Tedlar bags for transfer to the laboratory for measurements. These containers are inexpensive and disposable. Normally they have no carryover, as they are typically single use. They need to be verified for cleanliness, especially for compounds of interest. Maximum holding time is typically 3 days.² Reactive analytes can be lost with longer holding times, especially when exposed to light, as with 1,3-Butadiene. These bags are not easy to transport with dramatic changes to pressure and temperature as they can readily burst.



Figure 2. Typical Tedlar Bag.

C. Canisters

Stainless steel canisters are frequently specified in standard methods for analysis of ambient air and other source samples, including TO15. Prior to implementation for collecting, they must be cleansed and validated for absence of target analytes. When left with a final evacuation of less than 50 mTorr, the natural vacuum can be used to pull in sample with minimal associated hardware.

By simply opening up the canister valve at the sampling site, a grab sample can be collected from the differential of atmospheric pressure and canister vacuum. Grab samples must be pressurized at the laboratory to a value above atmospheric pressure prior to analysis, using



Figure 3 Typical 6L Canister.

pure nitrogen. The initial and final pressures are entered as correction factors to the final results to account for the dilution.³

Samples can also be loaded into canisters with a diaphragm pump.⁴ A mass flow controller maintains a constant flow into the canister over the desired sampling period. Final pressures up to 2 atm (30 psiA) are achievable. All materials in the sample flow must be non-reactive, such as stainless steel, Teflon[™], and Viton[™].

² Eurofins Guide to Air Sampling, 2014, www.eurofinsus.com/media/161448/guide-to-air-sampling-analysis-2014-06-27_revised-logos.pdf.

³ California Air Resources Board, Standard Operating Procedure for the Analysis of Greenhouse Gas Compounds In Ambient Air by Gas Chromatography Mass Spectrometry SOP MLD070, November 2015, ww2.arb.ca.gov/sites/default/files/2020-03/mld070.pdf.

⁴ California Air Resources Board, Standard Operating Procedures for Xonteh Model 901 and 901PC Canister Samplers AQSB SOP 805, April 2015, www.arb.ca.gov/airwebmanual/ aqsbdocs1/AQSB% 20SOP%20805%20(Xonteck%20901&910PC).pdf.

Passive sampling kits are available to control sample flow into an evacuated canister without an active pump. Installing hardware involving a critical orifice that yields a constant flow into the canister over time to achieve an average loading over a time interval. A variety of orifices are available to select the flow rate achieved over a predetermined time interval. Calibration of a critical orifice is affected by the vacuum changes in the canister. A flow controller with a metal diaphragm is mounted following the orifice. As the flow through the orifice must operate with a pressure differential between the sample pressure and the canister vacuum, its calibration fails when the pressure differential becomes small. Pressures above 0.766 atm⁵ (-7 "Hg) require a termination of the process, as the flow rate is not maintained when the canister gets so close to atmospheric pressure.⁶ Six-liter canisters with a maximum pressure reading after sampling of 0.766 atm can suffer from an additional dose of 1.2 nmol/mol for 1/8" interconnecting tubing or 0.25 nmol/mol for 1/16" interconnecting (see Table 1).

Canisters have a significant advantage with being easy to transport, even by air, are reusable and have extended holding times to 30 days for most analytes.⁷ However, they are expensive, must be cleaned and validated, and can be subject to component carryover from previous samples. Special operations are required to ensure that canisters to be cleaned must achieve vacuums below 50 mTorr, are free of any contamination, and do not leak.

D. Transporting Canisters by Air Freight

Canisters are rugged enough to be readily shipped by air to shortening the laboratory turnaround times for analytical results. Since these samples are frequently pressurized, they come under International Air Transport Association's Dangerous Goods Regulations.⁸ Ambient air samples are exempted, as their bulk gas is non-flammable, non-corrosive and non-toxic (the toxic components in the sample are at trace levels). If the pressure in the canister is maintained below 200 kPa [29.0 psiA,1.97 atm] at 20 °C, and contents are not liquefied or refrigerated-liquefied gases, no special labeling is required. Typical temperatures in the cargo hold of freight carriers can range from -18 °C to 90 °C and pressures down to 8.3 psiA (0.564 atm).^{9,10}

⁵ Relative to atmospheric pressure at sea level.

⁶ Restek "Passive Air Sampling Kits", 2015, .www.restek.com/pdfs/500-03-001.pdf.

⁷ US EPA, "Analysis of Volatile Organic Compounds in Air Contained in Canisters by Method TO-15, www.epa.gov/quality/analysis-volatile-organic-compounds-air-contained-canisters-method-15-sop-no-hw-31-revision, 2014, p.10.

⁸ "Dangerous Goods Regulations", Section 3.2.2.4.1, International Air Transport Association (IATA), 61st Edition, January 2020, www.iata.org/en/publications/dgr/.

⁹ "Fedex Packing Guidelines for Shipping Freight", 11/2016, www.fedex.com/content/dam/fedex/usunited-states/services/FreightPackagingGuidelines.pdf.

¹⁰ Singh, S. P., et al, "Measurement and Analysis of Temperatures and Pressure in High Altitude Air Shipments", Packaging and Technology and Science, 23, online onlinelibrary.wiley.com/doi/10.1002/ pts.877/abstract.

E. Addition of 150 µL Liquid Water

Ambient air samples will have humidity from < 0.5% V to ~ 4% V.¹¹ Most standards are likely to be anhydrous. To ensure that both samples and standards possess similar moisture content, canisters for standards and controls after evacuation can be dosed with 150 μ L liquid water to generate 204 ml gas¹² [40% relative humidity¹³]. This step yields equivalent effects of humidity on the concentration process independent of the selected sample or standard and minimizes active surface sites inside canisters, especially applicable to polar analytes like alcohols, aldehydes and ketones.¹⁴

F. Cross-Contamination with Canisters Below Atmospheric Pressures

Grab samples and samples generated with a critical orifice are very dependent on the pressure differential between the canister and atmospheric values. The process requires that canisters cannot be allowed to approach atmospheric pressure, as the flow rate into the canister is not maintained at the setpoint.

A risk of attaching subambient pressure canisters to the analytical instrument is backflow of previous sample/standard held up in the interconnecting tubing. Vacuum in the canister can pull enough cross-contaminants to change target analyte concentrations. Flushing the lines prior to canister hook-ups does not resolve the problem. As the automated sampler valve rotates to the active position, the interconnecting tubing can be exposed to a position with a pressurized sample/standard and fill up the tubing with this sample to its pressure level. Then, as the sampler advances to the desired position, this pressurized dose can backflow into the new sample. Tables 1 and Figures 4 and 5 provide data for likely cross-contaminations involved. Figures 6 through 9 illustrate the process for backflows into subambient sample canisters. The error contribution becomes an addition of 6 ml of the pressurized canister at 0.9 atm with 1/16" tubing and 27 ml at 0.9 atm with 1/8" tubing. If the higher pressure canister is a 100 nmol/mol standard, its addition becomes 0.1 nmol/mol for 1/16" tubing and 0.45 nmol/mol for 1/8" tubing This impact is not readily noticed, as it becomes additive to the native concentrations and is a systematic error that cannot be detected nor corrected. Often pressurized sample canisters are attached with calibration standards, and they themselves are not impacted.

¹¹ The MAC Humidity/Moisture Handbook, 2019, www.macinstruments.com/wp-content/uploads/ handbook.pdf.

¹² Volume of water vapor = 0.15 ml_(l) * 1 g/ml * 1mol/18 g * 22.4 L/mol * $(273+25)/273 = 0.204 L_{(g)}$ at 1 atm, or 1.2 %V at 40 psiG in 6L canister.

¹³ Restek "TO-15 Canister Relative Humidity: Part II (Examples and Calculations)," 2013, docs.google.com/spreadsheets/d/1xxYWufpwFqxyn4wU6hTjdgA6qVE--39_0qjuqM86RLQ/ edit#gid=0.

¹⁴ California Air Resources Board, "Standard Operating Procedure for the Determination of Non-Methane Organic Compounds in Ambient Air by Gas Chromatography Using Dual Capillary Columns and Flame Ionization Detection, SOP No. MLD 032", 2002.

Canisters that are already pressurized do not exhibit this effect, as pressure prevents the backflow effect and keep the contaminates in the interconnecting tubing at bay.

When samples arrive at the laboratory, canisters should be noted for their pressure as received. If below atmospheric pressure at the laboratory, they need to have nitrogen added to bring them to positive pressure to avoid this phenomenon. The initial pressure divided by this final pressure becomes a dilution factor for correcting the final results.

Sample Canister Pressure (atm)	Volume (ml) pulled in from 40 psiG 2.1 mm ID Tubing	Added Concentration (nmol/mol)	Volume (ml) pulled in from 40 psiG 1.0 mm ID Tubing	Added Concentration (nmol/mol)
1.00	0	0	0	0
0.95	14	0.23	3	0.05
0.90	27	0.45	6	0.10
0.85	41	0.68	9	0.15
0.80	54	0.91	12	0.20
0.75	68	1.14	15	0.25
0.70	82	1.36	18	0.30
0.65	95	1.59	21	0.35
0.60	109	1.82	24	0.40
0.55	123	2.04	27	0.45
0.50	136	2.27	30	0.50

Table 1. Summary of calculations for added concentrations to sample canisters from adjacent 100 nmol/mol standard canister.

G. Effects of Canister Vacuum of Errors in Quantitation Reporting

Analyzing sub-atmospheric canisters runs the risk of a dose of the previous sample adding to the analytes in the active canister. Even flushing the sample lines with vacuum or nitrogen prior to measurements does not minimize the problem. Let set up a scenario of Position 1 hooked up to pressurized nitrogen blank, Position 2 with 100 nmol/mol standard, and Position 3 with unknown passive sample at 0.766 atm. Position 1 is fully flushed with blank nitrogen. Position 2 needs to be flushed out with standard before trap is loaded to get representative standard in the interconnecting sample lines. When Position 3 is up, the natural vacuum in the canister will pull in 67 ml of the 100 nmol/mol standard and effectively add 1.1 nmol/mol to results, for 1/8" interconnecting lines. There is no ability to monitor the addition or correct the artefact. And interconnecting lines cannot be cleared.



Figure 4. Volume pulled into Canister versus Canister Pressure (1/8" OD, 2 m tubing).



Figure 5. Volume pulled into Canister versus Canister Pressure (1/16" OD, 2 m tubing).

Parameters involved in Cross-Contamination Assessment

Location of Automated Sampler – mounted in sample tower, Interconnecting tubing from Automated Sampler to First Trap in Concentrator

- Length 2 meters
- Inside diameter for tubing: 0.0.085" (OD 1/8")
- Total volume for interconnecting tubing: 73 ml
- Pressure of 100 nmol/mol Standard Canister: 40 psiG
- Pressures of Sample Canister: 0.5 atm



Standard Canister Volume: 6 L Original Canister Pressure: 40 psiG Concentration: 100 nmol/mol

Figure 6. Original canister forces standard into interconnecting tubing (1/8") from its pressure.



Figure 7. Advancing automated sampler to an adjacent sample canister allows a 136 ml dose of analytes from the original canister to be added to the Sample Canister.



Standard Canister Volume: 6 L Original Canister Pressure: 40 psiG Concentration: 100 nmol/mol

Figure 8. Original Canister forces standard into interconnecting tubing (1/16") from its pressure.



Figure 9. Advancing automated sampler to an adjacent sample canister allows a 30 ml dose of analytes from the original canister to be added to the Sample Canister.

The effect of this process is a systematic error to final results and is not correctable. Analyte concentrations from the higher pressure canister are dosed into the canister below atmospheric. The additional amount depends on the difference in pressure in the interconnecting tubing and the vacuum level in the receiving canister. Internal standard calculations will not correct for the error.

H. 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 10. 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 10. Comparison of peak size without pressure regulator (red) and with regulator (green).

I. Effects of Temperature at Sampling Site versus at Analytical Laboratory

Canister samples collected on site for both grab samples and samples generated with a critical orifice can have different temperatures than what is set in the analytical laboratory. If the sample temperature is above the laboratory (22.2 °C), a vacuum is created from the impact of Charles's Law. Table 2 lists several locations listing the record high or low ambient temperatures and the vacuum generated. To avoid the situation discussed in Section F, the canister's pressure must be increased by pressurization (Section J). Temperatures below the laboratory will not create this vacuum, but instead canister pressures will be above those at the lab.

City	- High Temperature (ºK)	Canister Pressure at Lab (atm)			
Phoenix, Az	323.1	0.91			
Riverside, Ca	320.9	0.92			
Las Vegas, Nv	320.3	0.92			
Dallas, Tx	318.1	0.93			
	Low Temperature (°K)				
Fairbanks, Ak	218.7	1.35			
Bismarck. Nd	230.9	1.28			

Table 2. Effects of temperatures at various US cities. J. Impact of Atmospheric Pressure on Sample Collection

Atmospheric pressure at the sampling site impacts the measurement of grab samples and the process involving critical orifices. This pressure does vary a bit over the day (Figure 11), but the change is relatively insignificant. Altitude for the site can have a bigger effect (Tables 2 and 3, and Figure 11) by altering the amount of sample loaded into a canister. For example, a sample collected in Denver will only come to 0.942 atm and will create a vacuum inside the container when analyzed in a laboratory at sea level. Based on discussions in Section F, as much as 0.23 nmol/mol from an adjacent 100 nmol/mol standard canister is added into the unknown sample for 1/8" interconnecting, tubing and 0.05 nmol/mol for 1/16" tubing.



Figure 11. Hourly barometric pressure readings of a typical summer day at Long Beach Airport illustrate routine variations realized over a 24 hour period.

Altitude (m)	Absolute Atmospheric Pressure (atm) ¹⁵
sea level	1.000
500	0.980
1000	0.964
1500	0.946
2000	0.929
2500	0.912
3000	0.894
3500	0.878
4000	0.857

 Table 2. Absolute atmospheric pressure versus altitude.

¹⁵ Altitude above Sea Level and Air Pressure, The Engineering Toolbox, www.engineering toolbox.com/ air-altitde-pressure-d_462.html, accessed April 6, 2020.



Figure 12. Plot of atmospheric pressure versus altitude.

Locale	Altitude (m) ¹⁶	Atmospheric Pressure (atm)
Long Beach	16	1.000
Dallas	131	0.995
Chicago	181	0.993
Phoenix	331	0.988
El Paso	1243	0.955
Salt Lake City	1288	0.954
Denver	1609	0.942
Independence Pass	3687	0.866

Table 3. Selected sampling locales and their altitudes and atmospheric pressure.

¹⁶ en.wikipedia.org/wiki/List_of_cities_in_the_United_States_by_elevation, accessed April 6, 2020.

K. Pressure Station (PS1) from Lotus Consulting

If a canister does not have some positive pressure, the sample aliquot to be measured will not be fully accounted, when a fixed sample loop will be below atmospheric pressure and most likely will not match the pressure for standards, thus yielding improperly low results. Or, if a mass flow controller is employed to dose in the sample into the measuring system, its calibration is suspect as the conditions are very likely to be radically different than the calibration certificate and will yield a systematic error, lowering the predicted volume to be measured. The problem is rectified by taking advantage of Boyles' Law that accurately predicts that concentration is directly proportional to pressure. By noting the initial sample pressure and then pressuring the canister to a final reading above atmospheric, the ratio of the initial and final becomes a dilution factor that must be applied to all results to correlate the final results with the condition of the original sample.

The Pressure Station (PS1) from Lotus Consulting provides the direct reading of the initial canister pressure. Utilizing the capabilities of the station, canister pressure can be boost above atmospheric pressure, with a display of the final pressure, and resulting dilution factor.



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