

## Expanding the Molecular Weight Range of Whole Air Sampling with Stainless Steel Canisters using Active SPME Sample Preparation and GCMS Analysis

### Application Note:

# A-3732-03

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### Abstract

A new preconcentration technique utilizing "Active SPME" has eliminated the deficiencies found with the canister technique, allowing recovery of heavy molecular weight compounds through C24 while being more compatible with thermally labile compounds than thermal desorption tubes. The multi-trap preconcentrator utilizes a "flow through" SPME stage where sample is actively introduced across the SPME film, eliminating the matrix and temperature variations found in classical "diffusive" SPME. Compounds from C10 and heavier are retained on the Active SPME stage, while lighter compounds are allowed to continue to a cold Tenax<sup>®</sup> trap for quantitative recovery of C2 and heavier compounds. Water is eliminated using a direct vapor to solid deposition in a cold trap, thereby avoiding loss of water soluble polar compounds. System flows are controlled using Dean's Switching rather than classical rotary valves, eliminating exposure to plastic rotors known to cause carryover and recovery issues. Data will be presented showing both the reproducibility and overall performance for EPA Method TO15 compounds, as well as the molecular weight extension provided by the Active SPME stage by comparing recoveries of a C10-C24 standard by direct GC injection verses preconcentration from commonly used 1.4L field sampling canister.

### Introduction

Whole air sampling into Stainless Steel Canisters



**7150 3-Stage Preconcentrator shown on Agilent 7890 GC.** Distance to GC column after preconcentration is minimized, providing enhanced recovery of semi-volatiles.

has been used to perform air monitoring of PPBv and sub-PPBv level volatile compounds in air for more than 30 years. The first EPA Method using canisters, Method TO-14, was first introduced in 1982, utilizing 6L SUMMA Canisters to collect whole air samples either by performing a rapid "Grab" sample in just a few seconds, to collecting a time integrated sample over 24 hours using an external flow controller. Since then, advances have been made to the art and science of whole air monitoring with canisters, including the introduction of a second EPA Method (TO-15, 1994) that expanded the range of amenable compounds, as well as the introduction of canisters with a fused silica lining that proved to be more inert than the original SUMMA canisters which utilized a NiCrOx lining.

Whole air sampling and analysis has several advantages over thermal desorption techniques, including recovery of thermally labile compounds and extremely low blank levels. Sampling is very easy as there is no need to measure the sample volume in the field. In fact, the amount of sample collected in the field does not even have to change with expected analyte concentrations, even with the very limited dynamic range of today's GCMS systems, since the

actual analytical volume introduced into the GCMS can be decided in the laboratory later. Furthermore, although the canister technique still relies on trapping and thermal desorption in the lab to concentrate the sample enough for measurement down to sub-PPB levels, this trapping system is fully blank and recovery checked prior to running samples, a process that would be far too expensive to perform on every thermal desorption tube sent to the field for sample collection. One of the few advantages remaining for field deployable thermal desorption tubes has been their recovery of higher molecular weight compounds, due both to the higher temperatures used during thermal desorption, and to the higher split flow rates used during sample preparation prior to GCMS injection. Although these higher molecular weight compounds were often limited to the more stable aromatic and aliphatic hydrocarbons, their recovery has sometimes been necessary to monitor for diesel range chemicals in air. The higher molecular weight range of tubes verses the more complete recovery of polar, non-polar, and reactive chemicals under C13 using canisters required the investigator to choose between them based on the information they were most interested in.

The system presented here has virtually eliminated the molecular weight range advantages of thermal desorption tubes, while maintaining the ability to recover thermally sensitive compounds that are not recovered from strong adsorbent traps. This has been accomplished in the following way:

1. The canister's interior surface has been changed to fused silica, allowing heating without catalytic loss of compounds which was typical on metal oxide SUMMA surfaces.
2. C10-C25 compounds are trapped on an Active SPME stage, requiring a much lower temperature for recovery compared to direct trapping on a thermal desorption trap.
3. Water is eliminated downstream of the Active SPME stage by utilizing a direct vapor to solid transition that allows extremely water soluble compounds to be recovered.
4. C2-C12 compounds are collected on a cold Tenax® trap after the cold dehydration trap, allowing up to 1000cc to be collected without loss of EPA Method compounds.

5. The Active SPME trap is cooled to -50C, allowing the Tenax® trap to desorb first to the Active SPME trap for dynamic refocusing, permitting splitless injection of the sample to the GCMS.

## Experimental

Standards containing the volatile TO-15 Compounds were blended from two 1PPM stock cylinders (Scott Specialty Gases) along with UHP Nitrogen to create 10PPB working standards in 6L Silonite™ coated canisters (Entech Instruments, Inc, Simi Valley, CA) using an Entech 4600A Dynamic Diluter. Canisters were precleaned using the Entech 3106 and 3120 canister cleaning systems to remove contaminants and to prepare the evacuated canisters with initial vacuums below 50mtorr.

A 1000ng/ul C10-C24 Hydrocarbon Standard in Methanol (Supelco) was diluted down to 50ng/ul in order to make direct injections into a split/splitless injector operated at 300°C on an Agilent 7890/5975 GCMS (Palo Alto, CA) in order to compare recovery of the same mix introduced to the GCMS through the 7150 Preconcentrator. A volume of 1.2ul of the original stock was injected directly into a 1.4L Silonite™ coated MiniCan™ with it's valve removed to insure complete transfer into the canister. The Entech Micro-QT™ valve was replaced, and the canister was pressurized to 15 psig, resulting in a mixture containing 46ng/100mL. For purposes of comparison, 100mL were drawn into the 7150 as described below.

The VOC and SVOC standards above were run through the 7150 using two different methods in order to avoid the interference created by the large methanol peak required as a carrier for the C10-C24 standard. Once calibrations are obtained, a single analysis can be used for analyzing actual samples over the entire range of approximately C3 - C24. The GC column was obtained from Agilent (HP1, 60m, 0.32mmID, 1um film). The MS was operated full scan.

The 65 component TO-15 analysis and calibration curve were generated by preconcentrating from 10cc to 1000cc of the 10PPB standard created in the Silonite™ 6L canister. The 6L canister was analyzed at room temperature. Conditions were as follows:

	Trapping	Water Bakeout	T1 Refocus	Desorb	Bakeout
T1 Active SPME Trap	50°C	50°C	-52°C	230°C	220°C
T2 Dehydration Trap	-40°C	160°C	60°C	60°C	150°C
T3 Tenax® Trap	-50°C	-50°C	200°C	200°C	210°C

The C10 - C24 data was generated by preheating the 1.4L Silonite canister to 150°C, and then withdrawing 100mL through the 3-stage 7150 using the following conditions:

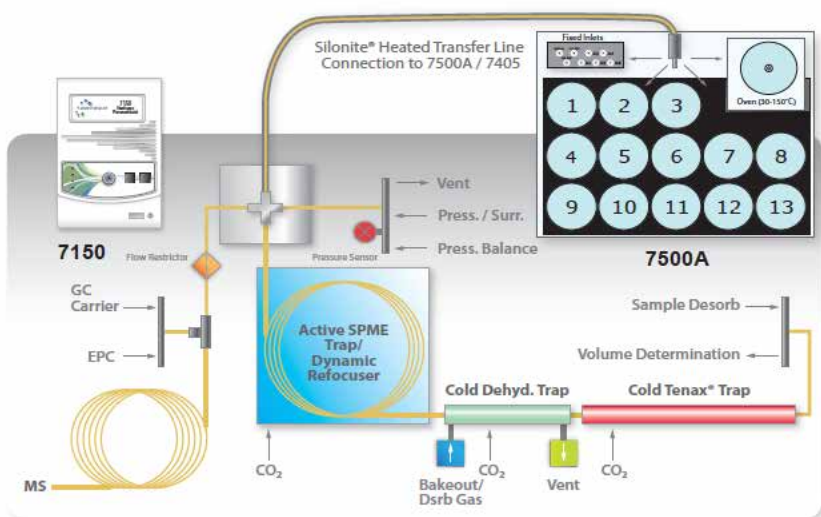
	Trapping	Water Bakeout	T1 Refocus	Desorb	Bakeout
T1 Active SPME Trap	50°C	50°C	-52°C	230°C	220°C
T2 Dehydration Trap	-40°C	160°C	60°C	60°C	150°C
T3 Tenax® Trap	-50°C	-50°C	200°C	200°C	210°C



**Figure 2** Bottle-Vac™ samplers can be used for both gas-phase and liquid/solid sampling. These samplers can be placed directly in a 7500A Autosampler tray along with Silonite Minicans™.



**Figure 1** 1.4L and 600cc Silonite™ coated MiniCan™ sampling canisters. MiniCans offer a no power, “pump free” sampling solution using an internal vacuum. The interior has a GC-like Silonite™ coating ideal for storing highly reactive compounds such as ammonia gas and phosphorous containing CWAs, allowing heating to as high as 150°C with very little increase in reactivity.



**Figure 3** 7500A/7150 Flow path. Rotary valves have been eliminated from the flow path to reduce the potential for leaks and contamination. The first trap in the system is an Active SPME trap which greatly extends the molecular weight range, while providing a dynamic refocuser when back desorbing the Tenax trap. CO<sub>2</sub> is used rather than liquid nitrogen, reducing the cost per analysis by roughly 10 fold.



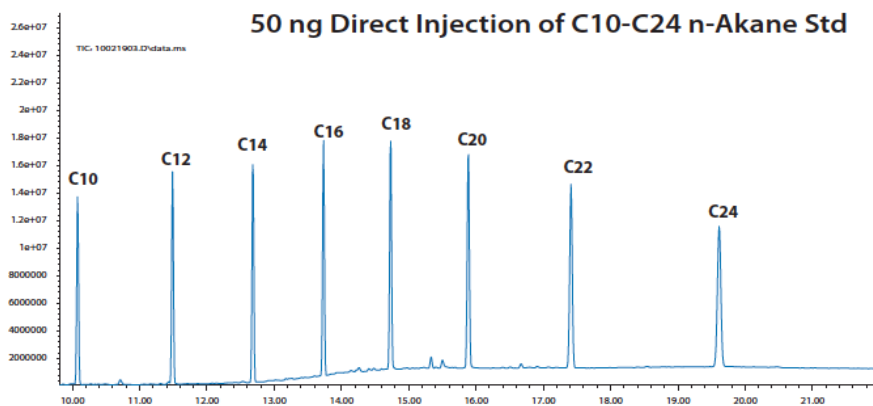
**Figure 4** 7150 Preconcentrator shown on an Agilent 7890/5975. The compact design was accomplished by using Dean's Switching rather than rotary valves for flow control. Separation of electronics and pneumatics modules allow the 3-stage trapping system to connect very close to the GC oven for improved SVOC recovery, while creating ideal modularity for an enhanced support strategy.

## Discussion

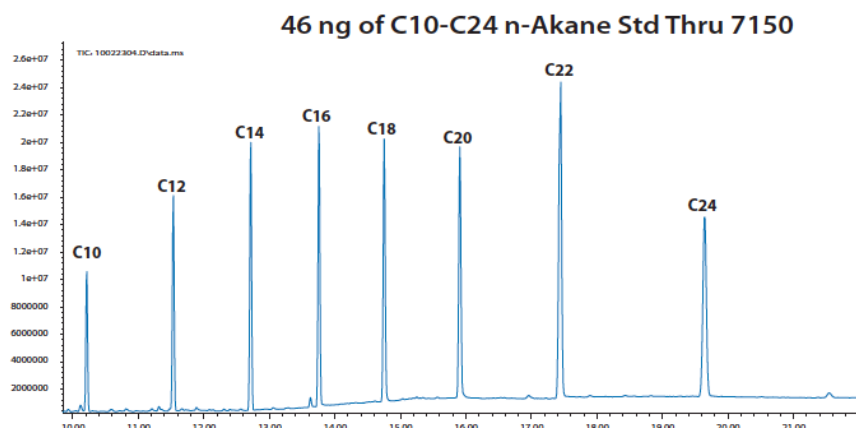
Figures 1 and 2 (p2) show the sample containers with the low volume, low thermal mass Micro-QT™ valves that allow much more rapid heating than classical canister valves. Proper heating of valves and a streamlined, inert flow path is critical for proper transfer of SVOCs into and out of the canister. Figures 3-4 (p2) show the picture and flowpath of the 3-stage, Dean's Switching 7150 Preconcentrator. SVOCs are effectively retained on the Active SPME trap, preventing any exposure to the down stream adsorbent trap. This is critical for a number of reasons. First, it allows recovery of the wide molecular weight range without having to overheat the traps and thermally stress the sampled chemicals. Secondly, preventing the SVOCs from reaching the high surface area adsorbent trap virtually eliminates the carryover inherent when exposing heavy SVOCs to an active adsorbent. Finally, keeping heavy compounds off of the Tenax® trap, and subsequent backflushing during bakeout is expected to increase the lifetime of the Tenax® adsorbent. To compensate for the fact that the T3 Tenax® trap is too large to directly allow a splitless injection into the GCMS, the T1 Active SPME trap is cooled to -50C to recombine the VOCs with the SVOCs after water removal in T2.

Figures 5-6 show the comparison of the direct injection of the C10-C24 standard, compared to the recovery through the 7150. The recovery of most of the compounds shown were actually better through the 7150, probably because of the expansion of the methanol and partial loss of standard upon injection into the 300 deg C injection port. The C22 hydrocarbon showing approximately 30% too high in the 7150 run relative to the other hydrocarbons was found to be due to the more rapid heating of the 1.4L MiniCan™ than the Micro-QT™ valve, causing a temporary coldspot and subsequent enrichment near the outlet of the canister. The heat distribution in the 7500A oven is being changed to eliminate this artificial enrichment.

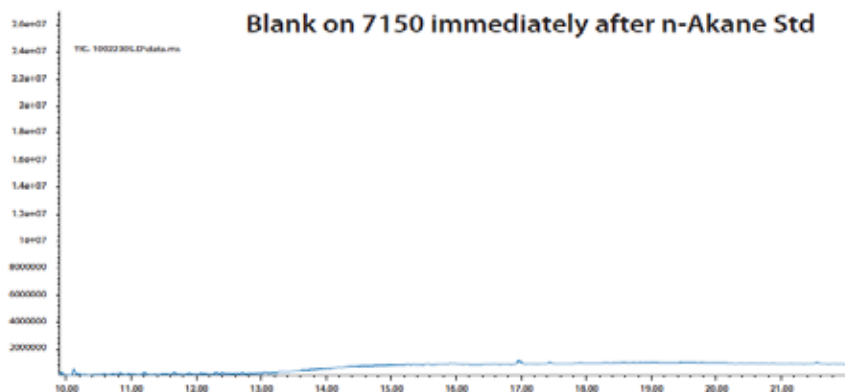
Figure 7 demonstrates the advantage of eliminating rotary valves and preventing exposure of the heavy SVOCs to the high surface area adsorbent trap. No carryover is visible in the blank run following the 46 ng injection.



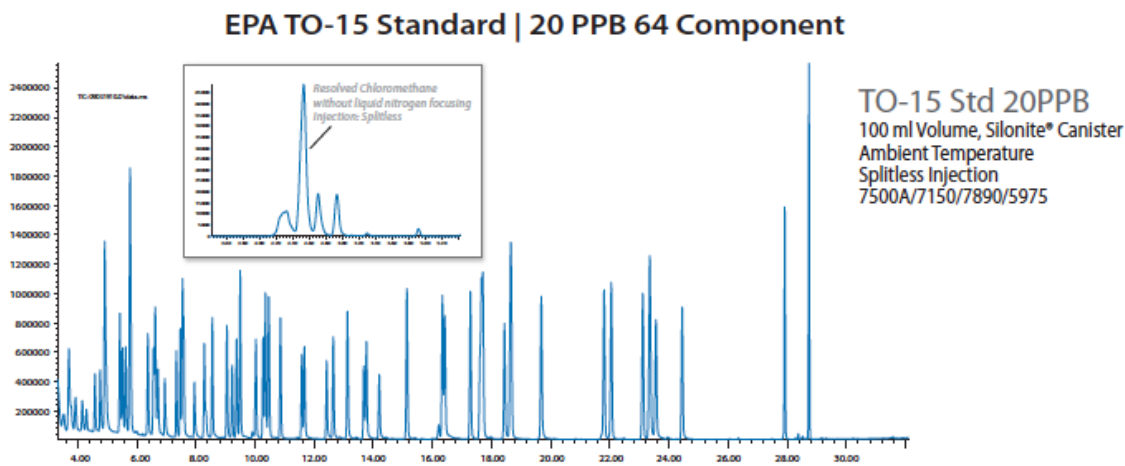
**Figure 5** Direct injection of 1ul into a 300 deg C injector on a 7890/5975 to show response indicating 100% recovery of the C10-C24 standard.



**Figure 6** 100cc sampled out of a 150 deg C Silonite canister containing a gas phase standard prepared to 46ng/100cc. Recovery of entire C10-C24 range is comparable to direct injection, except for a larger C22 response probably due to artificial enhancement during the canister heating process. This anomaly has been addressed and will be remedied in future oven designs.



**Figure 7** 100cc of blank nitrogen analyzed directly after a 46ng injection of the C10-C24 standard showing no detectable carryover.



**Figure 8** TO-15 analysis, 250cc, 10PPB, 64 Component Standard, 7500A/7150/7890/5975



## 7150 Calibration Curve (0.40 ppb to 20 ppb) Relative Response Factors (RRF)

Compound	0.40 ppb	1.0 ppb	2.0 ppb	4 ppb	10 ppb	20 ppb	Ave RRF	%RSD
Propene	6.93	6.49	6.87	6.18	5.54	5.84	6.31	8.9
Dichlorodifluoroethane	1.96	1.91	1.77	1.58	1.42	1.32	1.66	15.8
Chloromethane	6.26	5.85	6.11	5.63	4.92	5.23	5.66	9.1
Dichlorotetrafluoroethane	1.42	1.39	1.40	1.29	1.21	1.18	1.32	7.9
Vinyl Chloride	4.94	4.81	5.07	4.63	4.34	4.39	4.70	6.3
1,3-Butadiene	3.91	3.59	3.85	3.63	3.37	3.40	3.62	6.1
Bromoethane	6.44	6.23	6.49	6.02	5.56	5.64	6.06	6.5
Chloroethane	4.52	4.41	4.56	4.18	3.90	3.95	4.25	6.8
Bromoethene	6.77	6.82	7.15	6.66	6.29	6.26	6.66	5.1
Trichlorofluoromethane	1.88	1.84	1.94	1.81	1.71	1.67	1.81	5.6
Acetone	1.13	0.99	1.04	0.95	0.92	0.83	0.98	10.7
Isopropyl Alcohol	1.24	0.90	1.06	0.90	0.85	0.84	0.96	16.1
1,1-Dichloroethene	1.04	1.03	1.06	0.99	0.95	0.94	1.00	4.9
Trichlorotrifluoroethane	1.22	1.22	1.29	1.19	1.14	1.12	1.20	5.3
Allyl Chloride	2.57	2.62	2.69	2.47	2.39	2.37	2.52	5.1
Methylene Chloride	5.80	5.20	5.30	4.82	4.59	4.51	5.03	9.8
Carbon Disulfide	1.72	1.65	1.72	1.59	1.52	1.50	1.62	5.9
trans-1,2-Dichloroethene	8.03	7.87	8.47	7.81	7.48	7.31	7.83	5.2
Methyl tert-Butyl Ether	1.48	1.42	1.54	1.43	1.39	1.38	1.44	4.2
Vinyl Acetate	1.24	1.23	1.37	1.29	1.30	1.31	1.29	3.9
1,1-Dichloroethane	1.09	1.04	1.09	1.01	0.97	0.95	1.03	5.6
2-Butanone	1.86	2.08	2.29	2.17	2.19	2.21	2.13	7.1
Hexane	8.10	8.07	8.40	7.89	7.53	7.60	7.93	4.2
cis-1,2-Dichloroethene	7.40	7.33	7.79	7.21	6.95	6.94	7.27	4.4
Ethyl Acetate	1.00	1.08	1.18	1.11	1.13	1.15	1.11	5.6
Chloroform	1.14	1.12	1.19	1.11	1.06	1.05	1.11	4.8
Tetrahydrofuran	2.25	2.25	2.43	2.28	2.24	2.34	2.30	3.2
1,1,1-Trichloroethane	1.14	1.12	1.16	1.11	1.06	1.05	1.11	3.7
1,2-Dichloroethane	7.97	7.79	8.08	7.54	7.33	7.22	7.65	4.5
Benzene	1.91	1.78	1.79	1.67	1.60	1.56	1.72	7.8
Carbon Tetrachloride	1.15	1.13	1.19	1.12	1.08	1.07	1.12	4.0
Cyclohexane	8.65	8.65	9.02	8.51	8.16	8.12	8.52	4.0
2,2,4-Trimethylpentane	6.49	6.52	6.74	6.24	5.97	5.93	6.32	5.1
Heptane	1.44	1.44	1.49	1.35	1.32	1.32	1.39	5.1
Trichloroethene	1.82	1.82	1.86	1.73	1.67	1.68	1.76	4.5
1,2-Dichloropropane	1.56	1.52	1.56	1.45	1.42	1.43	1.49	4.3
1,4-Dioxane	1.40	0.91	0.75	0.70	0.72	0.76	0.87	30.9
Bromodichloromethane	2.63	2.73	2.84	2.67	2.64	2.65	2.69	3.0
cis-1,3-Dichloropropene	2.27	2.32	2.42	2.29	2.30	2.35	2.33	2.3
4-Methyl-2-pentanone	2.71	2.61	2.73	2.63	2.77	2.80	2.71	2.8
trans-1,3-Dichloropropene	1.92	1.86	2.10	2.02	2.06	2.12	2.01	5.1
Toluene	5.06	5.14	5.23	4.86	4.78	4.72	4.96	4.2
1,1,2-Trichloroethane	1.69	1.74	1.77	1.63	1.61	1.62	1.68	4.1
2-Hexanone	1.06	1.17	1.28	1.21	1.26	1.33	1.22	8.0
Dibromochloromethane	2.46	2.64	2.80	2.66	2.70	2.69	2.66	4.2
Tetrachloroethene	2.67	2.68	2.76	2.53	2.46	2.41	2.59	5.4
1,2-Dibromoethane	2.26	2.44	2.50	2.33	2.34	2.36	2.37	3.5
Chlorobenzene	5.19	5.20	5.15	4.79	4.60	4.53	4.91	6.3
Ethylbenzene	7.90	8.05	8.14	7.66	7.38	7.27	7.73	4.6
m&p -Xylenes	3.25	3.30	3.33	3.10	2.89	2.89	3.13	6.3
Styrene	4.27	4.66	4.72	4.59	4.59	4.62	4.58	3.4
o-Xylene	6.23	6.36	6.37	6.04	5.74	5.60	6.06	5.4
Bromoform	2.86	3.27	3.42	3.36	3.31	3.29	3.25	6.1
1,1,2,2-Tetrachloroethane	3.58	3.73	3.97	3.77	3.71	3.72	3.75	3.4
4-Ethyltoluene	9.35	8.71	8.20	7.80	7.87	7.82	8.29	7.5
1,3,5-Trimethylbenzene	7.80	7.89	7.21	6.64	6.63	6.63	7.13	8.4
1,2,4-Trimethylbenzene	7.70	8.18	8.19	6.97	6.64	6.63	7.39	9.9
1,3-Dichlorobenzene	5.89	6.24	5.96	5.00	4.59	4.63	5.38	13.6
Benzyl Chloride	5.62	6.29	6.65	5.65	5.16	5.41	5.80	9.7
1,4-Dichlorobenzene	5.92	6.02	6.00	5.20	4.58	4.57	5.38	12.9
1,2-Dichlorobenzene	5.43	5.64	5.72	5.21	4.34	4.27	5.10	12.6
1,2,4-Trichlorobenzene	4.48	4.88	5.10	4.61	4.32	4.04	4.57	8.4
Hexachlorobutadiene	4.22	4.61	4.81	4.31	4.01	3.76	4.29	9.0

Figure 9 5 point TO-15 calibration, 0.4 to 20 PPB, using 10-500cc from a single, 6L Silonite Canister.

## **Conclusion**

A new 3-Stage Preconcentrator for analysis of stainless steel and glass canisters has successfully demonstrated recovery of SVOCs out to C24, while maintaining successful, quantitative recovery of routine EPA Method TO-15 compounds. The linearity of the response for 65 typical TO-15 compounds is shown to be quite good, due to the reduction in absorptive and adsorptive surfaces stemming from the much shorter flow paths and elimination of rotary valves. Challenging the system with the C10-C24 standard, it was found that the Silonite™ coated MiniCans™ required heating to 100-150°C to insure recovery of the C16+ compounds. Using a first stage Active SPME trap provided good recovery out to C24, while preventing the introduction of the heavier compounds onto the adsorbent trap, allowing complete system cleanup as demonstrated by running a system blank right after a relatively high concentration C10-C24 standard. Transmission of SVOCs into the canister during time weight sampling over 24 hours will likely show losses of these heavier compounds using classical flow controllers. This problem has been resolved using a new time integrated sampling technique called Helium Diffusion Sampling, which eliminates the need for an external flow controller.

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