
Understanding Sampling Canister Technology

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Introduction

Stainless steel canisters offer a tremendous advantage over other air sampling media, namely Tedlar bags and adsorbent traps. Since their introduction in the late '70s, canisters have continued to grow in popularity due to their ease of sampling, long storage times, low blank levels, and the ability to perform multiple analyses in the laboratory. Like Tedlar bags, the concentration of the sample is not altered in the field. The sample is simply placed in a container that preserves the concentration until analysis is performed from days to weeks later in a laboratory. Whether the concentration is PPM level or Sub-PPB, the sampling is performed the same way, eliminating much of the responsibility on the part of the individual performing the sampling.

When canisters were first introduced, the "SUMMA" passivated canister was the only option available. Today, with the availability of electropolished, fused silica lined (Silonite and others), and glass canisters, as well as multiple valves and gauges to choose from, air monitoring personnel must be further educated on the advantages of each type and size of canister and their corresponding valves and gauges. This document gives an overview of canister technology, and addresses issues of importance for obtaining the highest quality data possible using canisters.

Chemical Inertness and Sample Storage

Canisters provide longer storage of a wider range of compounds, for multiple reasons. First, stainless steel is very dense, preventing the transmission of chemicals into and out of the canister through its walls. Unlike Tedlar bags, this absence of absorptive surfaces allows canisters to be cleaned up quickly, since outgassing and diffusion out of surfaces is unnecessary. In addition, the Tedlar itself contains plasticizers that may cause additional absorption and background contamination if applied too heavily during manufacturing.

For chemicals to remain in the gas phase, the internal canister surface must also be inert to minimize adsorption. Research efforts to create this level

of inertness have lead to the SUMMA, electropolished, fused silica lined, and deactivated glass canisters.

Types of Canisters and Their Differences

SUMMA Canisters

SUMMA Canisters were the first canisters to be used for EPA Method TO-14. These were originally developed by atmospheric chemists to study freons and other trace chemicals in the upper atmosphere. SUMMA canisters provide a thick Nickel/Chromium oxide layer on the surface that covers up the more reactive iron atoms that are also a constituent of 304 and 316 stainless steel. The liquid deposition technique essentially provides a ceramic layer that is not only inert, but is little affected by ozone and other oxidants in the atmosphere. This surface is very stable, providing many years of acceptable TO-14A and TO-15 compound recovery. Due to the ionic nature of the Nickel/Chromium oxide layer, it has been found that water vapor is needed to allow recovery of aromatic and polar compounds from SUMMA canisters. Generally, the amount of water found in ambient air is sufficient, except when sampling is to be performed under very arid conditions, or during cold winter months. For polar compounds, a minimum humidity of 40% is generally recommended. With SUMMA canisters, the sampling professional may want to add additional water to the canister prior to sampling during cold winter months. Although the relative humidity at 0°C may be 50%, this will drop to under 10% at 25°C in the laboratory. Once polar compounds are adsorbed onto the surface, it is unclear as to the ability to release them back into the gas phase by the post-sampling addition of water, so it is recommended to add water while the canister is still under vacuum prior to sampling. Generally, 50ul of purified water injected into a 6L canister will provide enough humidity.

Electropolished Canisters

Electropolishing of stainless steel creates a smoother, more reflective surface that improves the inertness of canister surfaces by lowering the surface area in contact with the sample while eliminating reactive iron on the surface. These

canisters can perform very well initially because they expose the sample to the same nickel/chromium oxide surface found in SUMMA canisters, but they are generally smoother than SUMMA surfaces, thereby reducing the overall surface area in contact with the sample. Unlike SUMMA polishing, a technique which adds approximately 600 to 1000 angstroms of oxide to the surface, the removal of material by electropolishing results in an oxide layer that is only 10-15 angstroms thick. This layer is too thin to prevent ozone from reaching the reduced metal below and initiating further oxidation. As additional sub-surface oxygen is added, the resulting stress will create bulging and cracking of the top layer, resulting in increased surface area over time. The cracked surface will also expose reactive iron which is just below the surface, causing further loss of canister inertness. Visually, this effect can be seen as a dulling of an electropolished surface that has been exposed to the environment over time.

Fused Silica Lined (Silonite®) Canisters

Another approach for providing an impermeable, ceramic layer that protects the reduced metal surface below is to add a layer of polymerized silicon dioxide, or fused silica. Silonite canisters provide a layer of fused silica that is similar to the oxide layer in SUMMA canisters, in that both are applied at a thickness of roughly 600 to 1000 angstroms. The fused silica in Silonite canisters has some added benefits over the oxide layer used to make SUMMA



Silonite coated (fused silica) canisters create a “GC-like” environment for sample storage, providing the most inert sampling solution available

canisters. First, silicon and oxygen form a less “ionic” bond than do chromium or nickel with oxygen. The result is a surface that is less likely to interact with EPA Method TO-14A or TO-15 compounds. The added inertness, in fact, makes it unnecessary to add water to the canisters, simplifying the sampling strategy under arid or cold sampling conditions. Secondly, Silonite is applied through a gas phase process, making it easy to achieve a high purity coating. The nickel/chromium oxide layer in SUMMA canisters is deposited while immersed in a low pH aqueous solution, which can become contaminated with iron over time. The chromium-containing solution is expensive to discard, so moderate iron contamination in the solution is usually tolerated, inherently creating inconsistencies in the abundance of surface-bound iron from one canister or batch to the next. In general, the more iron, the poorer performing the canister.

Silonite canisters are made by a very high energy chemical vapor deposition process that bonds the fused silica onto the metal surface. Although fused silica is colorless, a color generally forms due to a phenomenon call “Thin Film Interference” as light that bounces off the fused silica comes out of phase with the light passing through and bouncing off the metal surface below. Colors resulting from the interference pattern make a convenient means of determining the thickness of the coating inside the canister when viewed with a borescope.

Glass Canisters

The latest arrival on the canister scene is a new glass sampling canister called the Bottle-Vac™ sampler. This new technology (patent pending) utilizes deactivated amber glass bottles to tremendously lower the cost of canister manufacturing, resulting in a more economical price to the end user. These Bottle-Vac samplers meet every requirement of canisters, with a couple of technical advantages and disadvantages that need to be addressed. One significant advantage is that the amber bottles are cheap enough to be discarded after a few uses, so the filtering systems used to prevent particulate introduction into the canisters can be eliminated. Although the Bottle-Vac fittings use a Viton elastomeric seal, complete VOC elimination has been demonstrated even after exposure to high PPM



level samples, by vacuum baking these fittings using a standard canister cleaning system.

Bottle-Vac samplers are now becoming more widely accepted for Ambient Air analysis for EPA Methods TO-14A and TO-15. They are also ideal for making dilutions in the laboratory to perform analyses on sample concentrations well above the calibrated range. Finally, Bottle-Vac samplers are compatible with heated analysis on the Entech 7500 heated canister inlet, making them suitable for analysis of compounds that cannot be recovered from Tedlar bags or SUMMA canisters. They use the new Micro-QT Valve described later in this document.



The 16 and 32 oz Bottle-Vac™ glass canister samplers demonstrate vastly superior performance over Tedlar bags, and are fully reusable like other canisters

Large vs. Small Canisters

The first canisters to be introduced for EPA Method TO-14 were made from 9" diameter hemispheres that were cleaned and then welded at their mid-sections. The resulting internal volume was 6L, most of which was needed to reach down to 1-2 PPB detection limits with mass spectrometer detectors during the early 1980s. In order to conduct multiple analyses, as well as to allow sample retrieval by early laboratory preconcentrators that required a positive pressure in the canister, canisters were routinely pressurized with the sample in order to increase the effective volume collected. It is now understood that pressurized sampling causes water condensation inside the canister, resulting in loss of polar and reactive compounds. The condensate also promotes the formation of a white precipitate believed to be caused from polymerization reactions involving ozone and sampled polar compounds that dissolve into the condensate.

Today's laboratory analyzers are 100 times more sensitive than those used to initially develop method TO-14. Inlet systems no longer require pressurized samples in order to quantitatively extract multiple samples from canisters. In most cases, a 1.0-1.4L canister can be used to achieve full scan detection limits down to 0.05 PPB, or up to 10 times lower using SIM (Selected Ion Monitoring). Larger 6.0L canisters are still required for very long integrated sampling (2-7 days), and may have an advantage in reducing contamination when using packless valves (see section on Canister Valves).

Valves and "Inclusion Volumes"

There are several types of valves that have been used to control gas flow into and out of canisters. An understanding of the strengths and weaknesses of each type of valve is important in maintaining the highest integrity during sampling and analysis.

Packless Valves

Packless valves use a "metal to metal" seal to minimize sample absorption and carryover. Leakage out of the plunger assembly is prevented without the use of an elastomeric seal, either by using a welded bellows assembly or a set of flexible

diaphragms that form a compression seal at their edges. The most commonly used 6.0L canister valve is a Swagelok Nupro bellows valve, while both Parker and Swagelok make diaphragm valves that are often used. The Nupro bellows valve takes much less force to close reliably, but can be damaged by over-tightening. Once over-tightened, the valve becomes very difficult to seal, and often has to be replaced. Using the "two finger, one thumb" rule to tighten and loosen the valve allows these valves to be opened and closed hundreds of times without damage.

The sealing force using diaphragm valves must be transferred through three stainless steel diaphragms, the innermost one making the seal on a highly polished valve seat. This makes these valve more difficult to seal, but likewise makes them more difficult to damage. Placing a brass plug on the inlet of the canister will help to maintain a reliable vacuum when using diaphragm valves after canister cleaning. Although diaphragm valves are usually designed to allow disassembly and cleaning, the specific "set" that the diaphragms take during use generally requires them to be replaced with new diaphragms upon reassembly in order to create a proper leak-tight seal.

Quick Connect Valves

Unlike canisters with packless valves, canisters using quick connects can be attached to field samplers, laboratory analyzers, and cleaning systems without using tools. This makes them easier to use while saving valuable time. There is no concern over how much force to use while attaching the canisters to sampling lines, and there is no way to overtighten the valves during removal. Quick connects attach to other quick connects of the opposite gender, allowing both devices to be "closed" prior to attachment. This is extremely valuable when performing pressure or vacuum tests, as the mating quick connect and gauge can be pre-evacuated, resulting in very little potential for contamination. The small resulting volume that is introduced when making the connection is called the "inclusion volume". For packless valves, this volume could be as much as 1-2 mLs, depending on the volume of the test gauge, while for quick connects it is only 0.1cc, resulting in much less potential for contamination.

When using miniature quick connects, an external sealing cap should be used to provide better leak-free operation. These quick connects were not originally designed for vacuum applications, and even the heavier spring that Swagelok uses for this application is not always reliable to make a long-term seal. Also, since quick connects use elastomeric seals, they can become contaminated if higher concentrations than normal are stored in the canister. If contaminated, the canister should be cleaned, stored for a few days under vacuum, and then recleaned to eliminate residual contaminants.

Micro-QT Valves

A new valve has been introduced that works like a quick connect fitting, but was designed and optimized for canister sampling, to be more reliable under vacuum. The valve is very small, resembling a Quarter-inch Tube (QT) when assembled. Its geometry allows it to easily adapt to common samplers and inlets used for packless valves and quick connects. The entire valve is small and can be removed from the canister, allowing the valve to be vacuum baked in a standard canister cleaning system to remove all contaminants prior to reuse. The inclusion volume of this valve is 0.01cc, which is 10x less than miniature quick connects and several hundred times less than when making a connection to packless valves. The sealing spring is stronger than in the miniature quick connect to further prevent the potential for leakage under normal use. The valve comes in a standard QT version, or a QT2 version that allows "Around The Valve" or ATV sampling, which permits the quantitative capture of heavier semivolatiles without the chance for condensation in the valve. This new addition to the family of canister valves should allow more reliable sampling and analysis, and is compatible with robotic laboratory autosamplers (Entech 7405 and 7500) that have recently been introduced.

Gauges - Inline vs. External

Many canisters with packless valves have permanent compound gauges capable of reading the vacuum and pressure from 30"Hg vacuum to 30 psig. One reason for mounting a gauge directly onto the canister is to eliminate the air that would otherwise be introduced when testing the vacuum

or pressure through the packless valve. Miniature quick connect and Micro-QT Valves introduce so little air into the canister that an external gauge can easily be used without fear of adding measurable contamination to the canister.

Although the bourdon tubes used in mechanical gauges are stainless steel, their internal surfaces are generally not as clean and inert as the interior of the canister and canister valve. These gauges typically use NPT fittings and Teflon tape to make their connection to the canister. Teflon is known to absorb and outgas freons. Although each of these concerns may not result in significant losses of target compounds during a given sampling event, the presence of extra absorptive and adsorptive surfaces make a canister more difficult to clean, and can increase the carryover of contaminants from one sampling event to the next. This is especially true when a canister has experienced PPM level samples and is then returned to normal ambient air sampling. Since the inclusion volumes for quick connects and Micro-QT Valves are so small, external gauges should always be used to check the vacuum rather than risking added contamination.

Canister Cleaning

Canister cleaning is performed by attaching canisters to a vacuum manifold and then alternating between evacuation and filling with high purity UHP nitrogen or zero air to dilute out the canister impurities. A SUMMA canister's internal surface of nickel/chromium oxide is more effectively cleaned at room temperature, or at temperatures above 120°C. At mild temperatures of 50-100°C, the water vapor that was effectively shielding the surface and preventing aromatic and polar compound adsorption is driven off, causing this surface to be available to adsorb the more polar compounds. At temperatures above about 120°C, the polar and aromatic compounds no longer stick to this surface, and are driven out of the canister. It is for this reason that at least one cleaning cycle should be performed at room temperature prior to heating when cleaning SUMMA canisters.

Silonite (fused silica lined) and glass canisters do not exhibit this tendency. Any heating of the canister will only increase the elimination of higher

molecular weight contaminants because they do not rely on the presence of water to keep compounds from sticking to their surface. Heating Silonite and Bottle-Vacs to 100°C has shown complete transfer of diesel range compounds up to C25 to the gas phase where they can be recovered during analysis or eliminated during cleaning.

Bottle-Vac samplers can be prepared for sampling somewhat differently when Sub-PPB detection limits are not needed. This would include general indoor air quality and virtually all IH exposure monitoring. These bottles can be heated without fittings in an oven for one hour at 80°C, and then removed and flushed for five minutes using a tube dropped down into the bottle to flush the bottle with UHP nitrogen while the bottle is cooling. Attaching the fitting and pumping down the bottle with a dual stage diaphragm pump will prepare the bottle for field sampling. The preparation of one or more bottles to act as field blanks can be done to validate the preparation procedure.

Recovery Validation

SUMMA and Silonite canisters have a virtually unlimited lifetime unless severely abused. However, occasional testing of canister performance should be done to verify that the inside of the canister has not been compromised by the presence of foreign substances. Particles and/or heavy organics may build up enough in the canister to affect the recovery of larger compounds, and can also result in carryover to later sampling events as these surfaces slowly outgas their impurities. The quality of the canister can be re-evaluated about once every two years by filling the canister with a recovery standard. For canisters not meeting the required recovery (100%±25%), a more involved cleanup can be performed utilizing distilled water. The manufacturer of each canister type can be consulted for an exact procedure to accomplish the more extensive cleanup.

Only by regularly certifying canisters for recovery can this technique provide the kind of analytical accuracy that canisters are capable of. Users of canister technology should request certification from the laboratory or canister provider showing that the canisters used in their project have been properly tested for standard target compound recovery. The one to two week storage and recovery of the EPA Method

TO-14A list of 40 different compounds is a good way to show the overall inertness of a sampling canister, although laboratories should ultimately use the complete list of compounds that they are claiming to be able to successfully analyze.

Advancements in Canister Technology

Canister technology continues to improve, allowing more and more chemicals to be monitored with this highly accurate technique. New internal surface coatings such as Silonite have made it possible to include more reactive compounds like formaldehyde and hydrogen sulfide in the list of acceptable target analytes. Unlike the SUMMA surface that becomes more reactive at higher temperatures, the Silonite coating does not exhibit these properties, and actually allows higher molecular weight compounds to be recovered as the canister temperature is increased. In fact, nearly all compounds capable of passing through a GC column are candidates for sampling with Silonite coated canisters, as long as the laboratory's canister inlet system on their GCMS can handle these compounds at their specific concentrations. New and more advanced GCMS preconcentration systems are continually being developed to handle this growing range of canister-compatible compounds.

Reactive Compound Recovery

Reactive compounds such as hydrogen sulfide, mercaptans, and formaldehyde have demonstrated acceptable recovery in Silonite canisters. These compounds are generally not recovered from SUMMA canisters as their interaction with the oxide surface causes chemical alteration or permanent adsorption. The stability of both formaldehyde and H₂S is very heavily influenced by the presence of water vapor in the sample. At higher humidity (>70% RH), H₂S will drop off quickly even in a Silonite canister due to interactions with the thin film of water that forms on the canister's internal surface. H₂S should be stored at humidities under 30% RH if possible for maximum storage lifetime. The humidity can be lowered by starting the sampling with a canister that is one-half to two-thirds filled with dry UHP nitrogen, so that the resulting water content in the canister will be only half that at the sampling location.

Formaldehyde seems to be less affected by relative humidity. However, if the laboratory temperature is too much below the temperature of a given “humid” sampling site, then there may be condensed water in the canister. This will cause most or all of the formaldehyde to go into the condensed water. An easy fix is to make sure the canister is slightly warmed before analysis. The Entech 7500 auto-sampler is the only commercially available inlet that performs this pre-heating automatically. Currently, the 7500 can handle canisters from 40cc (glass vials) to 1400cc, providing heating from ambient to as high as 150°C.

Semivolatile Compounds

Semivolatile compounds, or SVOCs, are generally not recoverable from canisters. They tend to stick to surfaces at room temperature, whether or not those surfaces are inert. However, using an Entech 7405- or 7500-compatible Silonite canister, the molecular range recoverable with canisters can be extended to include SVOCs up to C25. Recoverable compounds include nerve agents, fatty acids, PAHs, pesticides, Mold VOCs, glutaraldehyde, and heavy industrial chemicals.

Sampling of heavy compounds may require some care to prevent transmission losses in the sampling train, since heating of the sampling devices cannot be easily done in the field. In most cases, the filters used in sampling VOCs cannot be used when monitoring SVOCs because these compounds will not pass through quantitatively. Also, time-integrated sampling cannot be done because the slow flow through these samplers will result in the loss of lower volatility compounds as well. Therefore, SVOC monitoring with canisters is currently limited to a quick grab sampling technique

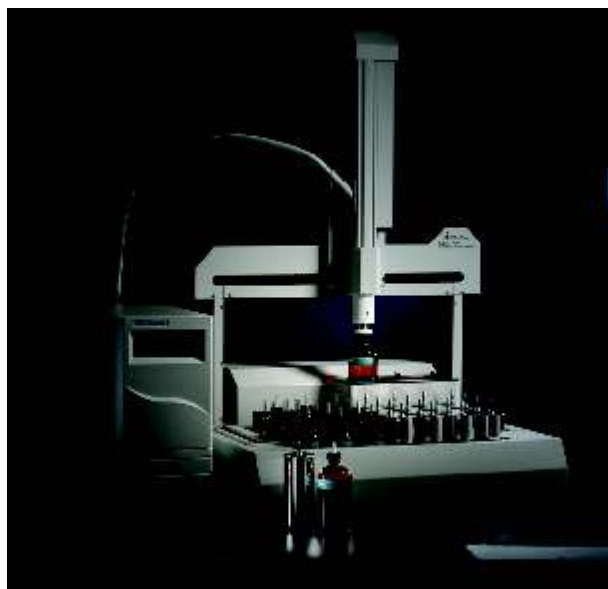
Micro-QT2 Valve canisters and Bottle-Vac glass canisters are both capable of “Around The Valve”, or ATV sampling. A small, removable plug-style valve allows the sample to flow directly into the canister without even having to pass through the valve. This completely eliminates any chance of adsorption in the valve, maximizing the quantitative transfer of the entire sample into the canister.

Silonite canisters currently compatible with SVOC monitoring and heated analysis on the 7500 autosampler include the following:

MC400QT2 (385cc)
MC600QT2 (600cc)
MC1400QT2 (1400cc).

Bottle-Vacs compatible with the 7500 include:

29-BV040A(40mL)
29-BV060A(60mL)
29-BV230A(8oz)
29-BV460A (16oz)
29-BV920A (32oz)



7500 Robotic Canister Autosampler preheating a 16oz Bottle-Vac glass canister prior to delivering a sample aliquot to the 7100A 3-stage preconcentrator during an extended TO-15 sample analysis by GCMS.