Fast, Accurate, and Precise: Learn how to Comply with EPA Method 325 a/b (Fenceline Monitoring for Benzene)

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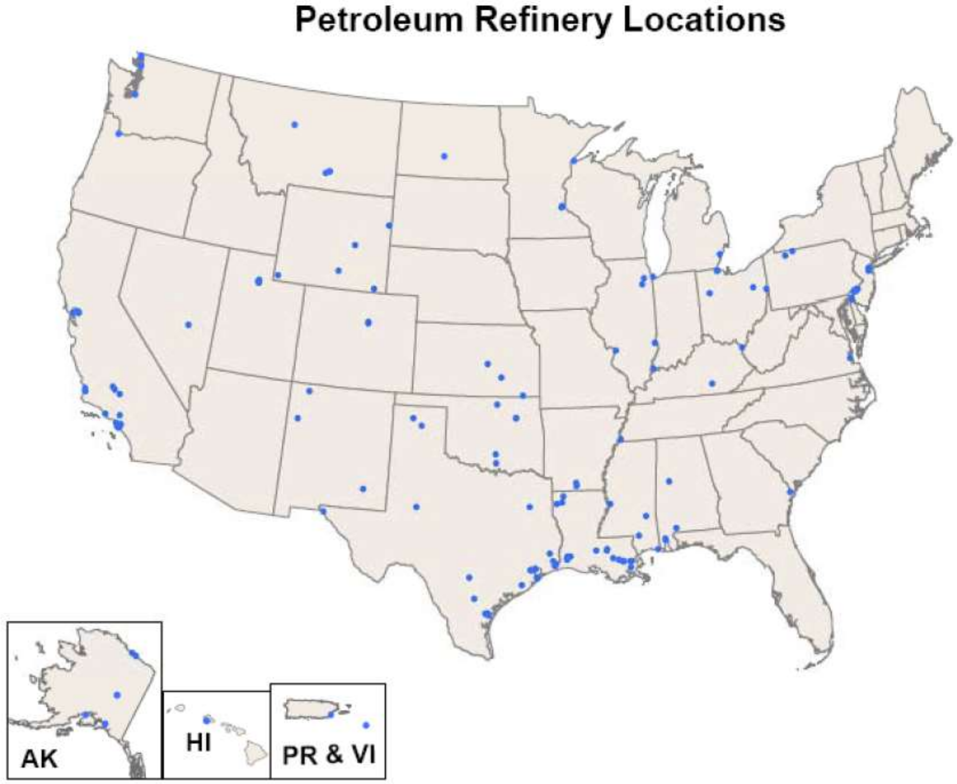
Welcome

- Method 325 Introduction
- Brief History of the Method 325
- Overview of the Passive Sampling Tube and Process
- Comparison of Passive and Active Sampling
- Operation of Thermal Desorption Process
- Analytical Method Parameters including Fast Chromatography
- Calibration

EPA Method 325: Promulgated, September 29, 2015



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

EPA Method 325

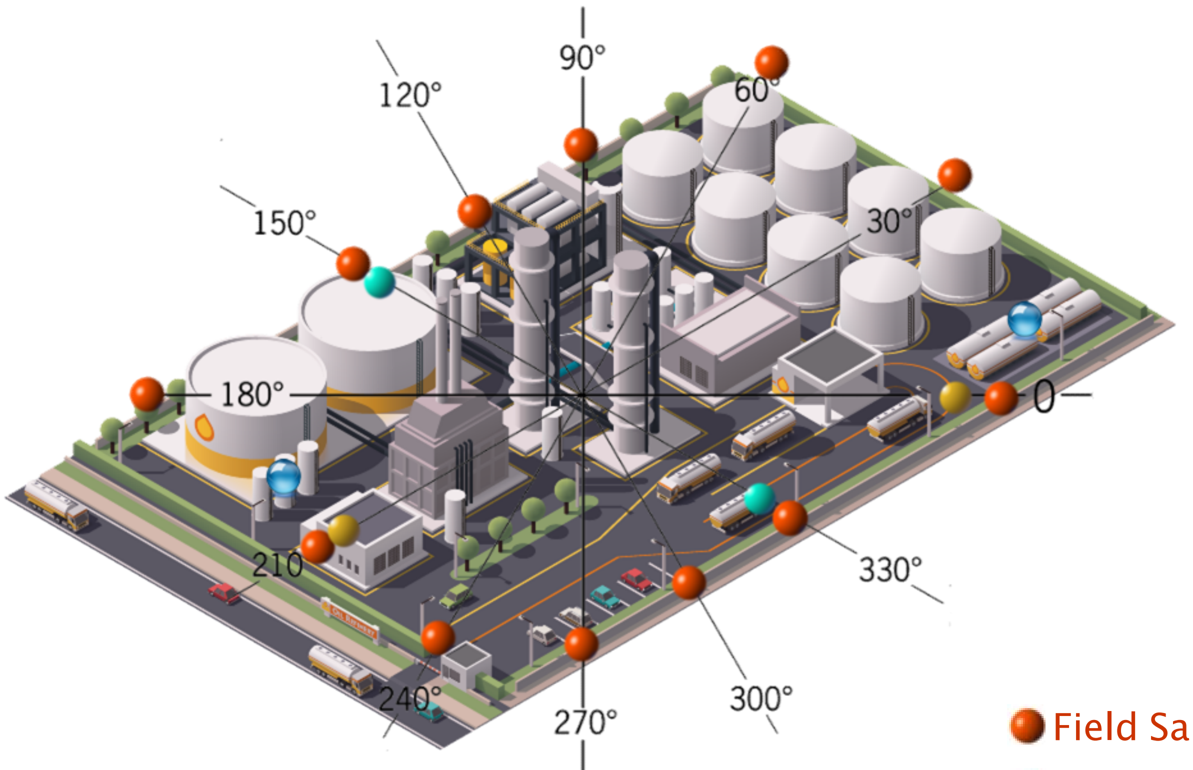
- 325 A: Deployment and collection of air samples
- 325 B: Analysis of the air samples

Schedule

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

Sampling Locations

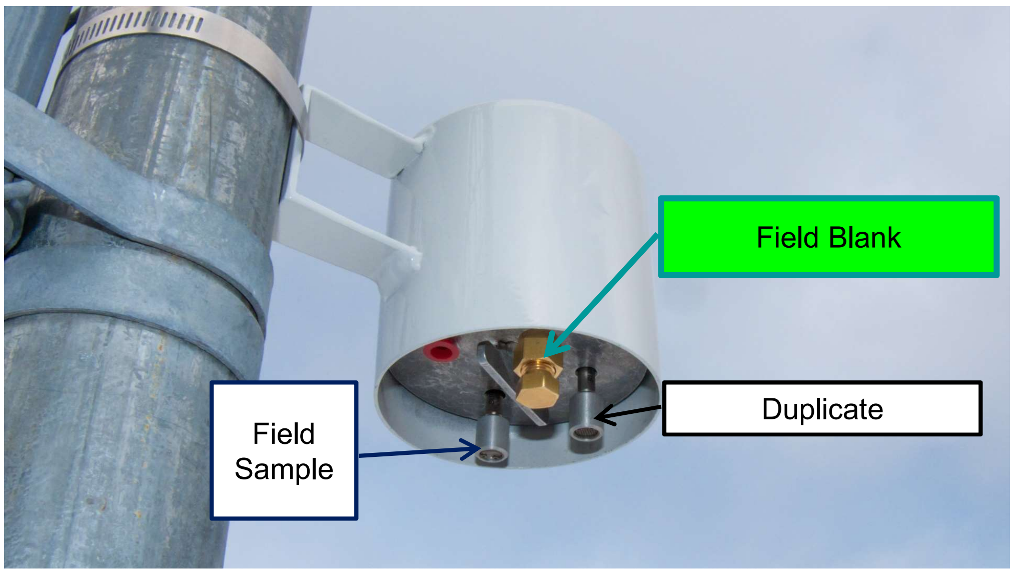
Option 1: Degree Angles	
Acerage of Refinery	Measured Angle
<750	30^{o}
750 to 1500	20^{o}
>1500	15^{o}



Field Sample
Duplicate
Field Blank
Extra Source Sample

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



- 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

Samples / site Depends on Size of Refinery

	Samples required for refinery (field)		
Refinery size	<750 acres	750 to 1500 acres	>1500 acres
Primary sampling	12	18	24
Duplicates per 10 samples	2	3	4
Near Source	~3	~6	~9
Field Blanks per 10 samples	2	3	4
Sample total at day 14	~16	~24	~32
Sample total at year end	~416	~624	~832
	Additional tubes required by the laboratory		
Calibration tubes	10	10	10
Labortory blanks	2	2	2
Quality Control tubes	14	14	14

Sampling Tubes for Method 325

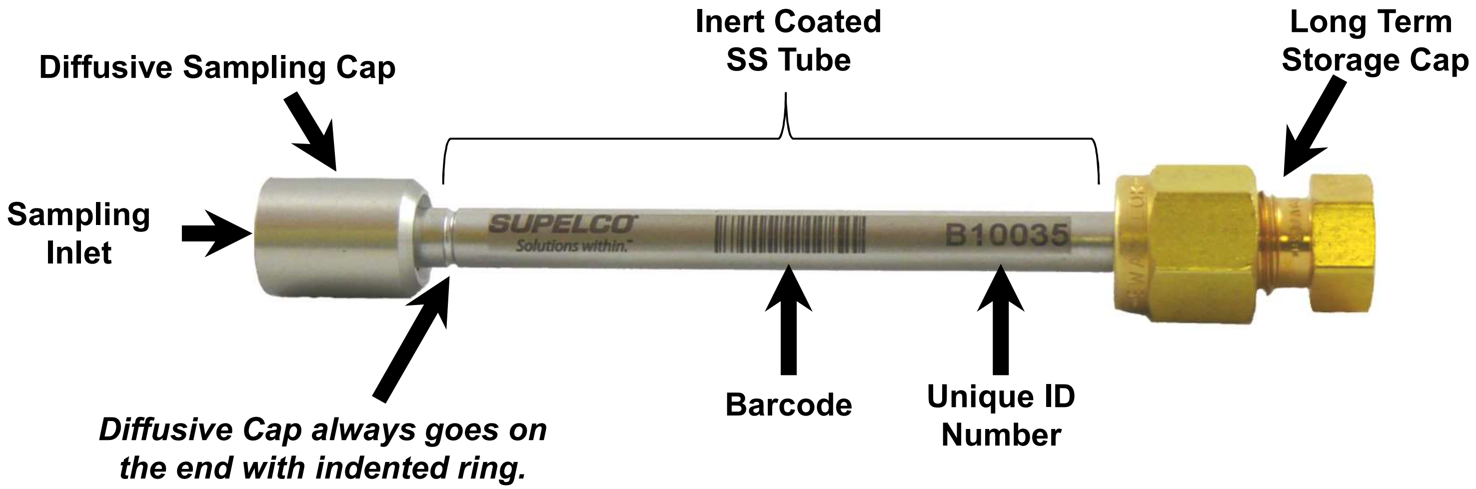
The development of the sampling tube began in 2003, with the U.S. EPA DEARS Study (Detroit Exposure Aerosol Research Study). 3-year field study (2004 to 2007)

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

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

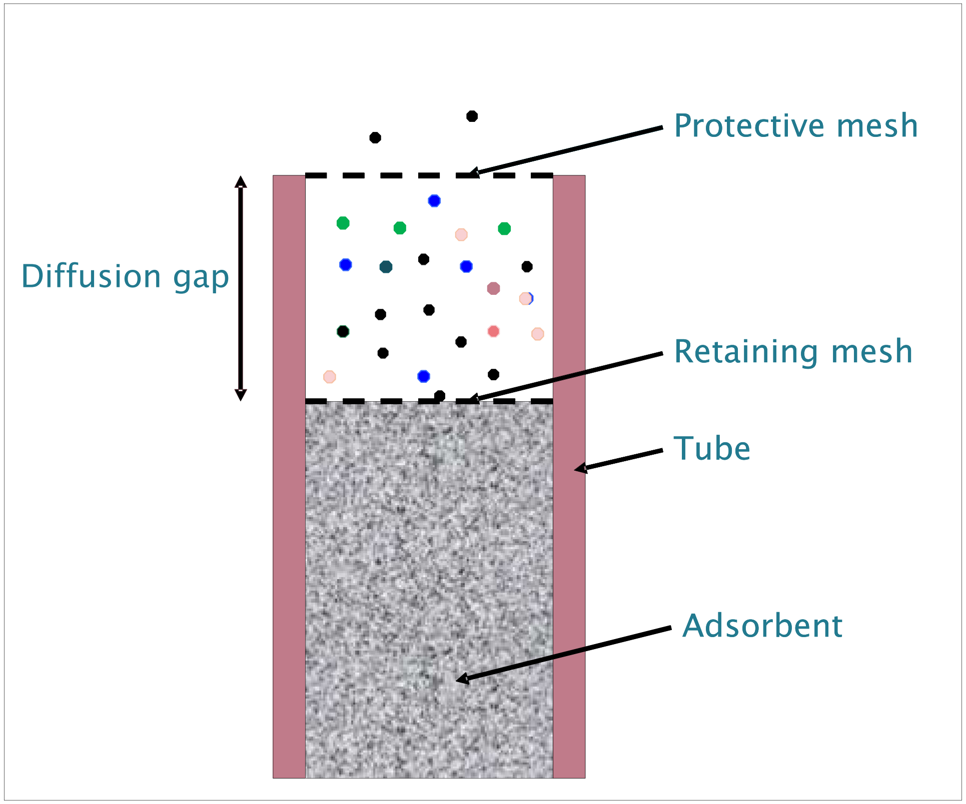


Supel™Coat is a deactivation process that produces a ceramic like protective coating to the stainless steel surface.

How the Passive Sampling Tube Works

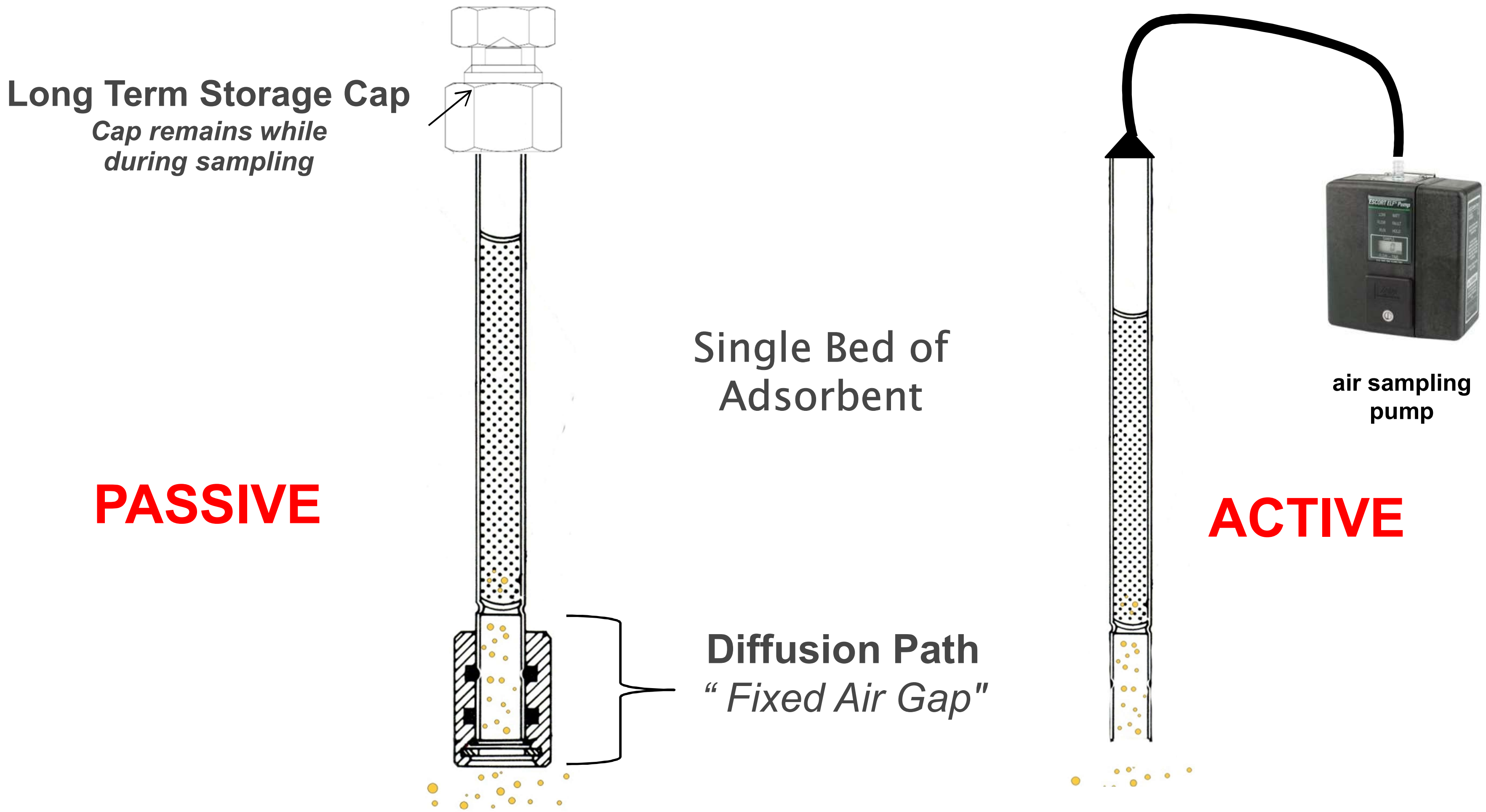
The Diffusive Sampling Process

- Diffusive Uptake Rate dependent on diffusion gap geometry and diffusion coefficient of analytes
- Only small surface area of a single adsorbent exposed
- 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.
- Because of this, diffusive monitoring <u>cannot</u> be used for applications with a wide range of analyte volatilities (e.g. TO-17)



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.



Differences

Active Sampling	Passive Sampling
▪ Very easy to ascertain volume on tube ▪ Can use multi-bed adsorbents for a wide boiling point target range determination ▪ Easy to apply several tubes but typically not necessary ▪ Requires a pump	▪ Excellent for long term sampling (time weighted averaging) ▪ Easy to apply several tubes ▪ Does not require a pump ▪ A single adsorbent so has a limited component range as compared to active sampling per tube. ▪ Uptake rates are adsorbent and component dependent (reason why we use the adsorbents with uptake rates calculated by EPA)

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

Method 325B

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

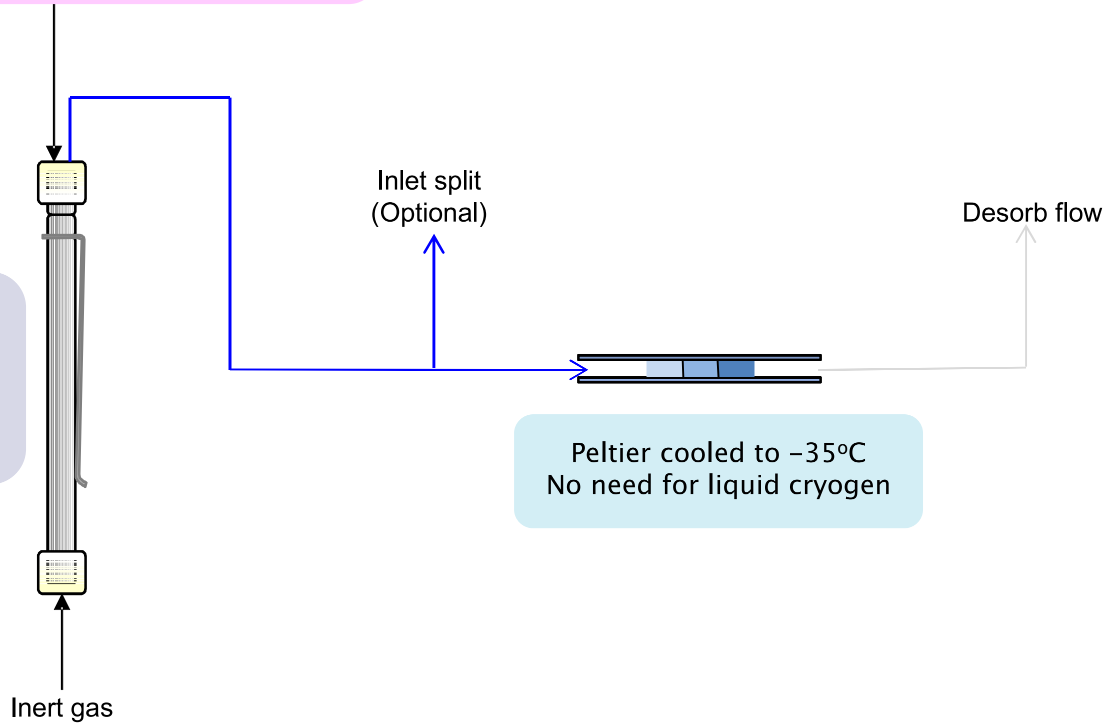
TurboMatrix Thermal Desorber
Clarus SQ8 GC/MS

Thermal Desorption: Operation

Primary (sample) Desorption

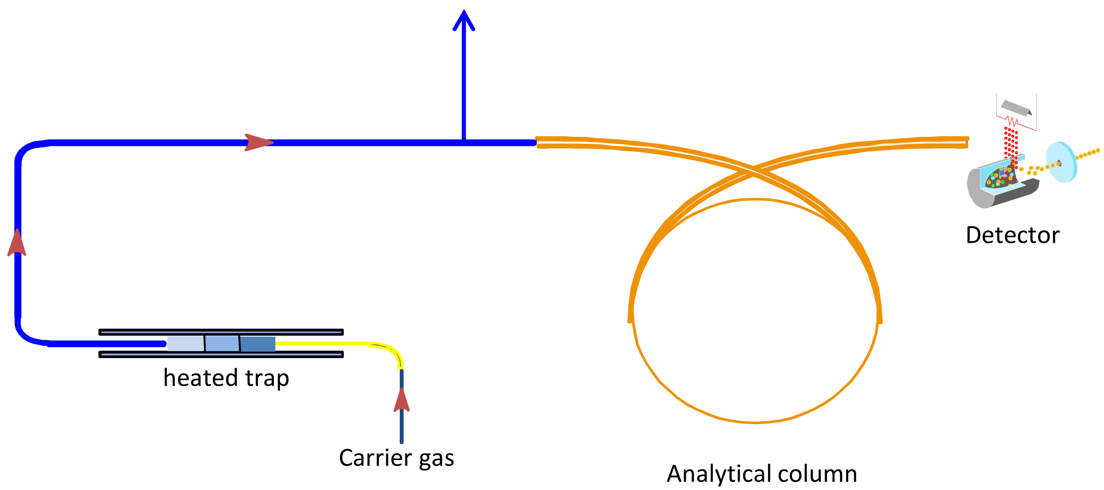
IS and/or Surrogate Spike (optional)
Impedance check (Optional)
Ambient or heated purge (at least 1min)

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



Secondary Trap Desorption

Optional Outlet Split or
Recollect on New or Same Tube

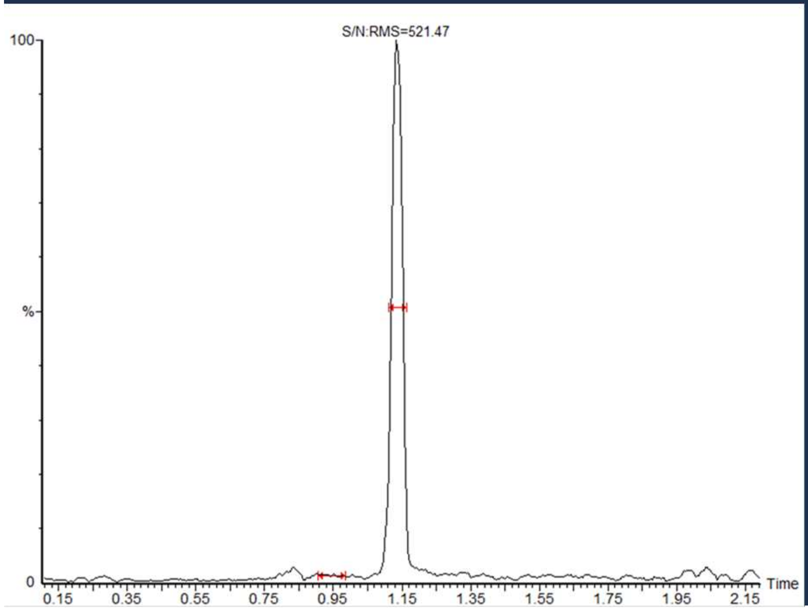


TurboMatrix Thermal Desorber
Clarus SQ8 GC/MS

Method Requirements

Quick Turnaround

Example: Benzene from Fast Method
Tube spike: 0.2 ng



One System Several Choices:

Fast 325B and a SVOC Setup

Both 325B and TO17 Setup

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

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

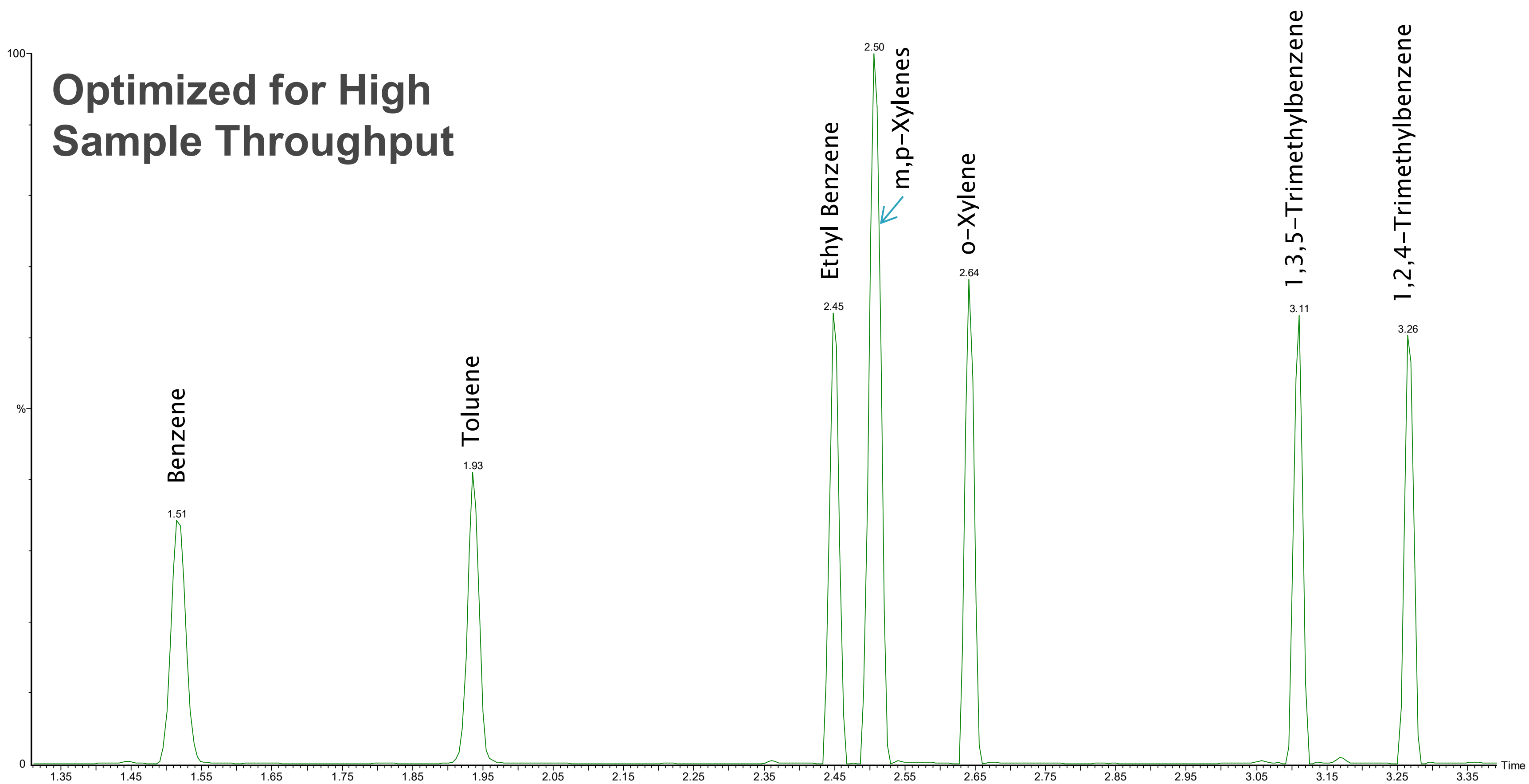
- Detectors
  - Mass Spectrometer (MS)
  - FID or PID
- MS Parameters
  - Scan range 35–300

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

Fast, Resolved Chromatography

VOC and SVOC Column



… Total Ion Chromatogram (TIC) at 10 ppb

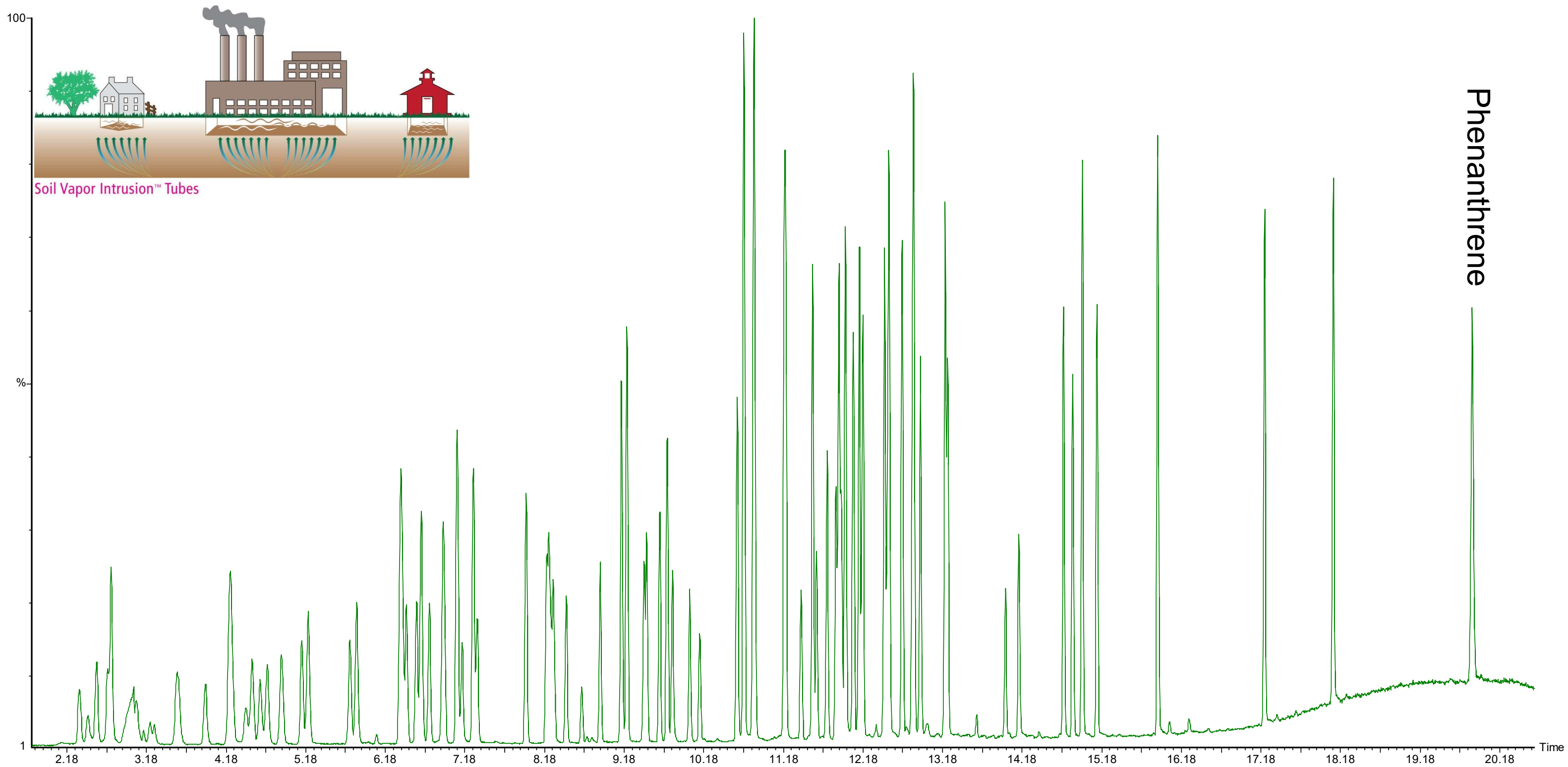
Performance Using Fast Method (325 and VOC and SVOC)

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

… processed using external standard calibration full scan acquisition

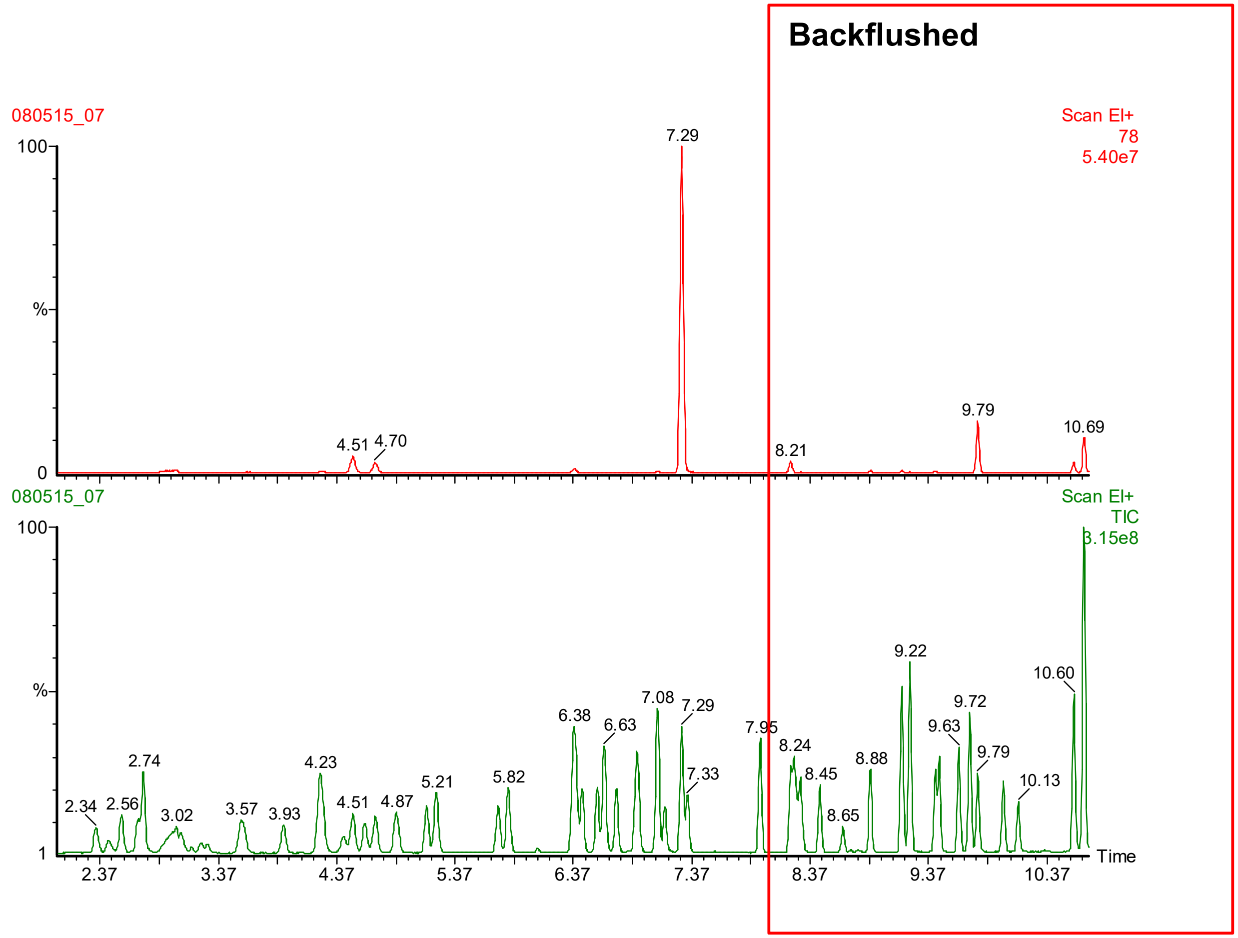
TO-17 Extended Range and 325 on Same System



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

… only outlet split was enabled

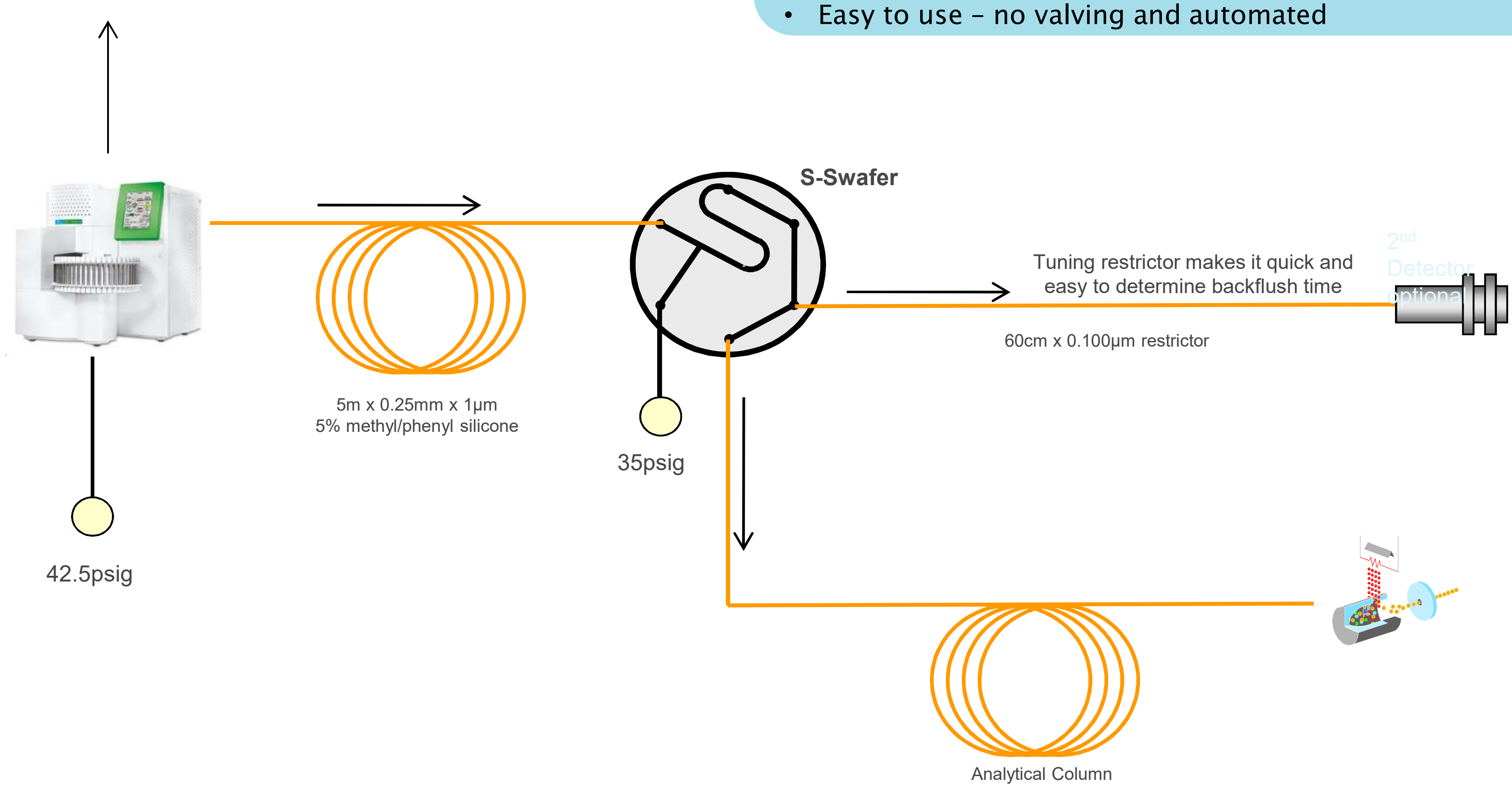
Expanded View and Mass Chromatogram for Benzene



Automated Backflushing

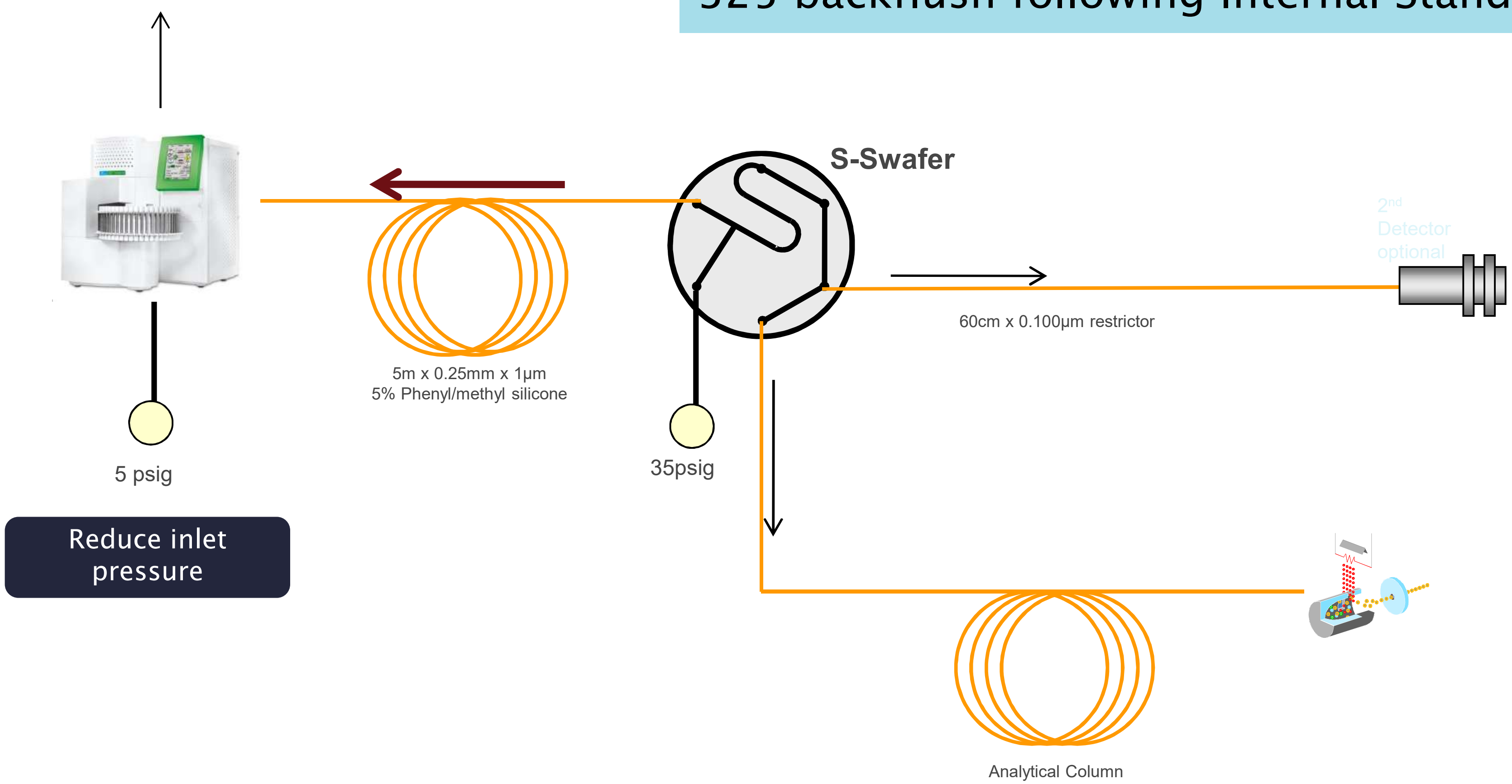
Swafer – Micro Channel Flow Technology

- 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



Acknowledgement

- Jamie Brown, R & D Manager, MilliporeSigma

- James Day, Sr Service Engineer, PerkinElmer

Summary

- Using FLM Carbopack X enables utilizing uptake rates calculated by EPA for enhanced accuracy
- Passive sampling tubes are easy to deploy
- Certification Specific for 325b does not Exist
  - NELAC certification is sufficient for a lab to run 325b
- The method has been optimized for enhanced sample throughput while maintaining excellent performance
- Meets or is better than EPA method criteria

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Thank you!

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