

The Importance of Air Sampling Media Cleanliness for Vapor Intrusion Investigations

Alyson Fortune and Michael Taday

Columbia Analytical Services Air Quality Laboratory, 2655 Park Center Drive, Simi Valley, CA 93065

ABSTRACT

The increase in regulatory oversight at vapor intrusion sites nationwide, as well as recent publication of Federal and local vapor intrusion guidance documents and screening levels has led to a need for reliable air phase (indoor air and sub-slab/soil vapor) data at extremely low concentrations. This paper will explore and discuss the importance of media cleanliness and certification to achieve typical low level data quality objectives.

Several potential pathways of media contamination will be examined, including: canisters, flow controllers/critical orifice assemblies, vacuum gauges, and canister pressurization/fill stations in the laboratory.

Several contamination situations will be explored and quantified. The resulting data will be used to support laboratory and field sampling best practice recommendations.

INTRODUCTION

Thorough cleaning and certification of canister media has long been an accepted practice in the laboratory community. However, similar cleaning, certification and general care with the associated canister sampling media (e.g. flow controllers and vacuum gauges) has been less commonly discussed and practiced. Since all of this equipment is cleaned and reused, it is critical, especially for ultra low level projects, to ensure that every piece of equipment used to collect a sample has been properly cleaned and certified by the laboratory performing the analysis.

In addition to being described in detail in the EPA TO-15 method¹, the importance of canister cleaning and/or the canister cleaning technique itself has been described in several historical documents, such as canister stability studies by Batterman et. al⁴, Ochai et. al⁵, and Brymer et. al⁶. These documents all describe a cleaning procedure using steam cleaning & heat. More recently, canister cleaning has been briefly described in the South Coast Air Quality Management District (SCAQMD) Multiple Air Toxics Exposure Study III (MATES III)⁷, in the literature by Wang et. al⁸, and at technical conferences⁹. To date, cleaning and other maintenance of associated canister sampling equipment (e.g. flow controllers, vacuum gauges) has not been described in great detail in the literature.

The EPA TO-15 method mentions cleaning of the “sampling system components” by rinsing with HPLC grade water and drying in a vacuum oven at 80°C¹. Restek Corporation recommends cleaning “the entire sampling train as you would the can to minimize introduction of contaminants into a clean can”². Entech Instruments recommends backflushing of flow controllers with nitrogen/zero air and/or baking the flow controllers in a 70°C oven for higher level applications.³

Since most commercial air analysis laboratories analyze canister samples from a variety of applications, including indoor/ambient air monitoring (typically lower concentration samples, sometimes in the low ppbV/high pptV range) and soil vapor/soil vapor extraction (SVE) system monitoring (typically higher concentration samples, sometimes in the high ppmV range), the potential exists for cross contamination and false positive results. The purpose of this paper is to explore the potential data quality implications of equipment cleaning & segregation practices (or the lack thereof) in the laboratory. Specifically, the issue of “carryover” or “memory” in air sampling equipment will be addressed.

PROCEDURE

One test sample was created in a 6L electropolished stainless steel (SUMMA) canister with elevated concentrations of a mixture of petroleum hydrocarbons and tetrachloroethene (this sample is referred to as Sample A). The study was split into two areas: contamination of flow controllers (defined as mechanical devices containing an orifice to restrict flow and a diaphragm to maintain consistent flow rate, used for passive time integrated sample collection) and contamination of vacuum gauges (used to check pressure upon receipt at the laboratory after sampling).

Flow Controllers

Sample A was pressurized to 29.4 psig (3 atmospheres) and allowed to equilibrate for 24 hours. It was then analyzed by Gas Chromatography/Mass Spectrometry (GC/MS) via EPA TO-15 to confirm the actual concentrations of selected target volatile organic compounds (VOCs) and to obtain a visual qualitative “fingerprint”. Refer to Tables 1 & 2 for instrument conditions; refer to Figure 1 for a GC/MS total ion chromatogram (TIC) fingerprint of Sample A.

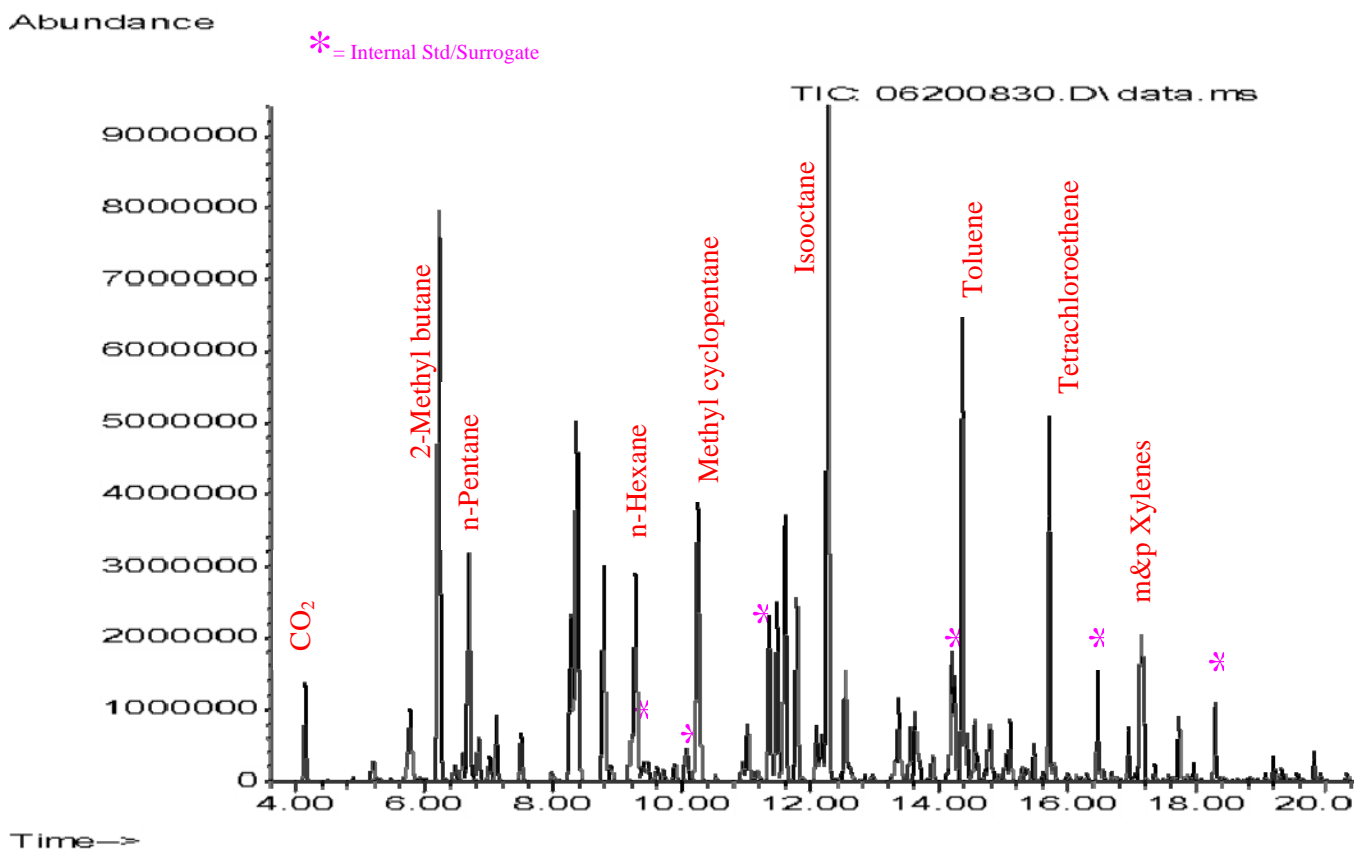
Table 1. Autosampler/Concentrator Conditions (EPA TO-15)

Instrument	Tekmar-Dohrmann AUTOCAN Autosampler, equipped with Concentrating Trap, Cryofocusing Module, and Vacuum Pump
<i>Adsorbent Trap</i>	
Set Point	35C
Sample Volume	Up to 1L
Dry Purge	400 mL
Sampling Rate	40-100 mL/min
Desorb Temp	230C
Desorb Flow Rate	10 mL/min Helium
Desorb Time	3 minutes
Bakeout after each run	8 minutes at 260C
<i>Refocusing Trap</i>	
Temperature	-180C
Injection Temperature	120C
Injection Time	1 minute

Table 2. GC/MS Conditions (EPA TO-15)

Instrument	GC/MS #16 (Agilent 6890 GC/5975C MS)
Column	J&W DB-1 MS 60m x 0.32mm ID, 1 µm film thickness
Carrier Gas	UHP Helium
Flow Rate	1 mL/min
Temperature Program	Initial Temperature: 35°C
	Initial Hold: 3 minutes
	Ramp Rate: 5°C/min to 125°C
	2 nd Ramp Rate: 20°C/min to 240°C; hold for 6 minutes
MSD Interface Temperature	280°C
Electron Energy	70 volts (nominal)
Mass Range	34-280 amu (SCAN mode)
Scan Time	Minimum 10 scans/peak, not to exceed 1 second per scan

Figure 1. GC/MS TIC Chromatogram of Highly Contaminated Sample (Sample A)
(0.5 mL analysis volume: 2000x dilution)



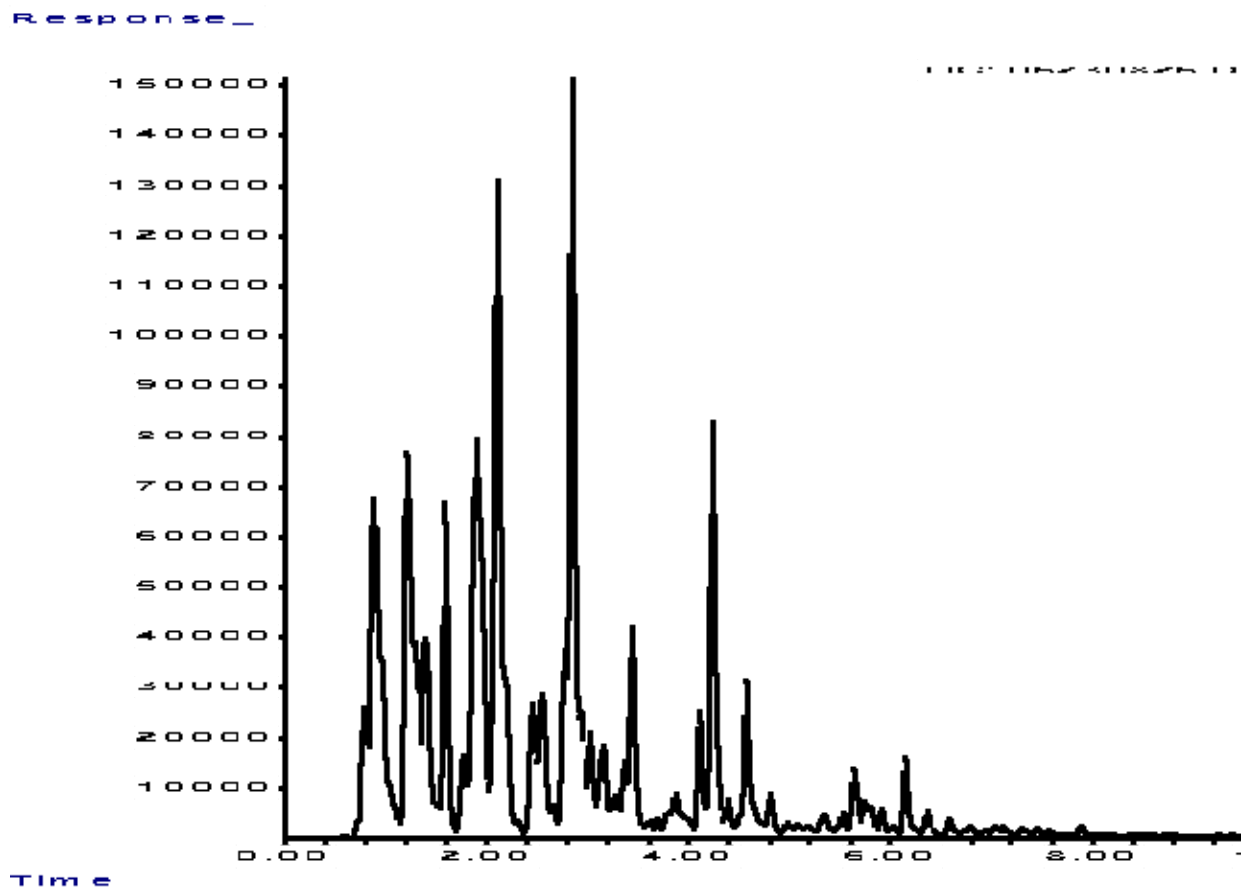
In addition, Sample A was analyzed by gas chromatography/flame ionization detection (GC/FID) to obtain a fingerprint. Table 3 lists GC/FID conditions used and Figure 2 presents the GC/FID fingerprint. For the purposes of this study, selected petroleum indicator compounds (n-hexane,

benzene, isooctane, and 1,2,4-trimethylbenzene (1,2,4-TMB), n-decane, n-undecane, and naphthalene) were tracked in the forthcoming data tables and/or chromatograms.

Table 3. GC/FID Conditions

Instrument	GC/FID #19 (Agilent 5890A GC equipped with Flame Ionization Detector)
Column	Restek Corporation RTX-1, 60m x 0.53mm ID, 5 µm film thickness
Carrier Gas	UHP Helium
Temperature Program	Initial Temperature: 60°C
	Initial Hold: 1 minute
	Ramp Rate: 12°C/min to 220°C; hold for 1.5 minutes
Injection Type	Manual (1 mL gas tight syringe)

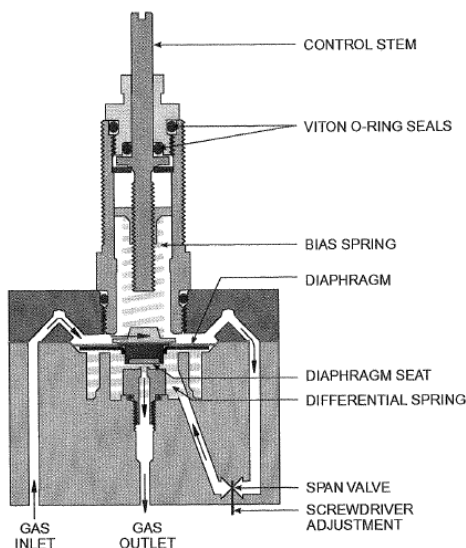
Figure 2. GC/FID Fingerprint Chromatogram of Highly Contaminated Sample (Sample A)



Contaminated air from Sample A was forced through two flow controllers (Vici Condyn Model 202, see Figure 3 for schematic) at a rate of 65 mL/min for 62 minutes (total volume passed through each flow controller was 4L). One of the flow controllers was then subjected to our laboratory's normal cleaning procedures (purged with high purity air at 30 mL/min in a 60°C oven for 2.5 hours); the other flow controller was used immediately to fill a cleaned and evacuated canister (Sample B) with humidified zero air over approximately one hour. After the first flow controller was cleaned, it was

then used to fill a cleaned and evacuated canister (Sample C) with humidified zero air over approximately one hour. Both Sample B and Sample C (having final pressures of approximately 5.0”Hg) were then slightly pressurized with humidified zero air (to 3.5 psig) analyzed via EPA TO-15. Concentrations above the reporting limit (0.1-0.5 $\mu\text{g}/\text{m}^3$) of target 91 target compounds were reported.

Figure 3. Schematic of Vici Condyne Model 202 Flow Controller



Vacuum Gauges

The pressure of Sample A was adjusted to approximately 10 psig. The pressure of Sample A was then checked with a TIF 9675 digital pressure/vacuum gauge (with necessary NPT/Swagelok tube adapting fittings attached, estimated dead volume in fittings is 0.5 mL), simulating the check done during sample log-in. Immediately after the high concentration sample, the pressure of a fully evacuated simulated “trip blank” canister was checked on the same vacuum gauge. This mock trip blank canister (Sample D) was immediately filled to 3.5 psig with humidified ultra zero air and analyzed via EPA TO-15. The process was repeated, only after reading the pressure of Sample A and before reading the pressure of the next mock trip blank, the gauge and fittings were evacuated with a vacuum pump three times, essentially flushing the dead volume with room air. After the flushing, the pressure of a fully evacuated mock trip blank canister (Sample E) was checked on the flushed vacuum gauge. Sample E was immediately filled to 3.5 psig with humidified ultra zero air and analyzed via EPA TO-15. Samples D & E (associated with Sample A at 10 psig) represent a “worst case” situation, since most real world samples are received at pressures <10 psig.

The entire procedure described above was repeated with Sample A adjusted to 0 psig, to simulate the receipt pressure of typical real world samples. Sample F is the mock trip blank without flushing; Sample G is the mock trip blank with flushing.

For clarity, a complete listing of all sample names/descriptions analyzed in this study is presented in Table 4.

Table 4. Sample Names and Descriptions

Sample Name	Description
Sample A	Highly Contaminated Canister
Sample B	Canister filled via uncleaned flow controller
Sample C	Canister filled via cleaned flow controller
Sample D	Mock trip blank, pressure measured after measuring pressure of 10psig Sample A (not flushed)
Sample E	Mock trip blank, pressure measured after measuring pressure of 10psig Sample A (flushed)
Sample F	Mock trip blank, pressure measured after measuring pressure of 0psig Sample A (not flushed)
Sample G	Mock trip blank, pressure measured after measuring pressure of 0psig Sample A (flushed)

RESULTS

A distinct difference was observed in the quantitative and qualitative analysis of samples from cleaned and uncleaned flow controllers, and flushed and non-flushed vacuum gauges. Figure 4 shows the GC/MS TIC chromatogram for Sample B (uncleaned flow controller); to contrast, Figure 5 shows the GC/MS TIC chromatogram for Sample C (cleaned flow controller). Figure 6 shows the GC/MS TIC chromatogram for Sample D (mock trip blank, not flushed, 10 psig); to contrast, Figure 7 shows the GC/MS TIC chromatogram for Sample E (mock trip blank, flushed, 10 psig). Results from Samples F (mock trip blank, not flushed, 0 psig) & G (mock trip blank, flushed, 0 psig) are presented in Figures 8 & 9, respectively. Numerical results and evaluations follow in the forthcoming subsections.

Figure 4. GC/MS TIC Chromatogram: Sample B
(Uncleaned Flow Controller)

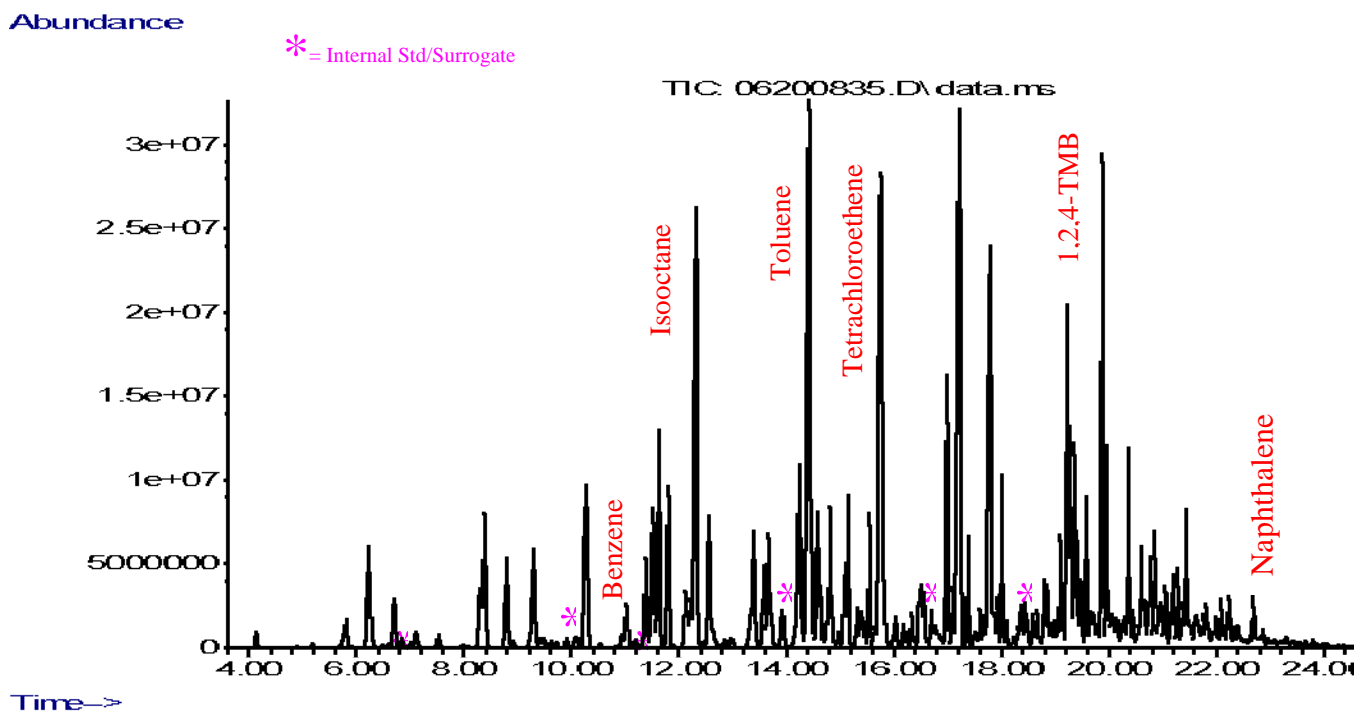


Figure 5. GC/MS TIC Chromatogram: Sample C
(Cleaned Flow Controller)

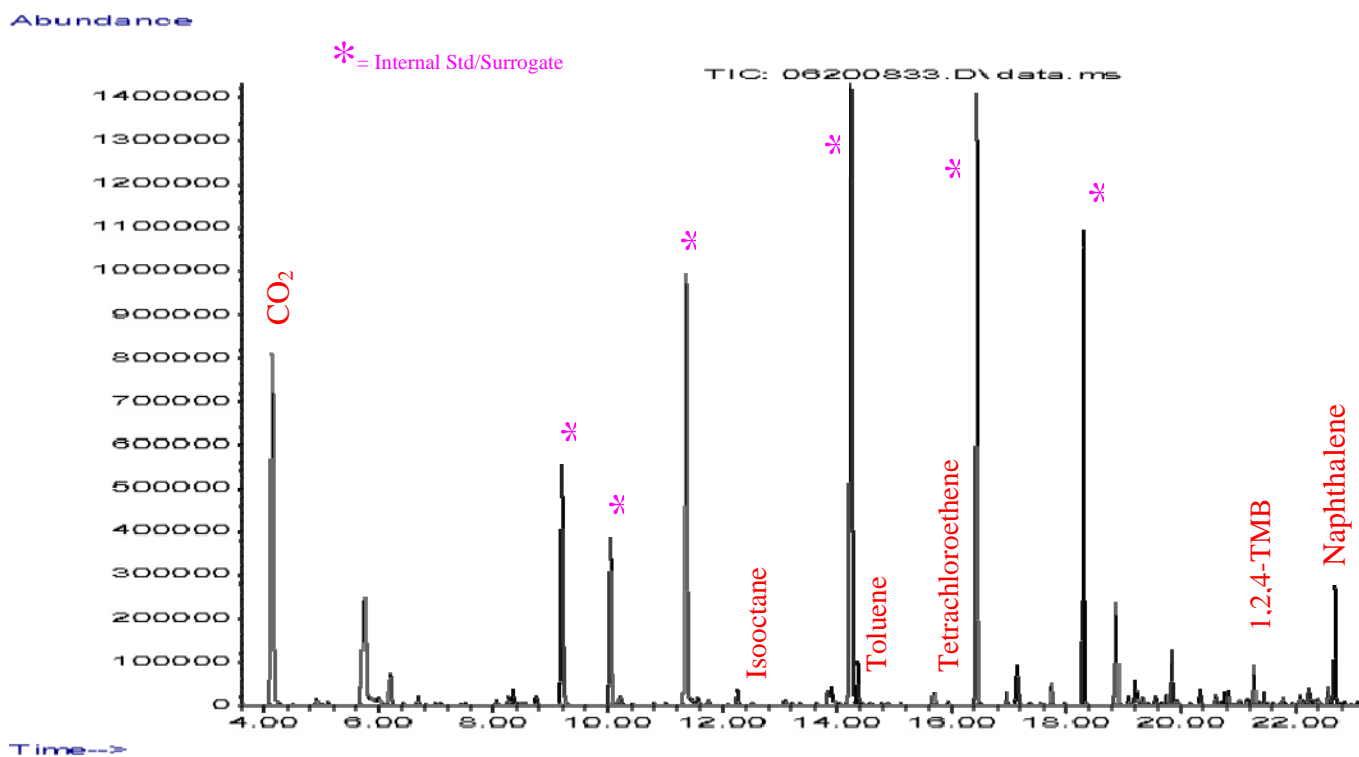


Figure 6. GC/MS TIC Chromatogram: Sample D
(Mock Trip Blank, not flushed, 10psig)

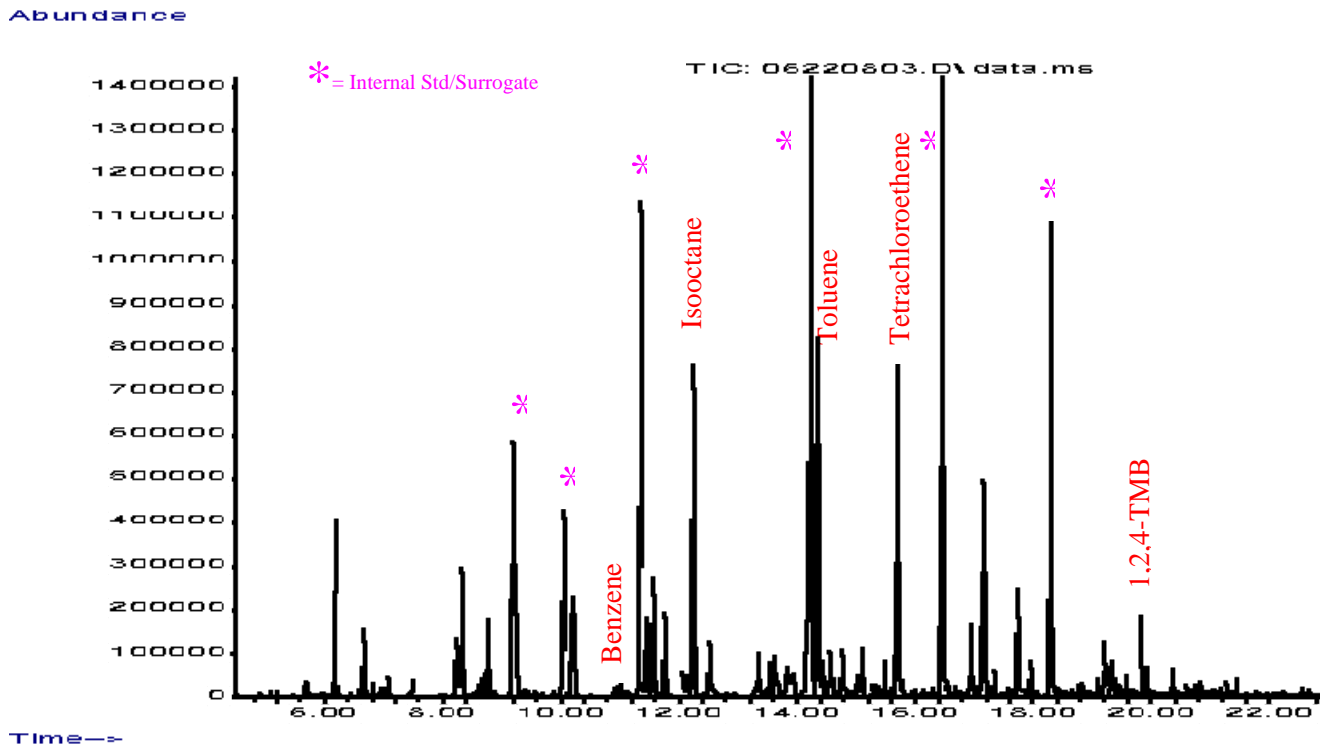


Figure 7. GC/MS TIC Chromatogram: Sample E
(Mock Trip Blank, flushed, 10psig)

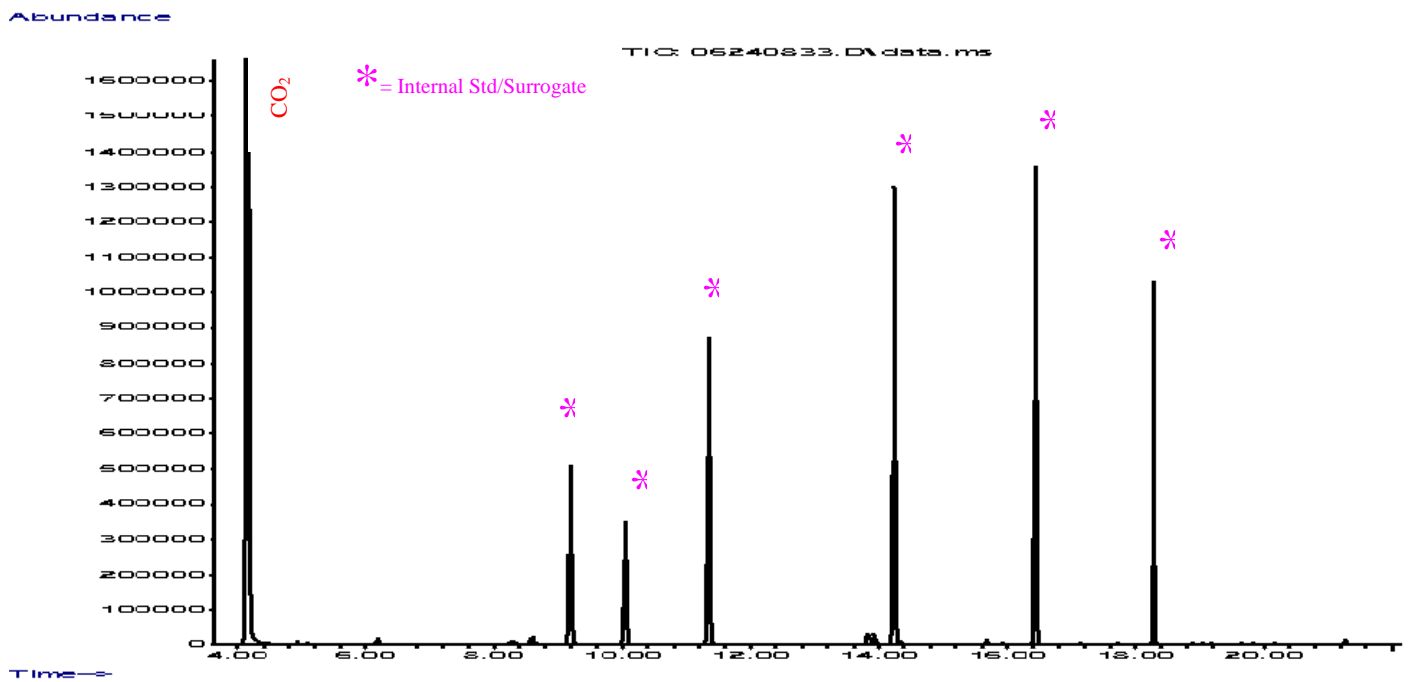


Figure 8. GC/MS TIC Chromatogram: Sample F
(Mock Trip Blank, not flushed, Opsig)

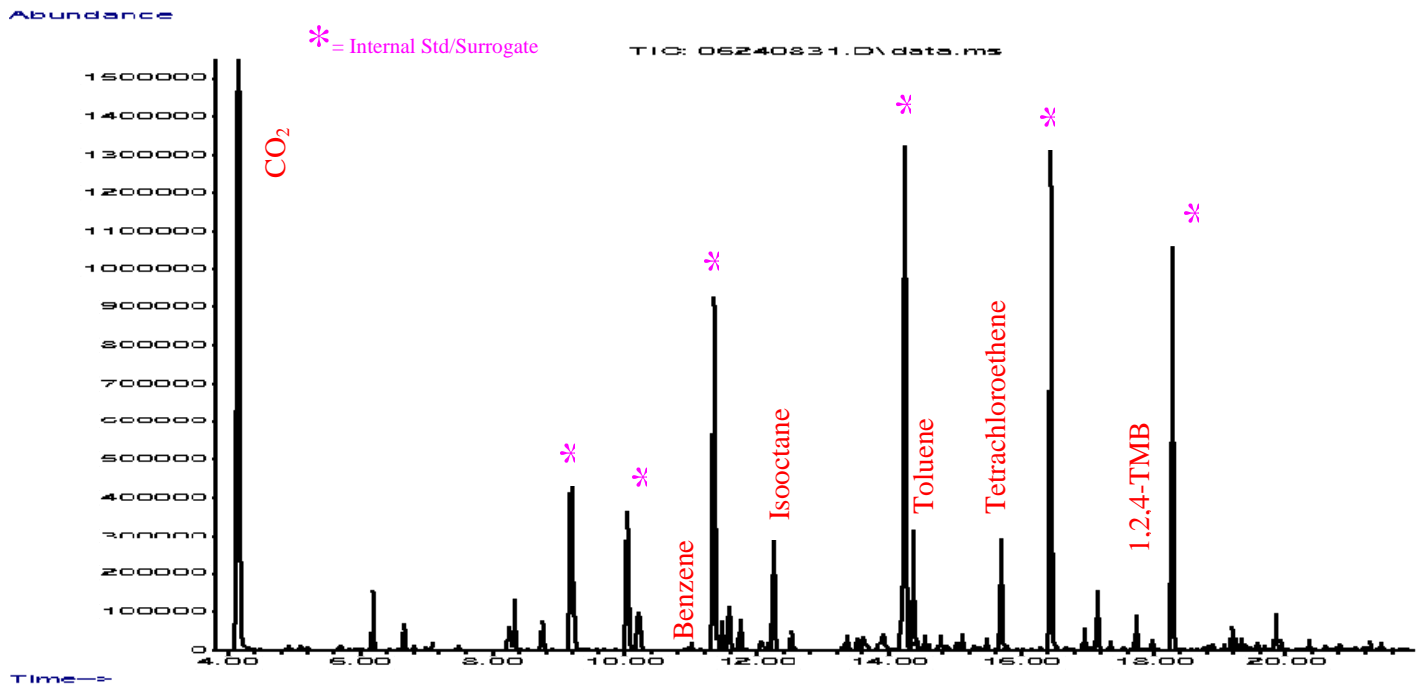
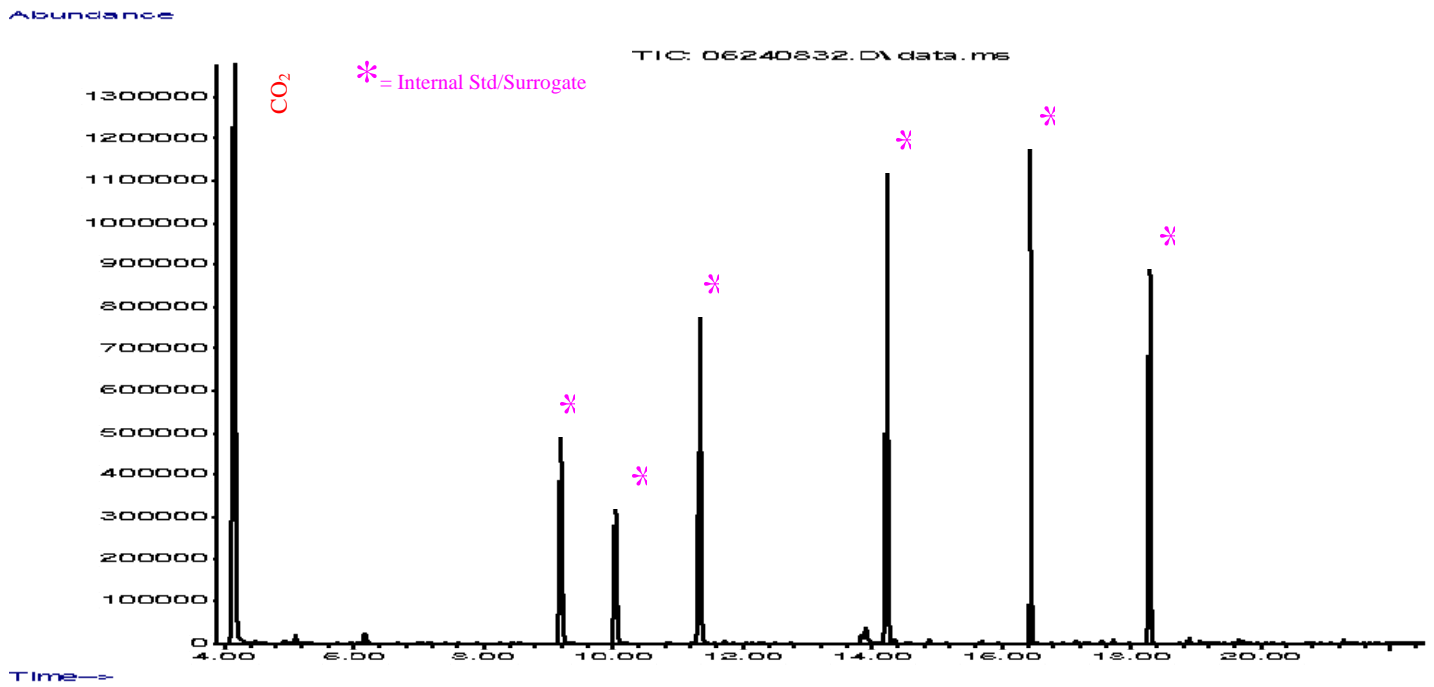


Figure 9. GC/MS TIC Chromatogram: Sample G
(Mock Trip Blank, flushed, Opsig)



Flow Controllers

Tetrachloroethene (PCE)

Tetrachloroethene carryover was seen in Sample B (uncleaned flow controller). Assuming a concentration of 250,000 $\mu\text{g}/\text{m}^3$ in Sample A, 10^6 ng tetrachloroethene were pulled through each flow controller; thus, Sample B (uncleaned flow controller) had 0.20% carryover and Sample C (cleaned flow controller) had 0.0002% carryover. While the percentages of carryover observed were very small, the nominal concentrations seen in the canisters as a result of this carryover exceed many established risk based concentrations for indoor air. Table 5 presents the concentrations seen in these samples, as well as the percent reduction in concentration between the cleaned and uncleaned flow controller samples.

Table 5. Tetrachloroethene Flow Controller Results

Sample A Concentration ($\mu\text{g}/\text{m}^3$)	Sample C Concentration ($\mu\text{g}/\text{m}^3$)	Sample B Concentration ($\mu\text{g}/\text{m}^3$)	% Reduction in Concentration from Cleaning
250,000 ^(E)	2.2	2000 ^(E)	99.89%

E=Estimated over calibration range

Petroleum Constituents

Petroleum product carryover was seen in Sample B (uncleaned flow controller). Looking at the eight individual marker compounds, Table 6 presents chemical information (molecular weight (MW) and boiling point (BP)), carryover information, and cleaning effectiveness information.

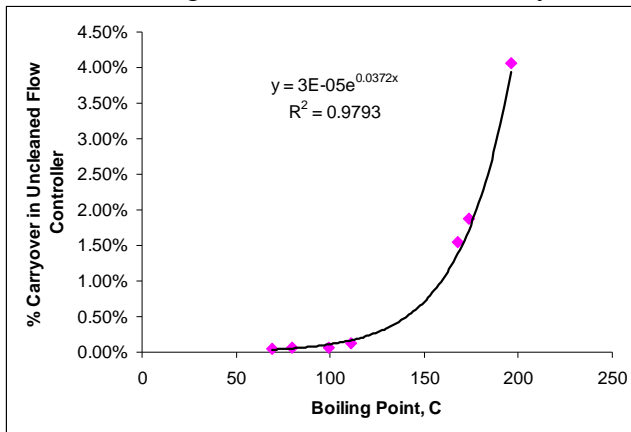
Table 6. Gasoline & Diesel Constituents Flow Controller Results

Compound	MW	BP (°C)	Sample A Concentration ($\mu\text{g}/\text{m}^3$)	Sample C Concentration ($\mu\text{g}/\text{m}^3$), % Carryover	Sample B Concentration ($\mu\text{g}/\text{m}^3$), % Carryover	% Reduction from Cleaning
n-Hexane	86.17	69	140,000	ND (0.75) NC	250 ^(E) 0.04%	99.8%
Benzene	78.11	80	36,000	0.23 0.0002%	100 0.07%	99.8%
Isooctane	114.23	99	300,000 ^(E)	0.84 0.0001%	810 ^(E) 0.07%	99.9%
Toluene	92.14	111	190,000	2.4 0.0003%	950 ^(E) 0.13%	99.8%
1,2,4-TMB	120.2	168	8,400	2.2 0.0065%	520 ^(E) 1.6%	99.6%
n-Decane	142.28	174	2,400	ND (0.75) NC	180 ^(E) 1.9%	99.9%
n-Undecane	156.31	196	610	ND (0.75) NC	99 4.1%	99.6%
Naphthalene	128.17	218	ND (1000)	4.7 NC	12 NC	61.3%

ND= Not detected (above reporting limit), NC= Not calculable, E=Estimated over calibration range

When plotting boiling point versus the percent carryover (Figure 10), the relationship appears to be exponential in nature. Thus, as the boiling point of the contaminant compound increases, the degree of carryover or memory in a flow controller appears to increase exponentially.

Figure 10. Plot of Boiling Point versus Percent Carryover in Sample B



Vacuum Gauges

Tetrachloroethene (PCE)

Tetrachloroethene carryover was seen in Sample D (mock trip blank, not flushed, 10 psig). The carryover concentration seen in Sample F (mock trip blank, not flushed, 0 psig) was reduced by approximately 50%. When the gauge was flushed out in between readings, the carryover concentrations seen in Samples E (10 psig) and G (0 psig) dropped dramatically, but low levels of tetrachloroethene were still seen. The ratio between the 10 psig and 0 psig readings remained similar (the 0 psig reading being approximately half of the 10 psig reading). Table 7 presents the numerical results of this experiment.

Table 7. Tetrachloroethene Vacuum Gauge (Mock Trip Blank) Carryover Results

Sample A Concentration ($\mu\text{g}/\text{m}^3$)	Sample D Concentration (not flushed, 10 psig) ($\mu\text{g}/\text{m}^3$)	Sample E Concentration (flushed, 10 psig) ($\mu\text{g}/\text{m}^3$)	Sample F Concentration (not flushed, 0 psig) ($\mu\text{g}/\text{m}^3$)	Sample G Concentration (flushed, 0 psig) ($\mu\text{g}/\text{m}^3$)
250,000 _(E)	19	0.36	8.0	0.24

E=Estimated over calibration range

Petroleum Constituents

Petroleum product carryover was seen in Sample D (mock trip blank, not flushed, 10 psig). The carryover concentration seen in Sample F (mock trip blank, not flushed, 0 psig) was reduced by approximately 50%. When the gauge was flushed out in between readings, the carryover concentrations seen in Samples E (10 psig) and G (0 psig) dropped to below the reporting limit. Tables 8A and 8B present the numerical results of this experiment.

Table 8A. Petroleum Constituent Vacuum Gauge (Mock Trip Blank) Carryover Results (Not Flushed)

Compound	Sample A Concentration ($\mu\text{g}/\text{m}^3$)	Sample D Concentration (not flushed, 10 psig) ($\mu\text{g}/\text{m}^3$)	Sample F Concentration (not flushed, 0 psig) ($\mu\text{g}/\text{m}^3$)
n-Hexane	140,000	3.4	1.7
Benzene	36,000	1.0	0.52
Isooctane	300,000 (E)	11	5.2
Toluene	190,000	10	4.6
1,2,4-TMB	8,400	2.4	1.1
n-Decane	2,400	0.78	0.32
n-Undecane	610	0.38	0.22
Naphthalene	ND (1000)	ND	ND

ND= Not detected (above reporting limit), E=Estimated over calibration range

Table 8B. Petroleum Constituent Vacuum Gauge (Mock Trip Blank) Carryover Results (Flushed)

Compound	Sample A Concentration ($\mu\text{g}/\text{m}^3$)	Sample E Concentration (flushed, 10 psig) ($\mu\text{g}/\text{m}^3$)	Sample G Concentration (flushed, 0 psig) ($\mu\text{g}/\text{m}^3$)
n-Hexane	140,000	ND (0.50)	ND (0.50)
Benzene	36,000	ND (0.10)	ND (0.10)
Isooctane	300,000 (E)	ND (0.50)	ND (0.50)
Toluene	190,000	ND (0.50)	ND (0.50)
1,2,4-TMB	8,400	ND (0.50)	ND (0.50)
n-Decane	2,400	ND (0.50)	ND (0.50)
n-Undecane	610	ND (0.50)	ND (0.50)
Naphthalene	ND (1000)	ND (0.50)	ND (0.50)

ND= Not detected (above reporting limit), E=Estimated over calibration range

CONCLUSIONS

The data demonstrate that laboratory best practices should include some type of decontamination for all canister sampling equipment, especially after exposure (or potential exposure) to elevated concentrations. The elevated concentrations of Sample A shown in this study (mg/m^3 range) are not atypical for samples collected from a SVE system or soil vapor samples collected near a subsurface contamination source. Thus, the potential exists for carryover and cross contamination of samples, unless care is taken by the laboratory to properly decontaminate and segregate equipment based on concentration level/application.

Even with very small percent carryover (as seen in Sample C), the nominal concentrations that may result from any type of equipment carryover can exceed human health risk based target levels for vapor intrusion investigations, resulting in false positives and potentially resulting in unnecessary cleanup work. The data demonstrate that this widely used style of flow controller (orifice/diaphragm assembly) has the potential for carryover, even after cleaning, when exposed to elevated

concentrations. In fact, for very boiling point contaminants (e.g. naphthalene), carryover may occur even at lower concentrations; this effect can be observed in the data presented in Table 6 (i.e. even with a moderate concentration less than 1000 $\mu\text{g}/\text{m}^3$ in Sample A, we observed naphthalene carryover in Samples B & C). To ensure optimum performance, this equipment should be used for low level (ambient/indoor) applications only. A simpler and less expensive critical orifice device (with less internal surface area and a less convoluted flow path) may be used for higher concentration applications.

Flushing out of the vacuum gauge in between sample pressure readings appears to be an effective practice to prevent carryover from highly contaminated samples to less contaminated samples. However, the data show that even after flushing, a low concentration carryover of tetrachloroethene was present (Samples E & G). This may present a problem for vapor intrusion investigations for human health risk assessments where ultra low level reporting limits are required. Therefore, to minimize the chances of this phenomenon occurring, the laboratory may segregate pressure gauges for low level vs. higher level work. On a related note, the data show that the issue of carryover from pressure gauges is exaggerated with positive pressure samples; under these circumstances, care should be taken by the laboratory to thoroughly decontaminate the system to prevent potential carryover.

It should be noted that additional sources/sinks of volatile organic compounds (VOCs) may exist in typical vapor intrusion sampling/analytical systems. There have been several recent technical presentations at national vapor intrusion conferences that have mentioned the influence of tubing type on VOC samples, including a comprehensive study performed by Hayes et. al.¹⁰ In addition, particulate matter or condensed VOCs entering a canister may act as a source or a sink for VOCs. On the canisters themselves, some older styles of canisters may have pipe thread (NPT) fittings connecting the valve stem to the canister body. These NPT fittings are wrapped with Teflon tape; over time and exposure to elevated concentration samples, this Teflon tape can also act as a source or a sink of VOCs.

To conclude, for low level vapor intrusion work, it is critical for the data user to consider each of these analytical issues and insist that proper decontamination and/or segregation of equipment occurs in the laboratory.

FUTURE WORK

Additional types of sampling equipment may be evaluated, including different brands, designs/configurations, and coating types of flow controller/critical orifice devices. Additional compounds may also be evaluated (other chlorinated VOCs, a better assessment of diesel/heavier hydrocarbons, etc).

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