ENTECH INSTRUMENTS

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Optimization of EPA Method 325

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Overview of EPA Method 325

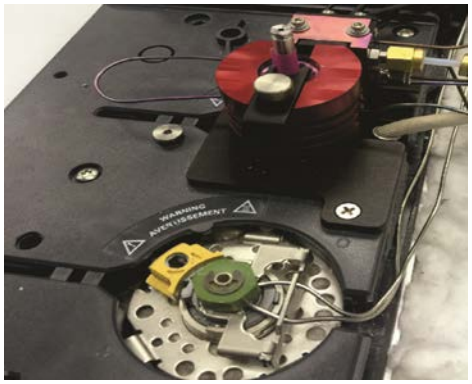
1. Improvements to current thermal desorption technology
2. Sample Collection
3. Calibration Technique
4. Sample Analysis
5. Analytical Results

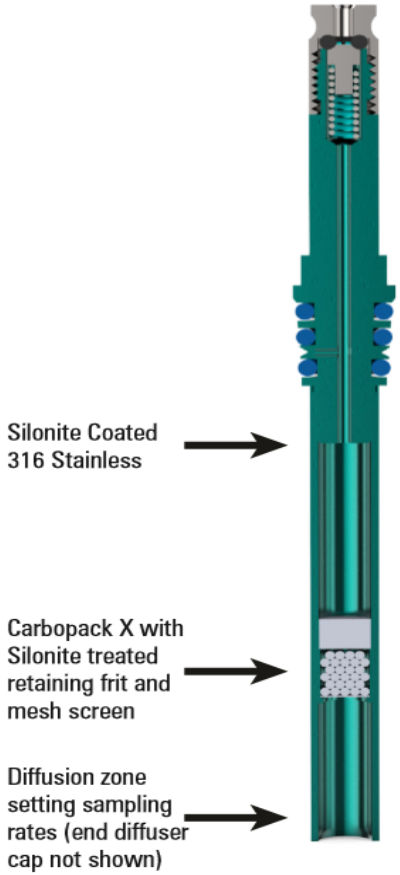
EPA Method 325 Summary

- Fence line monitoring for benzene at oil refineries for 1-2 week periods
- Diffusive Sampling tubes with known uptake rates specified in EPA Method 325
- Uptake rate is dependent on the design of the sorbent tube
  - Must be ¼" tube with 5mm ID and 15mm open volume prior to the adsorbent
  - For benzene, this yields an uptake rate of 0.67cc/min when using CarboPack X
- Thermally desorb sorbent tube to a Gas Chromatograph equipped with either Flame Ionization Detector or Mass Spectrometer

Improvements

- Newly designed 5800 thermal desorption system that sits directly on top of an open injection port of the GC to allow the sample to desorb right into the GC column
- Eliminates long transfer lines that can cause carryover
- Optimized design of the sorbent tube that incorporates a side port at the top of the tube that allows desorb gas to flow through the tube and into the GC column





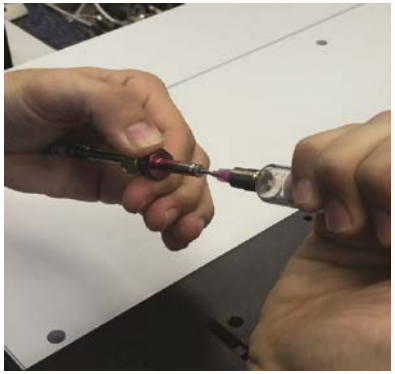
Sample Collection

- Sorbent Pens need to be thermally conditioned and blank tested prior to use
- Addition of a diffuser is required to prevent wind from disturbing the uptake rate
- Sample duplicates and blank collection is need at a 10% frequency
- Protective cover is also needed in case of rain that may occur during a 2 week period
- Comparison of Diffusive Sorbent Pen collection and canister sampling

Calibration Technique

- 5 different concentrations of the gas phase BTEX standards were prepared from the neat chemicals at 1-50ppm
- 2ccs of each calibration standard was spiked onto the Sorbent Pen yielding a concentration range of 0.3, 0.9, 3, 6, and 15 ppbv
- For a 2mL, 1ppm standard you will have injected:
  (1 µL/L)(0.002L) = 0.002µL of BTEX Vapor
- 1 week sample at 0.67cc/min uptake rate
- 6.75L will be collected on the Sorbent Pen yielding a concentration of:

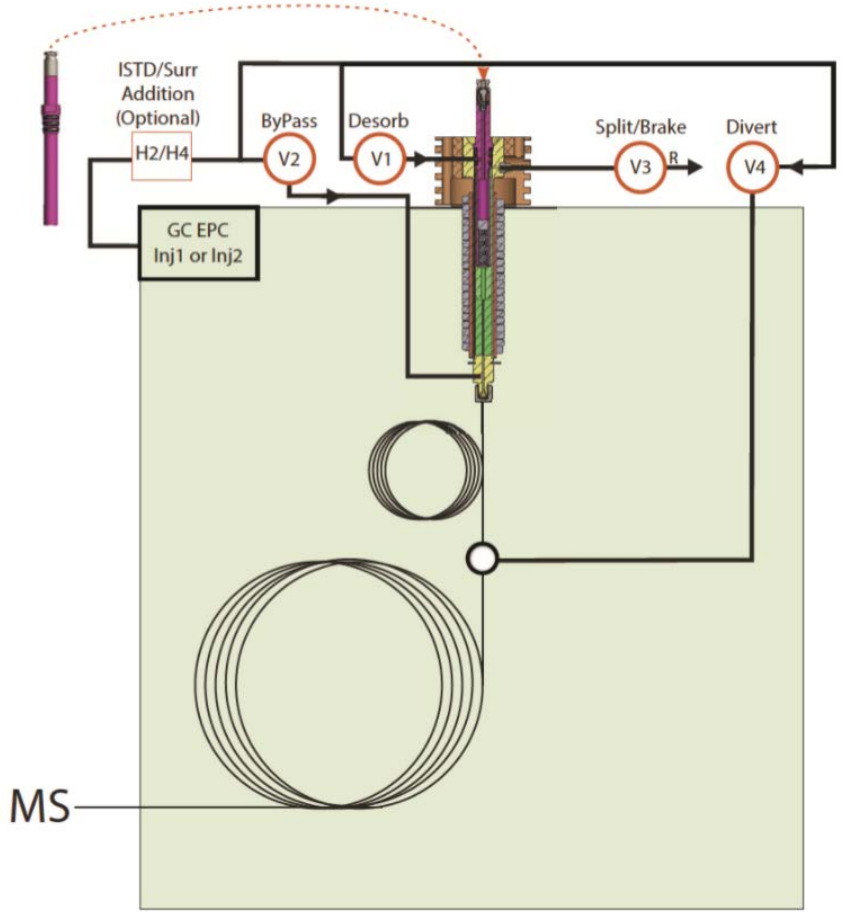
$$\frac{0.002\mu L}{6.75L} = \frac{0.3nL}{L} \text{ or } 0.3ppbv$$



	Concentration (ppbv)						
Compound	0.3	0.9	3.0	6.0	15	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-Xylenes	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

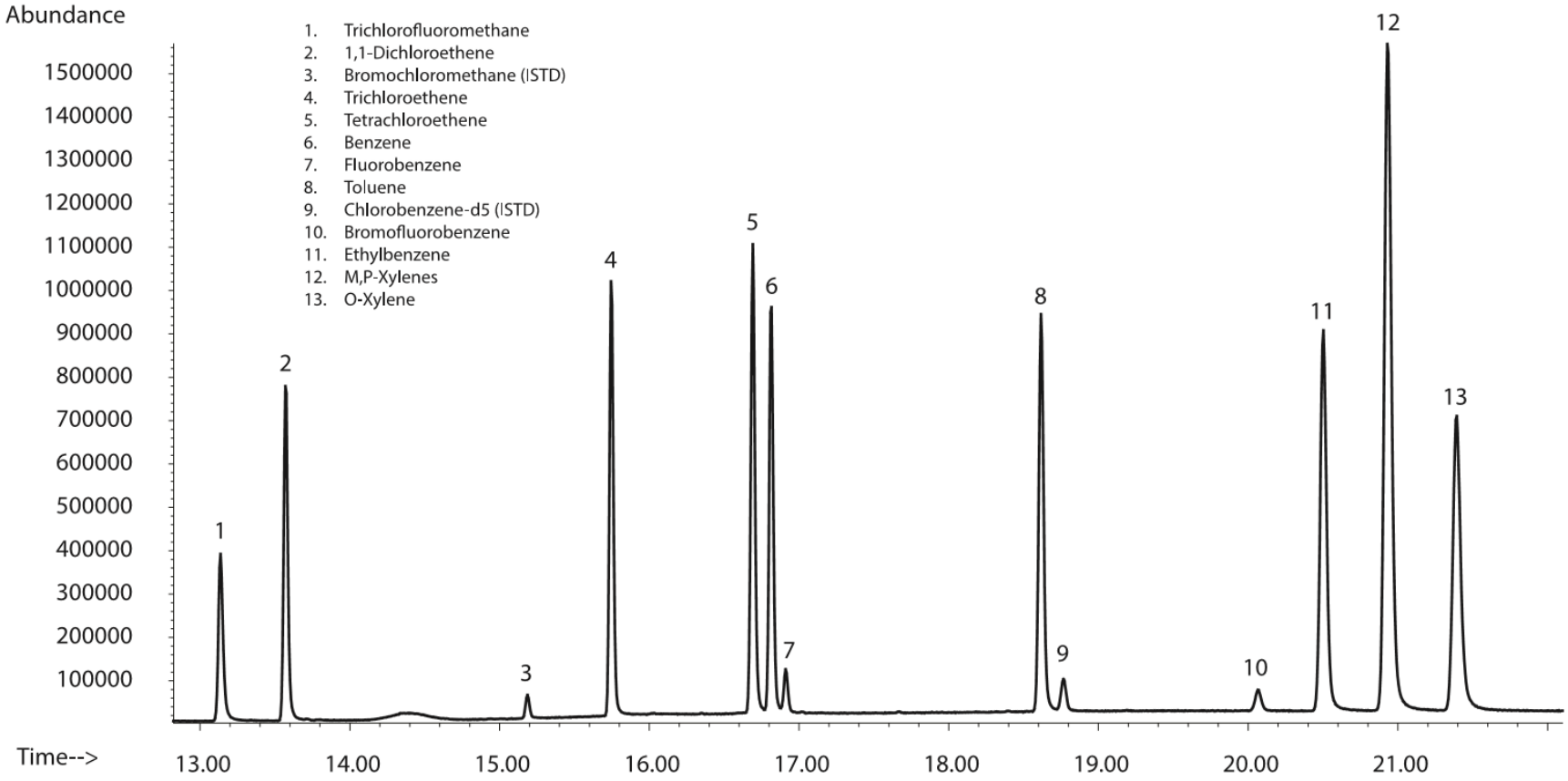
Sample Analysis

- 5800 Thermal Desorber (Entech Instruments) installed on a 7890B/5977 GCMS (Agilent Technologies) in open rear injection port
- Carrier gas flow to the desorber is supplied by teeing off from the line going to the front injector
- 5m x 0.25mm ID x 0.5μm DB-1 precolumn is used to prevent heavier, unwanted compounds from reaching the longer 30M CL-BTEX analytical column
- Tee between 2 columns allows the flow to be reversed through the precolumn after target analytes have passed onto the primary column



Perfect Peak Shape without LN2 Focusing

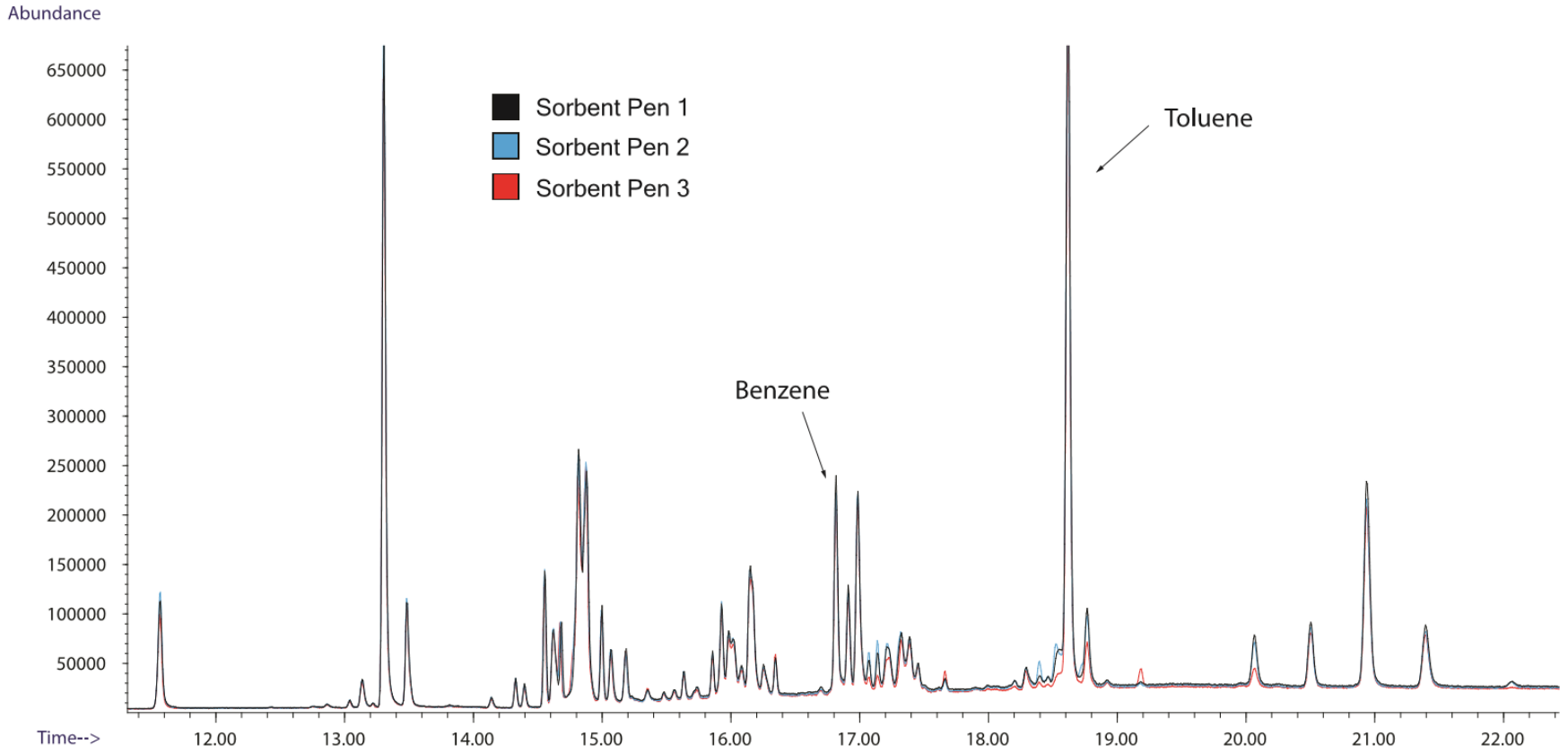
Back-flushing Eliminates Ghost Peaks and Reduces Run Times



BTEX Standard corresponding to 6 ppbv for benzene as sampled for 1 week

Triplicate Sampling of 325 Sorbent Pen

Virtually perfect overlap of BTEX Compounds

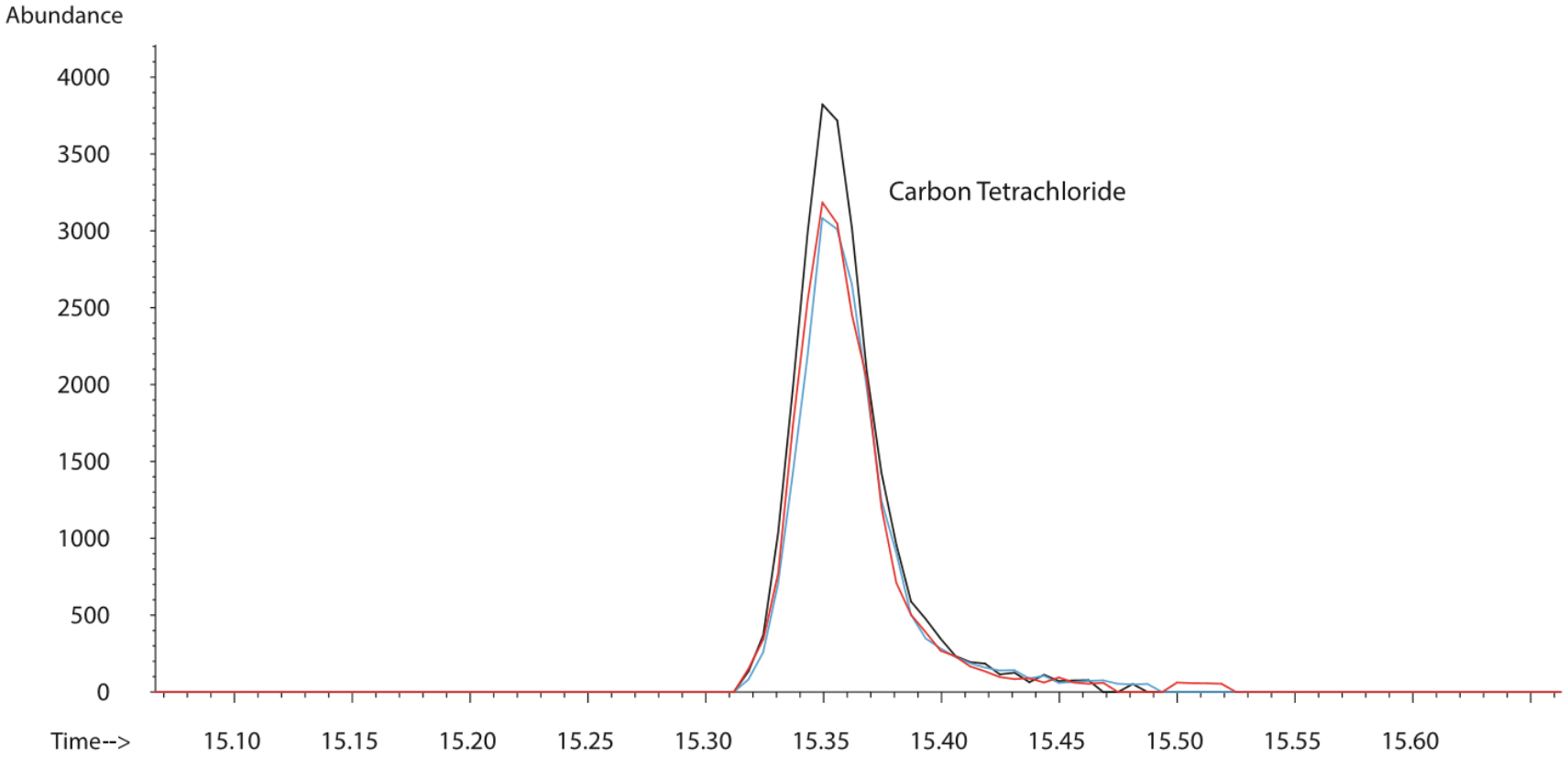


Triplicate Sorbent Pens placed in parking lot near parked vehicles to increase BTEX concentrations. Sampling was performed over a 1 week period.

Carbon Tetrachloride Ion Chromatogram

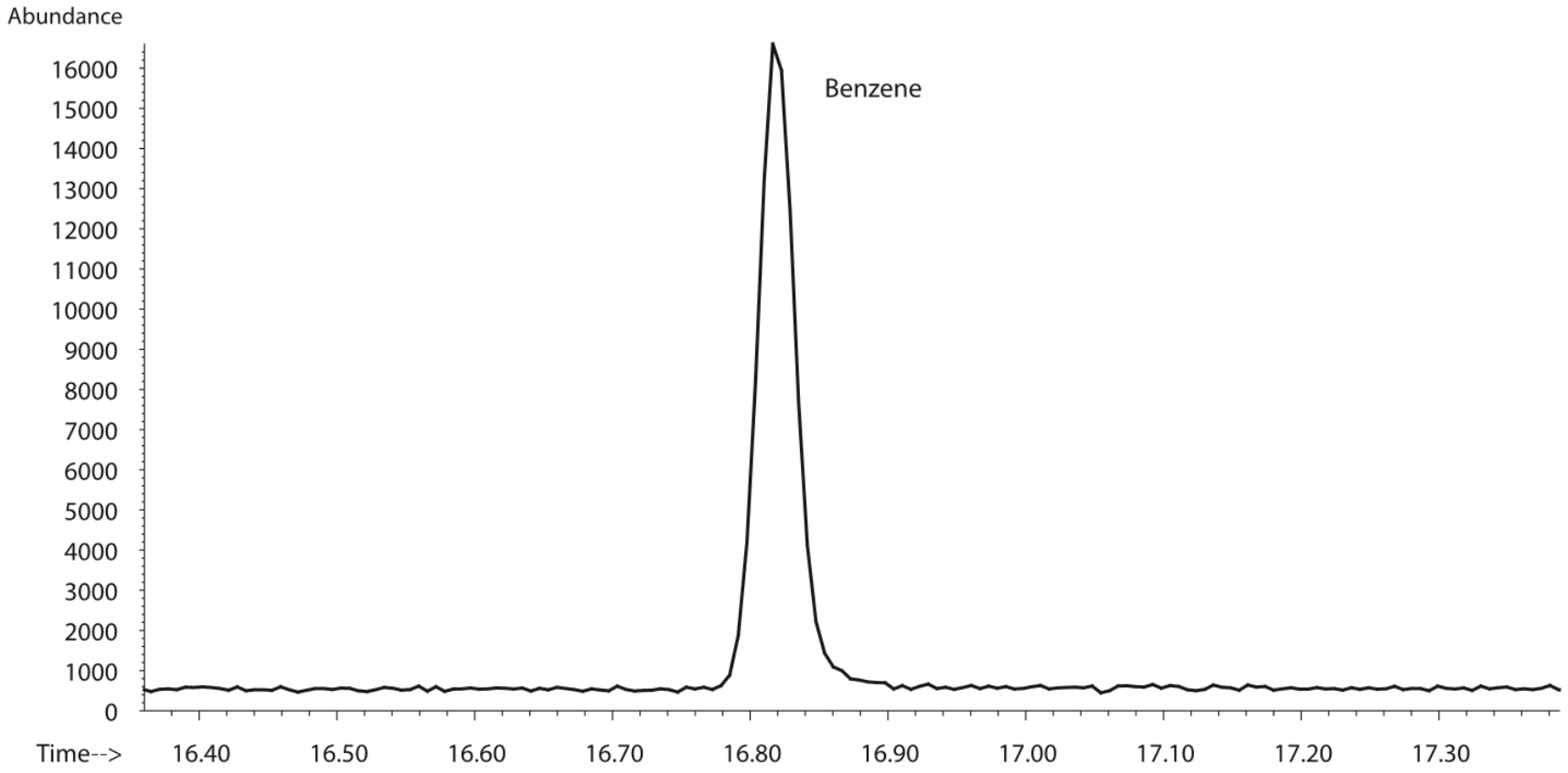
m/z = 117

Reproducibility at the global background of 0.070ppbv, helps to prove a successful sampling event slight variations of 10-15% are expected at levels nearing method detection limits



Benzene Single Ion Chromatogram

m/z = 78, from ambient tube sample with calculated concentration of 0.09ppbv



325 Sorbent Pen Comparison to Canister

Sampling and Triplicate Pen Results at Elevated Levels

	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%

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

- Diffusive sampling provides a simplified collection for long periods of time, such as 1-2 weeks
- Optimized Thermal Desorption Unit directly into the GC column eliminates carryover
- Data quality that surpasses requirements of EPA Method 325