Automated Thermal Desorption TO-17 Extended for Soil Gas and *NEW* EPA Method 325a/b Fenceline Monitoring of Refineries

Tom Mancuso, Product Specialist, PerkinElmer
Lee Marotta, Sr Field Application Scientist, PerkinElmer
Stephen Varisco, CARO Analytical Laboratories
Roberta Provost, Pace Analytical Laboratories

Outline

- Introduction
- Tube Design
- Active and Passive Monitoring
- Functioning and Operations
- Performance
- Ensuring quality
- Summary

History

- 1980 introduced the first automated thermal desorber
- 1990 introduced next generation ATD 400
  - Portable
  - Ease of use
  - Remote control software
- 2000 introduced the TurboMatrix (TMX) 50 and TMX 1
  - TMX-1 dedicated system for online sampling and ozone precursors
  - TMX-50 automated tube sampler
  - Touch Screen GUI for ease of operation
  - Optimized flow path
  - Ease of Maintenance
- 2005 introduced family of five thermal desorbers to five laboratory needs
  - Flexibility for customer needs and solutions
  - Many added features and benefits

Air Sampling Applications

- Environmental (Investigation of toxic compounds and / or ozone precursors in air) Using Sorbent Tube Sampling
  - Soil Gas (soil vapor intrusion)
  - Indoor/Outdoor air
  - Fence line monitoring including New EPA Method 325
  - Stack monitoring
  - Manufactured Gas Plant (MGP) sites

Innovations: Relevant to Air Analysis

- Electronic control of all flows
  - Program flow, velocity or pressure
  - Enhances RT precision
- **Automates** spiking internal standard as a gas
- **Automates** spiking a surrogate prior to sending tubes out for sampling
- **Automates** sample tube and cold trap impedance check to validate trap and tube
- **Automates** sample recollection: confirmatory analysis through sample recollection on the same or new tube
- **Automates** tube conditioning during analysis
- **Automates** leak check of tube and trap prior to each analysis
- Excellent water management

The Clarus TurboMatrix 650
Automated Thermal Desorber

Advantages

Sorbent Tube Recipe

Active and Passive Sampling

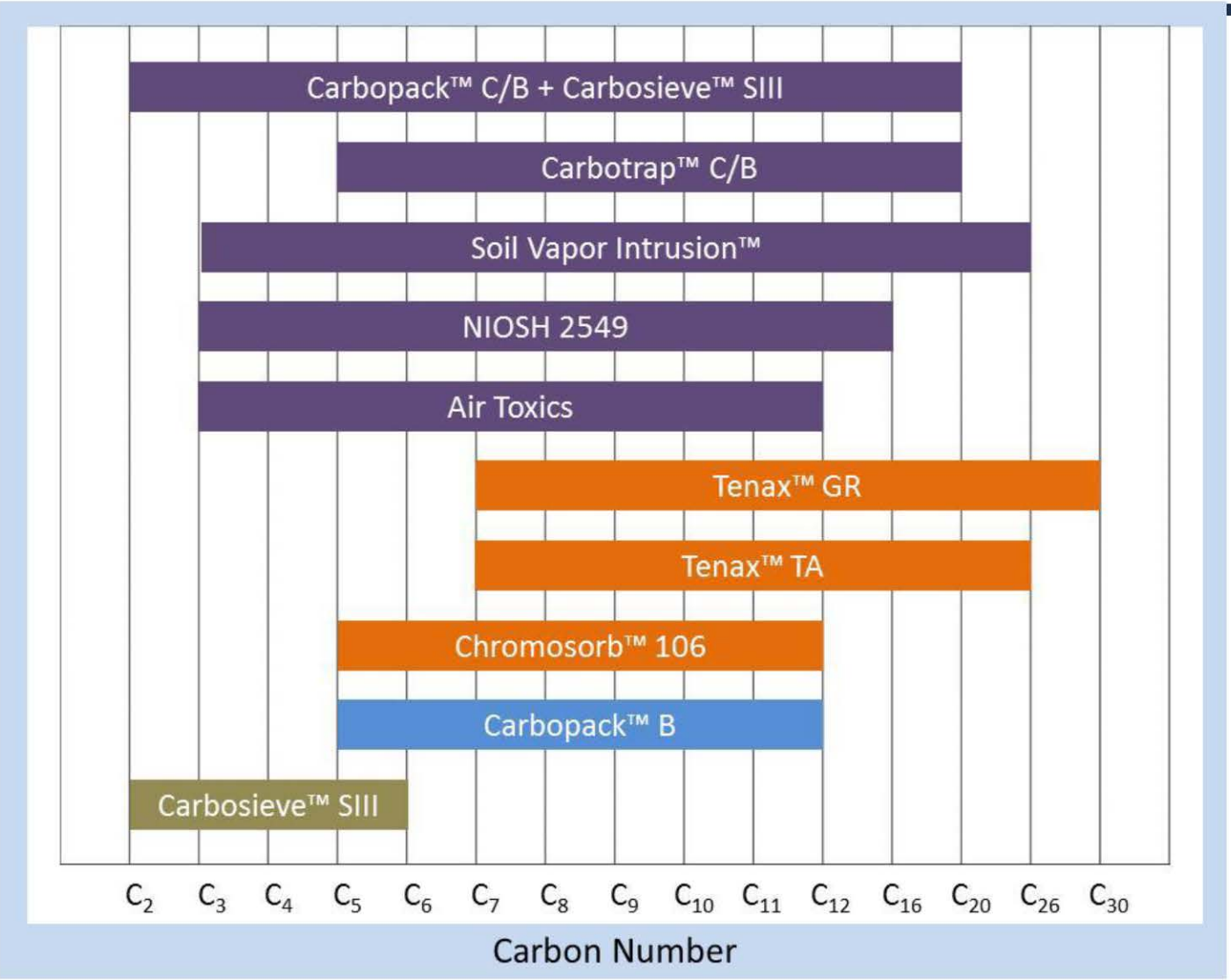
Advantages of Tube Sampling

- Established methodology
- Convenient and less expensive to transport
- Easy to clean, immediate reuse means fast turnaround
- Cost effective
- Larger sample volumes
- Suitable for non-polar and polar compounds
- Inherent Water Management
- Enables Recollection to preserve sample
- Enhances recovery of high boilers – extends analyte list
- Completely Automated

New Sorbent Tubes Investigated: Active Sampling

- **2010: Soil Vapor Intrusion (SVI) Tube (patented)**
  - (C_3 to C_{26})
  - Combines VOC & SVOC from the seven VOA gases to phenanthrene
  - Developed by PerkinElmer, CARO Analytical Services thanks for your help
- **2011: XRO-640 tube (patent pending)**
  - (C_6 to C_{40})
  - Combines VOC & SVOC from BTEX to benzo(g,h,i)perylene
  - Developed by PerkinElmer, Alberta Innovates Tech Futures and Pace Analytical Services thanks for your help
- **2013: XRO-440 (patent pending)**
  - (C_4 to C_{40})
  - Combines VOC & SVOC from 1,3-butadiene to benzo(g,h,i)perylene
  - Developed by PerkinElmer, Pace Analytical Services thanks for your help

Additional Tubes



Active (pumped) Sampling and Tubes

- 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 x min = volume)

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

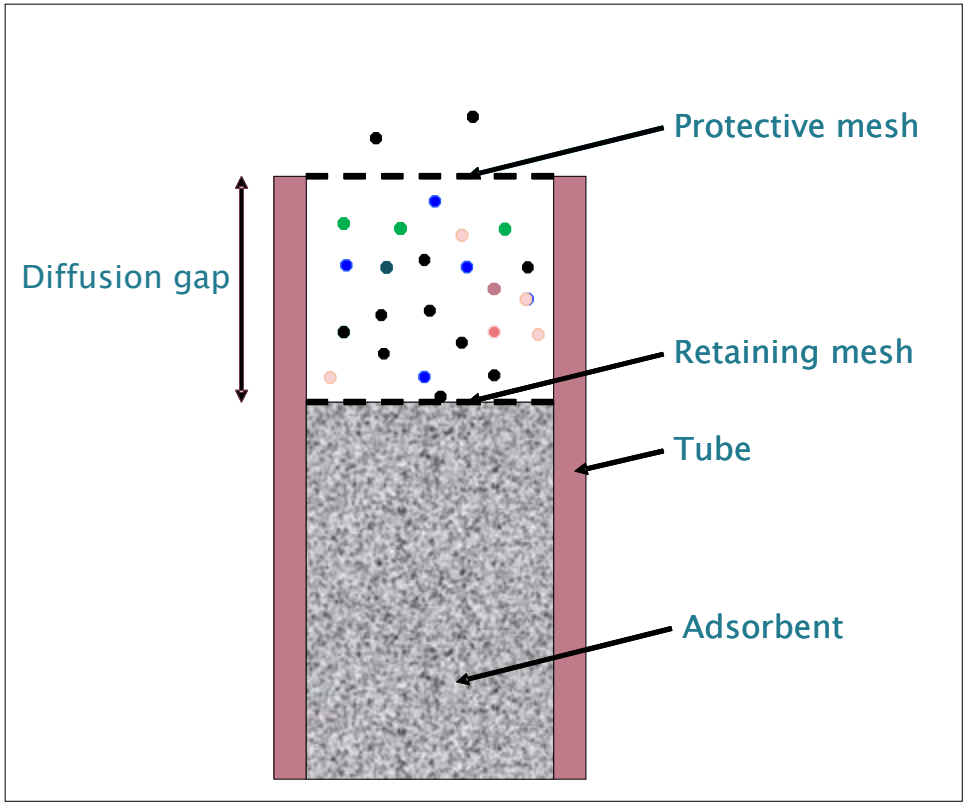
← Desorb the tube in the direction of strong adsorbent to weak adsorbent

Passive (monitoring) sampling

- Precise caps for diffusive sampling
- Tubes accommodate clips for personal monitoring
- Many uptake rates have been determined
- PerkinElmer uses the adsorbent tubes the EPA used in developing method 325

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 $U = \frac{D.A}{L}$
- 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)



Differences

PerkinElmer
For the Better

Active 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

Passive Sampling

- 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)

PerkinElmer
For the Better

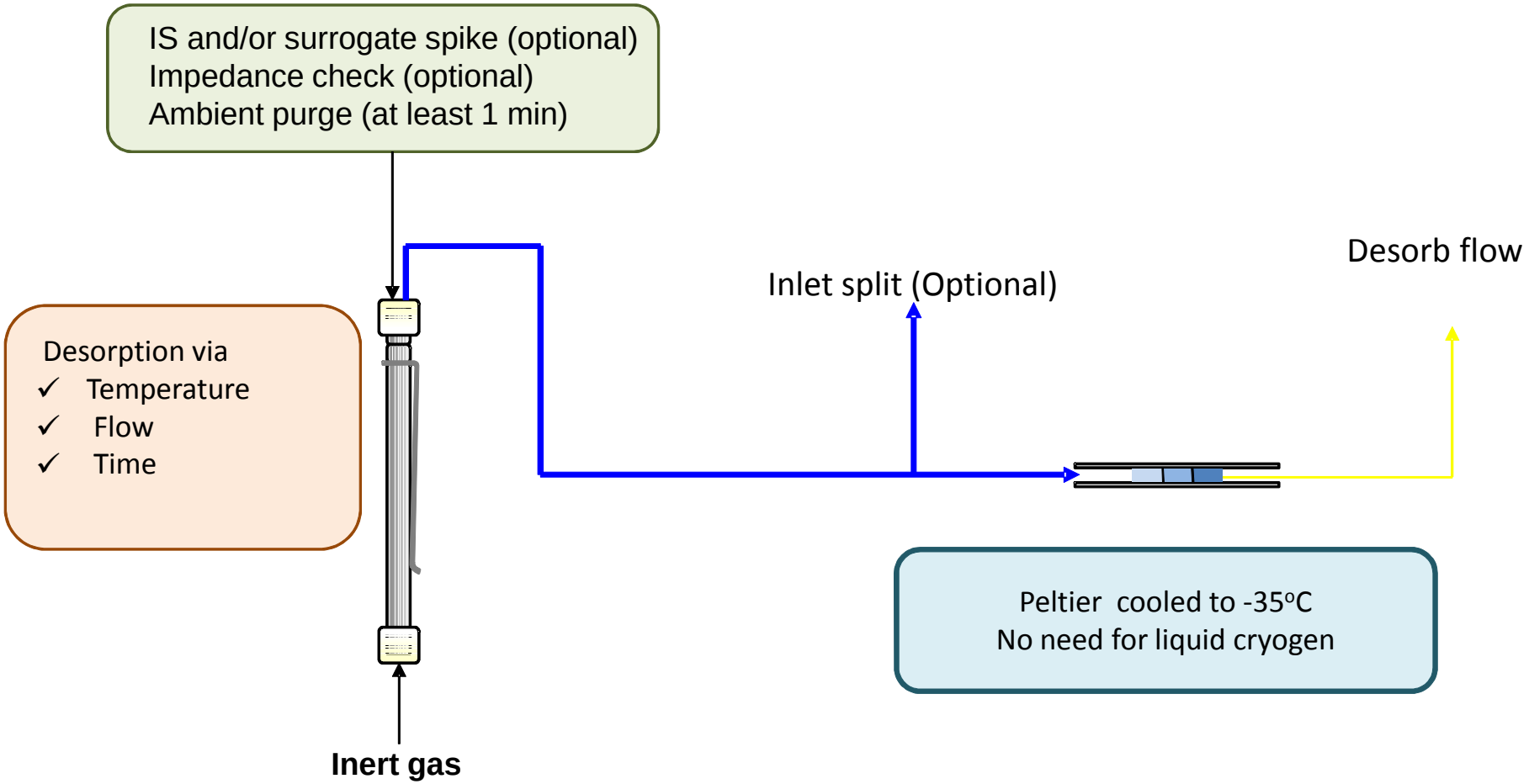
TurboMatrix ATD

Clarus SQ8 GC/MS

Thermal Desorption

Operation

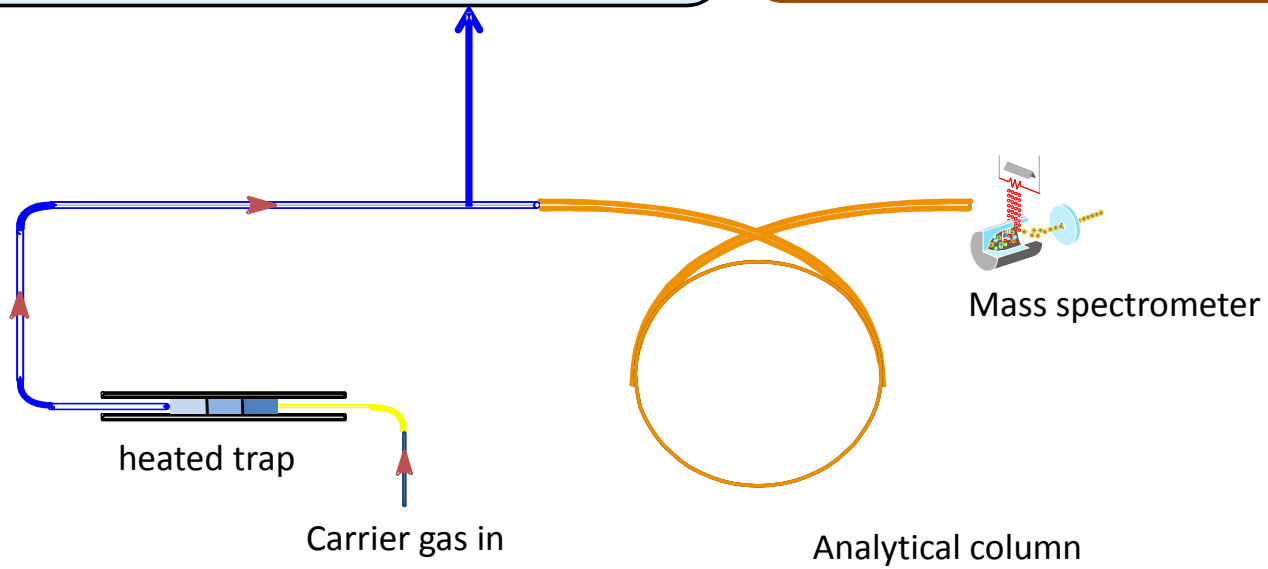
State 1: Sample Tube Desorption



Stage 2: Transfer of Sample to Instrument

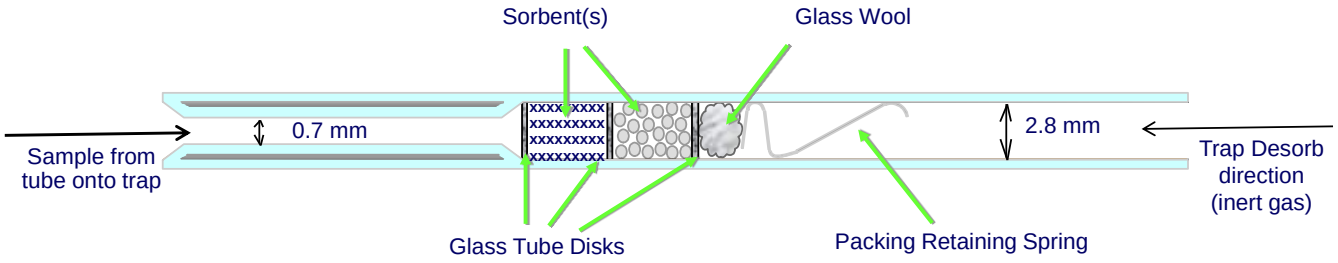
Optional ‘outlet’ split or
Recollect on same tube or new tube

Typical flows
Column Flow: 2.5mL/min
Recollect Flow: 10mL/min
%Recollected: 80%



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



PerkinElmer
For the Better

TurboMatrix ATD

Clarus SQ8 GC/MS

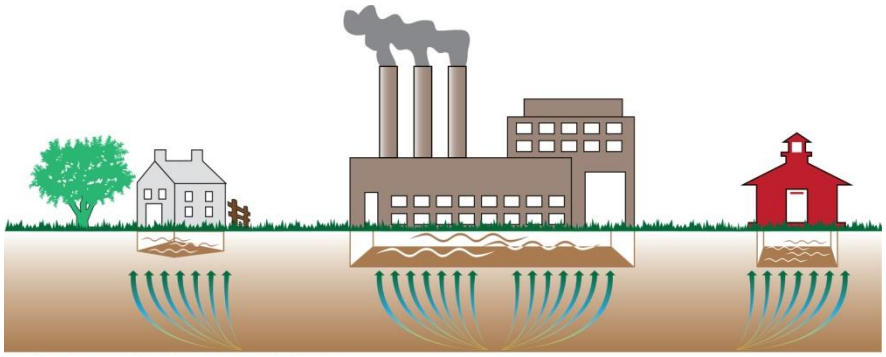
Applications

Soil Gas

and

Refinery Fenceline Monitoring

Soil Vapor Intrusion



Soil Vapor Intrusion™ Tubes

- Soil vapor intrusion occurs when toxic compounds that are present in the air space in soil of a contaminated location have pathways of entering a building, potentially creating a health risk
- These toxic vapors typically occurred because of a contaminated water and/or soil source

Challenges Sampling Soil Gas

- Soil vapor differs from other air sampling
  - High moisture content
  - Greater analyte range
  - Wider concentration range

Development of New Soil Vapor Intrusion Tube (SVI Tube)

PerkinElmer
For the Better

- Broad Compound Boiling Point Range
  - Dichlorodifluormethane to phenanthrene
  - nC3 to nC26
- Front adsorbent capable of recovering high boilers and protecting the stronger adsorbents
  - Prevents irreversible adsorption
  - Clean (compound recovery) after one desorption cycle
- Excellent recovery of high boilers while maintaining the gasses at high sample volumes

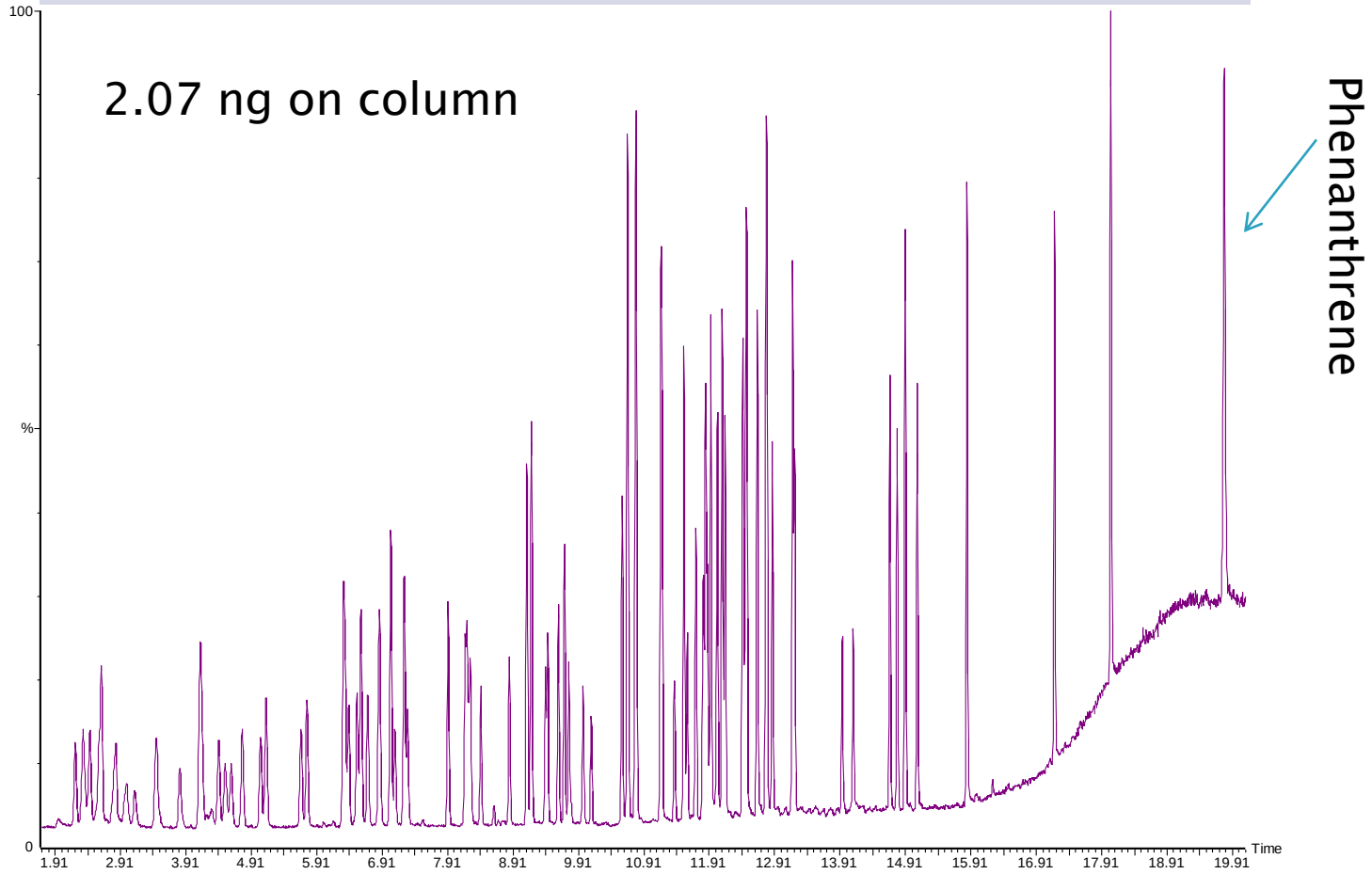
Achieved Goals for SVI tube

- Increasing sampling volume while ensuring retention of all volatiles
- Excellent recoveries of Polynuclear aromatic hydrocarbons (PAHs)
- Automated water management
- Recollection of sample
- Automated sample integrity

Analytical Performance Characteristics

Total Ion Chromatogram

SVI Tube: dichlorodifluoromethane to phenanthrene



Precision, Linearity, Single to noise (s/n)

PerkinElmer
For the Better

1 Liter sample volume
Reporting Limit 0.05 µg/m^3

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

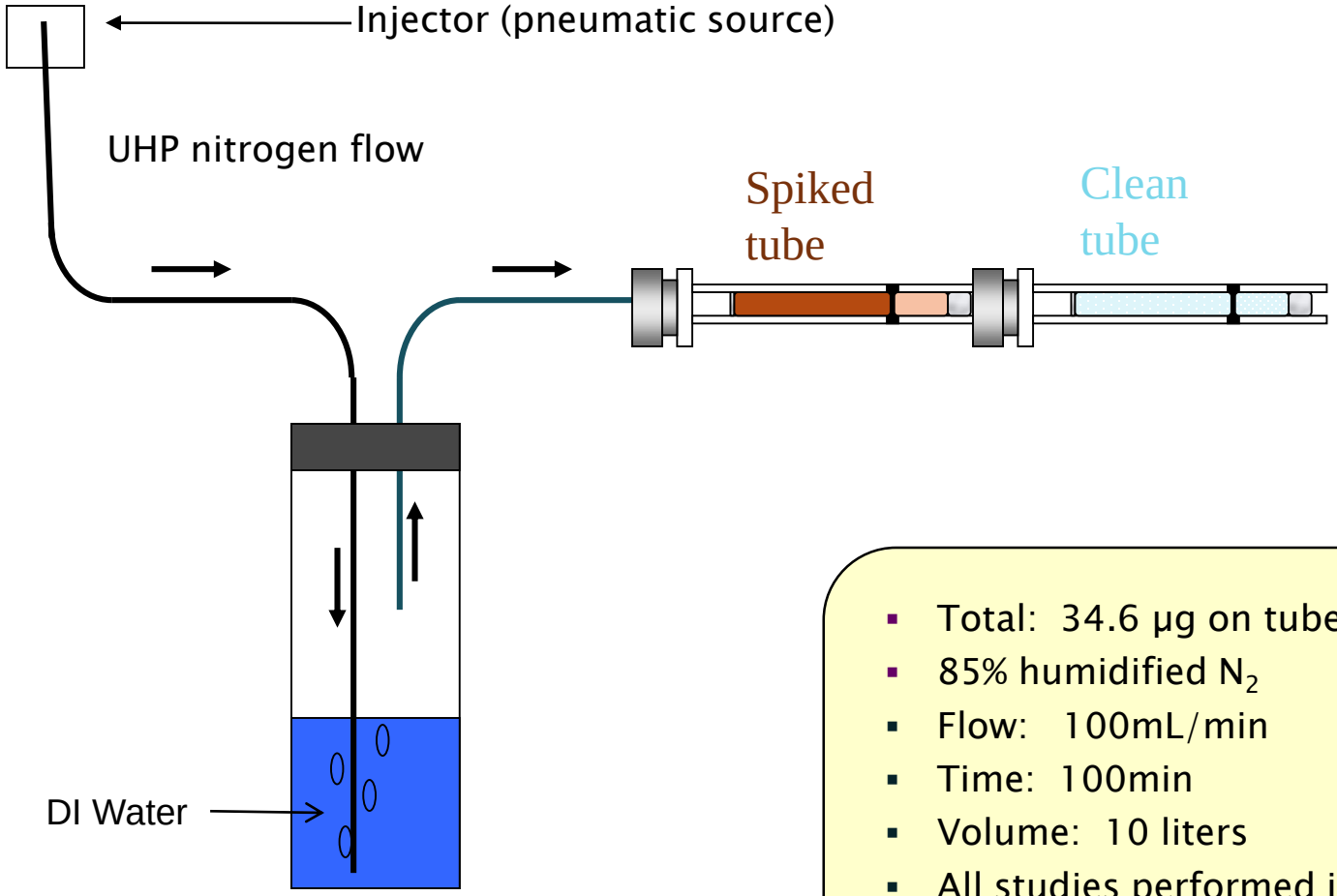
What's on Tube for Recovery and Breakthrough Experiments

- 300ng: 8260B Mega Mix (76 target analytes)
- 300ng: 502.2 volatile (voa) mix #1 (six gases)
- 300ng: 1,3butadiene
- 250ng: Four polynuclear aromatic hydrocarbons (PAHs)
- 10µg of diesel

Concentration on tube for experiments
24.6µg standard mixes plus 10ug of diesel: *34.6µg Total*

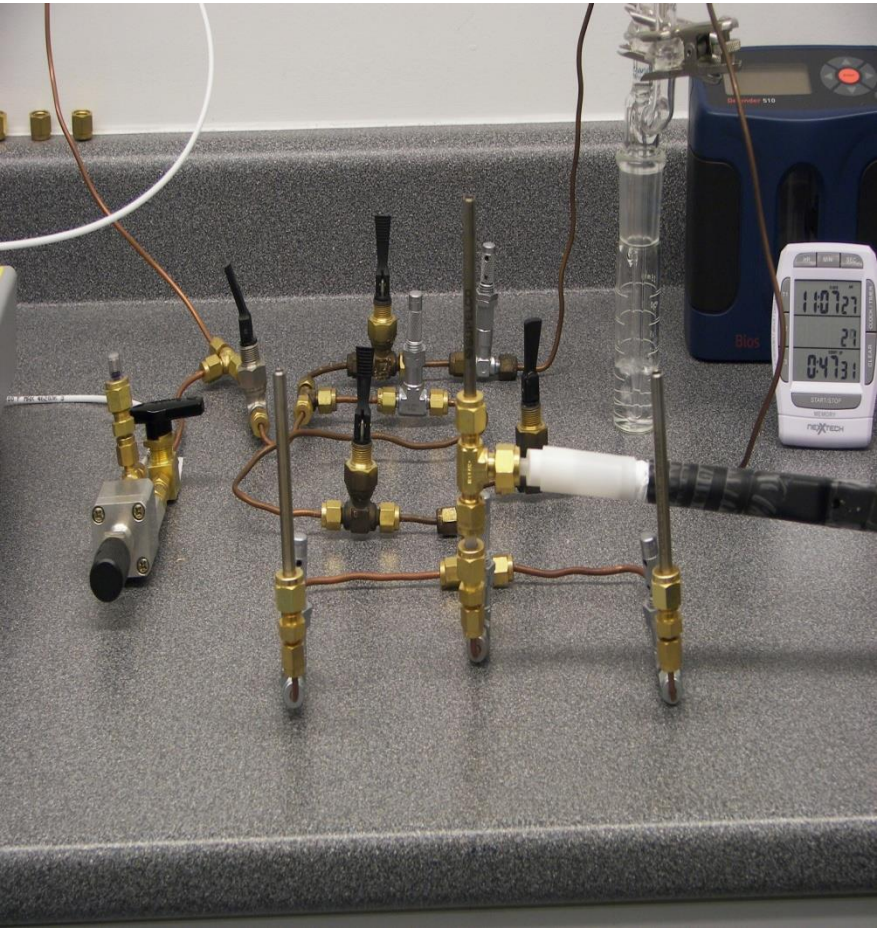
(Standard stocks courtesy of Restek Corp.)

Manifold Used to Ensure Volatile Retention



- Total: 34.6 µg on tube
- 85% humidified N_2
- Flow: 100mL/min
- Time: 100min
- Volume: 10 liters
- All studies performed in triplicate

Results from Breakthrough Experiments



- 10L Sample Volume
- 85% Humidity

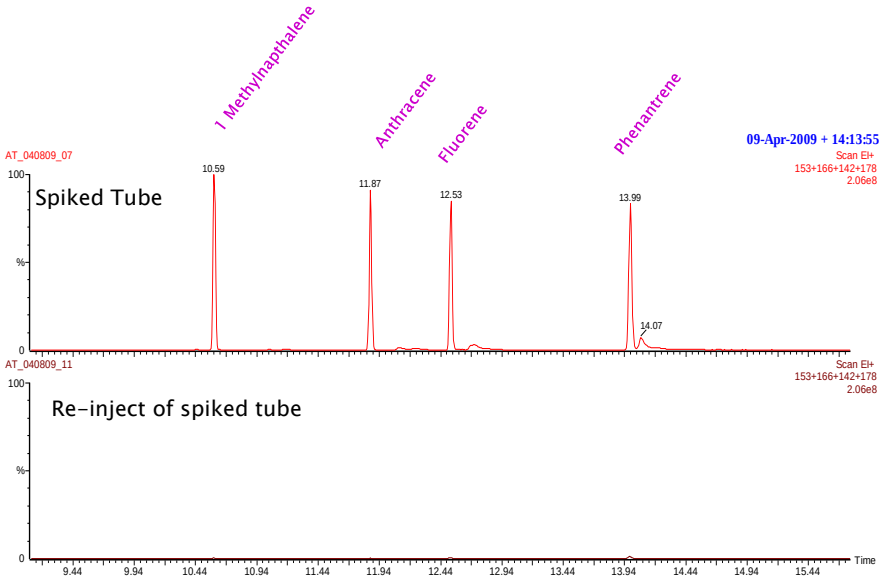
Component	% BT
Dichlorodifluoromethane	1.0
Chloromethane	5.4
Vinyl Chloride	nd
1,3-Butadiene	nd
Bromomethane	nd
Chloroethane	nd
Trichlorofluoromethane	nd

Recovery: Excellent from for all Targets

- Recovery procedure
  - Analyzed spiked tube
  - Analyzed trap
  - Analyzed blank tube
  - Re-analyzed spiked tube which should be clean

PAH Compounds	% Recovery
1-Methyl Napthalene	99.7
Anthracene	99.8
Fluorene	99.4
Phenanthrene	98.8

- Non-detectable carryover
  - Insignificant carryover of 4 heaviest PAHs
  - Significantly below method criterion

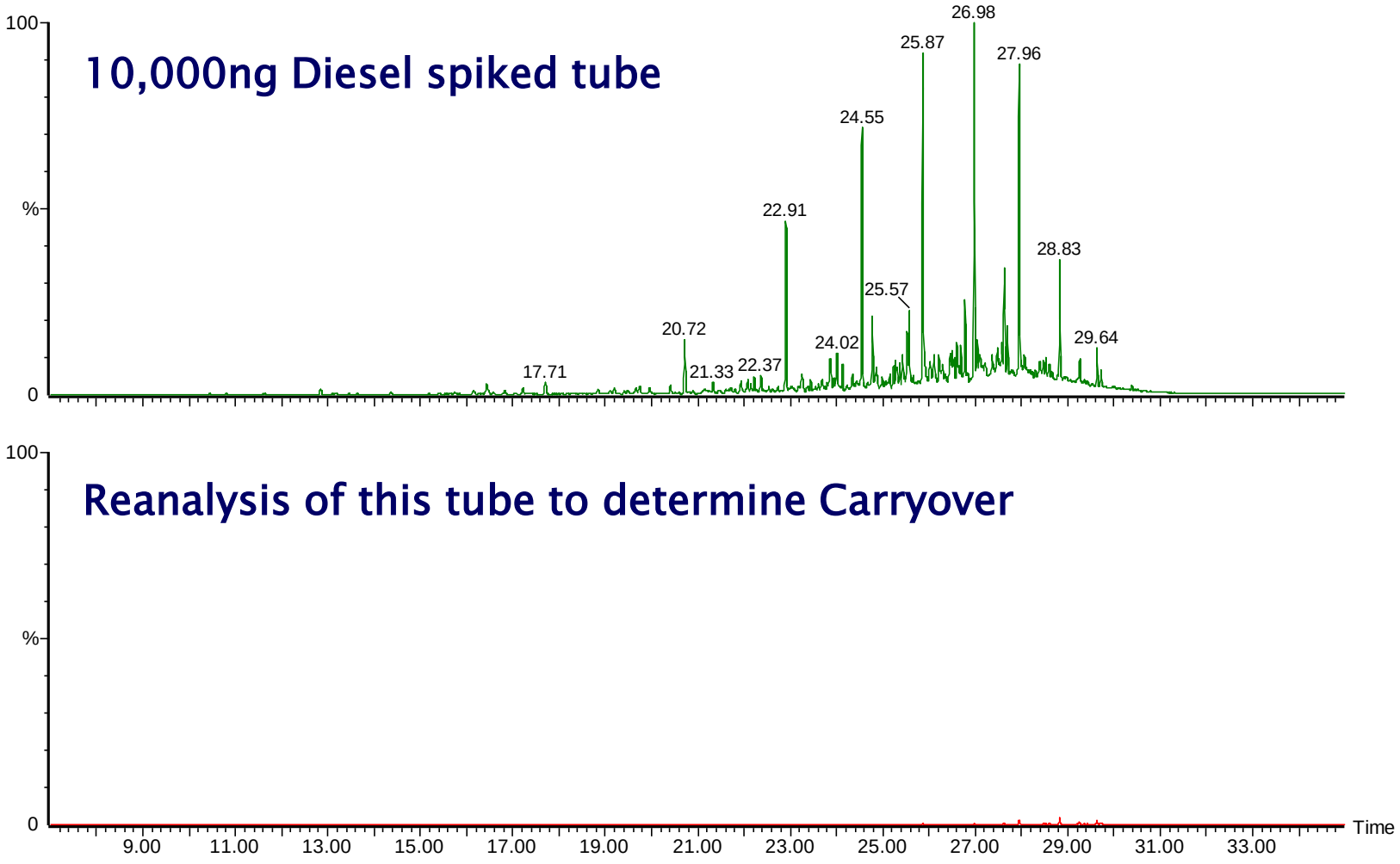


Excellent Recovery of Diesel

PerkinElmer
For the Better

Carryover <1%

Masses 57 + 69



PerkinElmer
For the Better

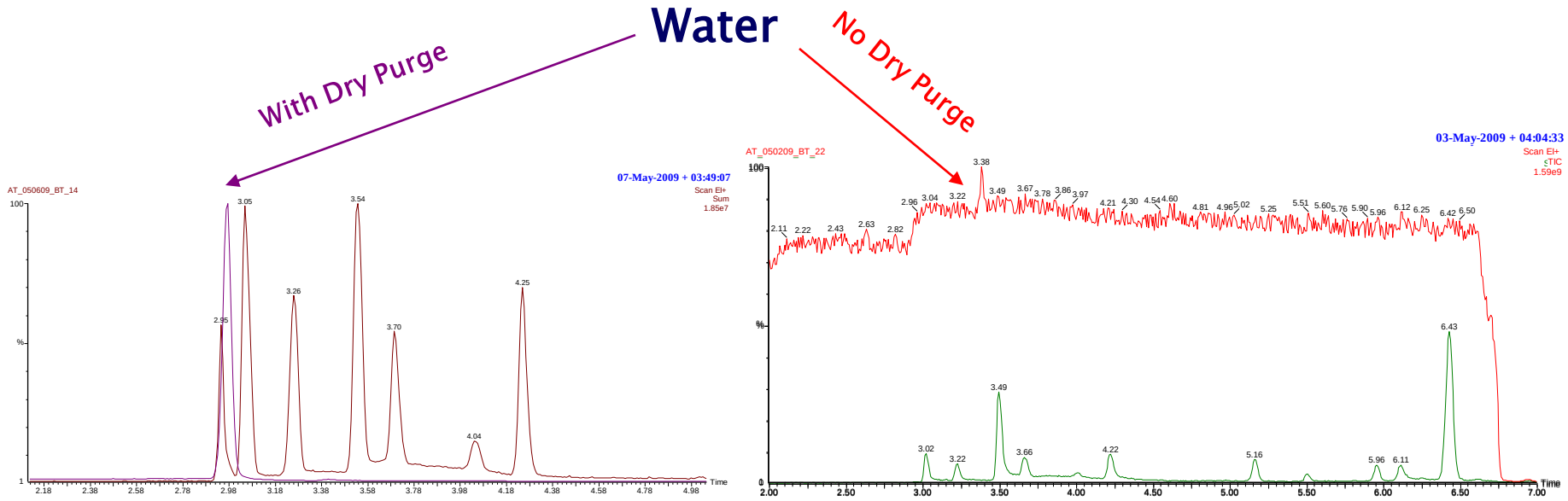
Water Management

Methods of Water Removal

- Nafion Drier / Desiccants
  - Polar Compounds Removed – Cannot be used for Air Toxics (TO-15/TO-17 Component list)
- Hydrophobic adsorbents
- Dry Purging!
  - Time depends upon sample humidity
  - 1 minute to rid tube of oxygen

Why Remove Moisture?

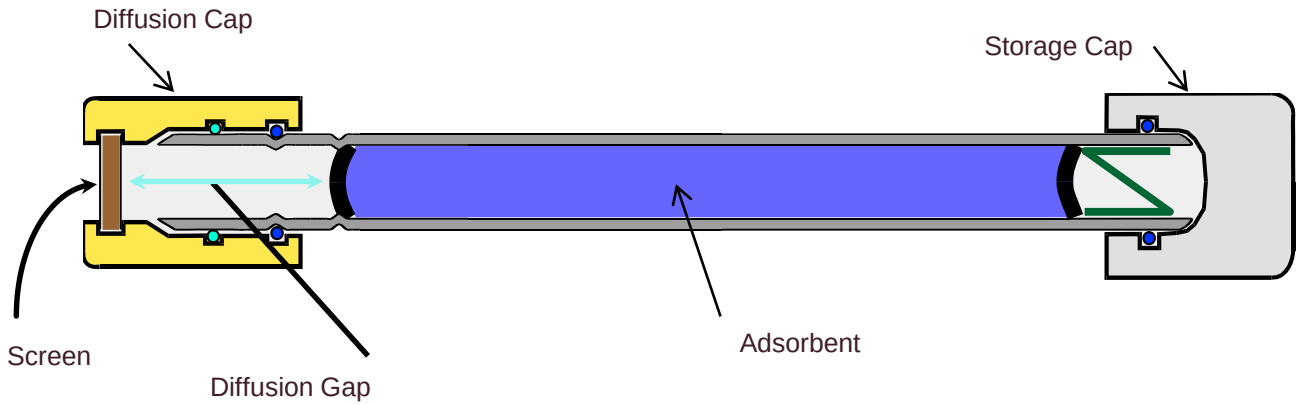
- Mass Spectrometer
  - Signal quenching
  - Increased maintenance
- Chromatography
  - Can effect peak shapes



EPA Method 325 a/b

Regulated Fenceline Monitoring of Refineries for Benzene

Method EPA 325a Sampling



- EPA calculated uptake rates for 20+ targets using Carbopack X specially treated tubes. PerkinElmer recommends and provides these tubes
- Sampling: Continuous – two weeks intervals
- Uptake rate on Carbopack X for the regulated target benzene is 0.67mL/min
- Volume on tube over a two week sampling period is 13.507 liters

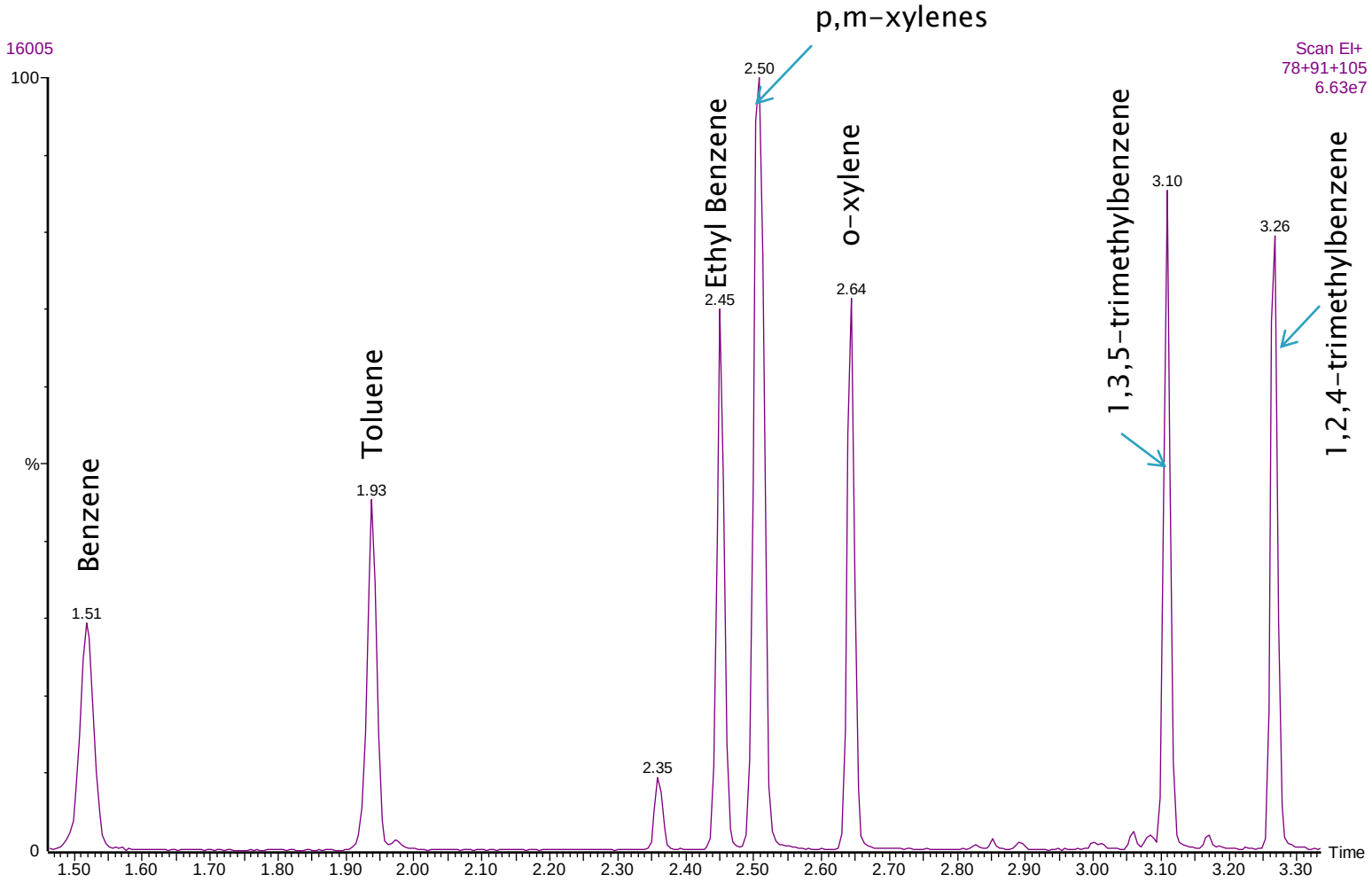
Samples / site Depends on Size of Refinery

	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 Shelter

- Optimized for accurate sampling
- Protected from weather and bugs, etc

Total Ion Chromatogram:



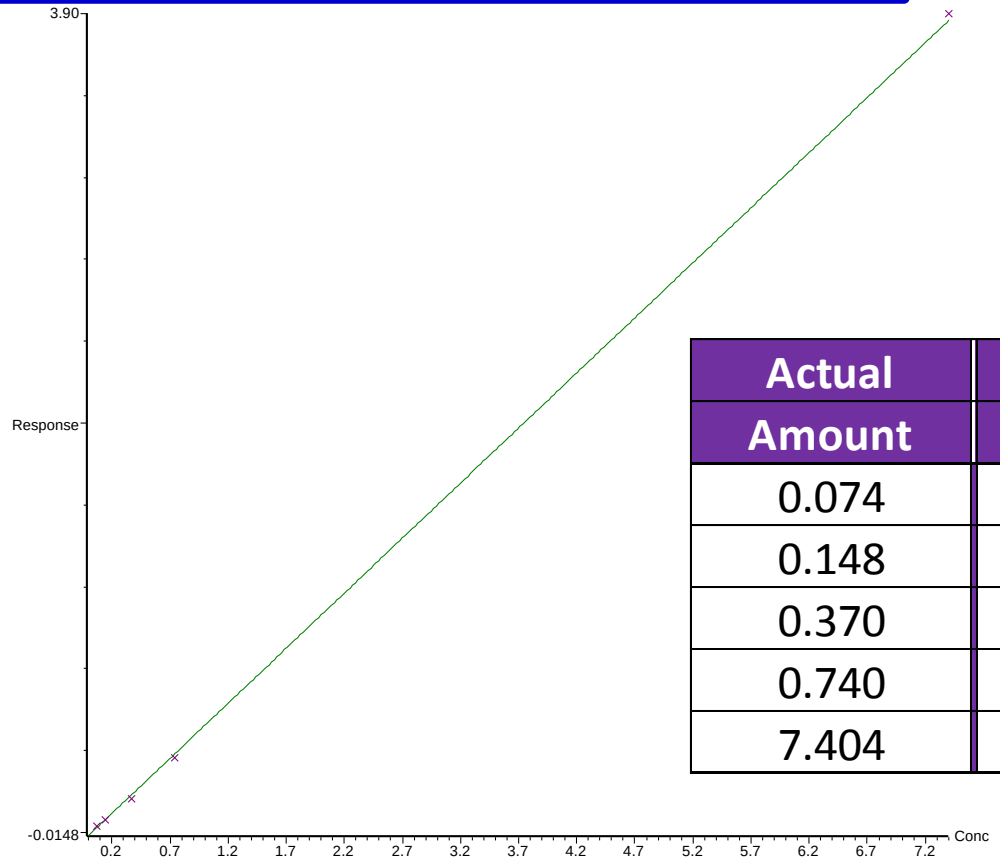
Bromofluorobenzene (BFB) Criterion

PerkinElmer
For the Better

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

Calibration for Benzene: 0.9999

Concentrations adjusted for 13.5 L volume
Range from 0.074 to 7.404 ug/m3
Correlation Coefficient: 0.9999



Actual Amount	Calculated Amount	%Dev	S/N @ RL
0.074	0.085	15	202 to 1
0.148	0.145	-2	
0.370	0.337	-9	
0.740	0.707	-4	
7.404	7.462	1	

Summary

- Advantages of tube sampling
  - Allows for sampling targets with a higher boiling point range
  - Easier and less expensive to transport
  - Polar and non-polar compounds
  - Passive sampling
  - Enhances detection limits … larger sample amounts

- PerkinElmer
  - Single Vendor Solution
  - Experts in thermal desorption and air sampling
  - Experienced sales, application specialists and service support
  - State of the Art solution from sampling to final report!!!!

PerkinElmer
For the Better

Solution for Measuring Toxic Compounds in Air

Thank you!

??? Please

thomas.mancuso@perkinelmer.com
lee.marotta@perkinelmer.com