Learn … how to Comply with *New* EPA Method 325

Fenceline Monitoring of Volatile Organic Compounds (VOCs) and Passive Sampling

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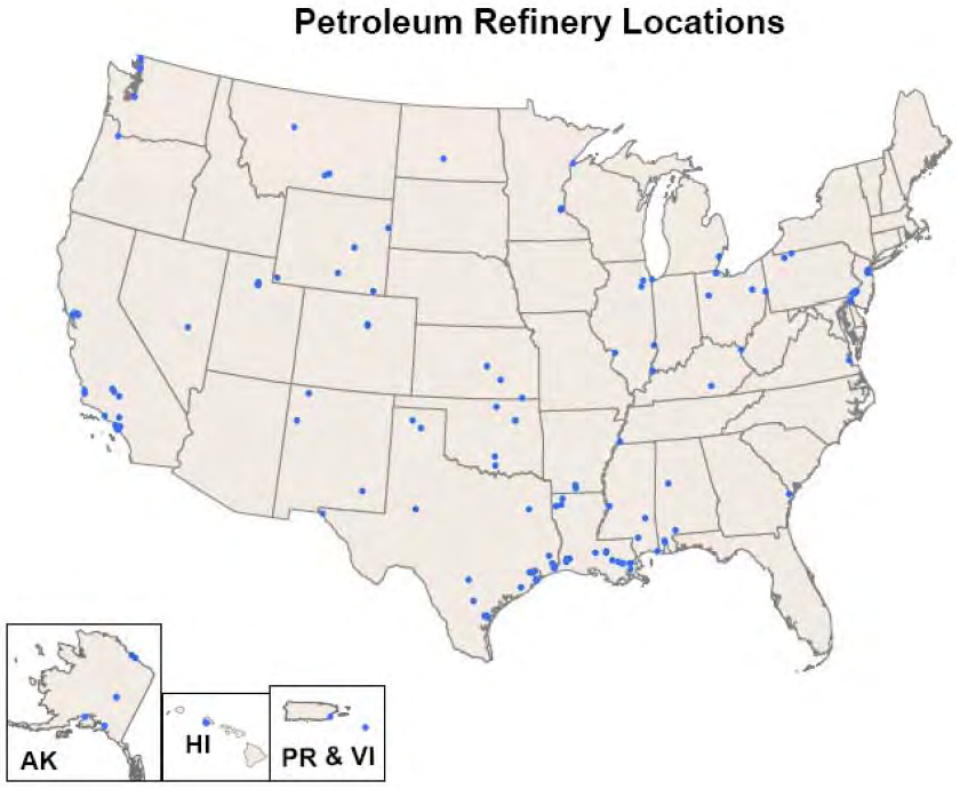
Welcome

- Method 325
- Overview of the Passive Sampling Tube and Process
- History of the Method 325 Sampling Tube
- Comparison of Passive and Active Sampling
- Operation of Thermal Desorption Process
- Analytical Method Parameters
- Calibration
- Tube Conditioning

What is Method 325?

- A new air sampling method for monitoring the fenceline of petroleum refineries
- Specific for monitoring the average air concentration of volatile organic compounds (VOC's), with Benzene being the target compound.
- Samples are collected by using passive sampling that are strategically placed along the fenceline
- The tubes are then sent to a laboratory to be analyzed using thermal desorption (TD) / gas chromatography (GC)

EPA Method 325: Promulgated, September 29, 2015



Source: http://www3.epa.gov/apti/video/10182011Webinar/101811webinar.pdf

EPA Method 325

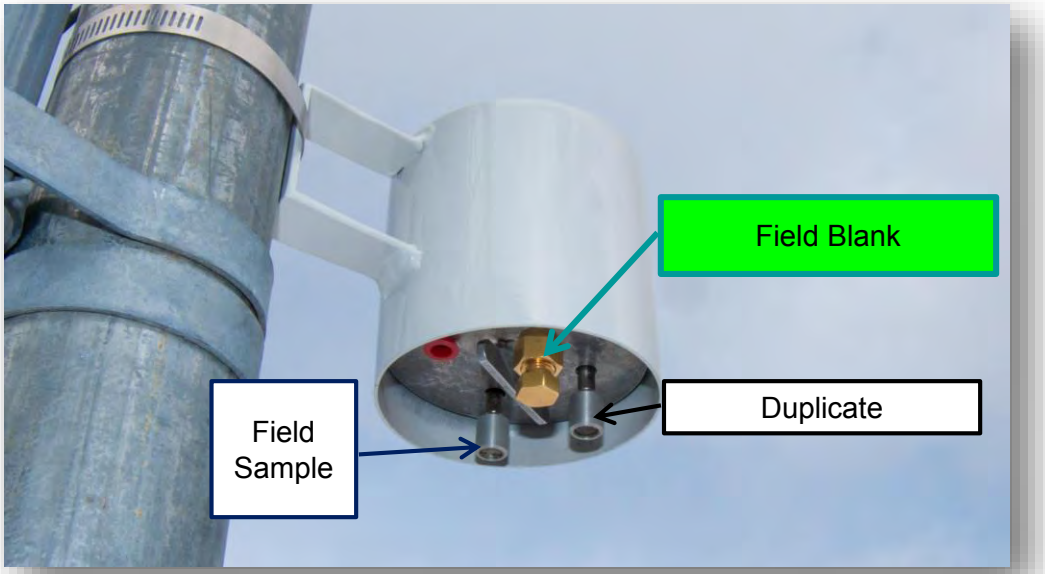
- 325 A: Deployment and collection of air samples
- 325 B: Analysis of the air samples

Schedule

- Petroleum refineries have 2 years to comply with this new regulation

Sample Deployment and Sampling

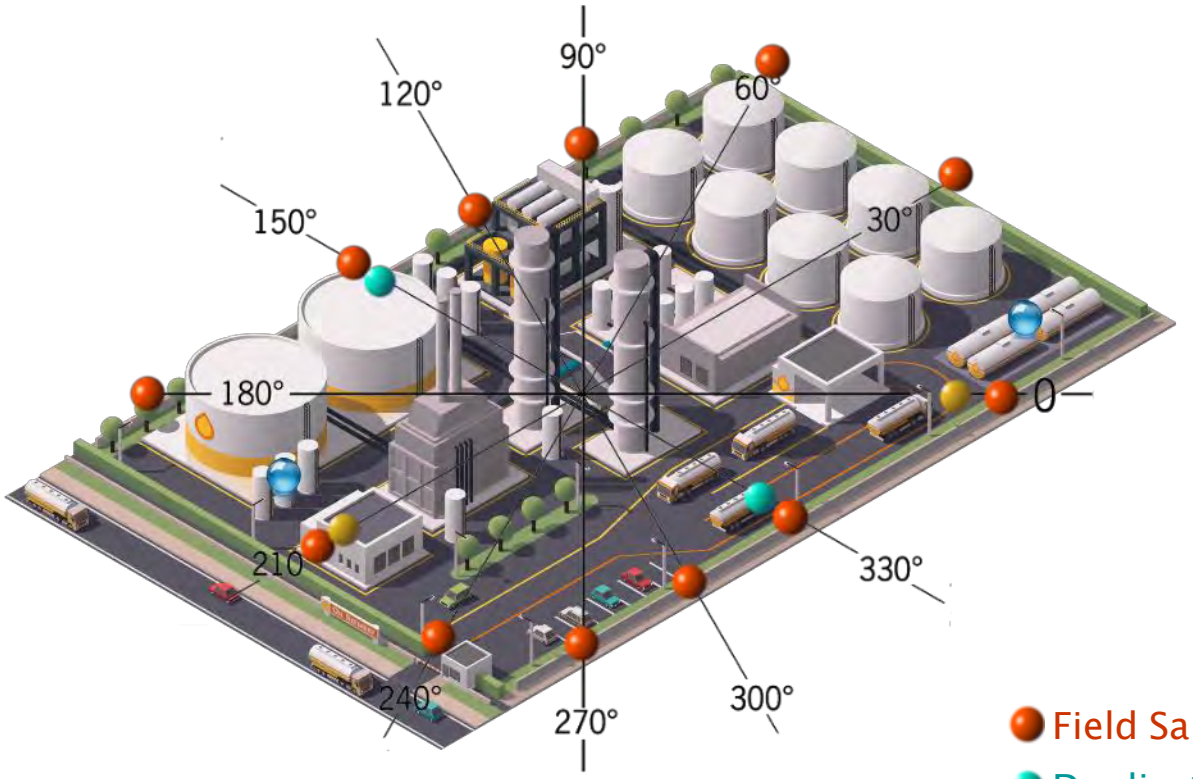
- Sampling shelters are mounted along the fenceline of the refinery
- The sampling tubes are placed in the shelter vertically with the inlet pointing down



Shelter provided courtesy of Enthalpy Analytical Inc. Durham NC

- The passive sampling 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
- Sampling takes place year round with 26 sampling events per year

Sampling Locations



Option 1: Degree Angles	
Acerage of Refinery	Measured Angle
<750	30°
750 to 1500	20°
>1500	15°

- Field Sample
- Duplicate
- Field Blank
- Extra Source Sample

Minimum Number of Tubes Required

Sample Tubes

Acerage of Refinery	Field Samples	Duplicates	Source Samples*	Field Blanks	Total
<750	12	2	~ 2	2	18
750 to 1500	18	2	~ 3	2	27
>1500	24	3	~ 5	4	36

* Extra source samples are required from emission sources within 50 meter of property line.

Laboratory tubes

Calibration	QC	Laboratory Blanks	Total
7	2	1	10

Sampling Tubes for Method 325

The Passive Sampling Tube used for Method 325

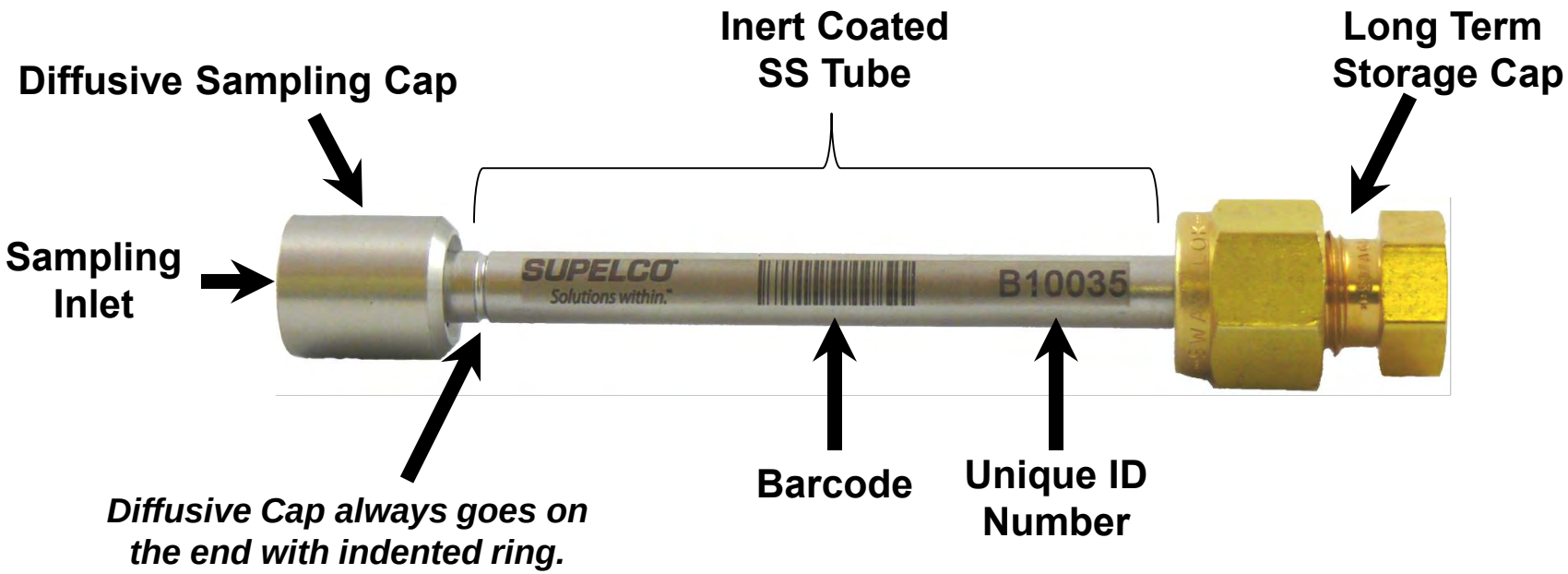
- Stainless Steel Tube 3.5” long x ¼” o.d.
- Tubes to have an Inert Coating
- Tube are etched with a unique Barcode, Serial Number, and Adsorbent Packing Identification
- Fixed Air Gap of 1.5cm at the Inlet

Inert Coated Tubes

Supel™Coat is a deactivation process that produces a ceramic like protective coating to the stainless steel surface.

- The coating covalently bonds to the steel surface and protects it from oxidation.
- Creates a reproducible surface on the inner diameter of the tubes.
- The inert coating is stable to 400°C, and withstands multiple uses.

Overview of the Passive Sampling Tube



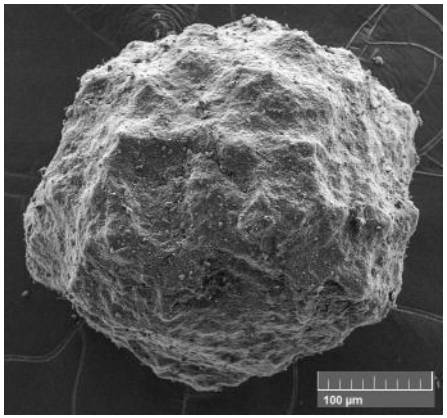
Tube Dimensions: 3.5-inches (89 mm) long x 1/4 inch (6.4 mm) o.d. x 5 mm i.d.

Adsorbent used in the Passive Sampling Tube

Carbopack X has the most validated uptake rates listed in the method

- Hydrophobic – low uptake of water vapor
- Retains & releases a wide range of volatile compounds
- It bridges the gap between other weaker graphitized carbon blacks, and the stronger carbon molecular sieves adsorbents

BET Surface Area	Density	Pore Diameter
240 m^2/g	**0.44 g/cc**	**100 Å**

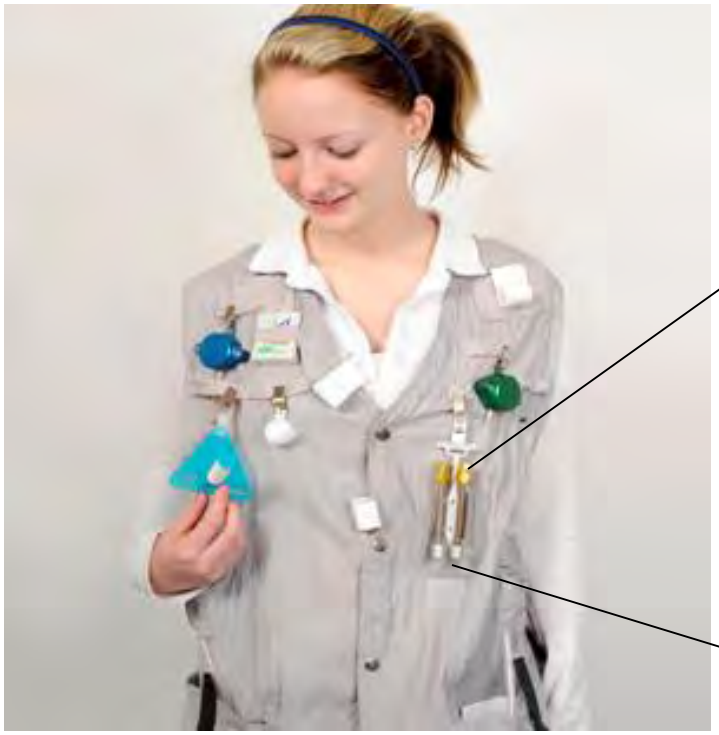


History of Method 325

Sampling Tubes

History of the Method 325 Passive Sampling Tube

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

History of the Method 325 Passive Sampling Tube (Cont.)

- **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 Moncure, NC**
  - 24-hour samples taken during summer and winter of 2007
  - 87 samples analyzed

How the Passive Sampling Tube Works

Passive Sampling versus Active Sampling

Passive Sampling

- Works without and air sampling pump
- Excellent for long term sampling
- Easy to deploy several tubes at a time
- Limited to a single adsorbent packed in the tube.
- Passive Samplers have fixed uptake rates (sampling rate) unique to the sampler's design, and how each component interacts with the adsorbent.
- (A reason why to use the adsorbents with uptake rates determined by EPA)

Active Sampling

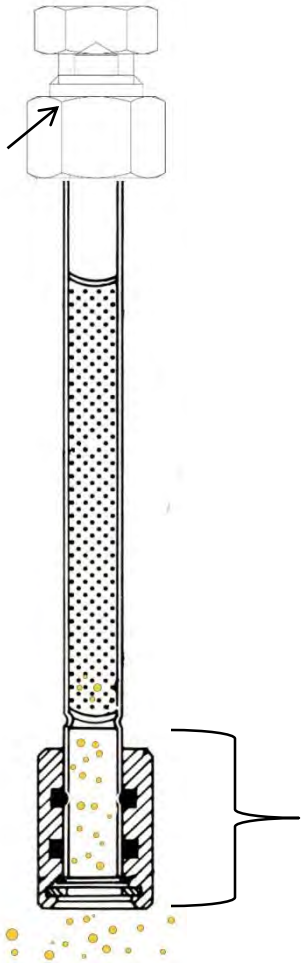
- Requires an air sampling pump
- Typically used for shorter term sampling.
- More difficult to deploy several tubes at the same time.
- Multiple adsorbents can be packed in the same tube, allowing a larger component range to be collected.

Comparison of Passive and Active Sampling

When used for passive sampling, 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.

Long Term Storage Cap

Cap remains while during sampling



Single Bed of Adsorbent

Diffusion Path

" Fixed Air Gap"

PASSIVE

air sampling pump

ACTIVE

Passive Uptake Rates for Carbopack X

Method 325B has validated uptake rates for 19 different VOC's when 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

How the Determine the Concentration

Determining the Concentration collected by the Tubes

$$C_m = \frac{m_{meas}}{U_{NTP} \times t} \times 10^6$$

Where:
C_m = The concentration of target compound in the air sampled (µg/m_3).
m_{meas} = The mass of the compound as measured in the sorbent tube (µg).
U_{NTP} = The diffusive uptake rate corrected for local conditions (sampling rate) (mL/min).
t = The exposure time (minutes).

Each chemical has it's own diffusive uptake rate, because each chemical interacts with the adsorbent differently.

The Difference Between the Tube Caps Described in Method 325

What's 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

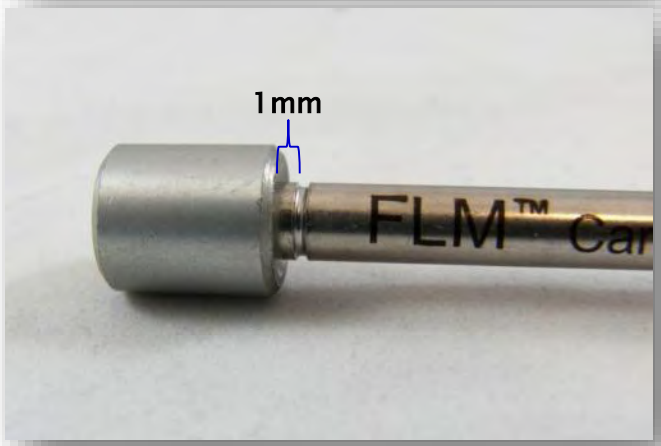
Purpose of Diffusive Caps

The diffusive cap serves several purposes:

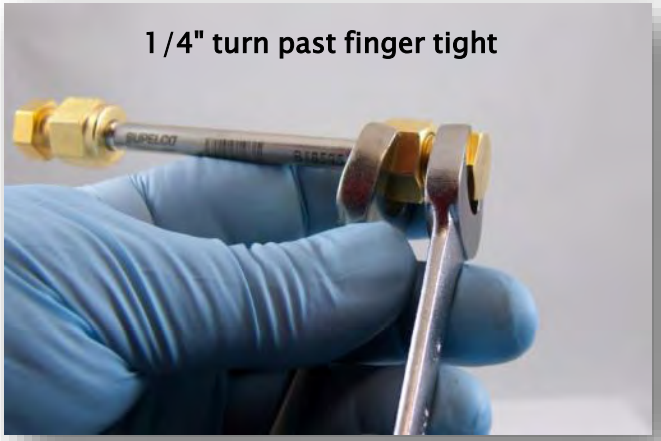
1. Defines the diffusive air gap inside the tube
2. Prevents air movement within the diffusive air gap during windy conditions
3. The screen in the cap prevents insects from entering the tube while sampling

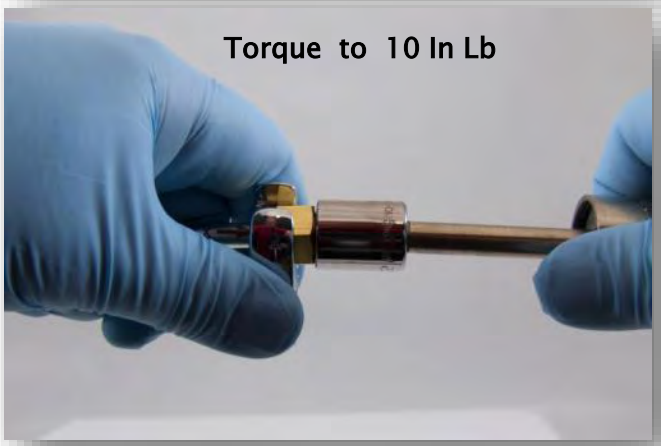
Use of Caps

- Diffusive Sampling Caps



- Long Term Sampling Caps

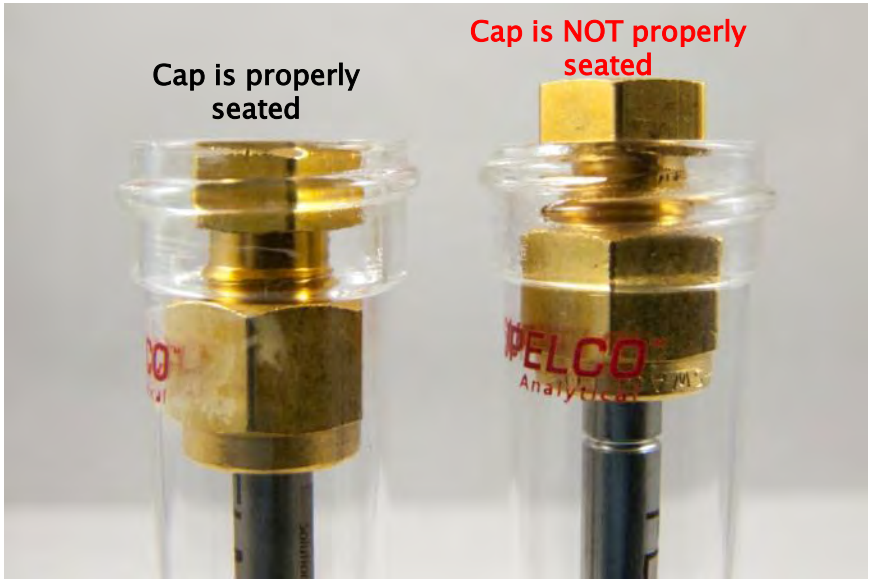




Secondary Storage Containers

- Method 325B specifies the use of a Shipping Container

Example of a non-permeable shipping container



The shipping containers can also serve a gauge to verify the long term sampling caps are seated properly

Tube Attributes

Sampling Tubes are Reusable

Sampling tubes are reusable. The method states the tubes need to repacked or replaced at least every 2 years or 50 uses, whichever comes first

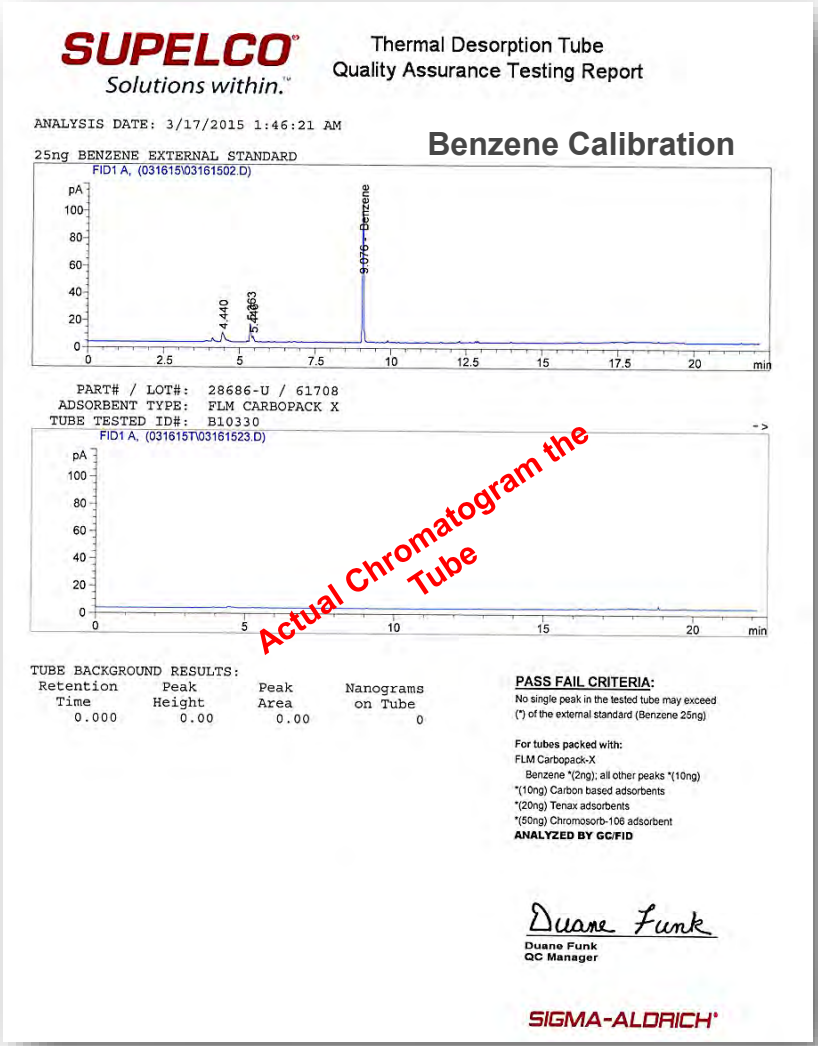
The most efficient way to re-condition tubes is by using an off-line tube conditioner

Recommendations:

- Conditioning Temp is 350°C or below
- Use good quality N_2 or He while the tubes are being heated. (50 to 100 mL/min) *Gas flow should enter through the back of the tube and exist through the sample inlet while conditioning*
- Re-conditioning Time: 15 minutes to 2 hours
- Maintain the gas flow until the tubes cools to ambient

Quality Sampling Tubes

- Choose an adsorbent specified in method 325- this reduces extra validation.
- Tubes with consistent backpressures – assures better performance.
- Preconditioned tubes- reduces the time required to condition new tubes before use.
- QC tested – assure low benzene background levels.



Barcoded Tubes

- Each tube is etched with a unique barcode and corresponding ID number
  - The Barcode is permanently "tattooed“ on the tube
  - Doesn’t require propriety equipment, or special programming
- The Barcodes and ID Numbers are still legible with repeated use

Source: DataLogic
PowerScan™ PD9530
Image Based Barcode Scanner

Solutions for Method 325B

Tubes are Sent to the Lab for Analysis

The long term storage caps are removed and PTFE analytical caps are used

How the Barcoded Tubes can be used in the Laboratory

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

TurboMatrix Thermal Desorber
Clarus SQ8 GC/MS

Thermal Desorption:

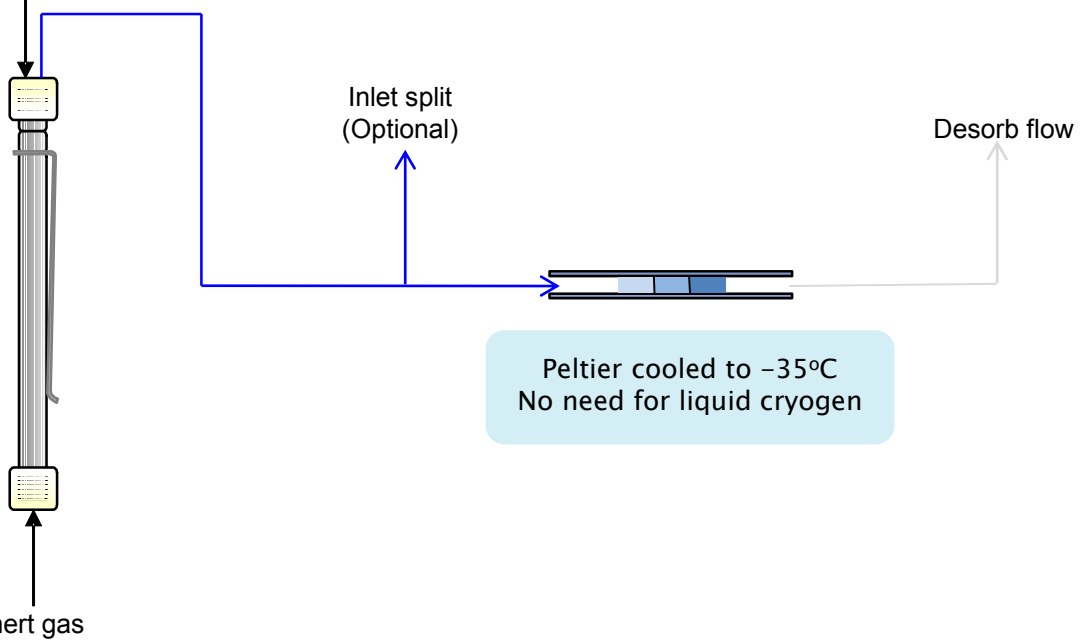
Operation

Primary (sample) Desorption

IS and/or Surrogate Spike (optional)

Impedance check (Optional)

Ambient or heated purge (at least 1min)

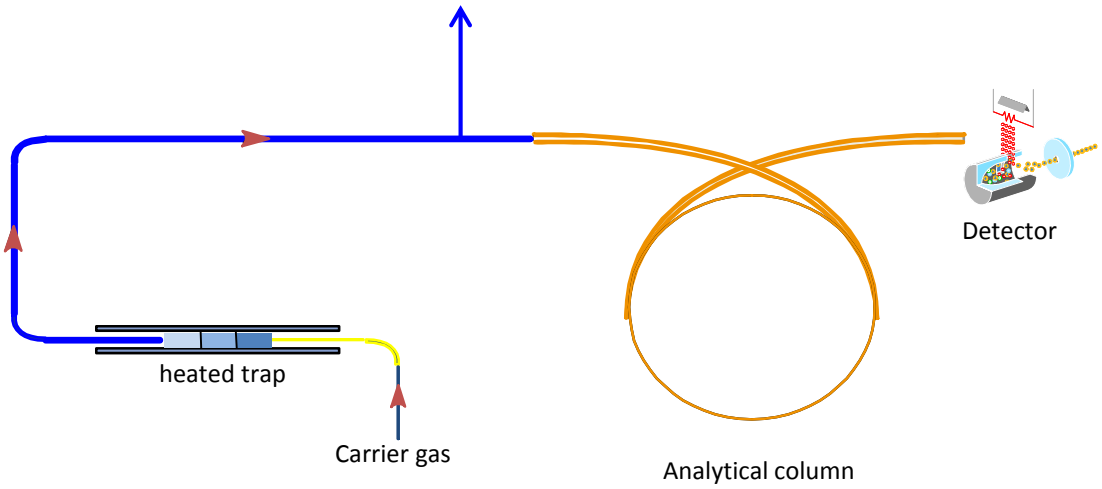


- Primary (sample) desorption
  - Temperature
  - Flow
  - Time

Peltier cooled to -35°C
No need for liquid cryogen

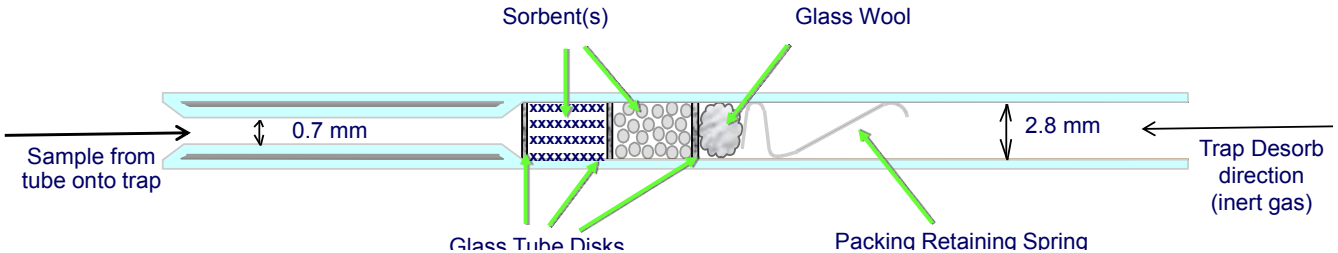
Secondary Trap Desorption

Optional Outlet Split or
Recollect on New or Same Tube



Cold Trap

- Reduced diameter outlet reduces analyte dispersion or band broadening for narrower, focused peaks
- Trap flow is reversed during desorption to enhance efficiency and ensure recovery of high boiling compounds



TurboMatrix Thermal Desorber
Clarus SQ8 GC/MS

Method Requirements

Results

Standard Preparation

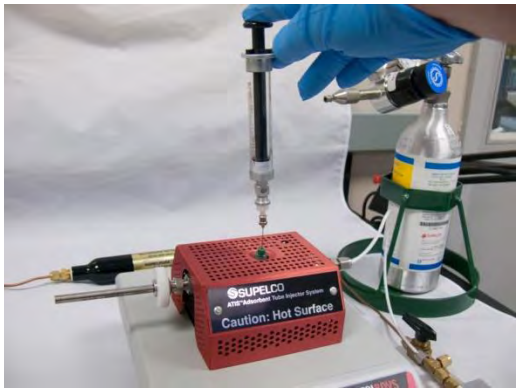
Tune Criterion for 325:
Compound 4-bromofluorobenzene (BFB)

- Detectors
  - Mass Spectrometer (MS)
  - FID or PID
- MS Parameters
  - Scan range 35–300

BFB Criteria for Method 325

Mass	Ref Mass	Range	Relative Abudance (%)
50	95	> 15% and < 40%	20.2
75	95	> 30% and < 60%	38.4
95	BPI	100%	100.0
96	95	> 5% and <9%	6.3
173	174	< 2%	0.4
174	95	> 50% and < 100%	71.8
175	174	> 5% and < 9%	6.8
176	174	>95% and < 101%	95.7
177	176	> 5% and < 9%	6.0

Standard Spiking Procedure
Liquid standards may be used

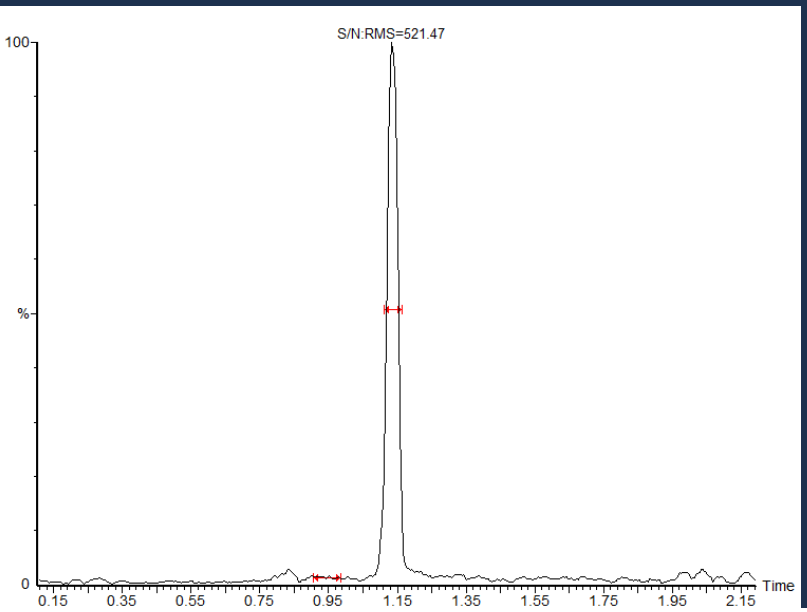


ATIS (Adsorbent Tube Injector System)

GC inlet w/Liquid Autosampler

“Homemade” Setup

Example: Benzene from Fast Method
Tube spike: 0.2 ng



One System Several Choices:

Fast 325B Setup

Both 325B and TO17 Setup

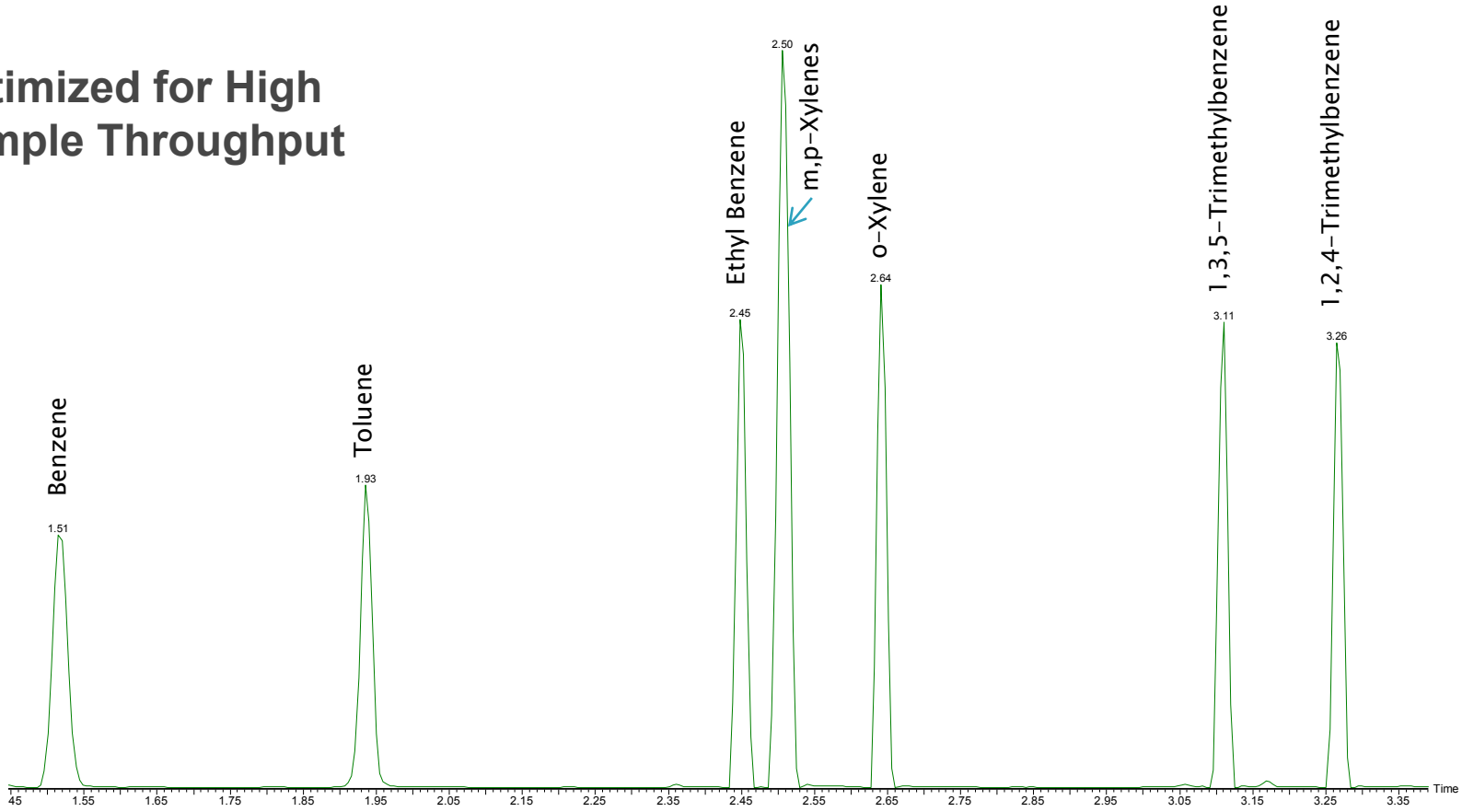
… fast method can be used for VOC and SVOC (BTEX plus 16 regulated PAHs)

Fast, Resolved Chromatography

VOC and SVOC Column

Inlet and outlet splits are enabled

Optimized for High Sample Throughput



Chromatogram courtesy of Pace Analytical Services, Minneapolis, MN

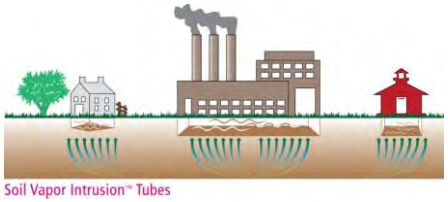
… Total Ion Chromatogram (TIC) at 10 ppb

Performance Using Fast Method (325 and VOC and SVOC)

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

… processed using external standard calibration full scan acquisition

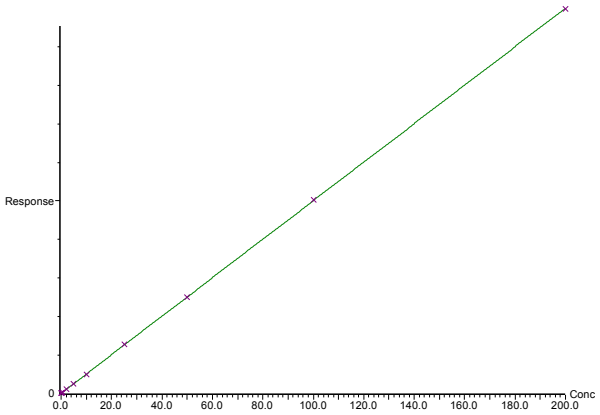
TO-17 Extended Range and 325 on Same System



Backflush after benzene
or stop run after last target of choice eluters

… only outlet split was enabled

Calibration of Benzene from Full TO-17 Target Analysis



Benzene Results

Range 0.05 to 200 µg/m^3

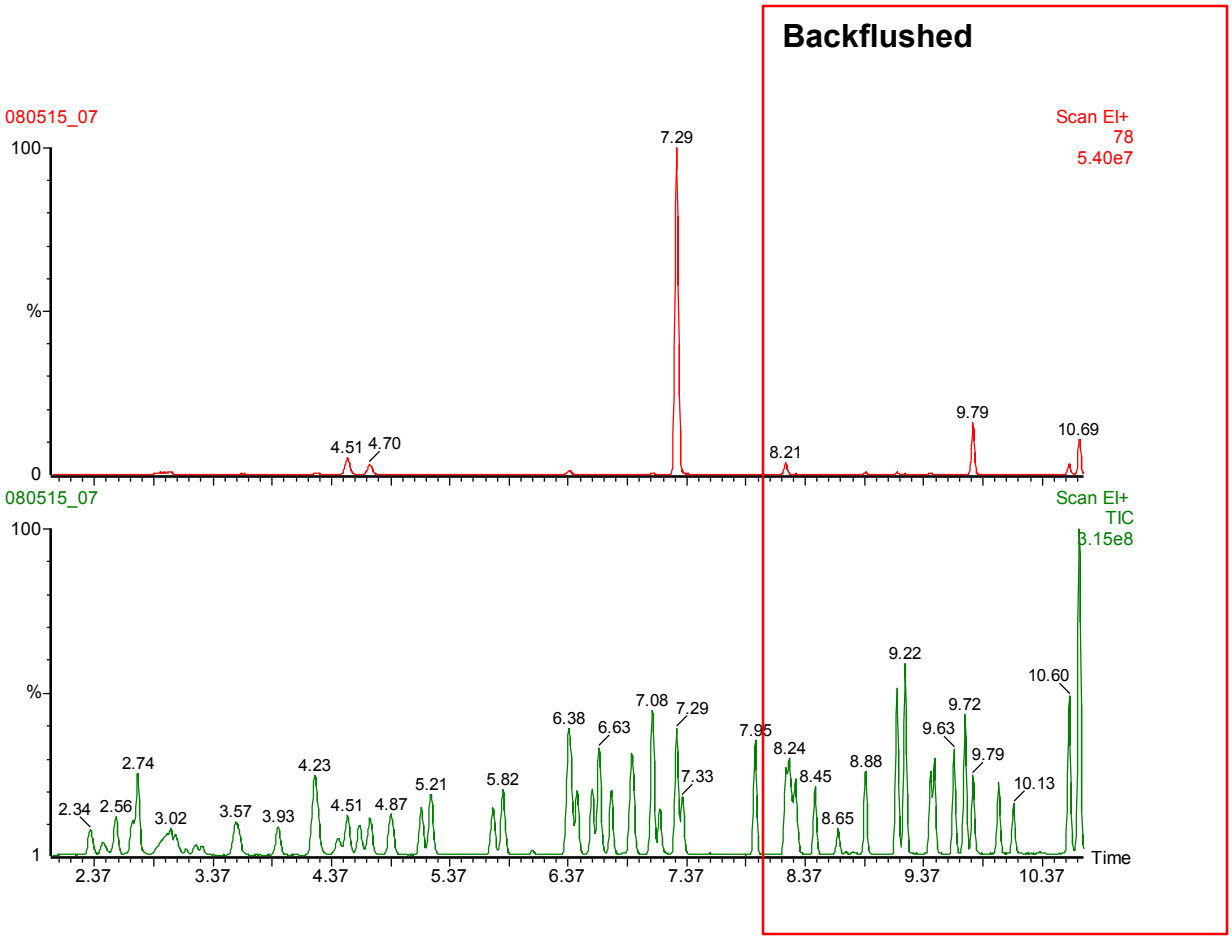
1 liter sample volume

S/N @ 0.05: 622 to 1

Performance of Targets from Soil Gas Method on Soil Vapor Intrusion (SVI) Tubes

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)	5	0.9997	8.69	3.56	570:1
others	13	0.9996	9.26	3.19	560:1

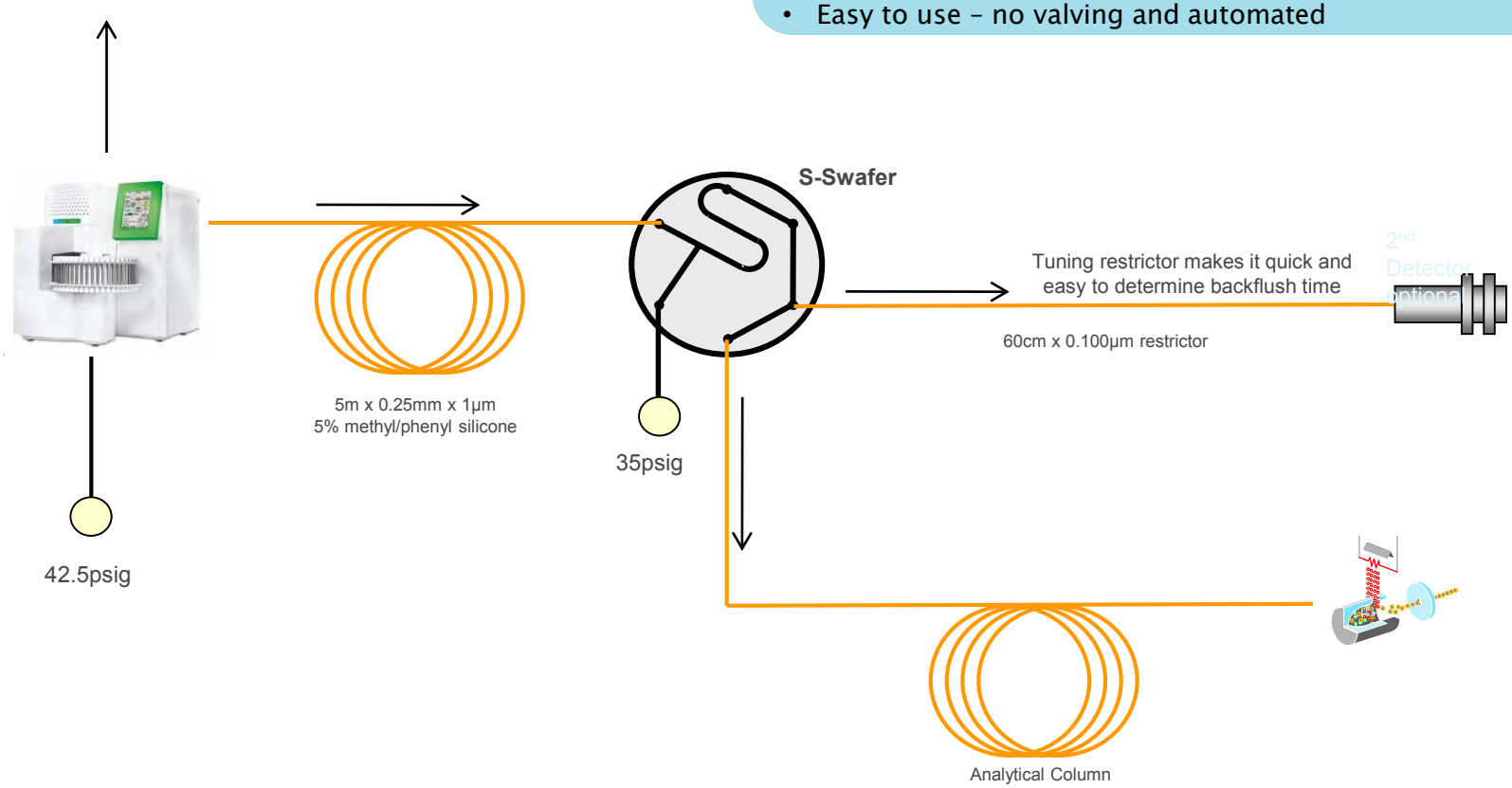
Expanded View and Mass Chromatogram for Benzene



Automated Backflushing

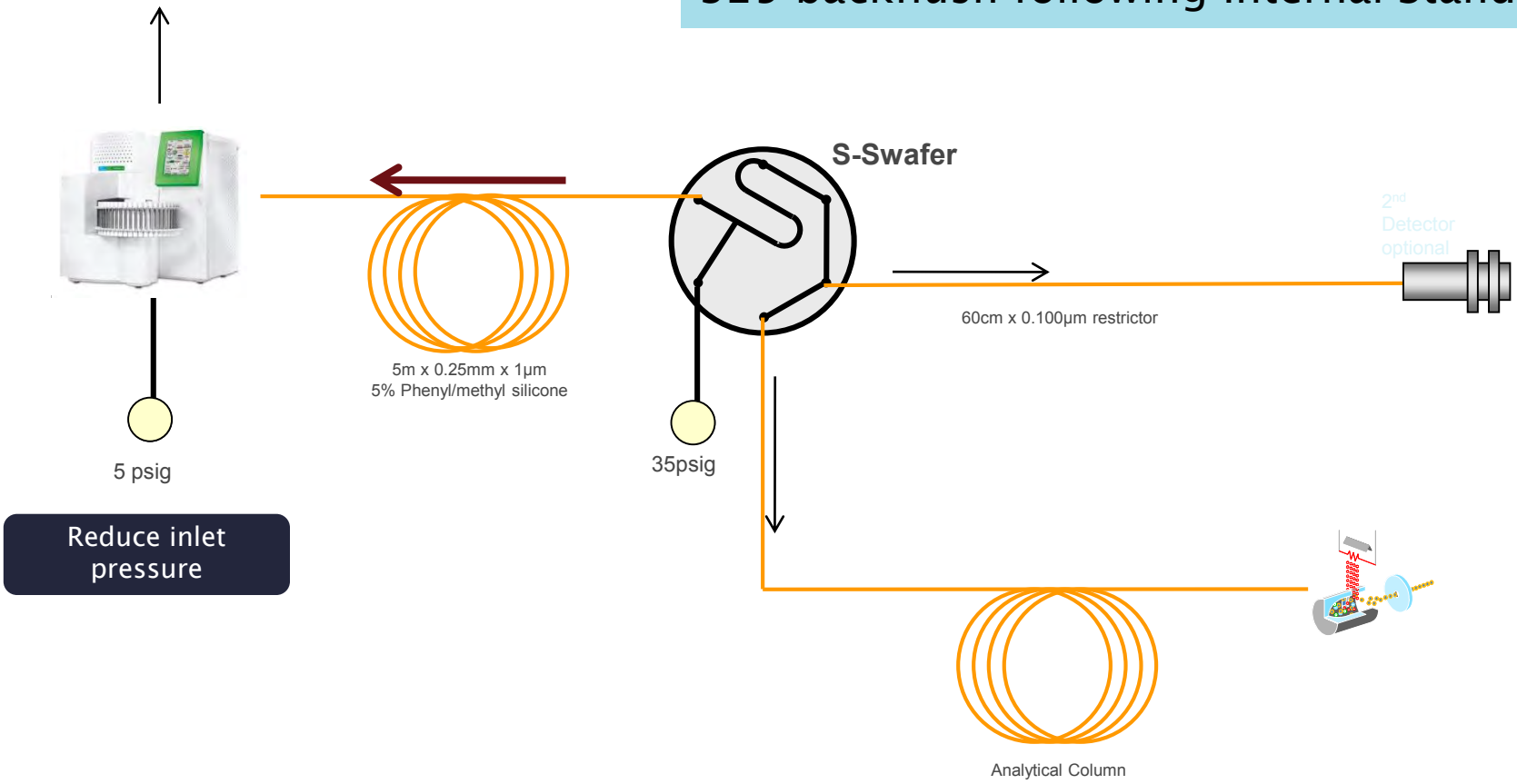
Swafer – Micro Channel Flow Technology

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



Same Configuration for TO-17 and 325

TO-17 do not enable backflush
325 backflush following Internal Standard



Internal Standard is Automatically Spiked onto Tubes

325 B one Internal Standard	TO-17 Internal Standards
Flurobenzene or	Flurobenzene
Chlorobenzene-d5 or	Chlorobenzene-d5
Perfluorobenzene	1,4-Difluorobenzene
4-Bromoflurobenzene (BFB)	4-Bromoflurobenzene (BFB)

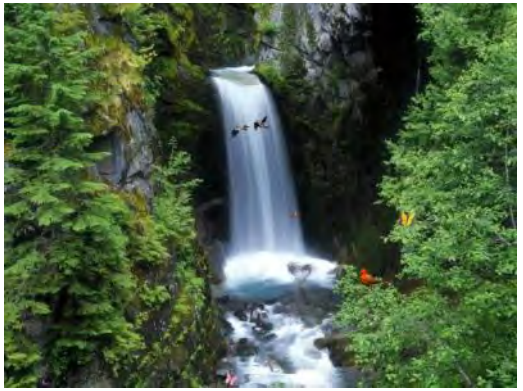
Precision for automated injection of Internal Standards

Internal Std	Fluorobenzene	1,4 Difluorobenzene	Chlorobenzene-d_5	BFB
Quant Ion	96	114	117	95
%RSD (n=15)	1.34	1.29	0.53	0.98

Let's Deal with Moisture

Example from Soil Gas (10 liter sample volume. 85% humidity)

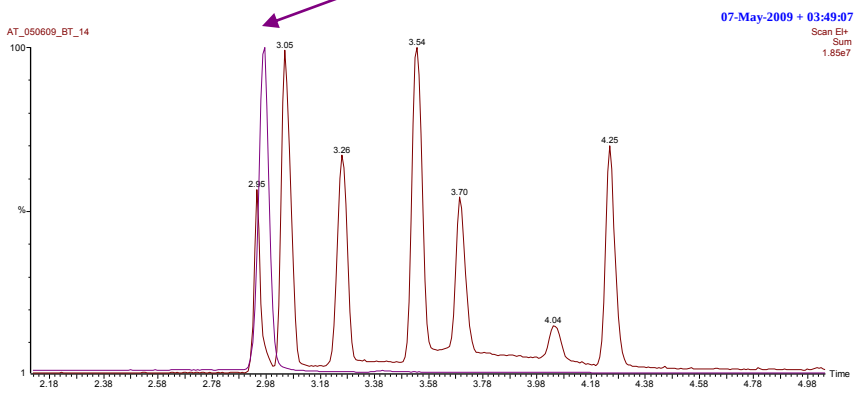
- Mass Spectrometer
  - Signal quenching
  - Increased maintenance
- Chromatography
  - Can effect peak shapes

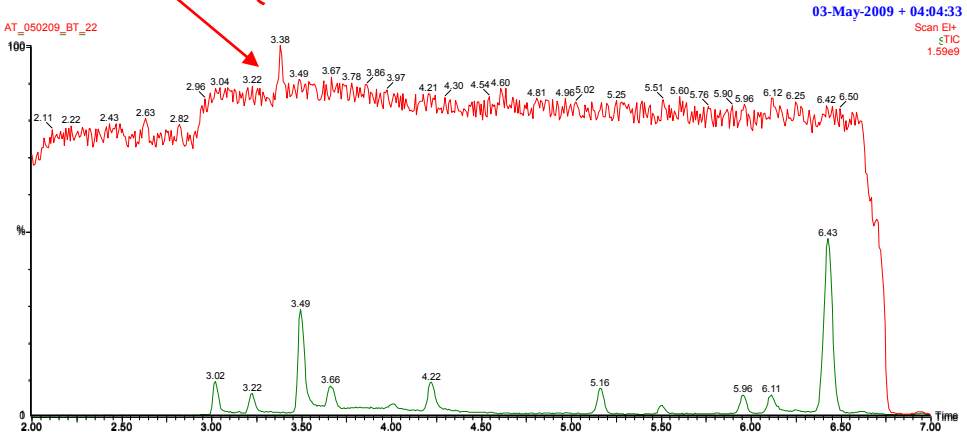


Water

With Dry Purge

No Dry Purge





Tube Conditioning and Off-line Dry Purge

- For soil gas, the automated tube condition can be used to perform an off-line dry purge at ambient temperatures
- For 325, a short instrument dry purge should be sufficient

… not only for conditioning!

Additional Comments

- Field and Laboratory Blanks
- 9 µg/m^3 of Benzene is the Action Level
- Benzene artifact on tube
  - ≤ 0.2 ppbv = ≤ 0.64 µg/m^3

Summary

- Using 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 is better than EPA method criteria
- We are here to help

Please contact us we are here to help!

Contact Info:

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Kristen.Schultz@sial.com

- View the complete portfolio of Air Monitoring products, find product literature, and more at: www.perkinelmer.com; www.perkinelmer.com/epa325; www.sigmaaldrich.com/air-monitoring

TurboMatrix 650 Thermal Desorber / SQ 8 GC/MS along with FLM™ Carbopack X

SUPELCO Solutions within.

PerkinElmer For the Better

Solution for Measuring Toxic Compounds in Air

Thank you!

???

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