

Extending the Hydrocarbon Range above Naphthalene for Soil Vapor and Air Samples Using Automated Thermal Desorption/Gas Chromatography/Mass Spectrometry (ATD/GC/MS)



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➤ Introduction

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➤ Thermal Desorption Technology and Operation

- Advantages
- Operation

➤ Tube Design and Adsorbent Optimization

- Objectives of new tube

➤ Tube Performance Characteristics

- Optimizing recovery, precision and detection limits
- Increasing safe sampling volumes in the most humid environment

- Environmental (Air Toxics)
 - Soil Gas (soil vapor intrusion)
 - Indoor/Outdoor air
 - Fence line monitoring
 - Stack monitoring

Innovations : Relevant to Air Analysis!

- Electronic control of all flows
 - Programmed flow, velocity or pressure
 - Enables consistent RT precision
- Automates spiking internal standard as a gas onto each tube
- 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
- Performs a leak check of tube and trap prior to each analysis
- Excellent water management



...ease of use, accurate, precise



Advantages of Tubes

Operation of ATD

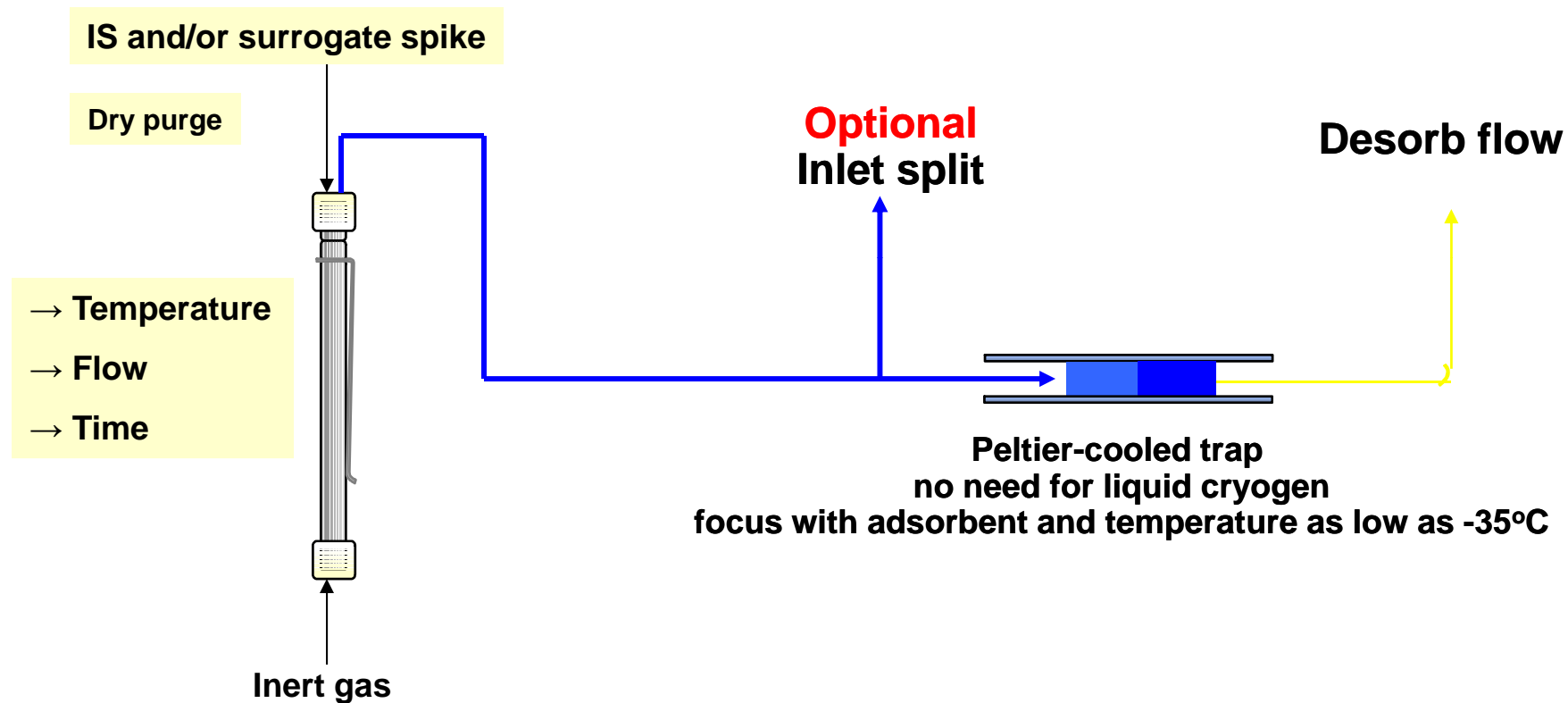
Sorbent Tube Recipe

Advantages of Tube Sampling

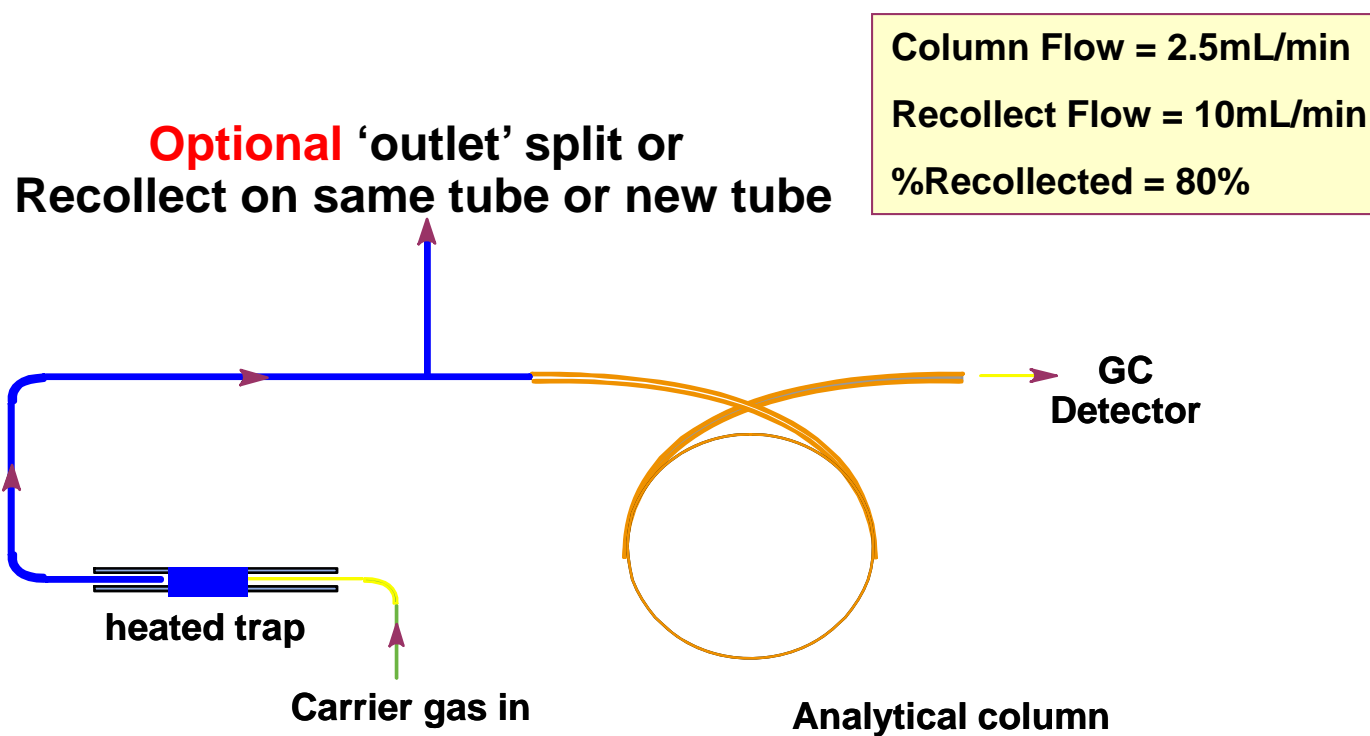


- Established methodology
- Convenient and less expensive to transport
- Easy to clean, immediate reuse means fast turnaround
- Cost effective
- Larger sample volumes
- Suitable for non-polar and polar compounds
- Inherent Water Management
- Enables Recollection to preserve sample
- Enhances recovery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

State 1: Sample Tube Desorption

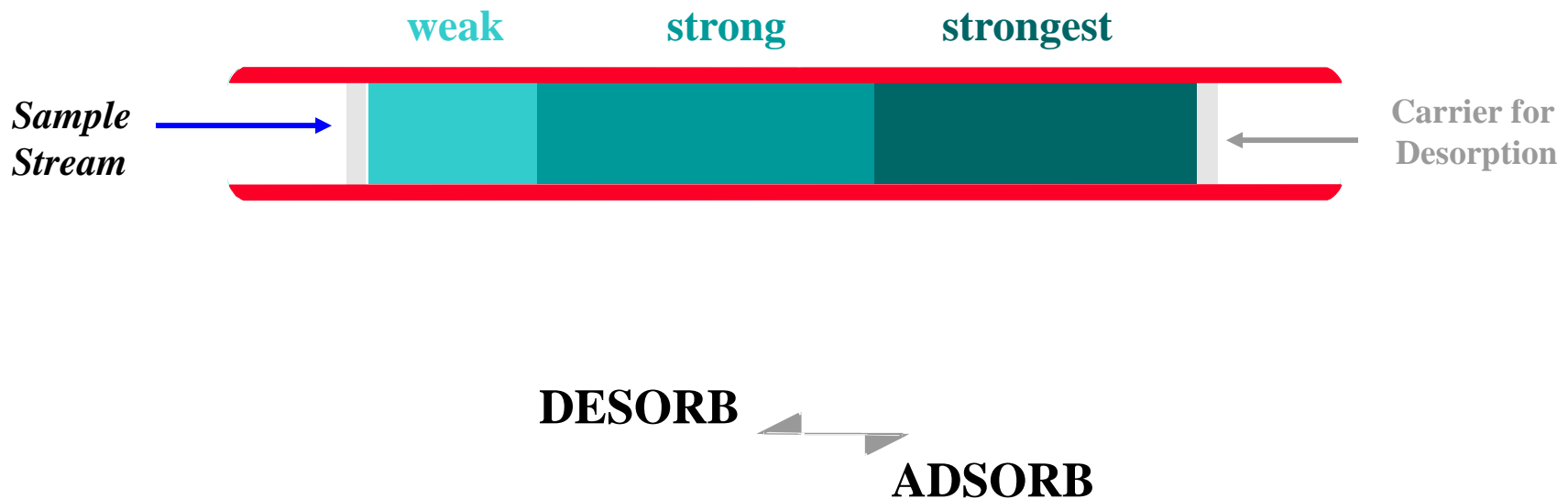


Stage 2: Transfer of Sample to Instrument



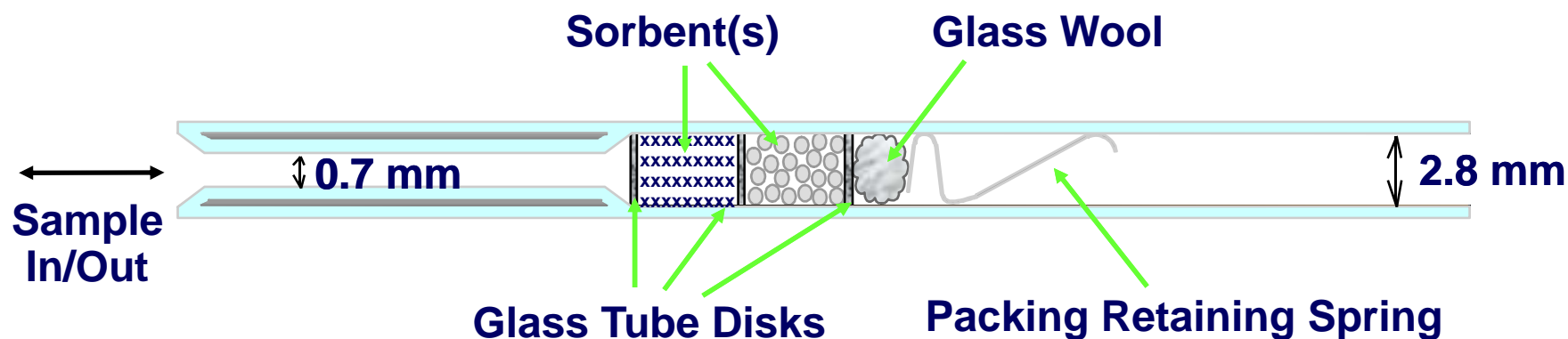
Thermal Desorption Tube

Multiple Adsorbents: *accommodate wide boiling point analyte range*



Cold Trap

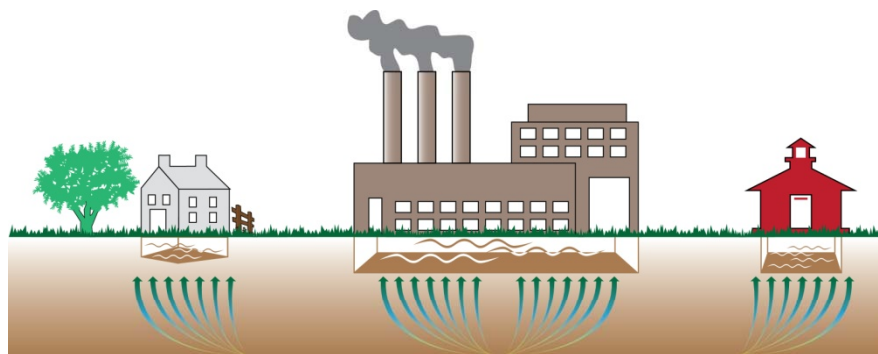
- Reduced diameter outlet reduces analyte dispersion or band broadening for narrower, focused peaks
- Trap flow is reversed during desorption to enhance efficiency and ensure recovery of high boiling compounds





*Enhanced Tube Design for
Soil Gas (Soil Vapor Intrusion) and
Ambient Air 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

Optimizing Air Sampling with *NEW* Tube Technology



- Increasing sampling volume ensuring retention of volatiles
- Excellent recoveries of semi-volatiles and diesel
- Automated water management
- Recollection of sample
- Automated sample integrity

.... Rugged for the most challenging soil gas analysis

Optimize a Tube for the Most Challenging Vapor - Soil Gas



➤ Soil vapor differs from other air sampling applications

- Higher moisture
- Greater analyte range
- Wider concentration range

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Characteristics of New Thermal Desorption Tube

- Broad Compound Boiling Point Range
 - dichlorodifluoromethane to phenanthrene plus
 - nC3 – nC26
- Protects the strong adsorbents
 - Prevents irreversible adsorption
 - Clean after one desorption cycle
- Excellent recoveries of high boilers

Regulations for Soil Gas (soil vapor intrusion)

- 23 US States regulate Soil Vapor Intrusion
- British Columbia Contaminated Sites Regulations, Schedule 11
 - Effective January 1, 2009
 - 118 regulated parameters: >90% via TD
 - Ex concentration regulations
 - Trichloroethene (TCE) – 1.0 ug/m³ (dry cleaning site)
 - Benzene – 1.5 ug/m³ (gasoline site)
- A thought??? Test water and soil first? Or ... Test vapor first?



Analytical Performance Characteristics

Total Ion Chromatogram of 82 compounds in 8260B

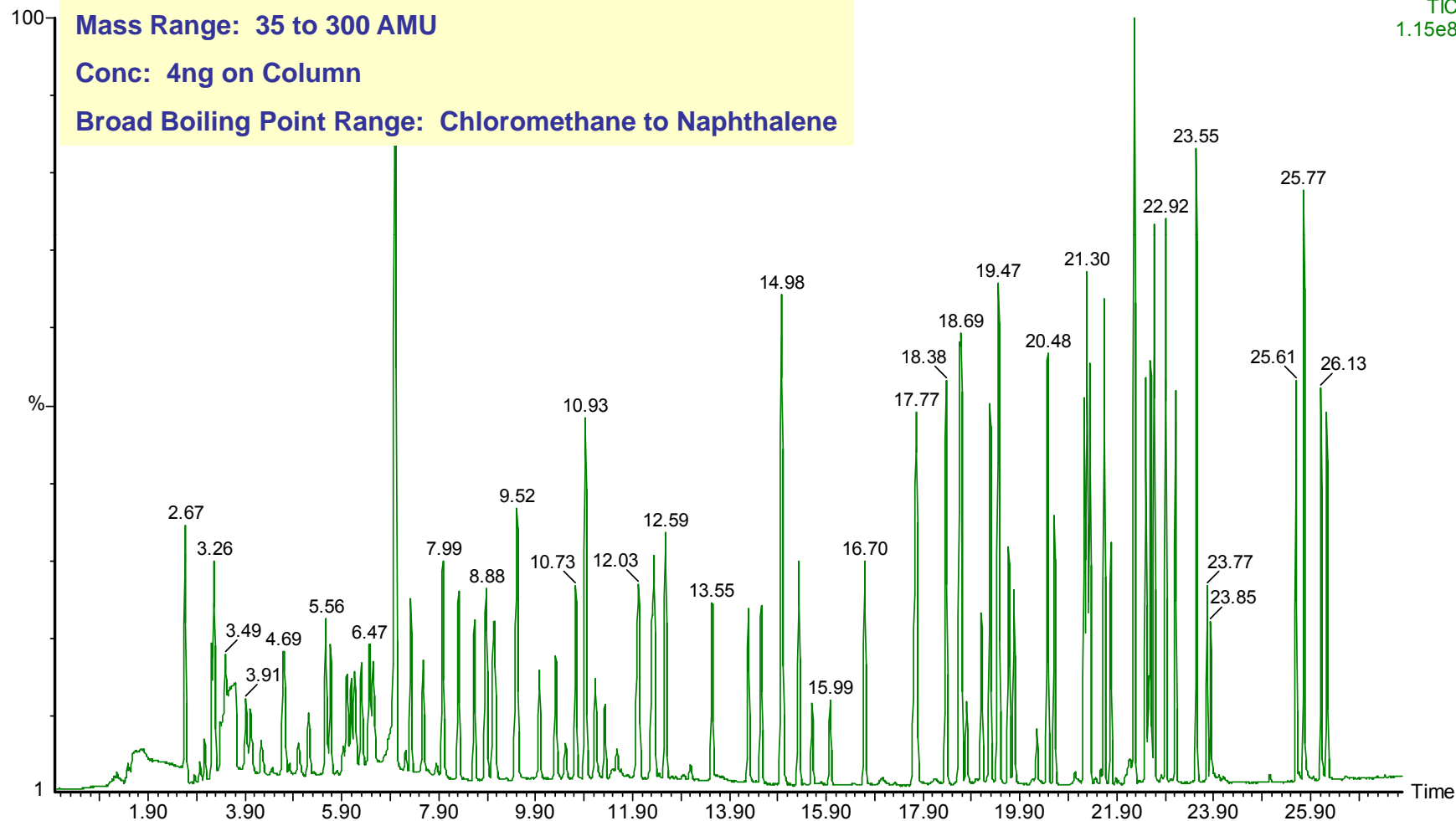


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Precision, Linearity, Reporting Limits and MDLs

Compound Class	# Cmpds	Precision	Correlation Coefficient	Reporting Limit	MDL
		(n=8)	0.1 to 200ng on tube	(10L Volume)	(10L Volume)
				unit ug/m3	unit ug/m3
Gases	6	6.9%	0.9952	0.05	0.02
non-Aromatic Halogens	33	2.7%	0.9985	0.02	0.005 to 0.01
Aromatics	15	1.4%	0.9995	0.02	0.005
Halogenated Aromatics	9	1.4%	0.9997	0.02	0.005

... exceeds method criteria

What's on Tube for Recovery and Breakthrough Experiments



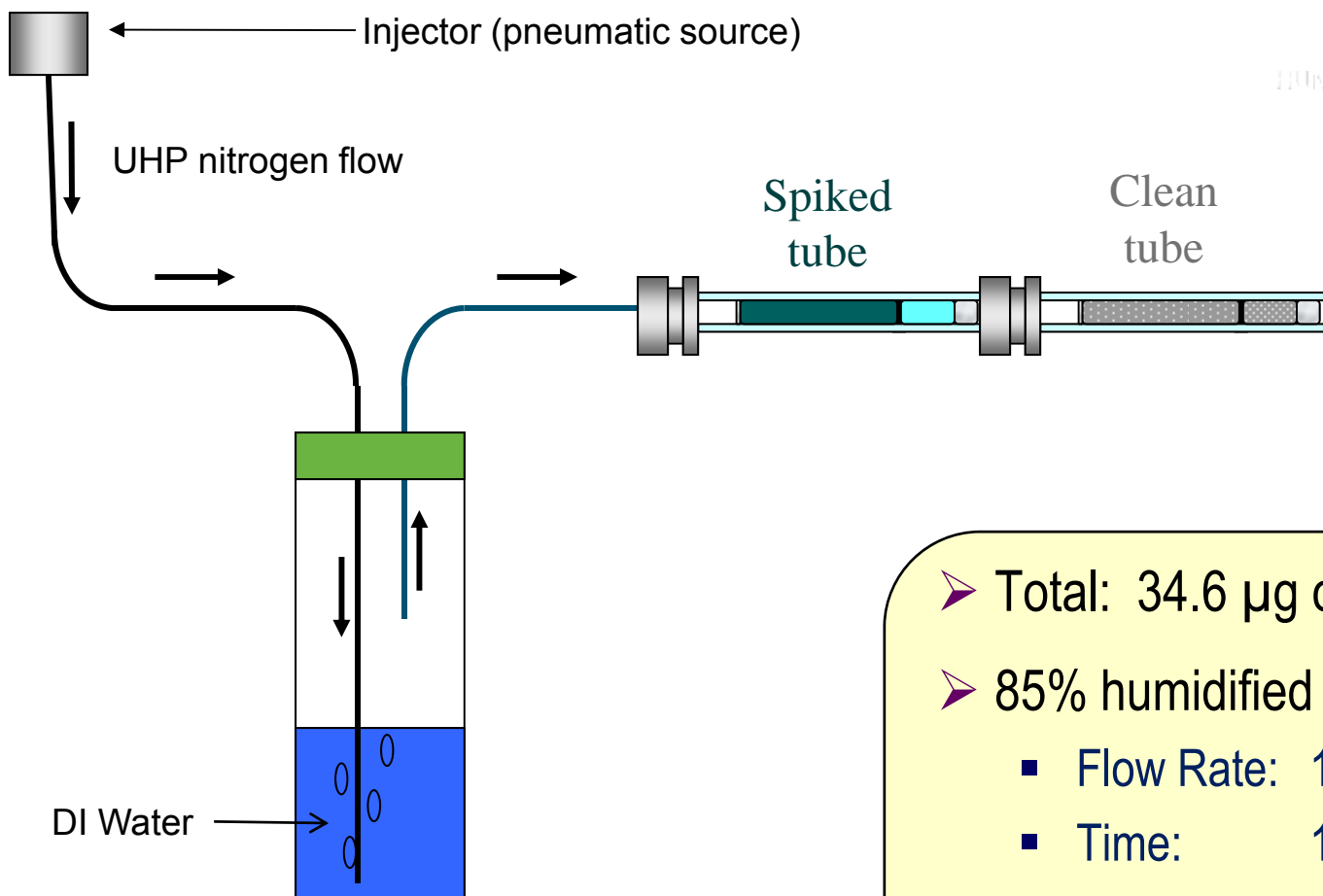
- 300ng: 8260B Mega Mix (76 target analytes)
- 300ng: 502.2 volatile (voa) mix #1 (six gases)
- 250ng: Four polynuclear aromatic hydrocarbons (PAHs)
- 10 μ g of diesel

Concentration on tube for experiments

24.6 μ g standard mixes plus 10ug of diesel: **34.6 μ g Total**

(Standard stocks courtesy of Restek Corp.)

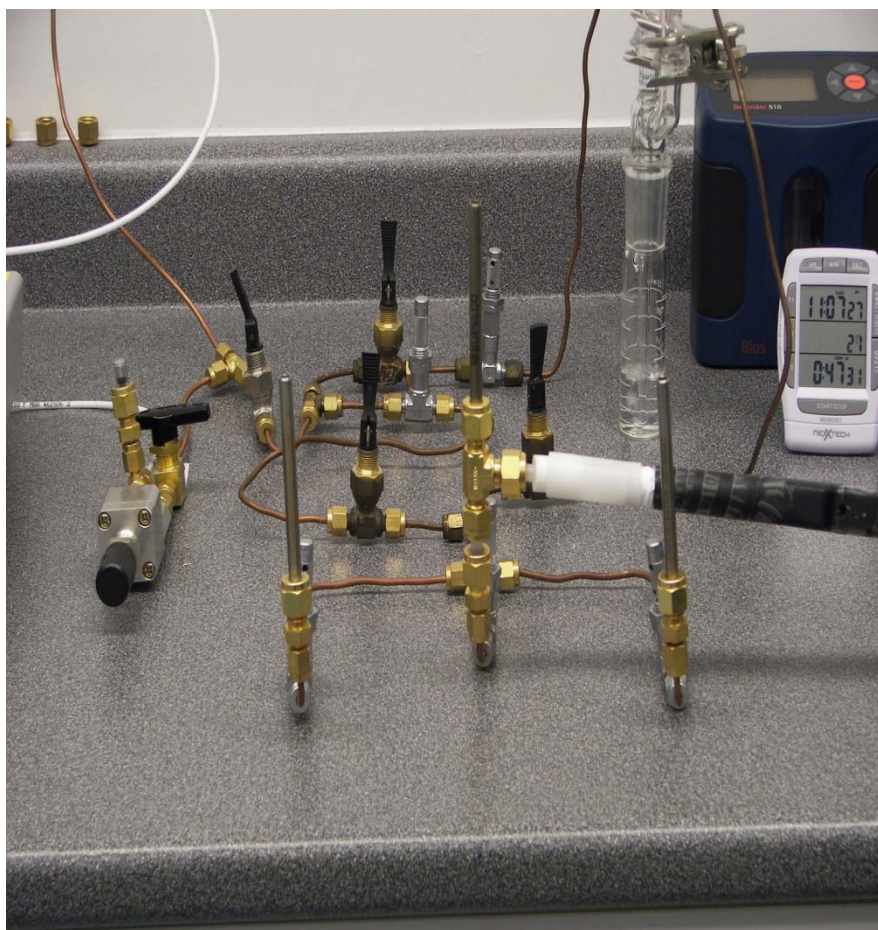
Manifold used for determining breakthrough & moisture retention



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- Total: 34.6 μg on tube
- 85% humidified N_2
 - Flow Rate: 100mL/min
 - Time: 100min
- Total volume 10 liter sampling
- All studies performed in triplicate

Results from rigorous breakthrough experiments



➤ 10L Sample Volume

➤ 85% Humidity

Component	% BT
Dichlorodifluoromethane	1.0
Chloromethane	5.4
Vinyl Chloride	nd
Bromomethane	nd
Chloroethane	nd
Trichlorofluoromethane	nd

Only two components with slight breakthrough

Recovery ... EXCELLENT (freons to phenanthrene)

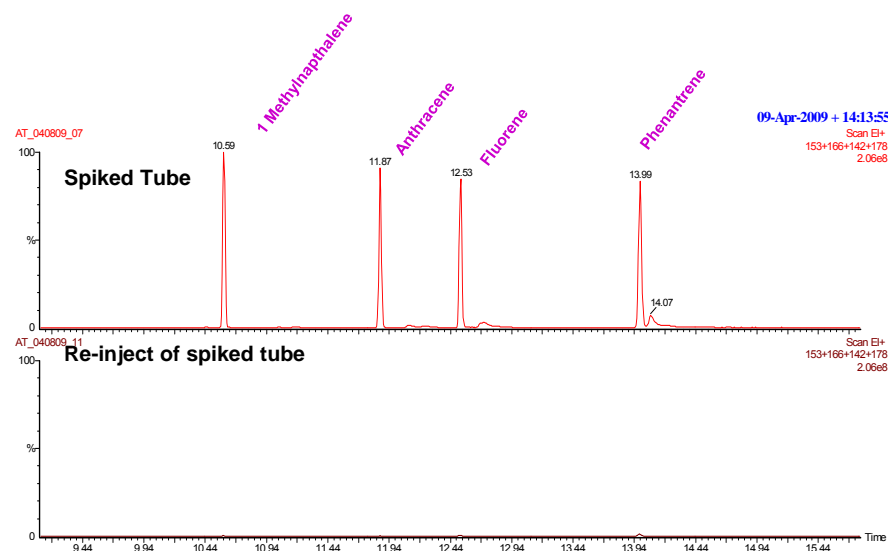
➤ Recovery procedure

- Analyzed spiked tube
- 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



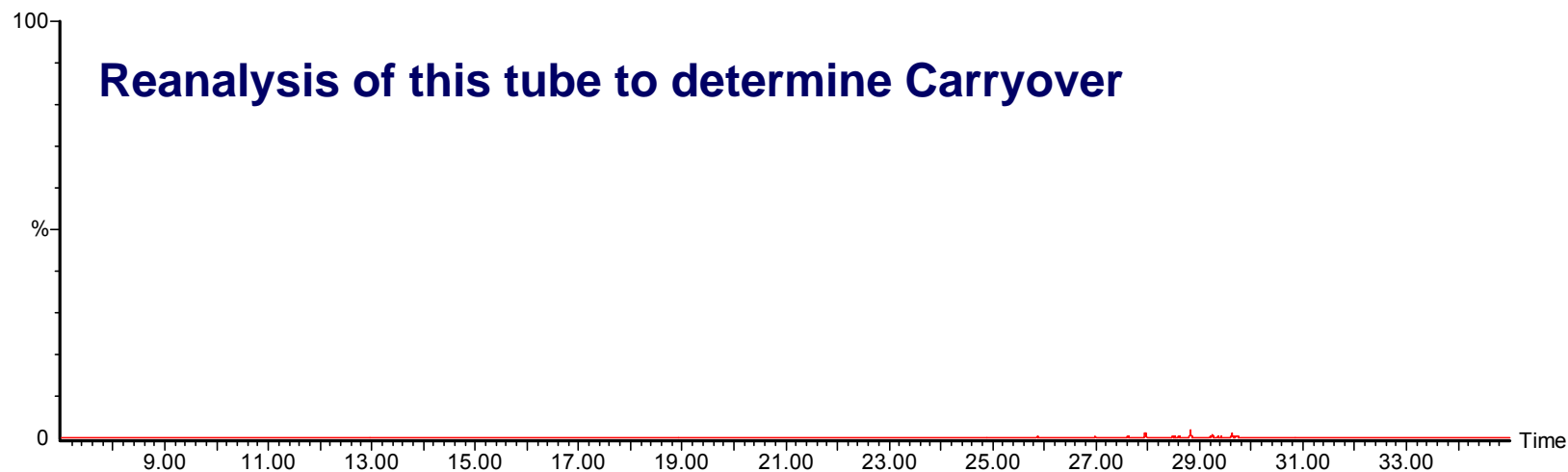
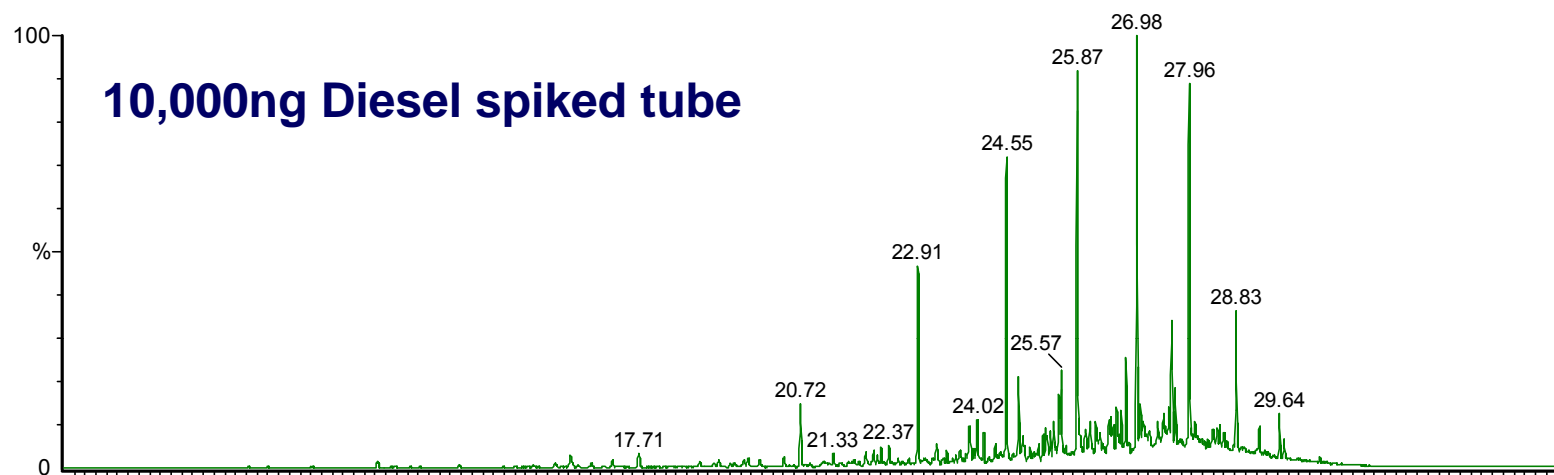
Recovery Results EXCELLENT (Diesel at 10ug)

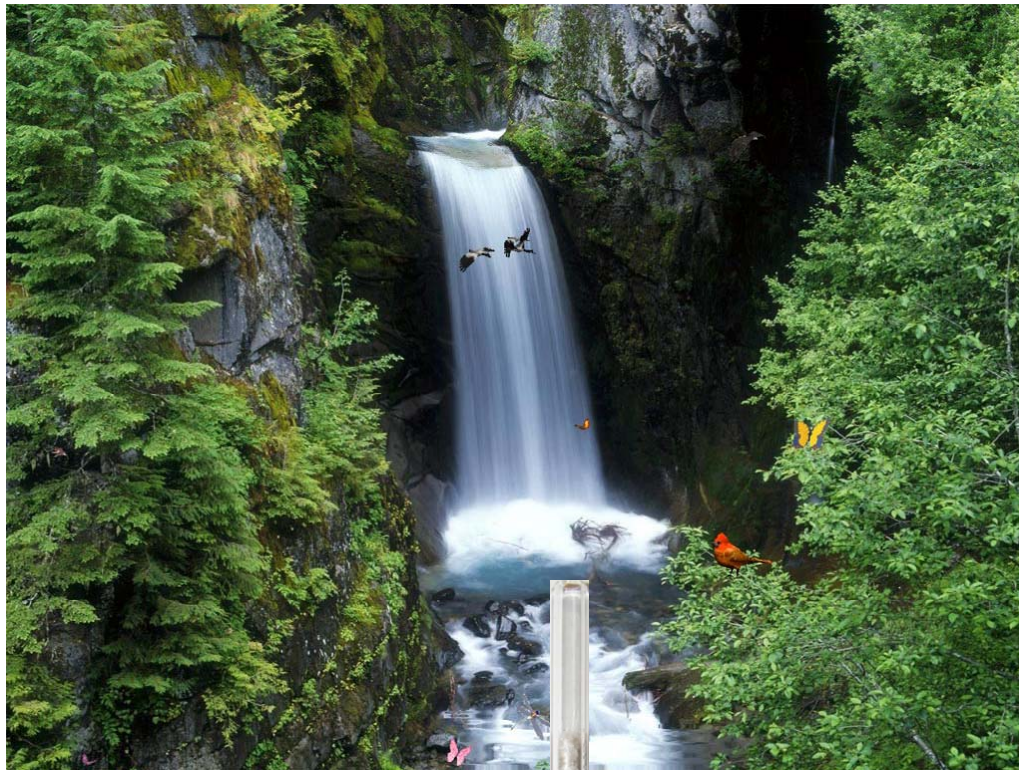


Carryover <1%

Masses 57 + 69

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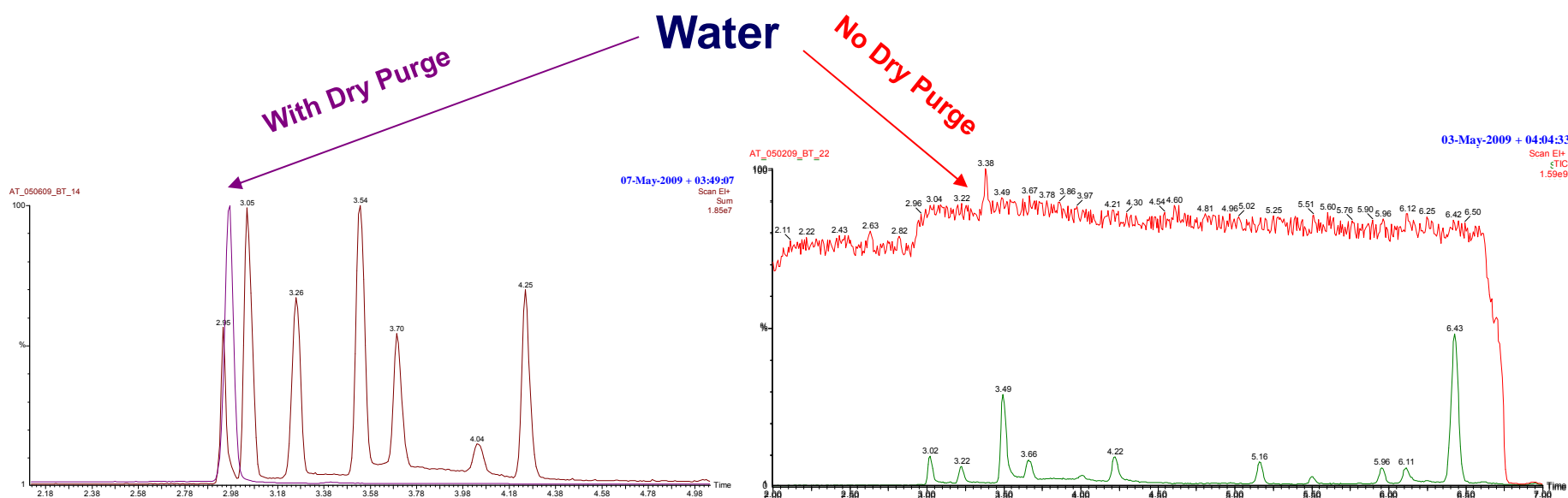


Water Management

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

Why Remove Moisture?

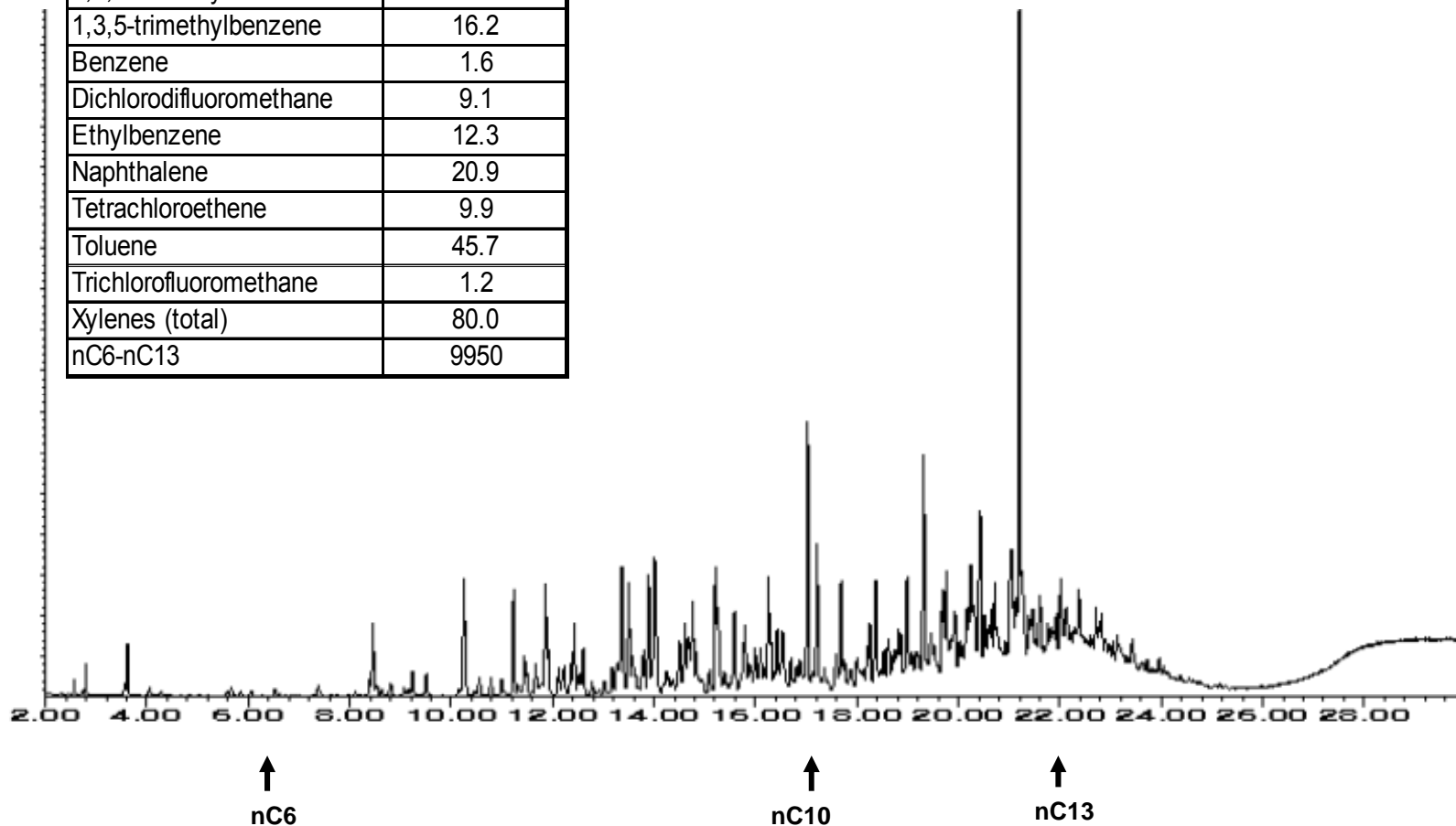
- Mass Spectrometer
 - Signal quenching
 - Increased maintenance
- Chromatography
 - Can effect peak shapes



Real World Sample – Petroleum Contamination (Tank Pull Site)

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Component	Result (ug/m3)
1,2,4-trimethylbenzene	72.7
1,3,5-trimethylbenzene	16.2
Benzene	1.6
Dichlorodifluoromethane	9.1
Ethylbenzene	12.3
Naphthalene	20.9
Tetrachloroethene	9.9
Toluene	45.7
Trichlorofluoromethane	1.2
Xylenes (total)	80.0
nC6-nC13	9950



Acknowledgements



- CARO Analytical Services, Richmond, BC
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 - Patrick Novak, Business Manager

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- Thermal Desorption Technology
 - Tubes well-suited for vapor intrusion investigations
 - Instrumentation Advancements → Analytical Integrity

- Team developed new Thermal Desorption Tube that Achieves
 - Broad Component Range
 - Protection of Strong Adsorbents
 - Excellent recoveries of high boilers
 - Excellent Safe Sampling Volumes
 - Optimal Water Management



... Air Toxic Analyzer

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Thank you

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