The Advantages of Passive Sampling to Measure Compounds in Air

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Welcome and Outine

- Introduction
- Adsorbents and tubes
- Comparison of passive and active sampling
- Applications and validation using passive sampling
- Operation of Thermal Desorption (discussed in second presentation today)
- Analytical method

Introduction: Air Sampling Applications

- The determination of toxic compounds – tube sampling
  - Soil gas
  - Indoor / outdoor air
  - Fenceline Monitoring (FLM)
  - Industrial stack emissions
  - Manufactured Gas Plants (MGP): volatiles and semi-volatile requirement
  - Worker exposure (industrial hygiene)
  - Off-gassing of materials ie building materials, automotive, etc. (could be irritant and not toxic)

- Ozone Precursor: typically on-line sampling
  - EPA target volatile organic compounds (VOCs) that promote ozone
  - Ground-level ozone is a "secondary" pollutant since it occurs when two primary pollutants react in sunlight and stagnant air. These two primary pollutants are nitrogen oxides (NOx) and volatile organic compounds (VOCs)

New Sorbent Tubes Investigated

- 2010: Soil Vapor Intrusion (SVI) Tube (patented)
  - (C_3 to C_{26})
  - Combines VOC & SVOC from the seven VOA gases to phenanthrene
  - PerkinElmer thanks CARO Analytical Services
- 2011: XRO-640 tube (patent pending)
  - (C_6 to C_{44})
  - Combines VOC & SVOC from BTEX to benzo(g,h,i)perylene
  - PerkinElmer thanks Alberta Innovates Tech Futures and Pace Analytical Services
- 2013: XRO-440 (patent pending)
  - (C_4 to C_{44})
  - Combines VOC & SVOC from 1,3-butadiene to benzo(g,h,i)perylene
  - PerkinElmer and Pace Analytical Services

Tubes and Adsorbents

Tube Material Used for Thermal Desorption

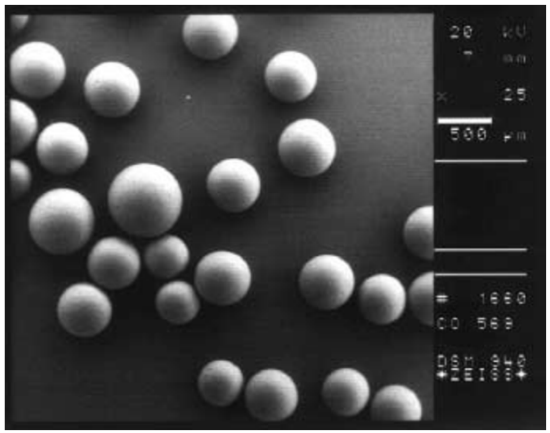
- Glass – adsorbents held by glass wool or glass frits
- Metal – adsorbents held by screen.
- Glass lined metal
- Deactivated metal

Adsorbent Choice and How It Works

- Choose an adsorbent (s) that will retain the components (without breakthrough) and release (recover) the target components of interest in the sample. Active sampling allows for the broadest component range
- Moisture management
- How it works
  - Smaller surface areas are for greater boiling point components and larger surface areas are for more volatile components

Adsorbents: Most Retentive

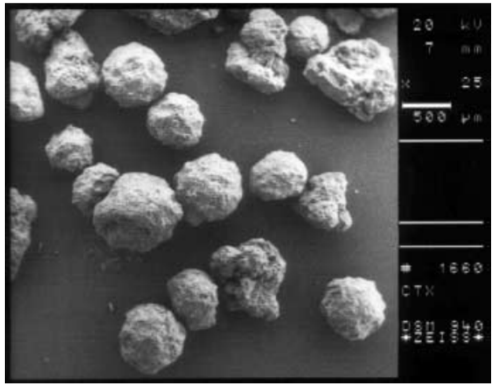
- Carbon Molecular Sieves
  - Spherical
  - Surface area 400 to 1200 m^2/g
  - Retains and releases light components: typically, C_2 – C_5; However, carboxene 2016 has a range from C_5 – C_{12}
  - Upper temperature limit: 400 ^oC
  - Moderate to very hydrophilic. Requires dry purge if sampled in humid conditions environment



Carboxen-569, W. Engewald et al.,
Anal Bioanal Chem (2002) 373: 490–500

Adsorbents: Broad Range

- Graphitized Carbons
  - Granular
  - Surface area 2 to 240 m^2/g
  - Retains and releases from C_3 to C_{28}
  - Strongest to weakest X>B>F>C>F
  - For instance; X has a range from C_3 to C_9
  - Upper temperature limit: 400 ^oC
  - Hydrophobic



Carbotrap-X, W. Engewald et al.,
Anal Bioanal Chem (2002) 373: 490–500

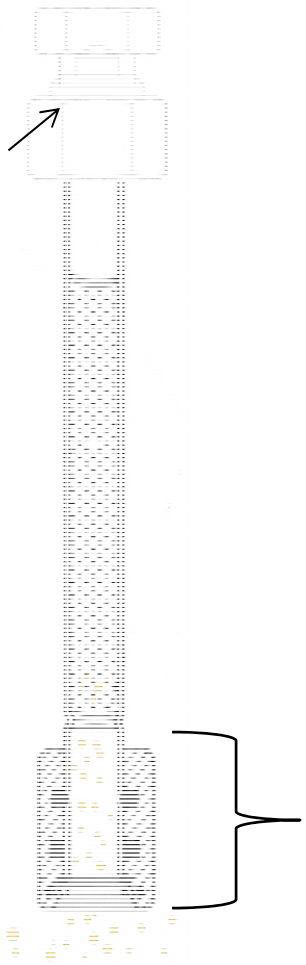
Adsorbents: Legacy (old)

- Porous Polymers (legacy)
  - Tenax TA and GR; Porapak N; Chromosorb 106; HayeSep D
  - Surface area 24 to 795 m^2/g
  - Retains and releases mid to high boiling point components C_7 to C_{30}
  - Temperature limit: 260 to 350 ^oC
  - Hydrophobic
  - Tend to produce high backgrounds, adsorbents can pyrolyze and cause significant contamination. Carbon based adsorbents are preferred
  - Let's move away from legacy and move into new technology

Active and Passive Sampling

Comparison of Passive and Active Sampling

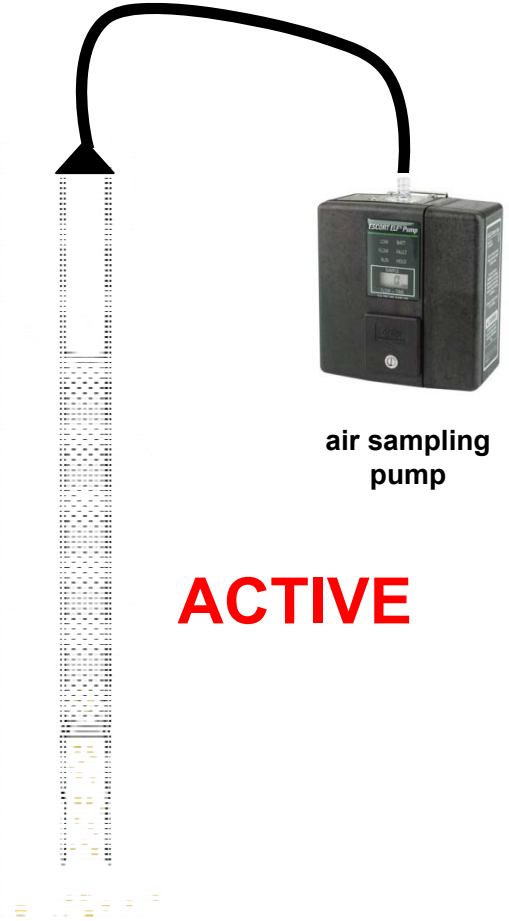
Long Term Storage Cap
Cap remains while during sampling



Single Bed of Adsorbent

Diffusion Path
" Fixed Air Gap"

PASSIVE



air sampling pump

ACTIVE

Active (pumped) Sampling Using TO-17

- Multiple Adsorbents: accommodate wide boiling point analyte range
- A known flow is pumped through the tube for a specified amount of time to attain volume desired: (mL/min) (min) = volume sampled

Sample the tube in the direction of weak adsorbent to strong adsorbent →

← Desorb the tube in the direction of strong adsorbent to weak adsorbent

Diffusive Caps

Diffusive Cap installed on the inlet of the sampling tube

- The diffusive caps
  - Defines the diffusive air gap inside the tube
  - Prevents air movement within the diffusive air gap during windy conditions
  - The screen in the cap prevents insects from entering the tube while sampling

Passive Sampling

- Precise caps for diffusive sampling
- Tubes accommodate clips for personal monitoring
- Many uptake rates have been determined to ensure a known volume uptake rate / compound
- PerkinElmer provides and recommends the adsorbent tubes the EPA used in developing method 325

The uptake of compounds of interest relies on the natural movement of the VOC molecules across the concentration gradient of the air gap in the inlet of the tube.

The Difference Between the Caps

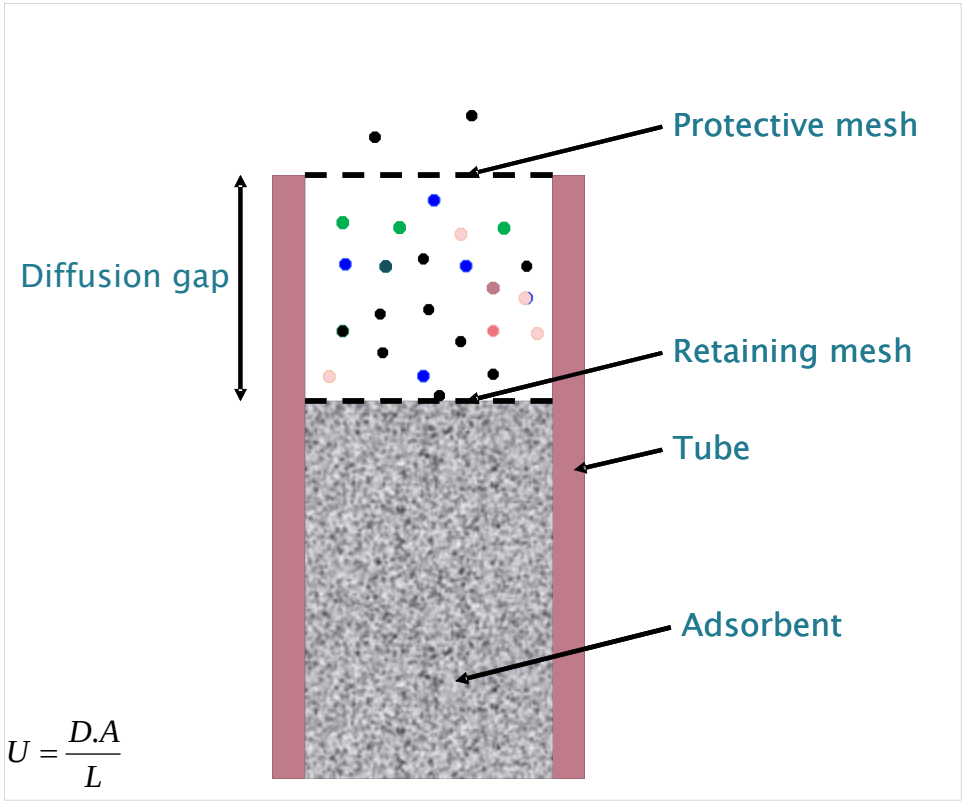
Long Term Storage Caps
Protects the tubes from contamination before and after sampling. PTFE ferrules are used in-place of the metal ferrules

Diffusive Cap
Placed on the tube (in the field) prior to putting them in the shelter

Analytical Caps
Seals the tubes on the thermal desorber carousel

The Diffusive Sampling Process

- Diffusive Uptake Rate dependent on diffusion gap geometry and diffusion coefficient of each analyte
- There is only a small surface area of a single adsorbent exposed to the sample
- If the adsorbent is strong, it will retain all analytes but may only release the lighter ones during analysis
- If the adsorbent is weak, it will retain just the heavier analytes
- Therefore, diffusive monitoring has a limited boiling point range compared to TO-17



Math☺ Of Course, Really Defines What's Happening

Fick's law – gas molecules will diffuse from an area of higher concentration to an area of lower concentration

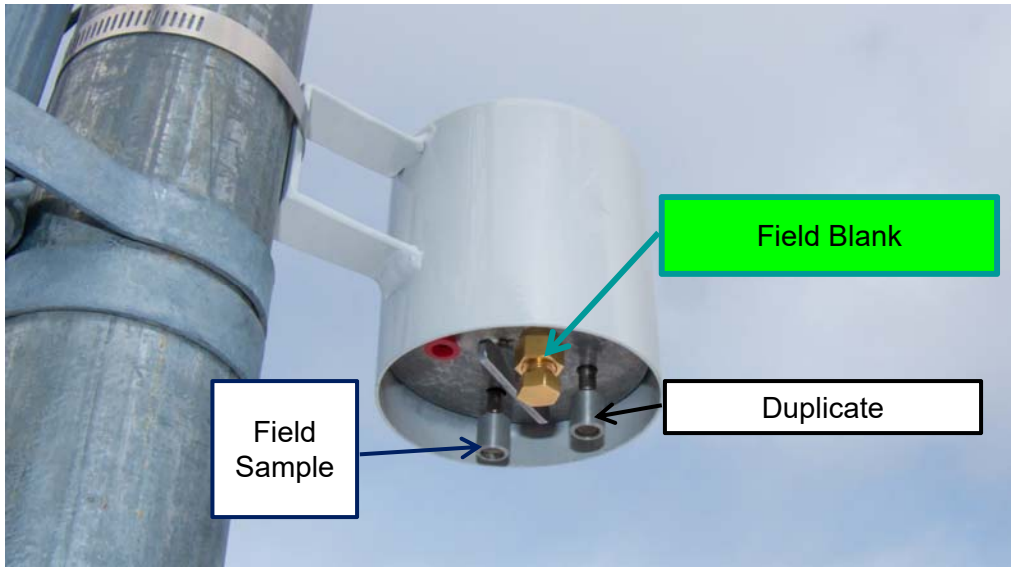
$$\frac{m = D\,(C_s - C_a)\,A\,t}{L}$$

Where:
m = mass uptake
D = diffusion coefficient
C_s = external concentration being sampled
C_a = concentration at adsorbent surface
A = cross-sectional area of the diffusion path
t = sampling time
L = diffusive path length

In Passive Sampling: Each chemical has it's own diffusive uptake rate per adsorbent because each chemical interacts with the adsorbent differently

Example of Tube Deployment

- Sampling shelters are mounted along the fenceline
- The sampling tubes are placed in the shelter vertically with the inlet pointing down



- For EPA method 325, the tubes are placed in the shelter for 14-days
- After 14-days the tubes are removed, capped, and a new set of tubes are placed in the shelter
- Samples are returned to the laboratory for analysis
- Sampling takes place year round with 26 sampling events per year

Shelter helps protect tubes from environmental conditions

In Summary, Let's Compare

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Active Sampling

- Very easy to ascertain volume on tube for quantitation
- Can use multi-bed adsorbents for a wide boiling point target range determination
- Easy to apply several tubes in series but typically not necessary
- Requires a pump

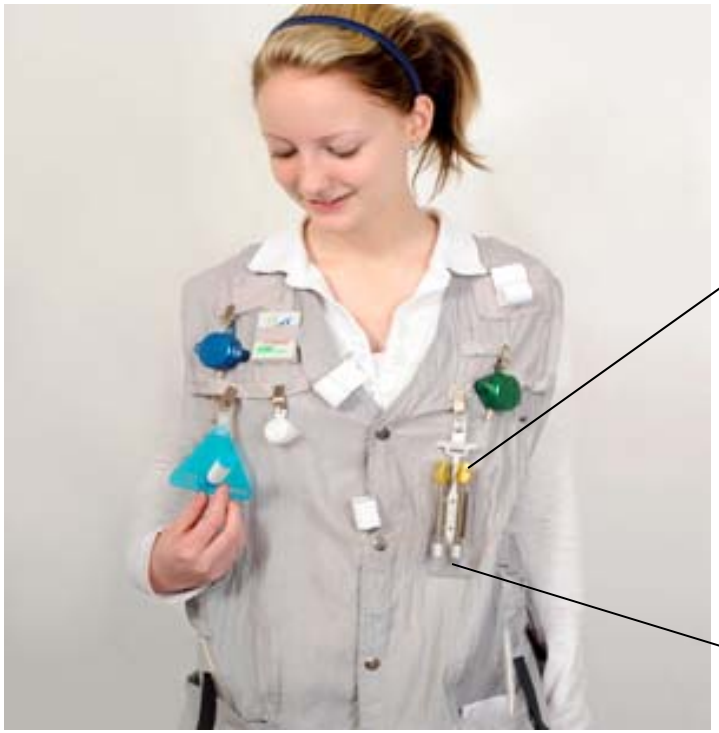
Passive Sampling

- Excellent for long term sampling (time weighted averaging)
- Several tubes may be required for wide range sampling
- Does not require a pump
- Using one adsorbent has a limited component bp range as compared to multi-bed used in active sampling
- Uptake rates are adsorbent and component dependent

Validating Passive Sampling

History of the Method 325

The development of the sampling tube began in 2003, with the U.S. EPA DEARS Study (Detroit Exposure Aerosol Research Study). 3-year field study (2004 to 2007)



Carbopack X Tubes used in the Dears Study

Sampling Vest used in the DEARS Study
Source: http://archive.epa.gov/heasd/archive-dears/web/jpg/dears3.jpg

Additional Examples of Validating Passive Sampling

- DCHS: Detroit Children's Health Study
  - 7-day samples taken during the summer of 2005
  - 200 samples analyzed
- DTREAX: Dallas Traffic Related Exposures to Air Toxics
  - 7-day samples taken during summer 2006 and winter 2008
  - 290 samples analyzed
- Beaumont: EPA Region 6 Air Toxics Monitoring Study
  - 7-day samples taken during the fall of 2007
  - 90 samples analyzed
- Moncure, NC
  - 24-hour samples taken during summer and winter of 2007
  - 87 samples analyzed

Passive Uptake Rates for Carbopack X

EPA has validated uptake rates for 19 different VOC's using Carbopack X

Compound	Carbopack X Uptake Rate (mL/min)
Benzene	0.67 ± 0.06
1,3-Butadiene	0.61 ± 0.11
Carbon tetrachloride	0.51 ± 0.06
Chlorobenzene	0.51 ± 0.06
3-Chloropropene	0.51 ± 0.30
p-Dichlorobenzene	0.45 ± 0.05
1,1-Dichloroethane	0.57 ± 0.10
1,2-Dichloroethane	0.57 ± 0.08
1,1-Dichloroethene	0.57 ± 0.14
1,2-Dichloropropane	0.52 ± 0.10
Ethylbenzene	0.46 ± 0.07
Styrene	0.50 ± 0.14
Tetrachloroethene	0.48 ± 0.05
Trichloroethene	0.50 ± 0.05
Toluene	0.52 ± 0.14
1,1,1-Trichloroethane	0.51 ± 0.10
1,1,2-Trichloroethane	0.49 ± 0.13
m,p-Xylene	0.46 ± 0.09
o-Xylene	0.46 ± 0.12

Source: Uptake Rates from Method 325b

Method 325b

Analytical Requirements

How the Barcoded Tubes Can be Used in the Laboratory

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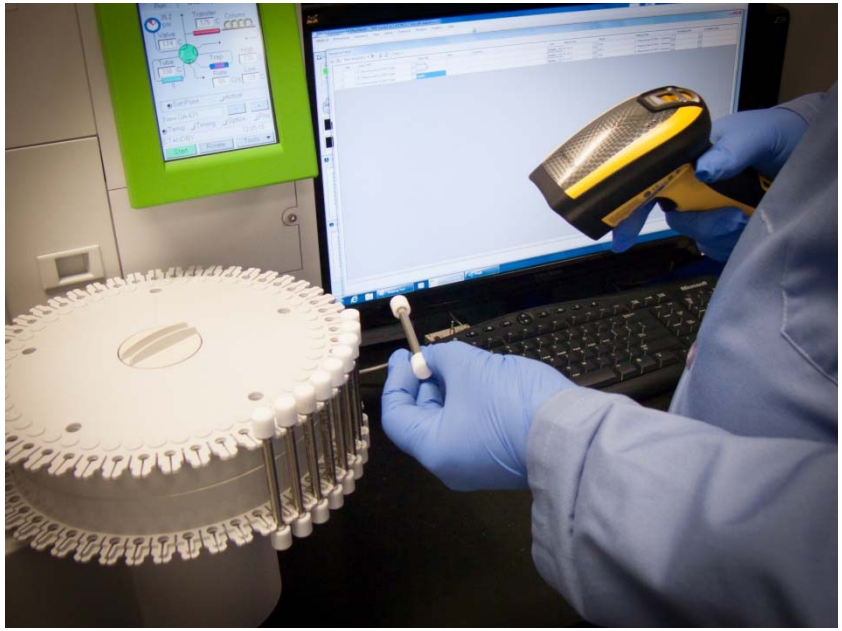
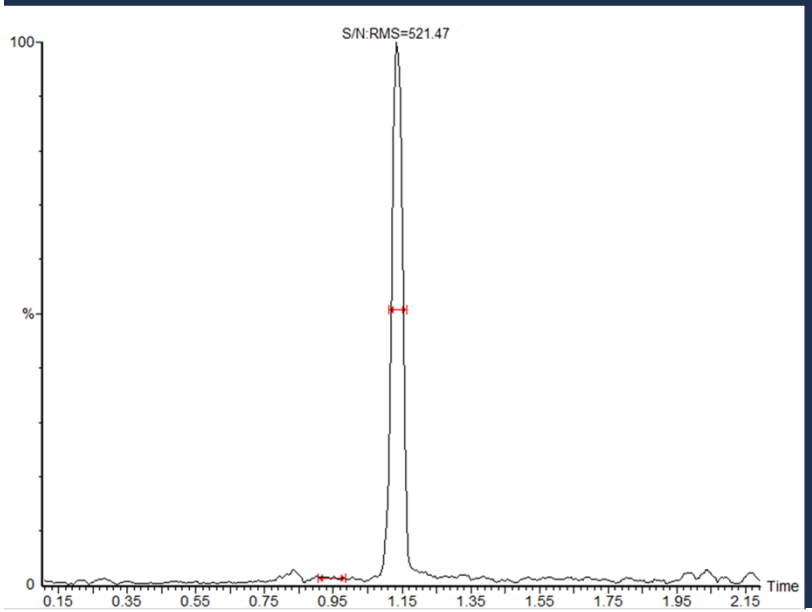
The serial number from the barcode can be scanned directly into your chromatographic sequence table

- This reduce errors (transposing numbers, wrong number being typed)
- Quick entry for the analysts



Example: Benzene from Fast Method
Tube spike: 0.2 ng



One System Several Choices:

Fast 325b Setup less than 4 min

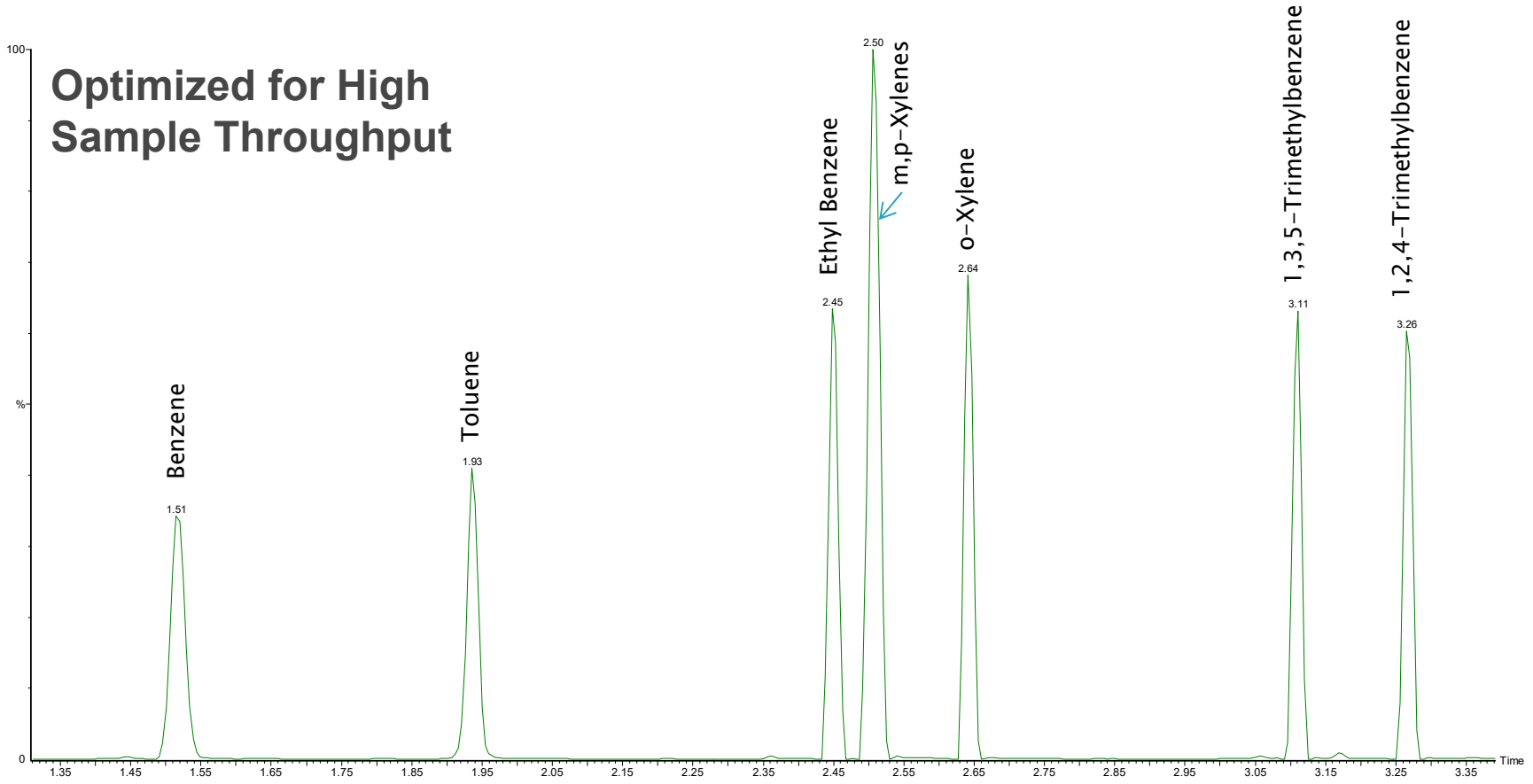
(can be used for VOC and SVOC)

Both 325b and TO17 Setup

… fast method can be used for VOC and SVOC (BTEX plus 16 regulated PAHs)

Fast, Resolved Chromatography

VOC and SVOC Column



… Total Ion Chromatogram (TIC) at 10 ppb

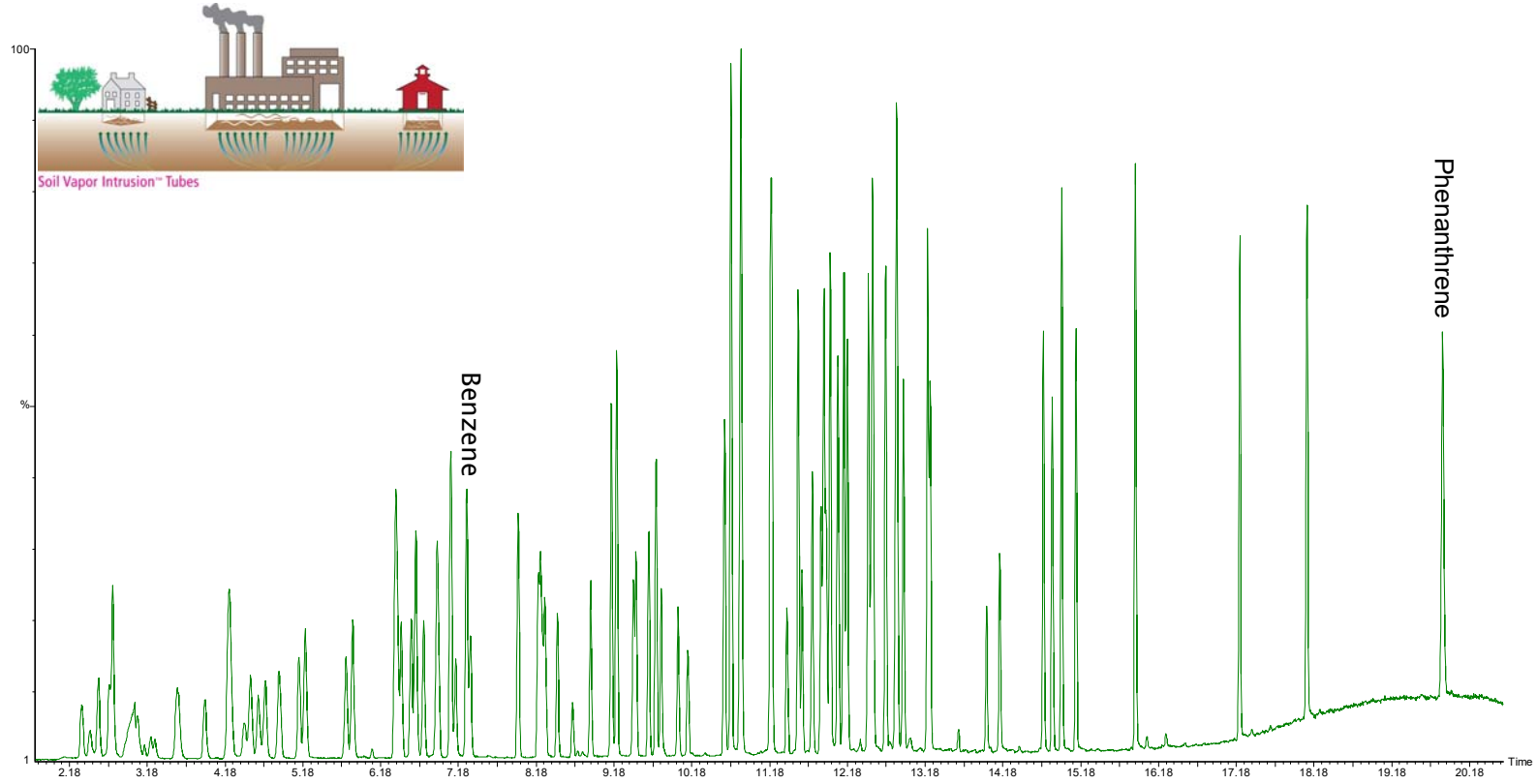
Performance Using Fast Method

Results are based upon a 1 liter sample volume Uptake

Target	Retention Time (min)	Precision (n=7) % RSD	Linearity (range 0.2 to 200 ng)	S/N @ 0.2 ng
Benzene	1.51	1.80	0.9999	520 to 1
Toluene	1.93	2.13	0.9999	651 to 1
Ethyl Benzene	2.45	3.01	0.9995	877 to 1
m,p-Xylene	2.50	2.69	0.9993	1021 to 1
o-Xylene	2.64	2.84	1.0000	902 to 1
1,3,5-Trimethybenzene	3.11	3.69	0.9999	823 to 1
1,2,3-Trimethybenzene	3.26	4.01	0.9999	819 to 1

Courtesy of Roberta Provost, formerly of Pace Analytical Services

Soil Gas Extended Range Components and 325 on Same System



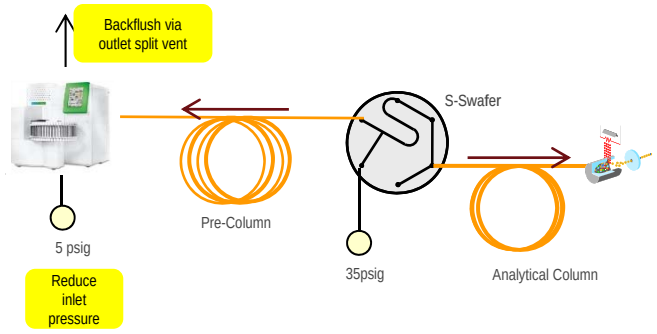
Backflush after benzene →

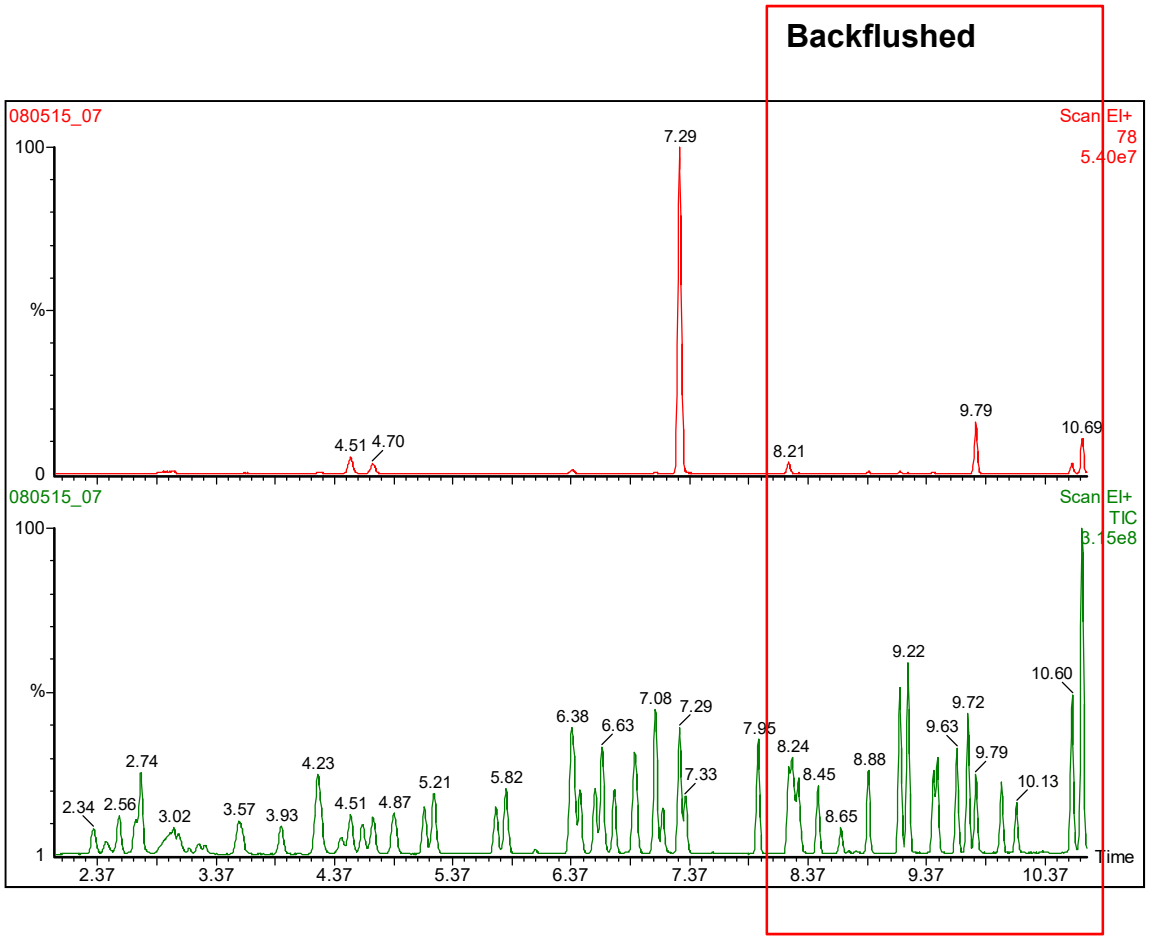
… gases, 8260 list, PAHs

Expanded View and Mass Chromatogram for Benzene for Dual Application Capabilities

Swafer – Micro Channel Flow Technology

- Enables backflushing during chromatography
- Prevents unwanted analytes to enter analytical column
- Can reside in GC Oven handles temperatures to 450 C
- Easy to use – no valving and automated





Analytical Results: Active Sampling

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1 Liter sample volume

Class of compound	# of analytes per group	Linearity (0.05 to 250 µg/m^3)*		Precision	Reporting Limit
		r^2	Ave RF	(n=10)	S/N at 0.05 µg/m^3)
Gases	7	0.9994	9.07	7.39	530:1
Aliphatic Hydrocarbons (halogenated)	35	0.9996	14.00	4.80	560:1
Aromatics (halogenated)	9	0.9997	13.30	2.58	1350:1
Aromatics (non-halogenated)	14	0.9996	10.27	1.91	1220:1
Polynuclear Aromatic Hydrocarbons (PAHs)	7	0.9997	8.69	3.56	570:1
others	13	0.9996	9.26	3.19	560:1

… better than method criteria

Summary

- Using FLM Carbopack X enables utilizing uptake rates calculated by EPA for enhanced accuracy
- Passive sampling tubes are easy to deploy
- The method has been optimized for enhanced sample throughput while maintaining excellent performance
- Meets or outperforms EPA method criteria

Solution for Measuring Toxic Compounds in Air

Thank you!

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