
Improving the Performance of Time Integrated Sampling of TO14 Compounds into Stainless Steel Canisters

Application Note: 902

Authors

Dan Cardin
Ken Langford
Vinay Shetty
Entech Instruments, Inc
Simi Valley, CA 93065

Abstract

Time integrated sampling of TO14 compounds into stainless steel canisters was evaluated under a variety of conditions. Four different flow controllers were tested at temperatures ranging from 4 deg. C to 40 deg. C to determine how well they maintained a constant flow rate despite changes in ambient temperatures. The three flow controllers with fixed restrictors maintained a relatively constant flow rate over the temperatures tested, while the flow controller with a variable flow restrictor showed an increase in flow of 1300% as the temperature was raised from 4-40 deg. C. The effect water has on recovery was also studied by sampling under dry conditions (RH=10%) and more normal conditions (RH=50%). Finally, individual parts that make up a passive canister sampler were evaluated to determine how each affects the recovery of TO14 analytes. Recoveries increased as flow path cleanliness improved and adsorptive surfaces were eliminated. The greatest improvements in recovery

were obtained by electropolishing the inside of inlet tubing, and by replacing the 2um stainless steel inlet filter with a deactivated glass frit.

Introduction

The use of both SUMMA and fused silica lined stainless steel canisters has become a standard technique for field collection of Volatile Organic Compounds (VOCs). Unlike sorbent tubes, the expected sample concentration does not affect how canister sampling is to take place, making it easier for the less technically experienced user to obtain accurate results. The sampling process requires no source of power as the canister uses its own vacuum to draw in an air sample. After filling, the valve is closed and the canister is returned to the laboratory for analysis. Acceptable holding times for EPA method TO14 compounds is typically 2 weeks or more.

Since VOC concentrations in air can vary due to changes in wind direction and fluctuations in source emissions, the determination of an average concentration is often desirable. This is accomplished using a passive flow controller capable of maintaining a constant fill rate into a canister over time. The constant fill rate allows the entire sampling period to be equally weighted so a true average concentration can be determined. Due to the tendency for sources and meteorological conditions to be on a diurnal cycle, 24 hour composite sampling into 6L canisters has become very common. The flow controller supplying the constant fill rate into the

canister must be stable as ambient temperatures fluctuate in order to avoid filling at a faster or slower flow rate during the sample integration period.

Substantial attention has been given to the interior surface of stainless steel canisters since the EPA first introduced Method TO14 over 15 years ago. SUMMA passivation provides an inert nickel/chromium oxide electropolished surface on the inside of canisters, while new coatings consisting of inert fused silica (eg. Silcosteel and Silonite™) provide an environment suitable for storing polar and sulfur compounds as well. However, little attention has been given to surfaces the sample is exposed to in the inlet system leading up to the canister. Even though the residence time in the inlet is shorter than the holding times in the canister before analysis, the narrow flow path found in passive samplers and inlet lines allows maximum exposure to these surfaces and ample opportunity for adsorptive or absorptive losses to occur. The general practice of “all stainless components” helps to reduce the adsorption experienced with other metals (copper, brass, aluminum) while eliminating the absorption that can occur into less dense polymers (Teflon, Tedlar, etc.). However, there may be a need to further increase the inertness of stainless steel surfaces using special deactivation techniques, such as electropolishing or fused silica lining. High quality 300 series stainless steel is made up of several different metals which differ in their tendencies to adsorb VOCs. The more reactive of these metals, iron, can be quite adsorptive if left on the surface. Electropolishing is an extraction process that preferentially removes the more reactive metal atoms in stainless steel, leaving a 40-500Å layer of less reactive nickel/chromium oxide. During sampling, this oxide layer is further isolated from the sample by a thin layer of water that forms on the surface. The oxide layer can be completely shielded by water as long as the surface is relatively smooth.

Passive canister sampling systems have 4 basic components: an inlet line usually made of 1/4” stainless steel tubing, a filter to eliminate particulates, a restrictor, and a back pressure flow regulator to provide the restrictor with a constant pressure drop while the canister is being filled. These components are shown in Figure 1. The

restrictor is commonly a sapphire orifice pressed into a stainless steel compression fitting. The back-pressure regulator maintains approximately a 0.5 to 1 psi pressure drop across the restrictor until the canister is within 1-2 psi of reaching atmospheric pressure, after which the regulator can no longer maintain a 1 psi differential across the orifice, resulting in a drop in flow rate. Flow rates and sampling times are usually chosen so that the filling process is stopped before the sample flow begins to drop off in order to obtain a time weighted average. To prevent the introduction of dust and particulates during sampling, a filter is used on the inlet of the flow controller. Stainless steel filters have been used for this purpose, although the potential adsorption of TO14 compounds has not been well investigated. Also, the cost of the filter is significant and is not likely to be considered disposable. This may cause the filter to be used long after particulates have gathered on the inlet side of the filter, changing the adsorptive/absorptive nature of the filter. An alternate filter design based on a disposable glass frit may provide a better short and long term solution.

Temperature Effects on Flow Rates

Flow vs Temperature data was collected for 4 different flow controllers; Veriflo models SC423 and SC423XL(Super 4), the Autoflow FC5104, and the Entech CS1200E. Each flow controller was calibrated to provide 3.3cc/min at 20 deg. C corresponding to a 24 hour fill time for a 6L canister.

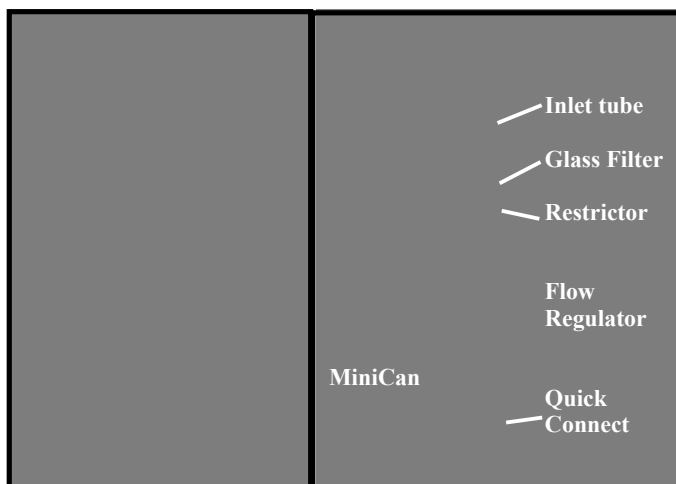


Figure 1 - CS1200E and 6L Silonite Canister (left). Flow controller components disassembled (right).

Transfer lines (3'x1/8") were attached to the inlet and outlets of the flow controllers allowing them to be placed in a temperature controlled enclosure while maintaining access to the vacuum canister and inlet flow meter. An Ashcroft 6" high-accuracy compound gauge (ANSI ref to 0.25% accuracy) was used to monitor canister pressure during sampling, while an Alicat model H12-10CCM flow meter displayed flow rates. After initial calibration at 20 deg. C, the temperature of each flow controller was brought to 4, 30, and 40 deg. C and the flow rates measured once temperature equilibration was achieved.

Figures 3 and 4 show the temperature stability of the 4 flow controllers at temperatures from 4 to 40 deg. C. Figure 3 shows a dramatic temperature effect on flow rate for the Veriflo SC423 variable flow rate passive sampler. Flow variations with this model are possibly due to expansion and contraction of the Viton elastomer in the needle valve used to control the flow rate. Flow rate changes due to ambient temperature fluctuations result in disproportionate weighting of daytime and nighttime sampling. If nighttime temperatures fall below 15 deg. C, for example, a 6L canister would be filled in just 6-12 hours of sampling, rather than the 24 hour rate for which it was calibrated. This prevents a true time-weighted average from being obtained unless a temperature controlled environment is provided.

Figure 4 shows 3 flow controller models having fixed restrictors consisting of a sapphire orifice pressed into a stainless steel fitting. The low coefficient of

Figure 2 - Pressure regulation diaphragms for Veriflo SC423XL (left) and Entech CS1200E (right).

thermal expansion in the sapphire orifice allows flow rates to remain relatively constant. Expansion and contraction of the small, sealing o-ring in the pressure regulator probably results in the small flow rate changes observed.

Although the flow deviations shown are small enough to allow all three models to be considered for non-temperature controlled sampling, the CS1200E was the only model to maintain less than a 10% flow change relative to the 20 deg. C calibration temperature. A total flow deviation of greater than 10% was not observed for the CS1200E until temperatures fell below -20 deg. C.

TO14 Compound Recovery Testing

TO14 compound recovery was validated for the CS1200E using several different configurations to determine conditions that would yield the optimum performance. A 30 PPB TO14 Standard was made daily in a Tedlar bag by diluting a 1 PPM Spectra Gas stock cylinder using an Entech 4600 Dynamic

Figure 3 - Deviations in flow rates with temperature. Veriflo variable flow sampler shows significant flow deviations with even minor temperature fluctuations.

Figure 4 - Fixed restrictor samplers show better temperature stability than variable flow models. The larger diaphragm in the CS1200E provides control to better than +/- 5% from 4 to 40°C

Diluter. The Tedlar bag was required to provide an atmospheric pressure sample to the inlet of the CS1200E flow controller. Three CS1200E flow controllers were connected via a 1/4" Swagelok cross and a 1/16" x 4" Teflon tube that protruded through the wall of the Tedlar bag to sample directly from the center of the bag. Three flow controllers allowed each experiment to be conducted in triplicate and averaged to reduce statistical variations in the data. The standard was drawn through the CS1200E flow controllers and into 0.4L MiniCans over 4 hours at a rate of 1.2 cc/min. This corresponds to a flow rate of approximately 35% of that required to fill a 6L canister in 24 hours (3.5 cc/min). After the 4 hour sampling, a fourth evacuated MiniCan was filled directly without flow control (5 seconds), representing a "100% recovery" sampling from the bag. The four MiniCans were analyzed using an Entech 7100 Preconcentrator and a 21-Position 7032 MiniCan Autosampler connected to an HP 5973 GCMS. MiniCans were pressurized with a 50 PPB fluorobenzene standard using the automated surrogate standard spiking feature in the 7032 autosampler. From each MiniCan, 100 cc were preconcentrated and injected onto a 60m, HP1, 0.32mm ID column with a 1um film and analyzed by scanning from 33 to 270 amu approximately 3 times per second. The response from the 3 CS1200E filled canisters were averaged and then normalized using the response from the quickly filled "Grab" sample to provide a percent recovery determination. Canisters were cleaned after analysis using an Entech model 3110 canister cleaning system by cycling between humid N2 pressurization and high vacuum evacuation. Recovery through stainless steel and glass filters, passivated and electropolished inlet tubing, and Nupro valve-quick connect valves were tested by keeping the flow controllers consistent and changing 1 element at a time when possible. Recovery using a 10% relative humidity standard was tested by only injecting 7 ul of water into a 4L Tedlar bag instead of 35ul needed to achieve 50% relative humidity.

Effects of Inlet Electropolishing

Stainless steel inlet tubing is typically used to raise the air inlet from several inches to several feet above the top of the canister. The top of the tube is usually

curved 180 degrees at the end, pointing down to prevent rain water or settling dust to enter the flow path. To test the effects of providing an ultra clean, electropolished surface, 6 tubes were first passivated to eliminate active surface metals and oxides. Three inlet tubes were then electropolished on the inside to provide a "SUMMA Like" surface. The tubes were placed on 3 CS1200E samplers in two different sampling experiments to compare recoveries using the sampling procedure described previously.

Table 1 and Figure 5 show the results of the recovery tests. With the non-electropolished inlet tubing, substantial loss of analyte begins to occur at the trimethyl- and dichlorobenzenes. With a required accuracy of +/-30% for method TO14, a sampling accuracy of better than +/-20% should be obtained to allow for errors during the analysis. Therefore, the last 4-5 compounds in the TO14 list would show a negative bias if they were sampled using a non-electropolished inlet. The final 2 compounds in the list are just barely classifiable as VOCs since they have boiling points over 220 deg. C. They appear to adsorb quite readily to active surfaces, such as the thick oxide coating on non-electropolished tubing.

Stainless Steel vs Glass Frit Dust Filtering

Dust should be removed from the sample before introduction into the canister or flow controller to prevent activation of surfaces or blockage of restrictor orifices. Nupro 2um stainless steel filters have been used for this purpose because of their

Figure 5

Table 1 - TO14 Recovery Data using CS1200E Passive Samplers

Test #	% Rel Humidity	Inlet Tubing	Filter	Valve
A	50%	None	None	Quick Connect
B	50%	Non-Electropolished	None	Quick Connect
C	50%	None	Nupro 2um Stainless	Quick Connect
D	50%	None	Glass 5um frit	Quick Connect
E	50%	Electropolished	Glass 5um frit	Quick Connect
F	50%	None	None	Nupro Bellows
G	10%	Electropolished	Glass 5um frit	Quick Connect

seals can reduce absorptive surfaces that can cause sample loss. Although not necessarily electropolished on the inside, the valves are clean and provide an inert flow path in and out of the canister.

Quick connect fittings are an attractive alternative to Nupro valves in certain cases as they make connection and removal from sampling and analytical systems much faster. Small o-rings provide leak-free seals allowing connections to be made with virtually no introduction of air during the connection process (<0.1cc). Recently, a new vacuum tight version of the Swagelok miniature quick connect has allowed them to be used on canisters in place of the Nupro valve. Although quick connects are not “packless”, the sealing o-ring is very small and is mostly concealed from the sample. The small, straight-through flow design of the mini quick connect fitting has much less volume than the Nupro valve and may have some advantages in reducing sample adsorption.

Table 1 shows the relative recoveries of TO14 compounds obtained using quick connect valves vs Nupro Valves. Even though the slow sampling flow rate provided ample exposure to the quick connect’s internal o-ring, no discernable sample loss is evident. This result is not unexpected considering the 4 passive flow controllers tested in this study all have internal o-ring seals that are exposed to the sample. As long as the packing is small and grease-free, the presence of an elastomer (Viton, Kel-F, Kalrez) does not appear to affect TO14 compound recovery.

Humidity Requirements for TO14 Recovery

It is well known that water plays an important role in VOC stability in a SUMMA, or electropolished canister. The VOCs in the canister need to be shielded from the nickel-chromium oxide on the surface in order to remain unreacted and in the gas phase. Although not tested here, polar or oxygenated VOCs have even a greater requirement for water vapor to be present. In a dry environment, the oxide surface may act as a weak adsorbent, removing polar compounds from the sample. Similarly, the flow path of passive samplers is primarily nickel-chromium oxide that could adsorb

Figure 6

availability. Like any fritted filter, the Nupro filter provides a lot of surface area that may result in sample loss if the surface contains active sites. Due to the cost of these filters, they are often reused over the lifetime of the sampler without concern for the potential loss in inertness created by particles that have accumulated on the inlet of the filter.

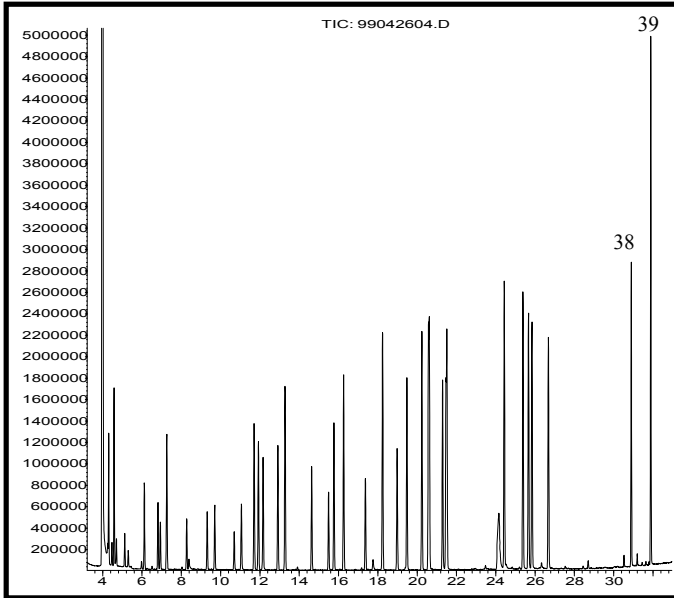
An alternate design based on a disposable glass frit allows regular replacement to provide a “like -new” flow path over the life of the sampler. Inherently more inert than stainless steel, these glass filters are further deactivated using a silanizing reagent to cover up free silanol (SiOH) functionalities on the surface of the glass.

Figure 6 shows the difference in recovery using Nupro stainless steel vs deactivated glass filters. There was a general decrease in TO14 compound recovery starting at about benzene and continuing through the heavier VOCs, although the most dramatic loss again occurred with the trichlorobenzene and the hexachlorobutadiene. These last two compounds did not meet the recovery criteria of method TO14 using Nupro filters, while deactivated glass filters allowed 90% recovery or better as compared to the direct sampling.

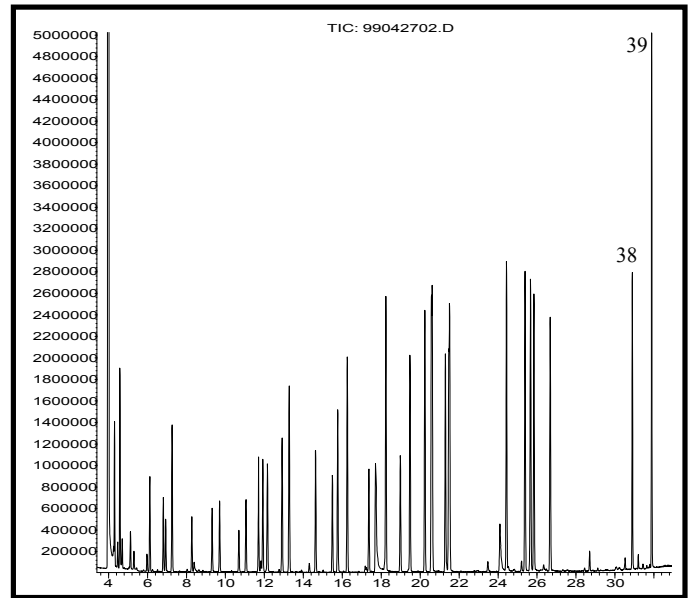
Nupro Valve vs Quick Connect Valves

Nupro bellows valves are the most commonly used valve when sampling into spherical stainless steel canisters. The bellows design eliminates the need for an elastomer or “valve packing” to make a seal along the valve stem. Therefore, they are referred to as “packless” valves. The elimination of elastomeric

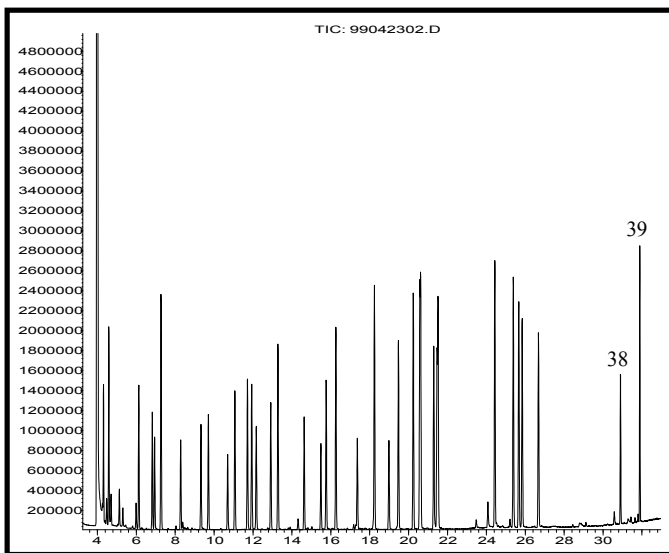
Chromatograms of TO14 Standard Collected Through CS1200E Canister Sampler



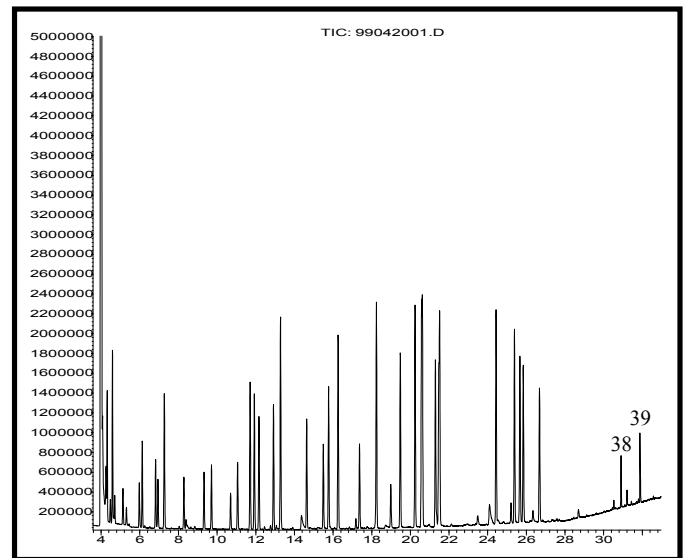
Non-Restricted sampling of 30 PPB TO14 Standard into 400cc Silonite Coated Canister. Quick sampling without flow control represents maximum achievable recovery.



30 PPB TO14 Standard Filled through 1/4" OD x 7" L electropolished inlet tubing and glass filter into 400cc Silonite coated MiniCan at 1.2 sccm. The canister valve is integrated into a miniature quick connect fitting.



30 PPB TO14 Standard Filled through a 2um Nupro stainless steel filter into a 400cc Silonite coated MiniCan at 1.2 sccm..



30 PPB TO14 Standard Filled through a passivated (non-electropolished) 1/4" OD x 7" L stainless steel inlet tube into a 400cc Silonite coated MiniCan at 1.2 sccm.

For more information, please contact us:

ExpotechUSA
10700 Rockley Road
Houston, Texas 77099
USA

281-496-0900 [voice]

281-496-0400 [fax]

E-mail: sales@expotechusa.com

Website: www.ExpotechUSA.com