

Sampling and GCMS Analysis of BTEX/TCE/PCE in Ambient Air using Diffusive Sorbent Pens and a Simplified “In-Oven” Secondary Trapping System

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Abstract

A new solution is presented for diffusive collection of BTEX/TCE/PCE over an extended period of time, followed by thermal desorption analysis by GCMS. Detection limits range from low part per trillion in ambient air, with support for higher concentrations in fenceline monitoring and other applications simply by increasing the split ratio upon GCMS analysis. Thermal desorption tubes called “Diffusive Sorbent Pens (DSPs)” were used to collect 2-week samples passively. Direct thermal desorption of the DSP samplers into a GCMS oven using a dual split technique with intermediate collection on a capillary column focusing trap inside of the GC oven was used to avoid the need for a complicated, external thermal desorption system. Two-week ambient level BTEX/TCE/PCE data is presented showing near perfect precision obtained using DSP diffusive sampling followed by dual split, “In-GC-Oven” focusing.

DSP
Sorbent Pen



Introduction

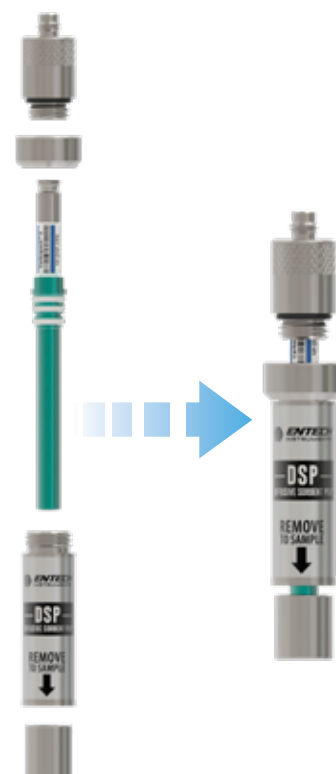
The accurate assessment of volatile organic compounds (VOCs) in ambient air is essential for understanding air quality, assessing environmental impact, and ensuring compliance with regulatory standards. Conventional approaches often involve active sampling techniques, such as canister-based or pump-driven methods. Nevertheless, for sampling of many VOCs such as BTEX and compounds of similar boiling points, passive or diffusive sampling has gained prominence as an effective approach due to its simplicity, portability, cost effectiveness, and ability to perform long-term time integrated sampling for more accurate risk assessment.

US EPA Method 325 utilizes diffusive based sorbent traps for fenceline monitoring of BTEX at high ppt to mid ppb levels. Classical TD systems analyze these samples using external focusing traps and split reduction of the total on-tube sample load using benchtop thermal desorption systems that include rotary valves and transfer lines in the flow path prior to sample delivery to the GCMS. These systems expose the sample to additional surface area and fittings during transfer to the GCMS, potentially increasing sample carryover while creating the opportunity for transfer efficiency to change over time due to the buildup of waxes and other heavy compounds that are not completely eliminated after each thermal desorption. A solution for passive sampling of BTEX range compounds is needed that not only simplifies sample collection, but also allows direct transfer of the sample into the GC oven to eliminate the need for external trapping and the limitations that come with it. Such a system is presented in this study.

Diffusive Sorbent Pens – Precision, Tool-Free Diffusive Samplers

Diffusive Sorbent Pens (DSPs) are specially designed thermal desorption tubes that are suitable for diffusive sampling. DSP Pens have a micro-seal valve built into one end, and use isolation sleeves and end plugs that are installed and removed tool-free, both in the lab and in the field. Rather than being made from tubes, Sorbent Pens are CNC machined to have exact internal dimensions, with barriers that keep the sorbent in exactly the same place on each Pen. The body of the Pen is Silonite coated to provide a surface similar to the inside of a GC column to minimize chemical reactions.

DSPs have an internal dimension of 5mm ID with a path length of 15mm leading up to the sorbent bed, to provide sampling rates consistent with US EPA Method 325. The sampling rate of VOCs into diffusive tubes of this geometry are shown in **Table 1** below. The total amount of sample accumulated on the tube increases linearly over time, provided that the sorbent's strength is sufficient to prevent the back-release of the collected compounds, ensuring their retention throughout the sampling event. Some compounds even lighter than those shown in **Table 1** such as 1,3-Butadiene can collect on sorbents such as Carbopack X with only a 1% loss per hour, allowing it to be collected over 8 hours during TWA personal monitoring. However, losses are too significant to allow quantitative analysis of 1,3-Butadiene over a period of 1 day or longer. The amount collected in 8 hours would provide detection limits for most compounds well below current OSHA and NIOSH methods that use solvent extraction of diffusive sampling badges. Future studies will look at these shorter sampling times, and the full range of compounds that can be recovered without significant reverse adsorption.



In this study, the DSP Pens packed with the Carbopack X sorbent were used to collect VOCs in the ambient air. The target analytes were BTEX and included Trichloroethylene and Tetrachloroethylene. A 2-week sampling time was used to optimize sensitivity and to obtain average concentrations at the sampling locations.

Compound	Carbopack™ X ^a	Carbograph™ 1 TD	Carbopack™ B
1,1-Dichloroethene	0.57±0.14	not available	not available
3-Chloropropene	0.51±0.3	not available	not available
1,1-Dichloroethane	0.57±0.1	not available	not available
1,2-Dichloroethane	0.57±0.08	not available	not available
1,1,1-Trichloroethane	0.51±0.1	not available	not available
Benzene	0.67±0.06	0.63±0.07 ^b	0.63±0.07 ^b
Carbon tetrachloride	0.51±0.06	not available	not available
1,2-Dichloropropane	0.52±0.1	not available	not available
Trichloroethene	0.5±0.05	not available	not available
1,1,2-Trichloroethane	0.49±0.13	not available	not available
Toluene	0.52±0.14	0.56±0.06 ^c	0.56±0.06 ^c
Tetrachloroethene	0.48±0.05	not available	not available
Chlorobenzene	0.51±0.06	not available	not available
Ethylbenzene	0.46±0.07	not available	0.50 ^c
m,p-Xylene	0.46±0.09	0.47±0.04 ^c	0.47±0.04 ^c
Styrene	0.5±0.14	not available	not available
o-Xylene	0.46±0.12	0.47±0.04 ^c	0.47±0.04 ^c
p-Dichlorobenzene	0.45±0.05	not available	not available

^a Reference 3, McClenny, J. Environ. Monit. 7:248-256. Based on 24-hour duration.

^b Reference 24, BS EN 14662-4:2005 (incorporated by reference-see §63.14). Based on 14-day duration.

^c Reference 25, ISO 16017-2:2003(E) (incorporated by reference-see §63.14).

Table 1. Sampling Rates of 18 VOCs using diffusive tubes with a 5mm ID x 15mm long path length leading to the sorbent bed.

Sample Collection using DSP Pens

Diffusive Sorbent Pens containing Carboxpack X were used to collect 2-week samples to determine levels of BTEX/TCE/PCE in an urban environment that was a reasonable distance from heavy industry. A pole or fence mountable shelter as shown in **Figures 2-4** were used to hold the DSP devices during sample collection, keeping them out of direct rain and sunlight. Three positions are included with these shelters to allow duplicate sampling and storage of a "trip blank" during 2-week sampling. To prevent convective transfer of the sample to the sorbent through the 5mm x 15mm diffusion zone, a wind screen was used to ensure collection rates were virtually constant during low vs high air movement outside of the DSP Pens. To start the sampling, the sealing plugs were removed by hand and placed on top of the Pens for safe keeping, and the wind screen in turn can be removed from the top of the Pens and placed on the bottom prior to snapping the pen into the shelter/holder. After two weeks, the Pens were sealed and transferred back to the laboratory for analysis.



Figure 3 - Sample site A at Entech in Simi Valley, CA

DSP Sorbent Pen Air Monitoring Components

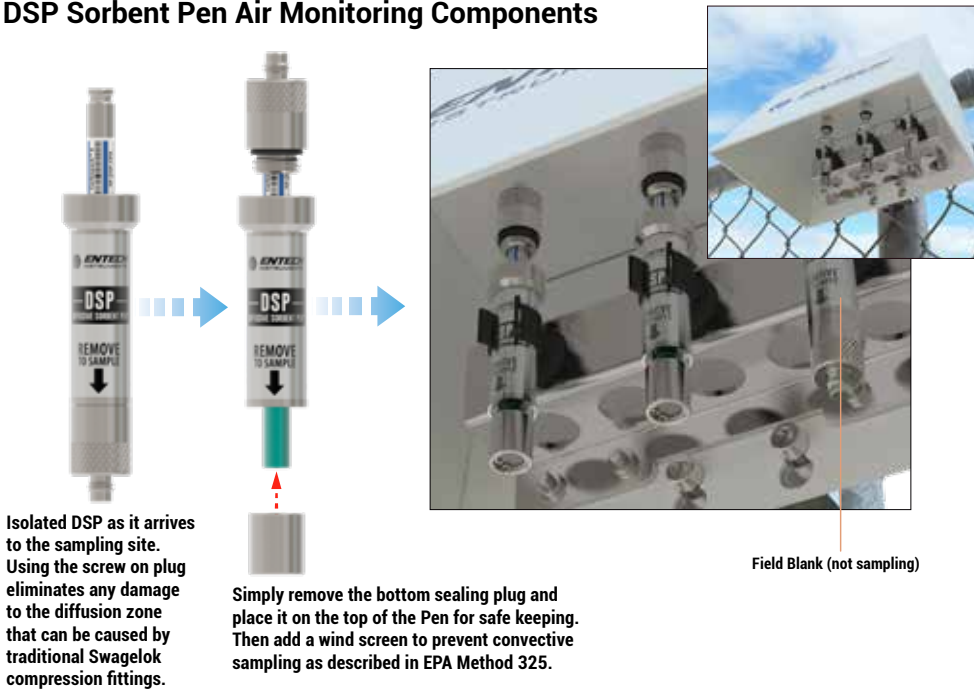


Figure 2 - Sorbent Pens in the sample collection configuration, shown mounted in the DSP shelter with wind screens attached. A 3rd position is included to support a trip blank if required.



Figure 4 - Sample site B at Entech in Simi Valley, CA shown with a canister enclosure to support both sample collection techniques.

Thermal Desorption of Diffusive Sorbent Pens

Simplified "Chemist Friendly" Thermal Desorption System

Figure 5 shows the analytical system used for the analysis of DSP Pens. No external, benchtop desorption systems were needed, as the 5800 SPDU (Sorbent Pen Desorption Unit) can utilize the first of two capillary columns inside of the GC oven as a focusing trap. Focusing of the sample prior to the second analytical GC column is needed due to the slow release rates of the target compounds from Carbopack X. By desorbing directly into the GC oven and using capillary columns to perform the focusing, the 5800 SPDU thermal desorption system is inherently easier to support, as GC chemists are familiar with how to change GC columns, but are not typically experts in repairing benchtop thermal desorption systems.

For this method, a 5m Megabore metal column with a 1 μ m 100% PDMS film was used to retain the analytes after they are thermally desorbed from the DSP Pens. External split modules were used to allow more advanced split control than found on today's GC systems. Some GCs use back pressure regulation when performing carrier gas pressure control in the SPLIT mode, while other use forward pressure regulation. With back pressure regulation, very little extra flow resistance is typically tolerated by the GC control algorithm before pressure control becomes unstable. This was an original problem with Purge and Trap systems, until P&T specific injection systems were developed. However, when all GC brands are placed in SPLITLESS mode, they simply maintain the required pressure, no matter how much or little restriction is present. This enables the use of external split control systems compatible with all GC models. Generally, major GC brands exhibit exceptional accuracy in pressure control. This precision greatly benefits any Thermal Desorption (TD) solution, like the 5800 SPDU, by leveraging this high-level accuracy to achieve remarkably consistent sample preparation and delivery to the analytical column.

As shown in **Figure 5**, 3 different split controls are available using the 5800 SPDU, 2 prior to the focusing column (Column 1), and 1 after. The Low Split prior to Column 1 was set to allow a 7:1 split, while the High Split flow provided a 30:1 split. The V5 Split after Column 1 was also set to allow a 7:1 split. After a 300° C DSP preheat, the Pens were desorbed for 3.2 min using a 7:1 split prior to Column 1, using only a 1.2cc/min flow through Column 1 to retain all of the compounds of interest. After desorption, the high split flow was momentarily turned on prior to Column 1 to eliminate the residual compounds left on the Pen. Then the V5 Split was turned on to achieve a 7:1 split as the sample was delivered to the second GC column for separation and delivery to the MS. The use of two 7:1 splits resulted in a 49:1 split (50:1 split), which is ideal for 2-week sample collections where the equivalence of 13.1L of Benzene will collect onto the Sorbent Pens. At a 50:1 split, this reduced the sample load to 260cc, which with today's MS systems allows full scan analysis down to 10-20 ppt levels. Using sequential 7:1 splits to achieve a 50:1 split uses far less carrier gas than using a single 50:1 split, which is very important for systems using Helium carrier gas.

Column 2 was a 30m x 0.25mm ID x 1 μ m, 100% PDMS column. After a fast transfer of the sample from Column 1 to Column 2, the flow can be returned to the V2 bypass, allowing Column 1 to be backflushed to eliminate any unwanted compounds and to shorten the Column 2 bakeout times.

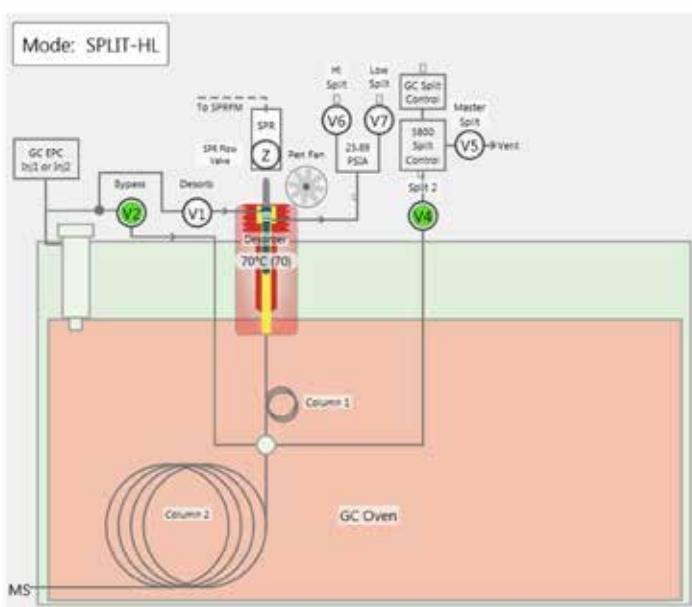


Figure 5 - Diagram of the 5800SPDU desorption, two-column focusing and separation, and high-low split system (idle status).

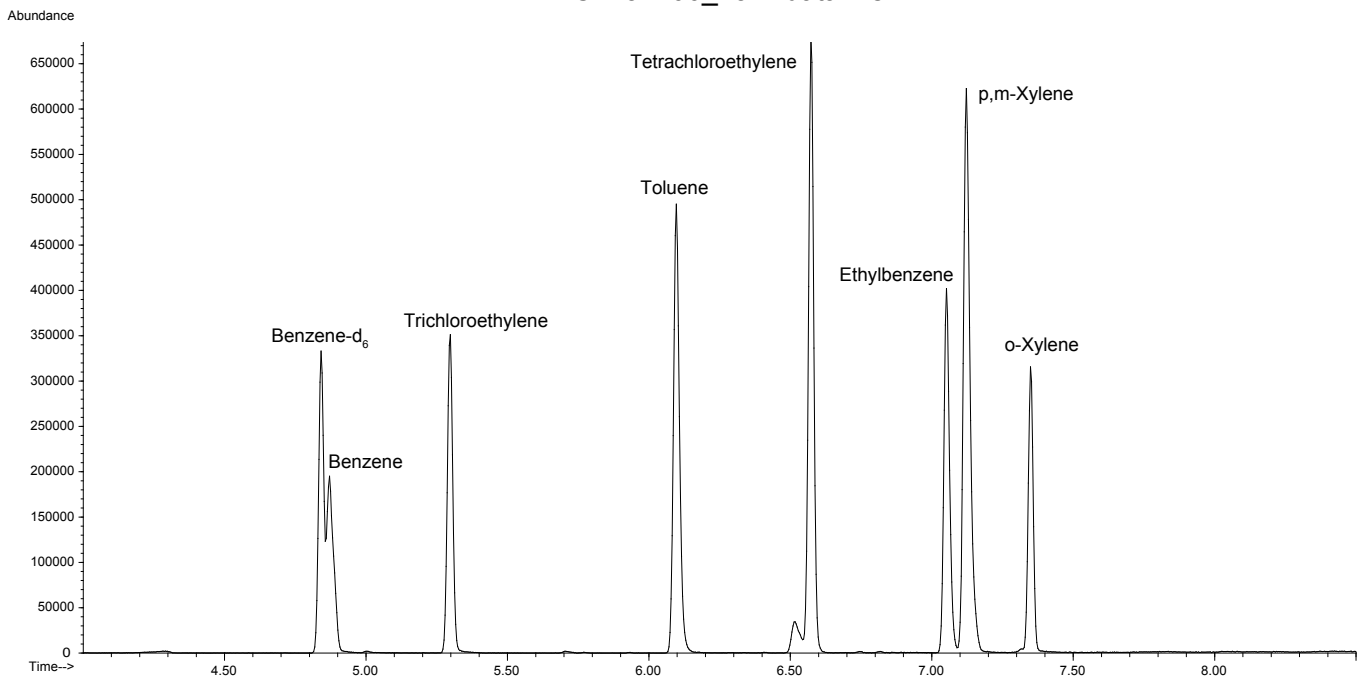


Figure 6 - Example of TIC of a calibration standard with the analytes at 3 ppb and internal standard at 5ppb.

Figure 6 shows a calibration standard at 3 ppb and a Benzene-d₆ Internal Standard at 5 ppb. Good peak shapes were obtained with peak widths of only 3 seconds. Compounds lighter than benzene are not quantitatively retained using Carboxen 100 sorbent during a two-week sampling period and thus are not included in the analyte list for this study. The exact time to start backflushing Column 1 was determined such that all compounds after o-Xylene would be prevented from reaching Column 2, allowing the total run time to be only 8.5 minutes. With sample handling, preheating, and cool down times added, the injection to injection cycle time was approximately 20 minutes. The capability to run 3 samples per hour with an automated system and efficient workflow gives laboratories high throughput and productivity.

Spiking and Calibration

Spiking of calibration and internal standards onto the DSP Pens is performed automatically at the VIPERS (Vapor Inlet Port Entech Rail System) spiking station as shown in **Figure 7**. Prior to Pen desorption, the SPR40 rail autosampler can pick up a Pen from the DSP Pen Tray for insertion into the spiking station for loading of calibration and internal standards. The SPR-FM flow module attached at the back of the SPR40 is capable of controlling the sampling rate and volume of gas added to the Pens. A 100cc reservoir is used to measure the volume drawn through the Pens, with re-evacuation as needed for larger spike volumes. For calibration curves, two 2.5L canisters were used with Benzene prepared at 2.7 ppm and 54 ppb, with the appropriate amounts drawn through the DSP Pens to create calibration curves from 0.008 to 10 ppb. All other BTEX, TCE, and PCE compounds were added to the cylinder at concentrations that would give the same equivalent concentrations to those of Benzene based on their relative diffusive sampling rates onto the DSP Pens, as presented in **Table 1**. Spiking 2, 5, 15, and 50cc from each of these 2 standards created the desired 8-point calibrations at 0.008, 0.02, 0.06, 0.2, 0.4, 1, 3, and 10 ppb. Benzene- d_6 at 5 ppm in a 2.5-L canister was used as the internal standard.

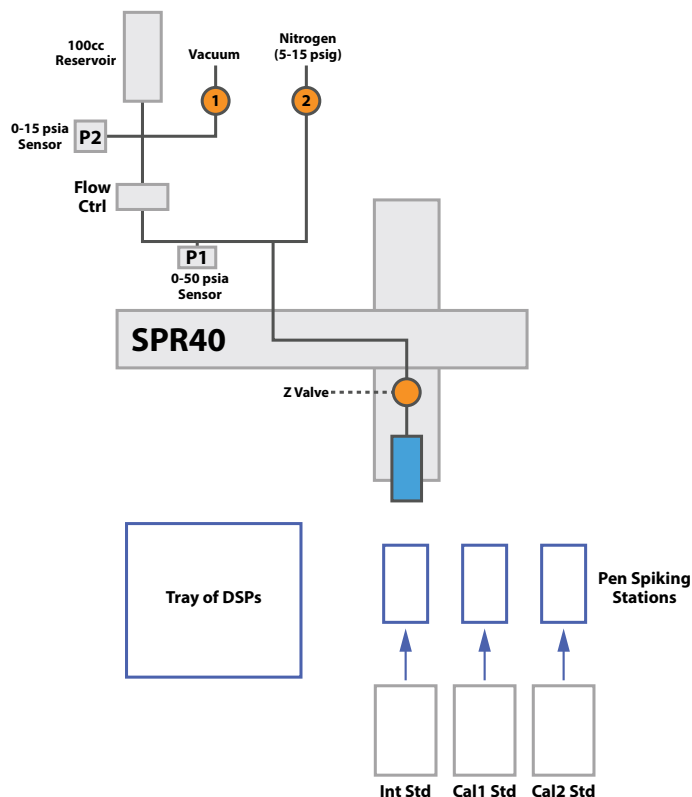


Figure 7 - Diagram of the Internal Standard and Calibration Standard Spiking System.



Figure 8 - SPR40, 5800SPDU, Hi/Lo SPLIT Module, DSP Pen Tray, VIPERS spiking system, and calibration and internal standard canisters mounted on an Agilent GCMS system.

Figure 9 shows the reproducibility of a 3 ppb standard spiked onto 3 different DSP Pens using the SPR40 automated spiking system. This is the response equivalent to an average of 3 ppb being exposed to the DSP Pens over a 2-week period. For monitoring over an 8-hour period, the collection would be 14 days x 3 8hr/day = 42x less, so this would be equivalent to a $3 \times 42 = 126$ ppb (0.126 ppm) average concentration, which is right in the range that many Industrial Hygiene methods show as a maximum allowable exposure limit (0.1 – 1 ppm).

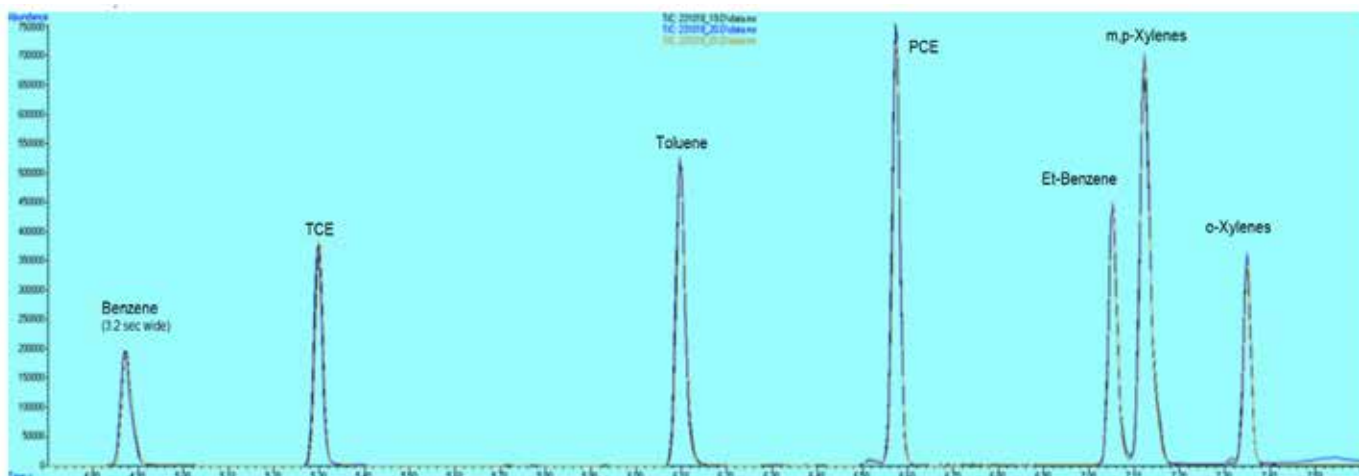


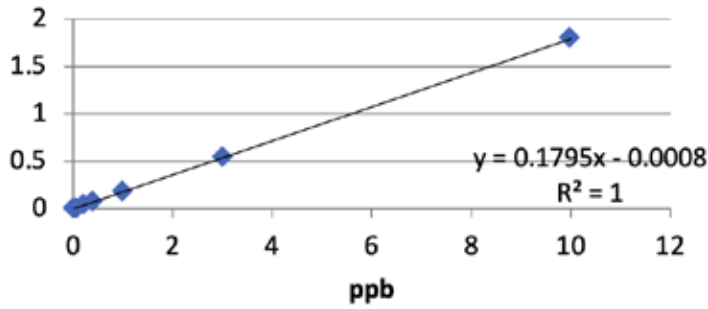
Figure 9 - Near perfect overlap of BTEX/TCE/PCE Standard spiked on 3 different DSP Pens at 3 ppb, the Action Limit for Fenceline Monitoring of Benzene by US EPA Method 325.

As shown in **Table 2**, all analytes had good linearity ($r^2 > 0.9980$) over the range of 0.008-10 ppb. The method detection limits (MDLs) were within 0.003-0.01 ppb, which is below the MDLs found in most other BTEX/TCE/PCE ambient air methods. Note that this method was performed using a relatively old Agilent 6890GC/5973 MS system using Full Scan mode. A modern GC-MS system with a more advanced ion source operating in SIM mode would further improve method sensitivity. Likewise, a higher split ratio (example 20:1 followed by 20:1 equal to 400:1) would allow the calibration range to be shifted up considerably into the high ppb to low ppm range, again without the consumption of too much GC carrier gas.

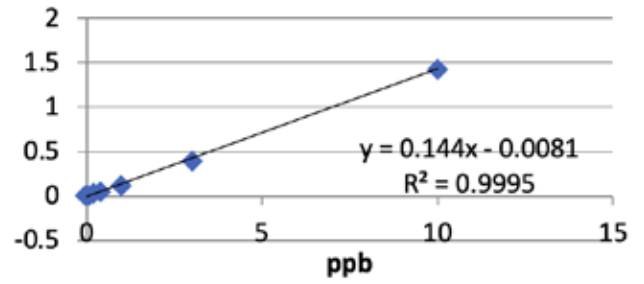
	Linear range (ppb)	r^2	MDL (ppb)
Benzene	0.008-10	1	0.0064
Trichloroethylene	0.008-10	0.9995	0.0032
Toluene	0.008-10	0.9995	0.0090
Tetrachloroethylene	0.008-10	0.9987	0.0057
Ethylbenzene	0.008-10	0.9990	0.0086
p,m-Xylene	0.008-10	0.9985	0.0095
o-Xylene	0.008-10	0.9992	0.0045

Table 2. Calibration curve information and method detection limits (MDLs) for the target analytes.

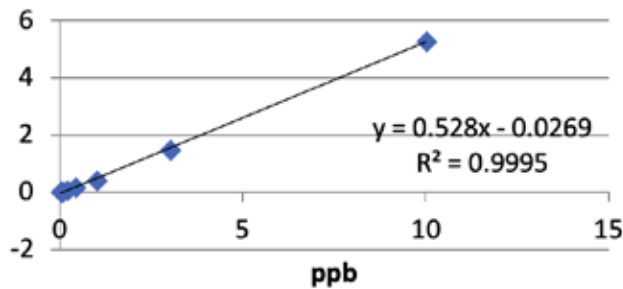
Benzene



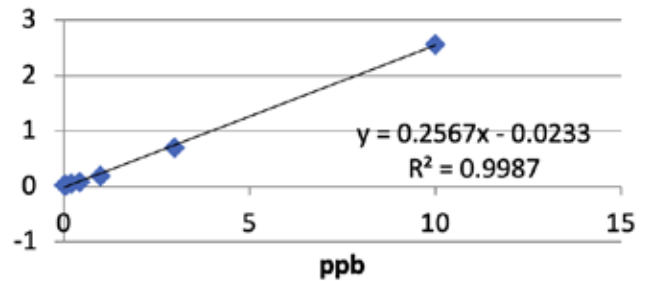
Trichloroethylene



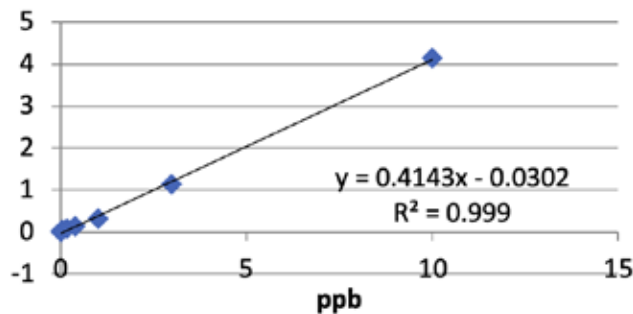
Toluene



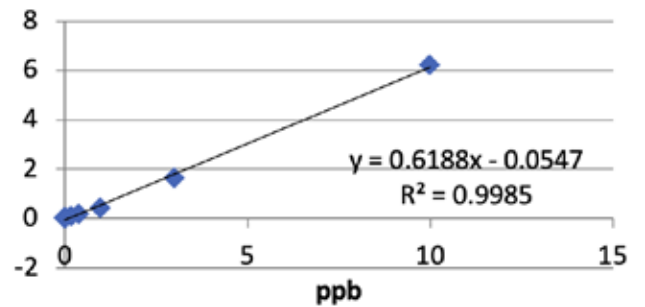
Tetrachloroethylene



Ethylbenzene



p,m-Xylene



o-Xylene

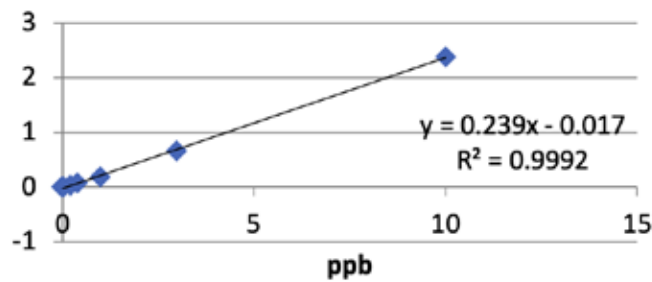


Figure 10 - Calibration Curves of BTEX/TCE/PCE from 0.008 to 10 ppb (1200x range).

Experimental Conditions

5800 SPDU

- Preheat: 2 min to 300° C
- Transfer to Column 1: 3.2 min Split 1 (before Column 1 Trap): 7:1
- Remove Pen Residual: 0.3 min Split 1 30:1
- Desorb: 3 min at 300° C (GC starts) Split 2 (after Column 1 Trap): 7:1
- Back Flush: 4 min
- Cool Down: 1.5 min

GC-MS (Agilent G1530A GC / 5973 MS)

- GC Oven: 35° C, 2 min hold, 25 °C/min ramp to 185° C, 0.5 min hold
- Column 1: Quadrex UAC-1 (5m x 0.53mm x 1µm)
- Column 2: Quadrex 007-1 (30m x 0.25mm x 1µm)
- Column flow: He, 1.2 mL/min
- MS Scan range: 46-200 amu

Air Sampling and Analysis

Several two-week air samplings were performed at the two parking lots (A and B) at Entech Instruments (Simi Valley, CA). Duplicate samples were collected at each sampling site for each two-week sampling period to assess the combined reproducibility of BTEX/TCE/PCE uptake rates, and the reproducibility using dual column thermal desorption inside of the GC oven. The 5-ppb internal standard was spiked after the sampling and before the analysis. **Figure 11** shows a TIC of a two-week parking lot air sample using the developed method. Peaks with high signal-to-noise ratio were observed for most of the analytes except for Trichloroethylene, which was not detected in any of the samples above the 0.01-ppb MDL. An example overlay of two replicates at the same sampling site over the same sampling period is also shown in **Figure 5** to demonstrate the precision of the method. Besides the analytes of interest, there were also relatively high amounts of 1-Chloro-4-trifluoromethylbenzene and Styrene detected in the samples.

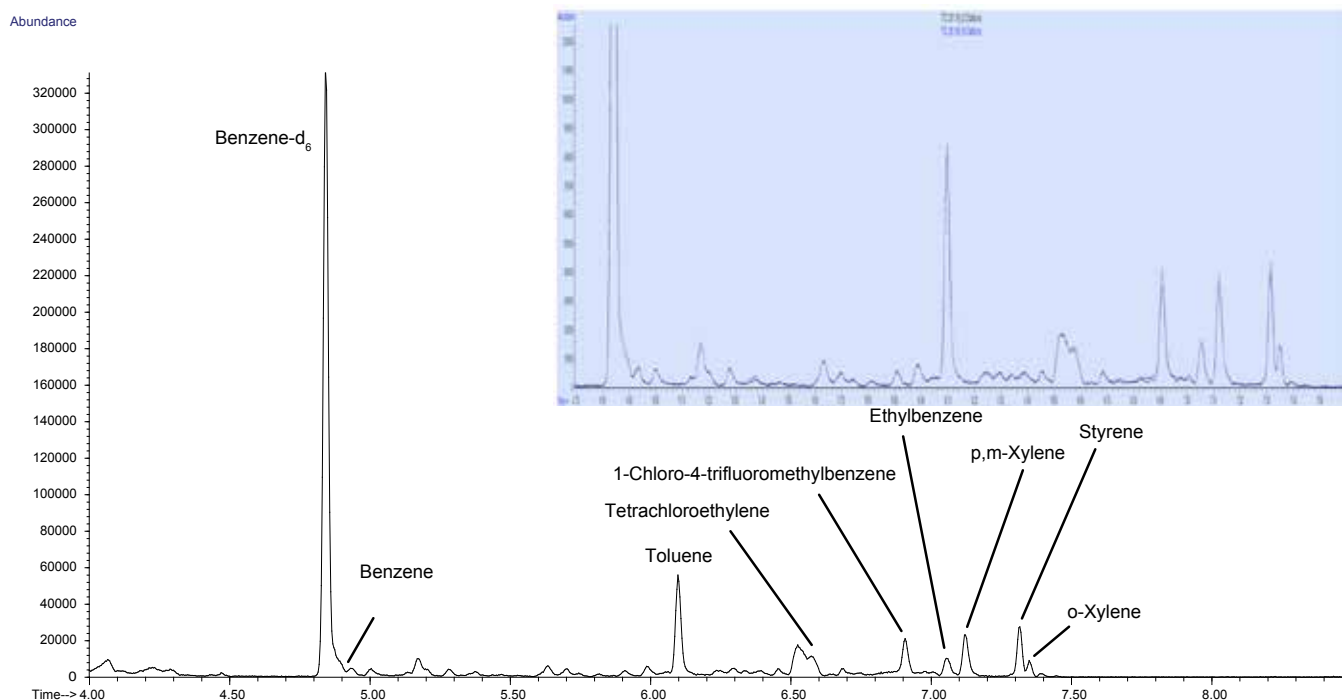


Figure 11 - TIC of a two-week parking lot air sampling. The blue insert is an overlay of two replicates at the second sampling site over the same sampling period, showing near perfect chromatographic overlap. A flat baseline after the Xylenes was the result of Column 1 backflushing to prevent the transfer of heavier compounds onto Column 2, eliminating the need for a longer oven bakeout.

Location A	1a1	1a2	mean	RSD (%)	2a1	2a2	mean	RSD (%)	4a1	4a2	mean	RSD (%)
Benzene	0.173	0.169	0.171	1.67	0.1442	0.1391	0.1416	2.55	0.1158	0.1218	0.1188	3.56
Trichloroethylene	ND	ND	-	-	ND	ND	-	-	ND	ND	-	-
Toluene	1.2248	1.1811	1.203	2.57	0.3319	0.3242	0.3280	1.66	0.2671	0.2650	0.2661	0.56
Tetrachloroethylene	0.0157	0.0181	0.0169	10.1	0.0973	0.0975	0.0974	1.51	0.0948	0.0949	0.0948	0.07
Ethylbenzene	0.1981	0.1932	0.1957	1.75	0.1267	0.1276	0.1271	0.51	0.1161	0.1150	0.1156	0.66
p,m-Xylene	0.4811	0.4765	0.4788	0.68	0.1769	0.1729	0.1748	1.61	0.1601	0.1583	0.1592	0.80
o-Xylene	0.1406	0.1368	0.1387	1.92	0.1341	0.1408	0.1374	3.41	0.1292	0.1262	0.1277	1.69

Location B	2b1	2b2	mean	RSD (%)	3b1	3b2	mean	RSD (%)	4b1	4b2	mean	RSD (%)
Benzene	0.1426	0.1451	0.1438	1.25	0.1472	0.155	0.1510	3.66	0.1129	0.1114	0.1122	0.97
Trichloroethylene	ND	ND	-	-	ND	ND	-	-	ND	ND	-	-
Toluene	0.3258	0.3337	0.3297	1.70	0.319	0.3158	0.3174	0.71	0.2574	0.2566	0.2570	0.22
Tetrachloroethylene	0.0968	0.0972	0.097	0.30	0.1004	0.0969	0.0986	2.46	0.0948	0.0948	0.0948	0.07
Ethylbenzene	0.1254	0.1243	0.1249	0.58	0.1244	0.1232	0.1237	0.68	0.1138	0.1117	0.1127	1.30
p,m-Xylene	0.1758	0.1751	0.1755	0.28	0.1698	0.1711	0.1704	0.52	0.1515	0.1528	0.1522	0.60
o-Xylene	0.1352	0.1318	0.1335	1.76	0.1357	0.1363	0.1359	0.30	0.1145	0.1148	0.1147	0.16

Table 3. Results of two-week parking lot air sampling at two locations (A and B) with two replicates. Results shown in ppb.

The results of the two-week parking lot air sampling at the two locations (**A and B**) with two replicates are shown in **Table 3**. Toluene was recovered at higher concentrations than the other analytes, which is typical in urban air samples. The first set of samples at parking lot A had Toluene concentration over 1 ppb potentially caused by a release in the area, but then the rest of the measurements were in the range of 0.2-0.4 ppb. The concentration of the other analytes were mostly within a range of 0.1-0.5 ppb. The RSDs for most measurements were below 4%, except for Tetrachloroethylene in the same samples that showed the higher Toluene levels. Otherwise, the precision was extremely good, and typically 10x better than required by US EPA Method 325.

Conclusion

A simple, sensitive, and reproducible approach for sampling and analysis of BTEX/TCE/PCE was presented in this study. Diffusive Sorbent Pens with built-in micro seal and tool-free plugs provided reproducible sampling over a 2-week period for the target compounds that were able to diffuse onto and be retained by the Carpack X sorbent.

An automated thermal desorption system with a capillary focusing trap inside of the GC oven was utilized to desorb, split, and focus the sample, thereby eliminating the need for external transfer lines, rotary valves, and additional packed traps. The entire flow path was simple, short, and inert. Thanks to the special design of the two-column system, after elution of the last target analyte from the capillary trap, heavier compounds were backflushed prior to introduction onto the second capillary column to substantially reduce the run time while lowering the maximum oven temperature needed to remove all contaminants. Consequently, the frequency of column and ion source maintenance while operating at the lower oven temperatures should be reduced.

Although Carpack X was proven the most suitable sorbent for this application, the use of other sorbents may allow either lighter or heavier compounds to be sampled and analyzed, while being matched to stronger or weaker focusing traps and separation columns to optimize the analysis of compounds recoverable using a diffusive sampling approach. This approach will also be further investigated for other applications such as indoor air monitoring and personal monitoring.



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