Optimizing Sampling and Analytical Parameters for Soil Vapour Samples using Automated Thermal Desorption / Gas Chromatography / Mass Spectrometry (ATD/GC/MS)

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Outline

Objective: Soil Vapour Tube

- **Background**
  - **CARO Analytical Services**
  - **Soil Vapour Regulations**
- **Thermal Desorption Technology**
  - **Advantages**
  - **Operation**
- **Tube Design and Adsorbent Optimization**
  - **Limitations of current tubes for soil vapour samples**
  - **Objectives of new tube**
- **New Tube Performance Characteristics**

Background information on CARO Analytical Services

- **British Columbia based**
  - **Full Service Environmental Testing Capabilities**

- **Technical Leadership in Soil Vapour**
  - **Co-authored BC SV Reference Methods**
  - **ISO 17025 Accreditation for SV (www.cala.ca)**

- **Client Collaboration**
  - **Knowledgeable & Accessible Staff**
  - **Equipment Rentals, Client Training**

- **SR&D Projects**
  - **VOC Artifacts in Tubing (www.caro.ca/soilvapour)**
  - **Custom TD Tube Development**
  - **VOC Sorption on Tubing – in progress**

Regulatory Background

- **23 US States regulate Soil Vapour Intrusion**

- **British Columbia Contaminated Sites Regulations, Schedule 11**
  - **Effective January 1, 2009**
  - **118 regulated parameters: >90% via TD**
  - **Stringent regulations**
    - **Trichloroethene (TCE) – 1.0 ug/m^3 (dry cleaning site)**
    - **Benzene – 1.5 ug/m^3 (gasoline site)**

- **Why is soil vapour important?**
  - **Protection of Human Health**

- **Test water and soil first? Or … Test vapour first?**

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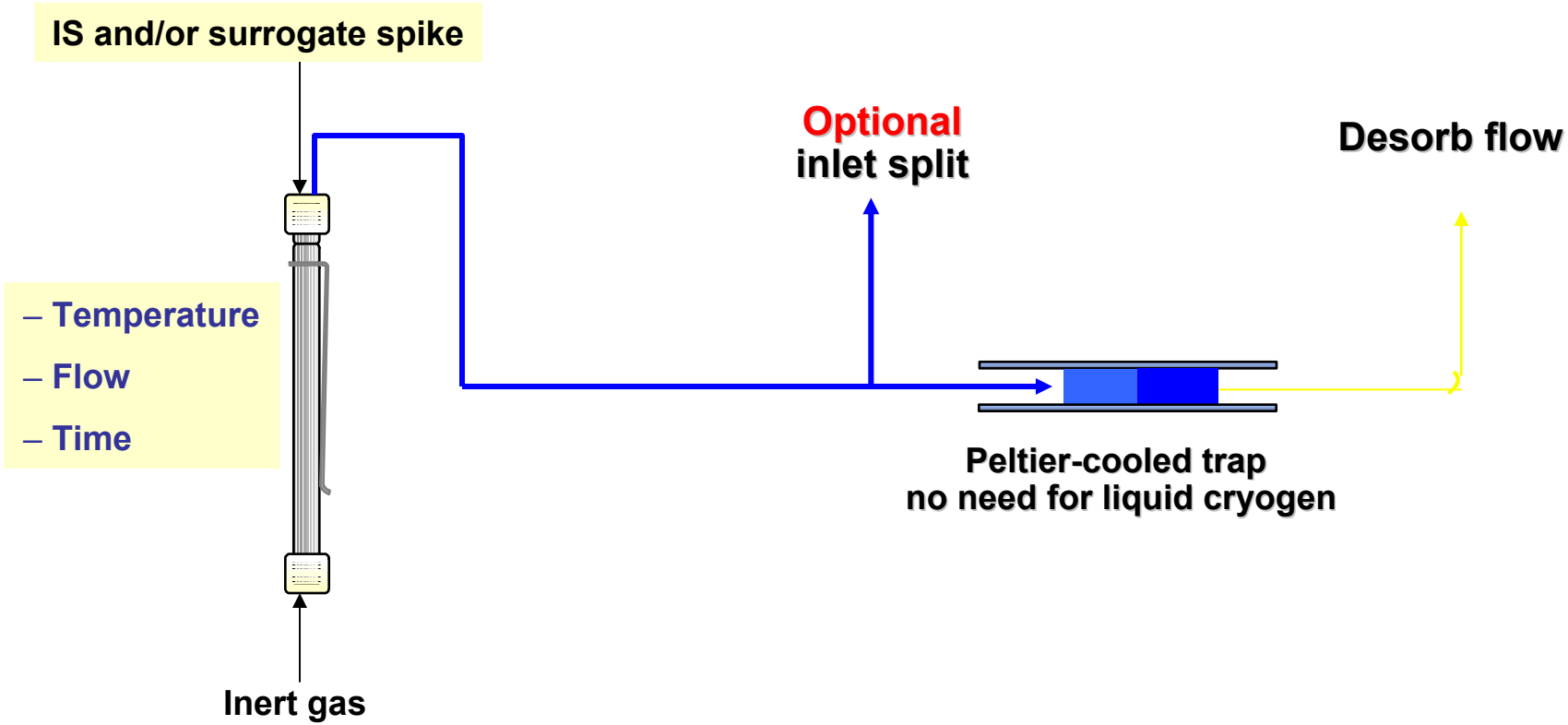
Advantages and Operation of Thermal Desorption Technology

Advantages of Thermal Desorption Technology

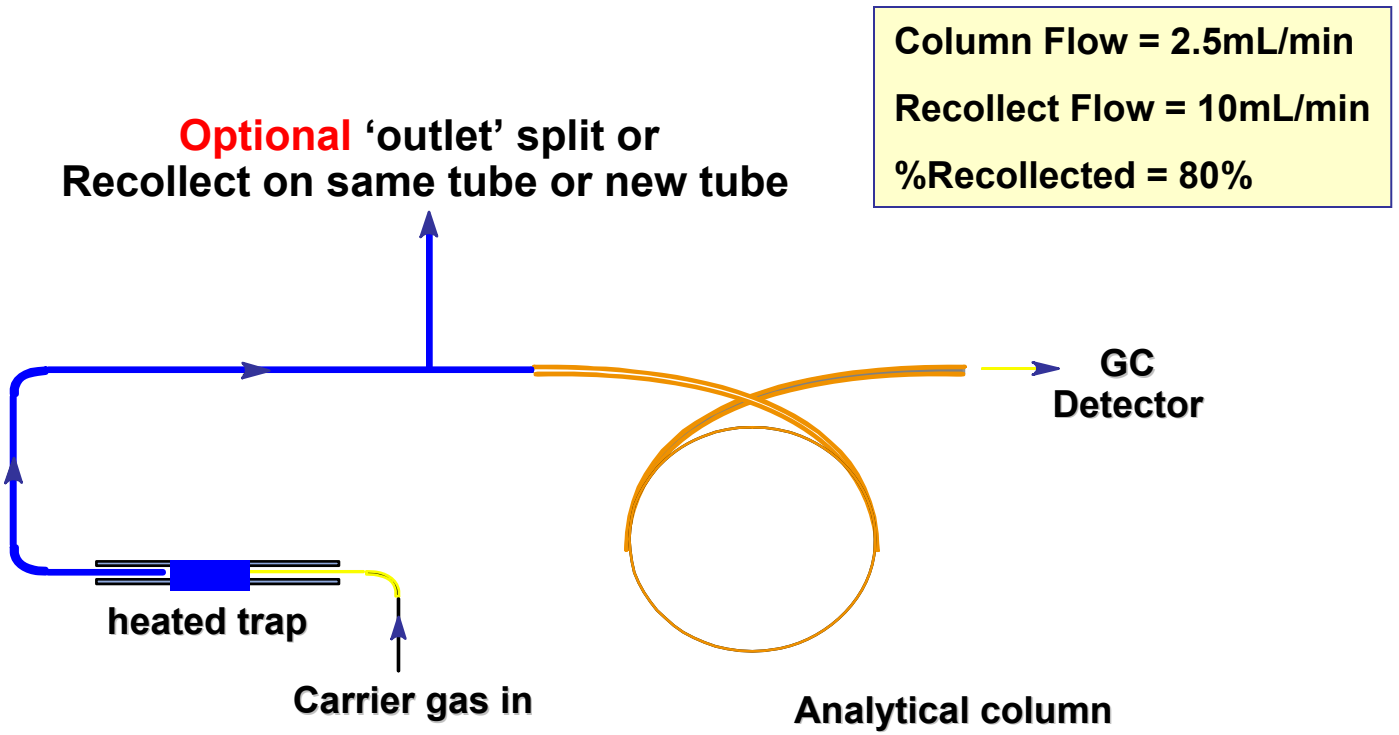
Air Toxics ≠ Charcoal Tubes

1. **Established methodology**
2. **Convenient transport**
3. **Easy to clean … immediate reuse … fast turnaround**
4. **Cost effective**
5. **Large sample volumes**
6. **Suitable for non-polar and polar compounds**
7. **Inherent Water Management**
8. **Enables Recollection to preserve sample**

State 1: Sample Tube Desorption



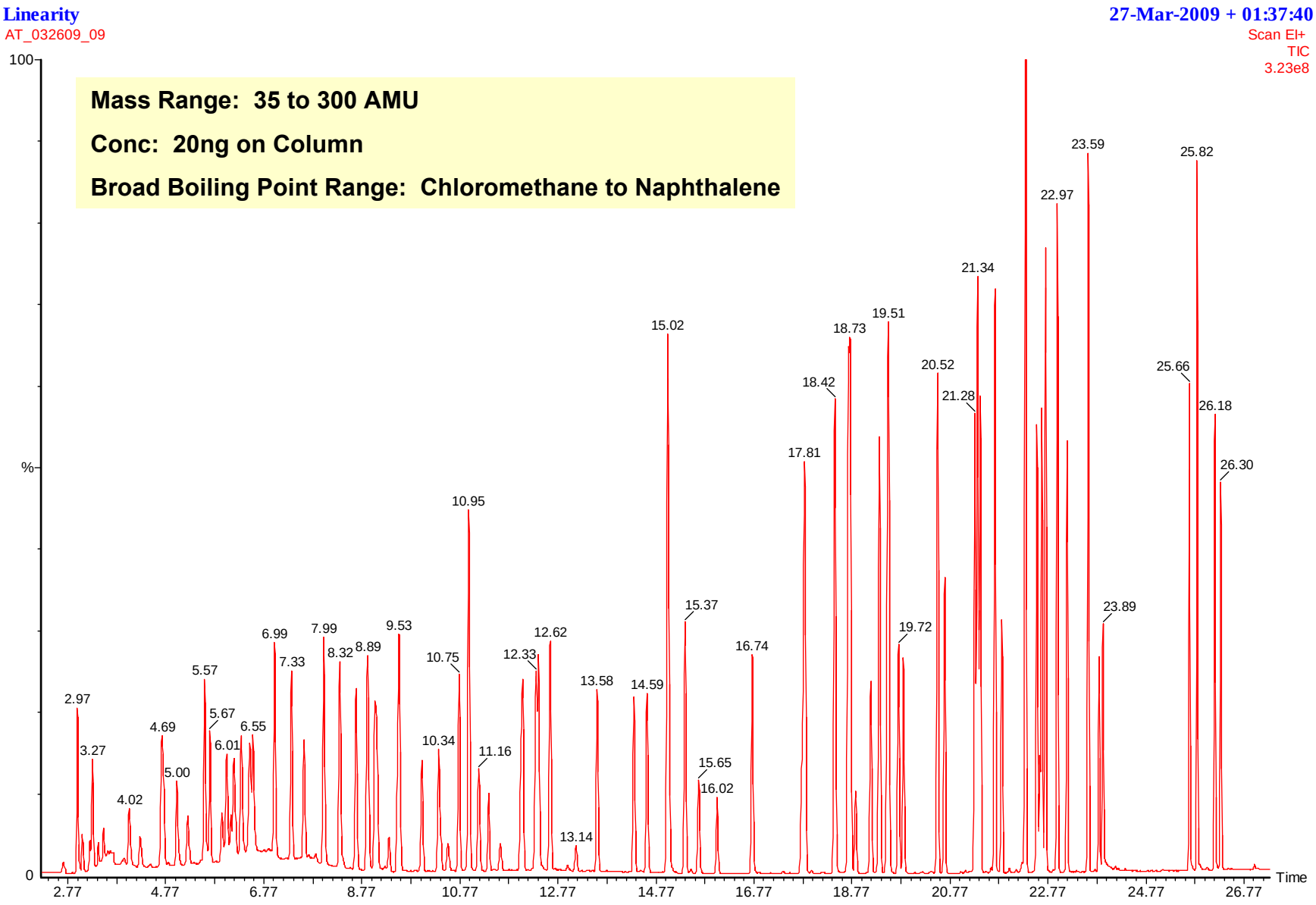
Stage 2: Transfer of Sample to Instrument



Optimizing Sample Integrity with Thermal Desorption

- **Automatic Internal Standard addition**
- **Recollection onto the same tube or new tube**
- **Automated Leak Checking**
- **Impedance Testing**
- **Excellent Water Management**

Total Ion Chromatogram of a 74 TO-15 and TO-17 Component Mix



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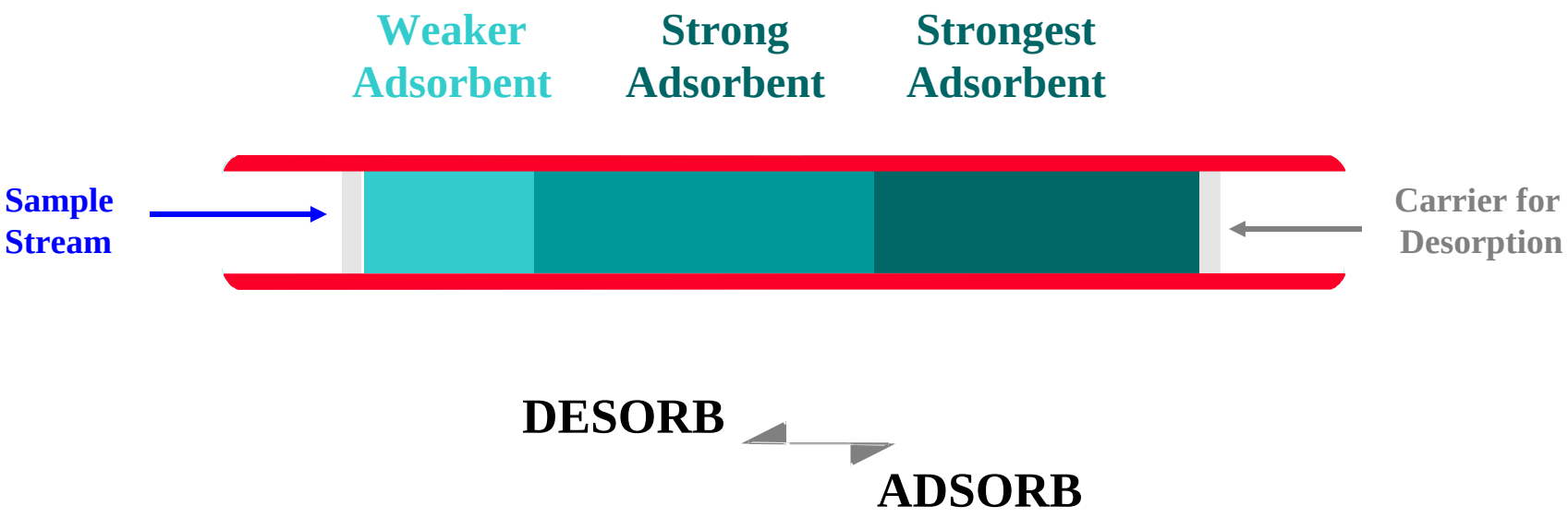
Tube Design and Adsorbent Optimization

Thermal Desorption Tube

Multiple Adsorbents

- accommodate wide boiling point range sample



Goal – Optimize a Tube for Soil Vapour Intrusion Sampling

- **Soil vapour differs from other air sampling applications:**
  - **Higher moisture**
  - **Greater analyte range**
  - **Wider concentration range**

- **Limitations of current industry-standard sorbent tubes:**
  - **Lack of a weak adsorbent prevents release beyond nC12**
  - **Ensure Safe sampling volumes for the low boilers**

Characteristics of New Thermal Desorption Tube

- **Broadest Analytical Range**
  - **dichlorodifluoromethane to phenanthrene**
  - **nC3 – nC22+**
- **Protects the Strong Adsorbents**
  - **Prevents irreversible adsorption**
  - **Clean after one desorption cycle**
- **Good Safe Sampling Volumes**
- **Optimal Water Management**

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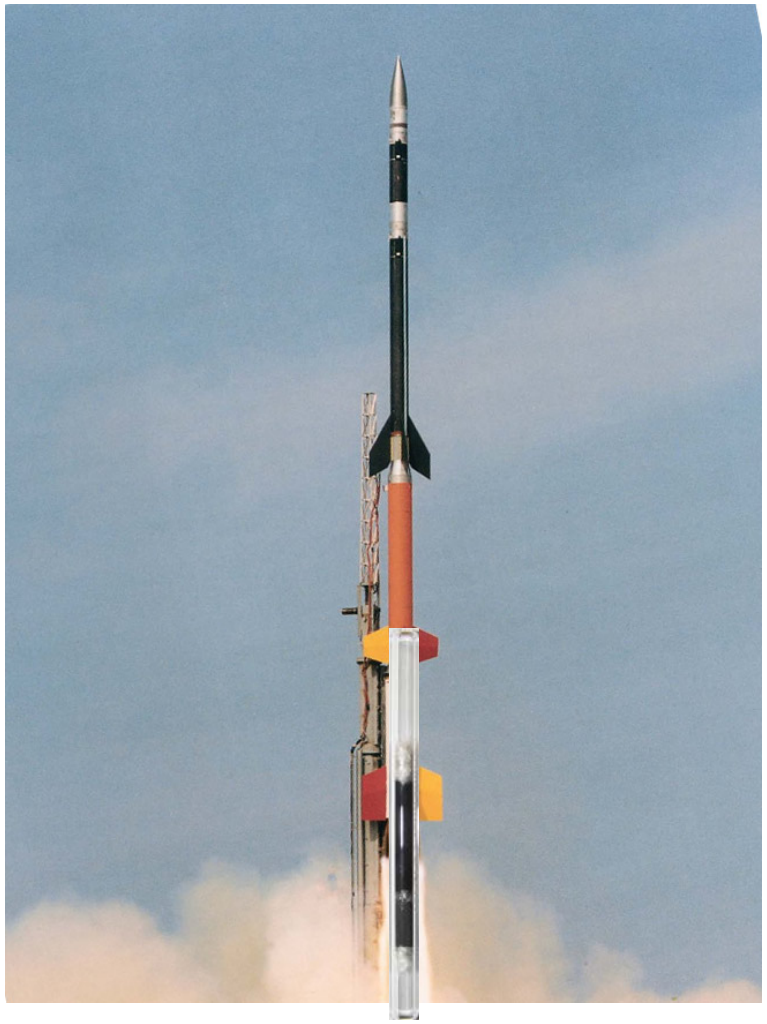


Soil Vapour Intrusion Tubes
Performance Characteristics

Precision, Linearity (average for Class) and Reporting Limits

Instrumentation:

PerkinElmer TurboMatrix 650 Thermal Desorber

PerkinElmer Clarus 600 GC/MS

Compound Class	**# Comp**	**Precision (%RSD)**	**Dynamic Range**	**Reporting Limit**	Outliers
		n=8	0.2 to 200 ng	10 liter sample (FS)	on RL
Gasses	6	6.9%	0.9952	0.05 ug/m3	
non-Aromatic Halogens	33	2.7%	0.9985	0.02 ug/m3	$CHCl_3$=0.05ppb
Aromatics	15	1.4%	0.9995	0.02 ug/m3	
Halogenated Aromatics	9	1.4%	0.9997	0.02 ug/m3	
Others	10	2.7%	0.9965	0.05 ug/m3	

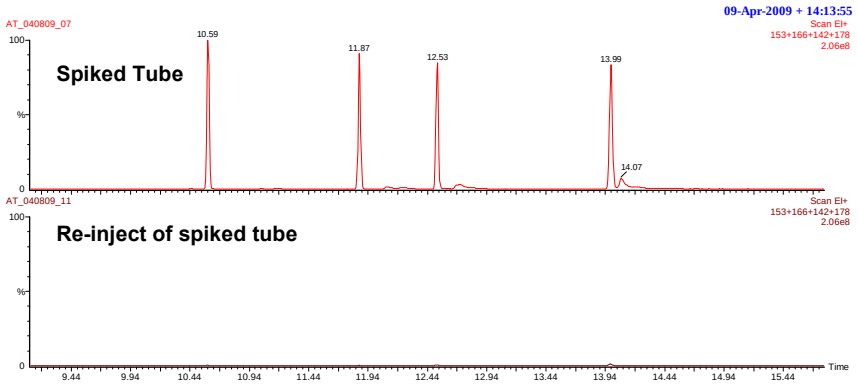
Recovery Results EXCELLENT

- **79 components investigated**
  - **400ng VOC mix + 250ng PAH**
  - **Range: difluorodichloromethane to phenanthrene**

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

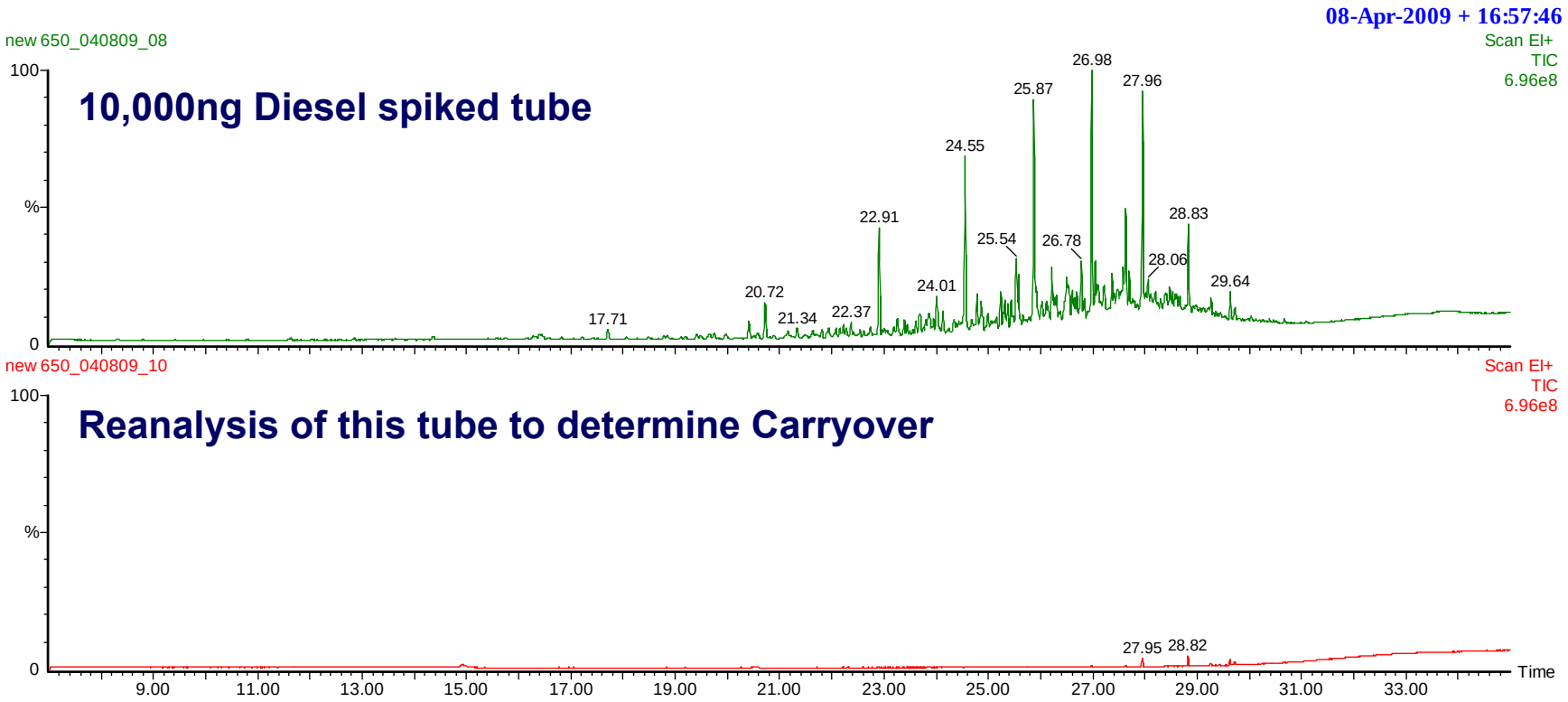
- **Non-detectable carryover**
  - **Slight carryover of 4 heaviest PAHs**
  - **Significantly below method criterion**

PAH Compounds	% Carryover
	(very low)
1-Methyl Napthalene	0.3
Anthracene	0.2
Fluorene	0.6
Phenanthrene	1.2



Tube Robustness – Diesel

Carryover <1%



What is Breakthrough?

- **Goal: Regulated compounds do not break through**

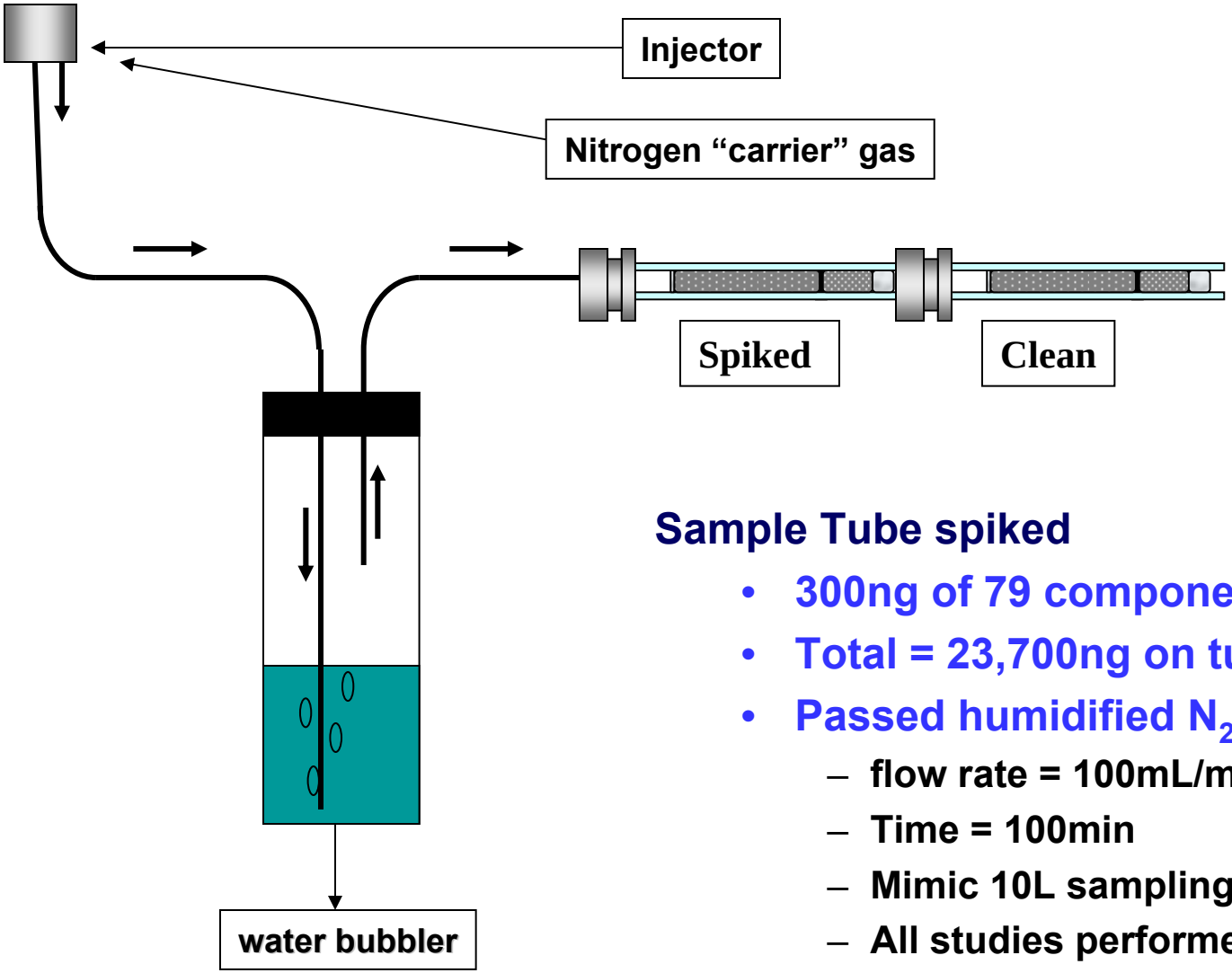
- **EPA TO-17: "**The volume sampled when the amount of analyte collected in a back-up sorbent tube reaches a certain percentage (typically 5%) of the total amount collected by both sorbent tubes"

- **Calculation: BT / (BT+spiked)*100%**
  - **BT = concentration of back tube**
  - **Spiked = concentration of front tube**

- **Safe Sampling Volume (SSV): 2/3 of Breakthrough Volume**

- **Assessing breakthrough in the real-world:**
  - **Sampling in series**
  - **Sampling in parallel (distributed volume pairs)**

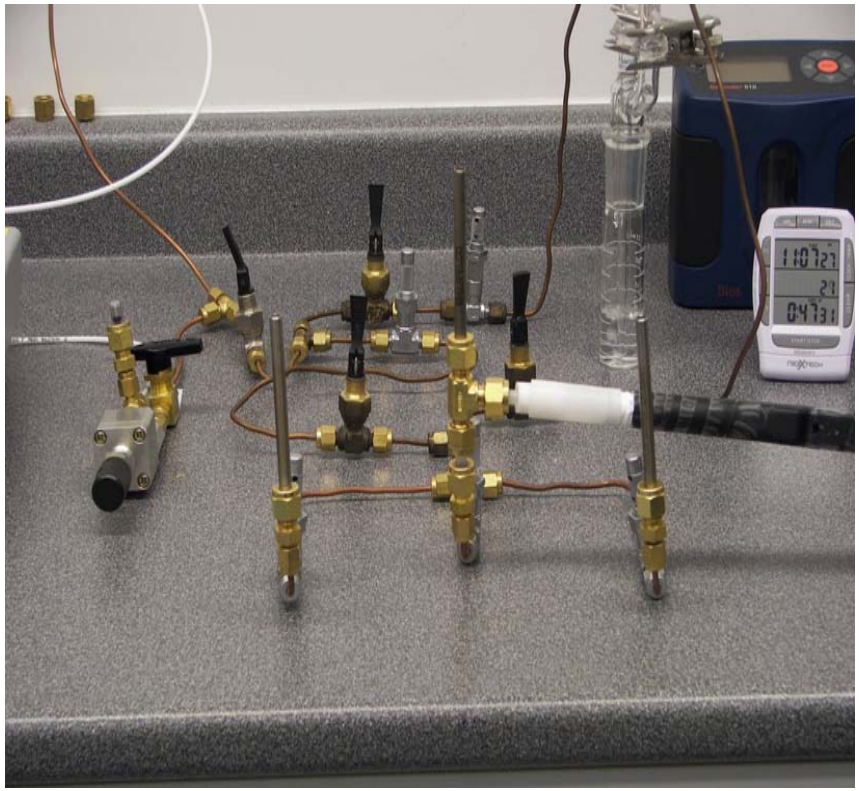
Manifold used for determining breakthrough & moisture retention



Sample Tube spiked

- 300ng of 79 components
- Total = 23,700ng on tube
- Passed humidified N_2 through tube
  - flow rate = 100mL/min
  - Time = 100min
  - Mimic 10L sampling
  - All studies performed in triplicate

Slight Breakthrough of only two Components out of 79 VOCs



VOC gasses:

- **10L of sample**
- **70% humidity**

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

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Water Management

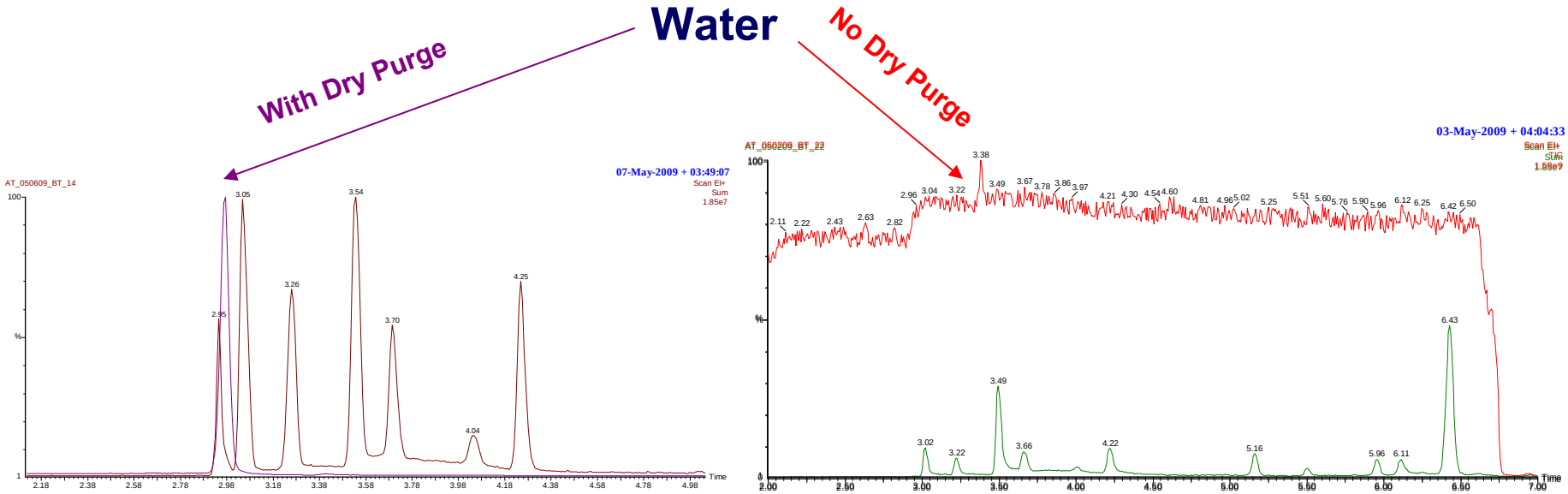
Methods of Water Removal

1. **Nafion Drier / Desiccants**
   - **Polar Compounds Removed - Cannot be used**
2. **Hydrophobic adsorbents**
3. **Minimize sampling volumes while maintaining regulated detection limits**
4. **Dry Purging**
   - **Typically not required for indoor air**

Why Remove Moisture?

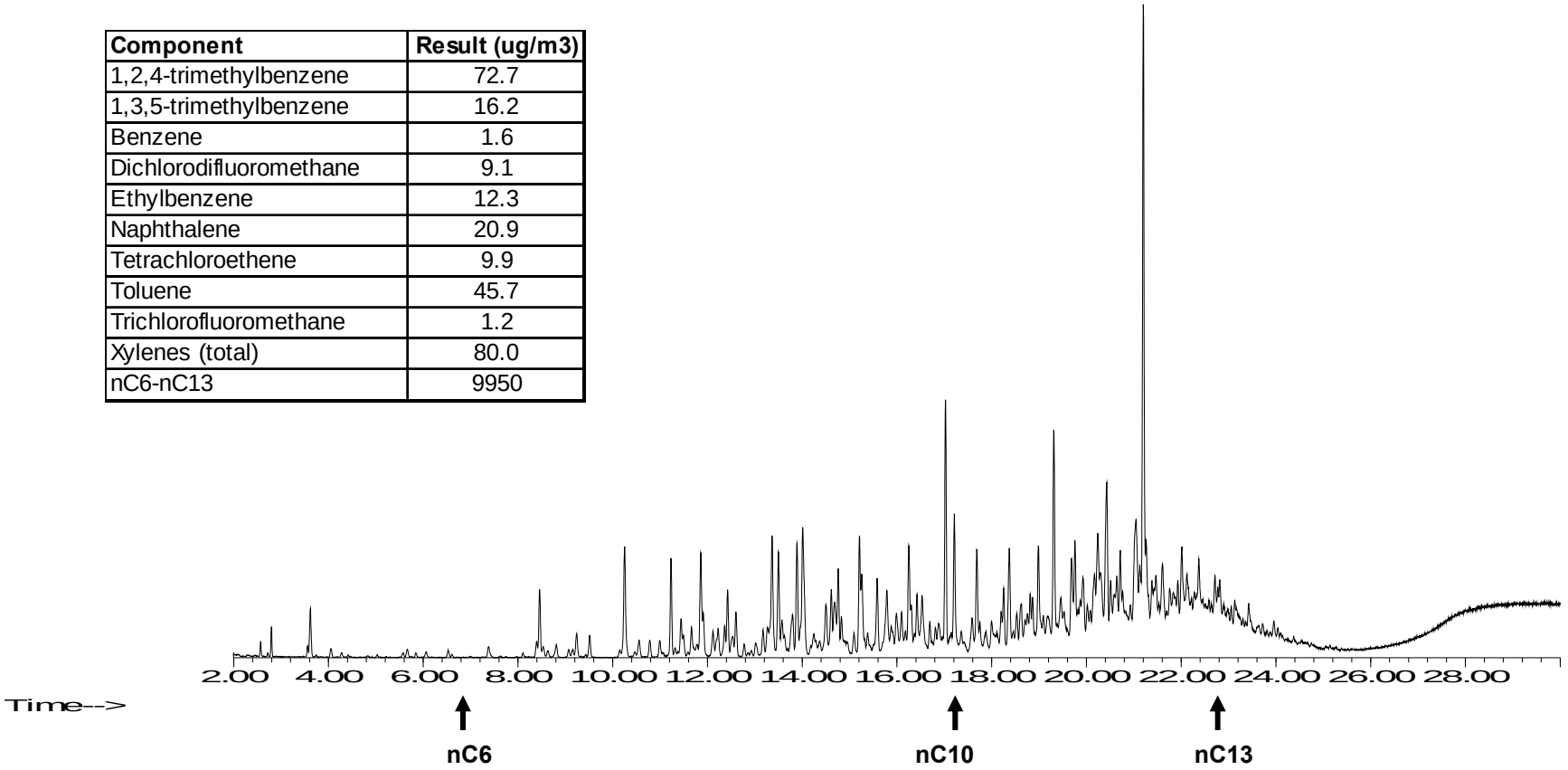
- **Mass Spectrometer (detector) problems**
  - **Signal quenching**
  - **Increased maintenance**

- **Poor chromatography**
  - **Can cause false negatives**



Real World Sample – Petroleum Contamination (Tank Pull Site)

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



Summary

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

- **Team developed new Thermal Desorption Tube that Achieves**
  1. **Broadest Analytical Range**
  2. **Protection of the Strong Adsorbents**
  3. **Good Safe Sampling Volumes**
  4. **Optimal Water Management**

- **Presentation available for download at www.caro.ca or www.perkinelmer.com**

Acknowledgements

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- **PerkinElmer:**
  - **Lee Marotta, Senior Product Specialist**
  - **Miles Snow, Senior Product Specialist**