Passive Collection of Volatile Compounds in Air using a Novel Adsorbent Sampler with Direct, Rapid Injection into a Capillary GCMS without Secondary Focusing

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Abstract

A new solution for the passive monitoring of Volatile compounds to sub-PPB levels in air is presented. New adsorbent based sampling devices called Sorbent Pens are used to passively collect air samples for 24 hours to 2 weeks, depending on the sensitivity and period of time weighted averaging desired. For this study, Carbopack X was used to specifically target BTEX compounds, although the adsorbent can be changed to recover lighter compounds such as Vinyl Chloride and Chloromethane, or much heavier compounds into the Semi-Volatiles range. A novel Sorbent Pen thermal desorption unit is introduced that rapidly transfers the collected sample directly into a GC, eliminating the need for a secondary focusing trap. Direct GCMS sample introduction results in far less carryover and system contamination than those solutions that perform secondary trapping and then transfer through long, heated lines to the GC. A pre-column inside the GC oven is used to backflush and eliminate heavier compounds that would otherwise contaminate the primary GC column, thereby reducing GC bakeout times. Data showing a calibration curve from 0.3 PPBv to 15 PPBv is presented, along with analytical precision when collecting duplicate and triplicate Sorbent Pens during a 1 week sampling period. Comparison were made to co-located 1 week sampling into two Silonite coated, 6L stainless steel canisters to prove the accuracy of the technique and to validate sample collection rates for BTEX compounds.

Background

Analysis of chemicals in both outdoor and indoor air down to sub-PPB levels has been shown using both thermal desorption tubes and whole air sampling canisters. The desire to simplify the sampling strategy led to the original development of whole air sampling canisters, as this avoided pumps and batteries, and increased the range of recoverable compounds relative to any one adsorbent.

Recently, completely passive tube methods such as US EPA Method 325 are emerging to further simplify the sample collection strategy. As with active tube sampling, the correct adsorbent must be selected for the range of compounds desired. However, unlike active sampling, a multi-bed trap is ineffective at collecting a wider range of compounds when performing diffusive air monitoring. For highly volatile chemicals, a strong adsorbent such as Carboxen 1000 is used to allow non-reversible adsorption of these light chemicals during the sampling period. Mid-range compounds such as Benzene, Toluene, Ethyl Benzene and Xylenes require a moderately strong adsorbent such as Carbopack X for reliable retention. There is the

potential for shifting this range even further out using weaker adsorbents like Tenax.

Typically, adsorbent traps are made of tubing that is 1/4" OD, with lengths varying from 3.5" to 7", with the 3.5" version being the most common. This tube geometry was adopted in the 1970s, and has not been updated much since. Due to the internal volume of these tubes, secondary preconcentration systems are used in the laboratory to further condense the sample to allow rapid injection onto a capillary column. This added path length between the original tube and the GC column can result in both sample loss and carryover, creating more variability in the analytical data. Since the first thing the air sample touches is the adsorbent in the tube, there is no way to prevent the collection of very heavy compounds, even non-volatiles that can break down into heavy semi-volatile compounds upon thermal desorption (pollen, spores, bacteria, plant fragments, particles with adsorbed SVOCs, etc). As heavy breakdown products continue to collect in the sample flow path, target compound recovery and carryover potential can be affected.

A new adsorbent tube / desorber combination is introduced that allows direct desorption into the GC by minimizing mixing volumes prior to the GC column . The desorber is installed into an unused GC injector port position, and pre-pressurizes the adsorbent tube using the carrier gas pressure without release of the adsorbed sample, allowing sample preheat prior to GC injection. A pre-column in the GC acts as a low pass filter, allowing only target compounds to reach the second column before the first column is backflushed to eliminate the heavier compounds. This keeps the system much cleaner, and considerably shortens GC run times. Changing the liner in the desorber replaces the entire flow path between the Sorbent Pen sampler and the GC columns, ensuring long term reliability in system performance. The effectiveness of this technique for capturing and quantifying BTEX in air was investigated for reproducibility and accuracy relative to ceramic coated canisters that are considered to be the "Gold Standard" of air monitoring.

Figure 1 - One week sampling into two Silonite coated 6L canisters and 3 Diffusive Sorbent Pens with Carbopack X. Diffuser caps are used to prevent over-sampling due to windy conditions. Also shown is a proposed sampling station for collecting multiple tubes potentially filled with different adsorbents to optimize recovery of lighter or heavier compounds.

Experimental

Gas phase standards were created by injecting liquid phase BTEX standards (Sigma Aldrich) into 6L Silonite canisters (Entech, Simi Valley, CA) to generate 1-50PPMv level working standards. Sorbent Pens (Entech Instruments) designed for US EPA Method 325 containing Carbopack X (Supelco) were spiked with 2cc of each gas phase standards to create a calibrated method that could be used to calculate the concentration in sample tubes by multiplying the ratio of the spiked tube volume to the known rate of diffusive sample collection multipled by the sampling time . To ensure sampling rates equivalent to those stated in US EPA Method 325, the Sorbent Pen was designed with the same ID and adsorbent packing depth as specified in the 325 method (5mm ID and 15mm open volume prior to adsorbent). Considering the sampling rates from 0.67cc/min for Benzene to 0.46cc/min for Xylenes listed in the method, a total volume of from 4.64L to 6.75L would be sampled over a 1 week period, which is far too much to inject into a GCMS without splitting. Therefore, a split ratio of 35:1 was chosen to bring the effective injection volume down to about 133 for Xylenes and Ethyl Benzene, to 193cc for Benzene, which is enough sample to achieve MDLs below 0.04 PPBv using full scan GCMS. The same gas syringe spiking technique was used to add 2cc of a 1PPM 1,4-Difluorobenzene internal standard to all standard, sample, and blank tubes.

Two sets of samples were collected in triplicate, one set along with two whole air sampling 6L canisters using CS1200E5 Flow Controllers (Entech) that we calibrated to fill at a constant rate over a 1 week period. The second set of 3 tubes were placed in a parking lot near parked vehicles to enhance the level of BTEX compounds. As specified in Method 325, difusers were placed over the sampling end of the tubes to prevent convective transfer during windy conditions which would otherwise increase the update rate of BTEX.

A 5800 Sorbent Pen Desorber Unit (Entech) was installed onto the back unoccupied injector port on a 7890B/5977 GCMS (Agilent), and carrier gas flow was supplied to it by teeing off of the carrier gas going to the front injector. Operating the front inlet in the splitless mode accomodated variable flow rates to the 5800 and columns attached to it. A pre-column (5m, 0.25mm ID, 0.5um PDMS) was used to prevent heavier, unwanted compounds from reaching the second, longer analytical column (60m, 0.32mm ID GasPro - Agilent). A tee between the two columns allowed flows to be reversed through the pre-column after target compounds were safely on the second column, eliminating the potential for system contamination by heavy volatile and semi-volatile compounds.
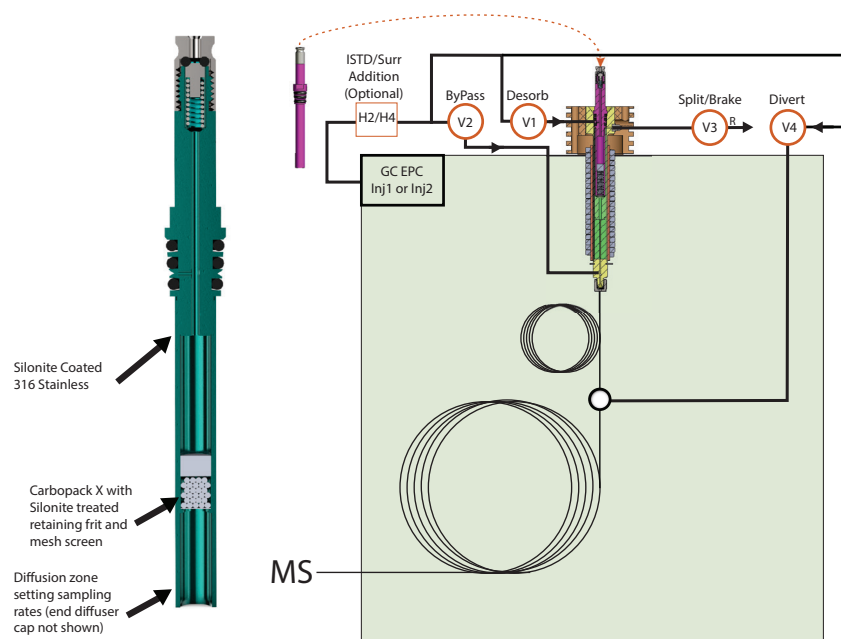

Figure 2 - Diffusive Sorbent Pen developed for BTEX monitoring over 8 hours to 2 weeks. The Carbopack X adsorbent is positioned to create reliable sample collection rates. The 5800 SPDU allows rapid injection into the GC, and controls the diversion of the carrier gas to back flush off heavy compounds before they reach the highly retentive Gas Pro Column.
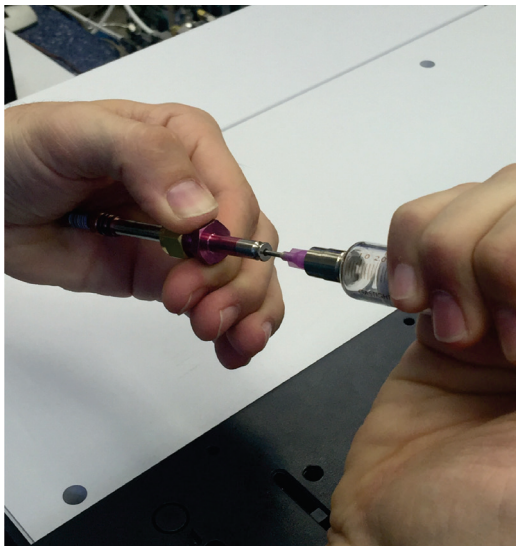
Figure 3 - Spiking of gas phase calibration standards and internal standards onto each tube is performed using gas tight Micro QT valves, and a 5-10cc glass gas-tight syringe with a 16 gauge needle.
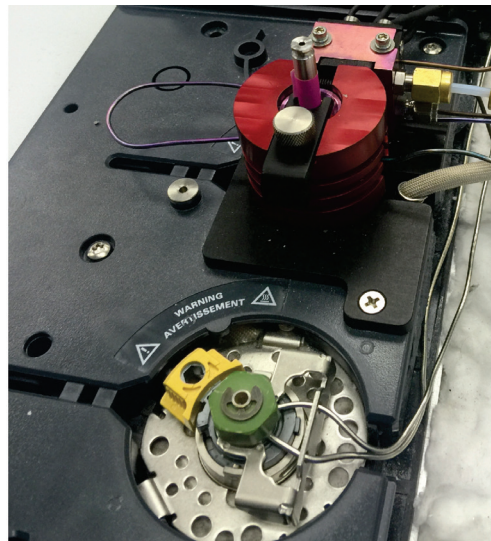

Figure 4 - The 5800 SPDU mounted on a 7890 GC. The 5800 is controlled through a SmartLab 2 interface (Entech) operating on the same WIN7 PC as the GCMS data system.

Discussion

Figure 3 shows the spiking of the Sorbent Pen with a gas phase standard. It is critical to introduce the standard onto the tube in the gas phase when using diffusive sampling tubes in order to deposit the standard onto the adsorbent the same way it will be during sampling. The Micro QT valve shown attached to the sampling end of the tube simplifies this process, as they were designed to interface with a 16 gauge needle. Table 1 shows the excellent linearity that was achieved, with all compounds under 6% RSD. The desorption of the Sorbent Pens into the dual column GC created the chromatography shown Figure 5, without the need for secondary focusing. The divert valve was opened after 6.3 minutes to backflush the 5m precolumn to prevent the introduction of heavy compounds onto the Gas Pro column. Figure 6 shows overlays of the 3 tubes collected for a week in a parking lot. Most compounds overlapped perfectly, indicating the overall precision of this approach. Figure 7 shows Benzene at 0.09 PPBv as collected on one of the Sorbent Pens exposed for a week in ambient air, still with plenty of signal to noise to allow measurements at lower levels. Figure

8 shows the overlay of Carbon Tetrachloride m/z=117 in the 3 parking lot diffusive samples. The global background for Carbon Tetrachloride has been dropping at 1-2 part per trillion per year over the past 20 years, and is currently at about 70 part per trillion. This concentration is easily detected, and its consistency from tube to tube can help to prove that each sampling event was successful. This is in contrast with other diffusive samplers where you can't prove whether the device sampled at the anticipated rate.

Table 2 shows the results for the 1 week sampling events. What started out to be 3 ambient tubes ended up being 2 due to an MS data collection error. The ambient air results were below the low level standard, but close enough that they should be fairly accurate. The canister data is also shown, and supports the results obtained with the two diffusive tube samples for BTEX. The slightly increased level of Toluene in the canister data is being investigated. The triplicate parking lot data shows the true potential of this technique when levels are in the calibrated range. The BTEX compounds were in virtually perfect agreement, with data quality

comparing to the best canister data in terms of reproducibility. The optimized design of the Sorbent Pen and the "on-column" desorption offered by the 5800 combine to create a solution where transferline losses and carryover are reduced to near zero.
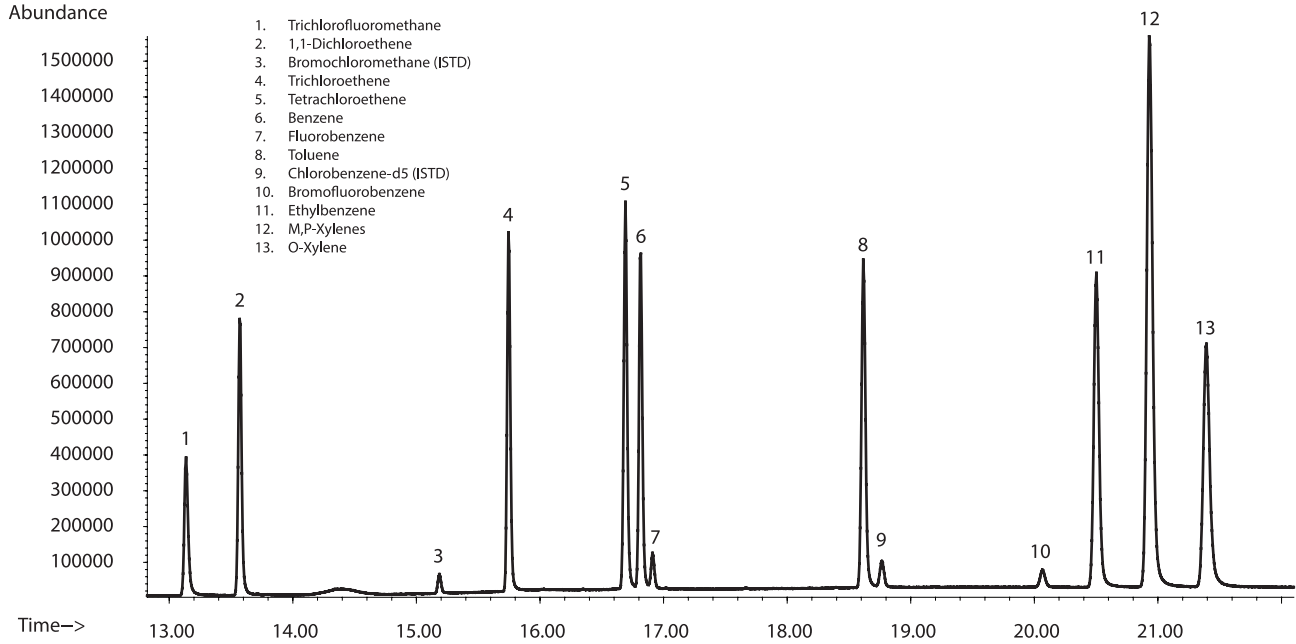

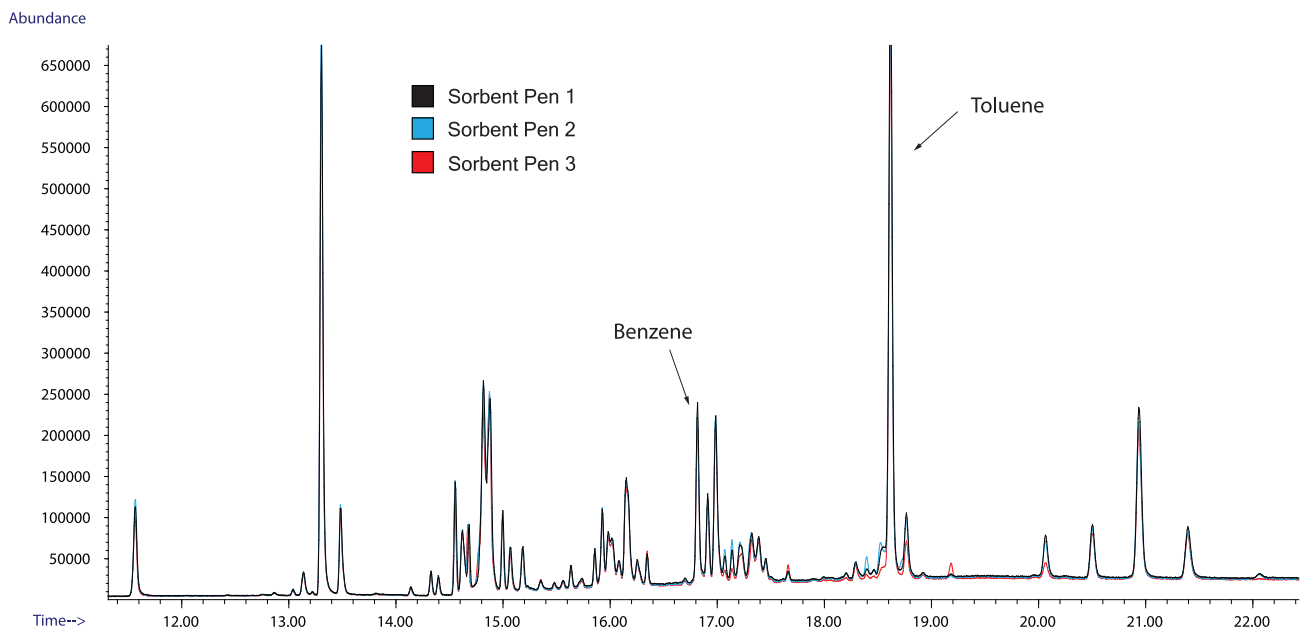**Figure 5** - BTEX Standard Corresponding to 6 PPBv for Benzene as sampled for 1 week.

Figure 6 - Triplicate tubes placed in parking lot near parked vehicles to increase BTEX Concentrations. Sampling was performed over a 1 week period. Overlap of BTEX is virtually perfect.
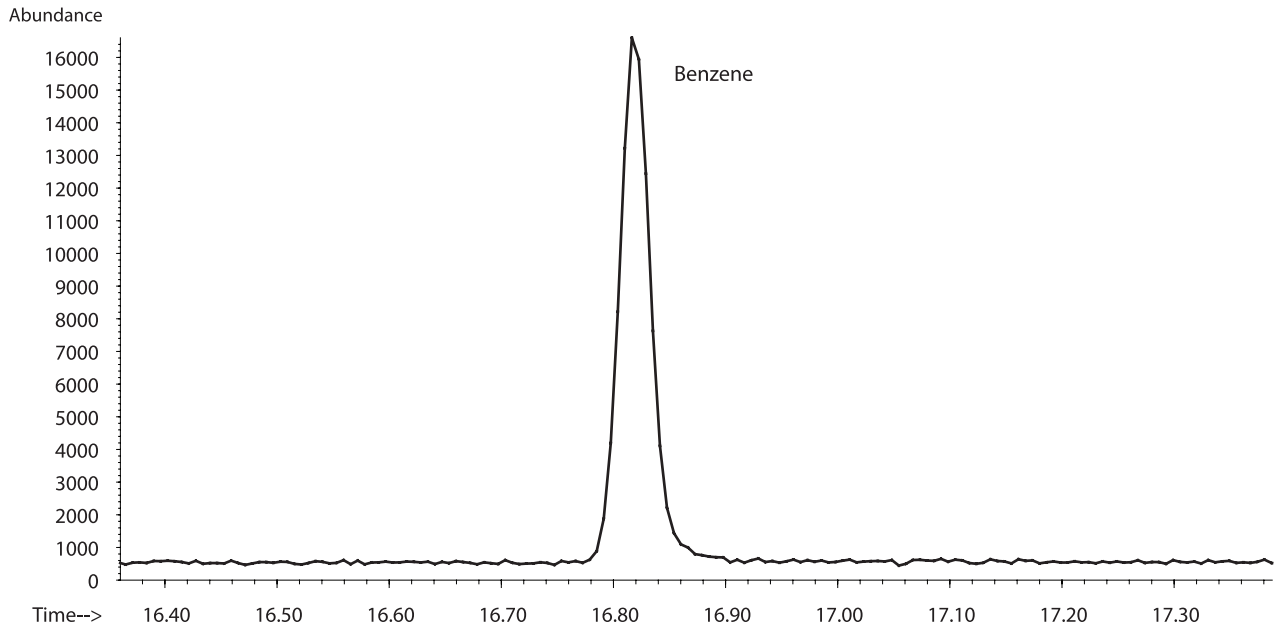
Figure 7 - Benzene m/z=78 from Ambient tube sample, with calculated concentration of 0.09 PPBv.
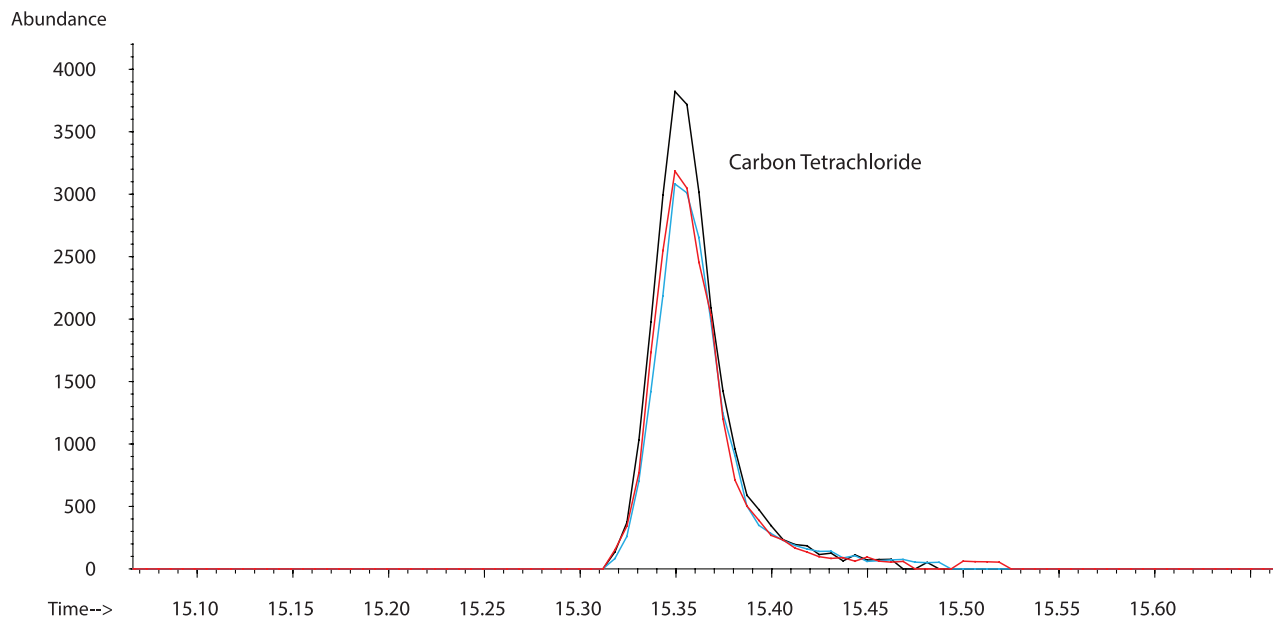

Figure 8 - Carbon Tetrachloride m/z=117 reproducibility at the global background of 0.070 PPBv, helps to prove a successful sampling event slight variations of 10-15% are expected at levels nearing method detection limits.

Calibration in PPM-mL/2								
		1	3	10	20	50	Average	%RSD
Benzene		1.233	1.152	1.094	1.083	1.054	1.123	5.65%
Toluene		1.232	1.155	1.117	1.120	1.102	1.145	4.08%
Ethylbenzene		1.246	1.177	1.121	1.191	1.115	1.170	4.13%
m,p-Xylene		3.154	2.963	2.811	2.972	2.767	2.933	4.67%
o-Xylene		1.525	1.406	1.328	1.397	1.317	1.395	5.33%
4-BFB		0.904	0.931	0.886	0.914	1.019	0.931	4.99%

Table 1 - BTEX Calibration data. Five different canisters were made up from 1 to 50 PPM to spike 2mL into each Sorbent Pen before desorption. For a 1 week diffusive Sorbent Pen sampling for Benzene collecting at 0.67cc/min, this corresponds to a 0.3 to 15 PPBv Calibration range.

	Benzene	Toluene	Ethybenzene	m,p-Xylene	o-Xylene
Rate of Collection:	0.67+-0.06	0.52+-0.14	0.46+-0.07	0.46+-0.09	0.46+-0.12
Total Volume, 163 Hrs	6553	5086	4499	4499	4499
			Concentrations (PPBv)		
Ambient Air Tube#1	0.101	0.185	0.044	0.111	0.040
Ambient Air Tube#2	0.089	0.173	0.036	0.098	0.040
%RSD Amb Air Tubes	9.09%	4.66%	13.31%	7.96%	0.00%
Ambient Air Canisters (Ave)	0.076	0.340	0.043	0.109	0.045
Parking Lot Tube #1	0.63	2.98	0.31	1.08	0.36
Parking Lot Tube #2	0.62	2.89	0.30	1.06	0.35
Parking Lot Tube #3	0.63	2.91	0.29	1.06	0.36
%RSDs ParkLot Tubes	0.49%	1.68%	2.75%	0.89%	1.32%

Table 2 - BTEX Data for 1 week duplicate diffusive samples compared to 6L canister samples, and triplicate 1 week diffusive tubes at elevated levels . The reproducibility was better than anticipated for a diffusive technique, and the ability to inject the sample directly onto the GC column probably contributed to the consistency in the results.

Conclusion

A solution has been presented that simplifies the collection and analysis of BTEX in air. This technique should work equally well for indoor or outdoor air monitoring. The ability to split during thermal desorption allows even higher concentrations to be monitored, including at the fenceline around refineries. The high level standard in this study was approximately 10-50 times below the mass spectrometer's saturation point for BTEX compounds, suggesting this technique could be used to monitor in more contaminated areas. The ability to successfully monitor Carbon Tetrachloride at its global background level provides a built in surrogate standard that further enhances the reliability of this approach for BTEX monitoring in air.

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