Soil Vapor and Air analysis : Extend the Hydrocarbon Range with Novel ATD tube Design

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History – Experience with Thermal Desorbers

- 1980 introduced first Automated Thermal Desorber
- 1990 introduced Automated Thermal Desorber 400
  - Portable
  - Ease of use
  - Remote control software
- 2000 introduced TurboMatrix (TMX) 50 and TMX 1
  - TMX-1 dedicated system for online sampling
  - TMX-50 automated tube sampler
  - Touch Screen GUI for ease of use
  - Minimizing plumbing
  - Ease of maintenance
- 2005 introduced family of five TurboMatrix Thermal Desorbers
  - Many improvements and features for air monitoring

Air Sampling Applications

- Environmental (Air Toxics)
  - Soil Gas (soil vapor intrusion)
  - Indoor (VDA 278, ISO 16000……)
  - Outdoor air (Ait Toxic EPA Method TO-15 (VOA) and TO-13 (SVOA), Ozone precursor……)
  - Fence line monitoring
  - Stack monitoring
  - Manufactured Gas Plants (MGP) sites

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
- Automates leak check of tube and trap prior to each analysis
- Excellent water management

…ease of use, accurate, precise

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Advantages of Tubes

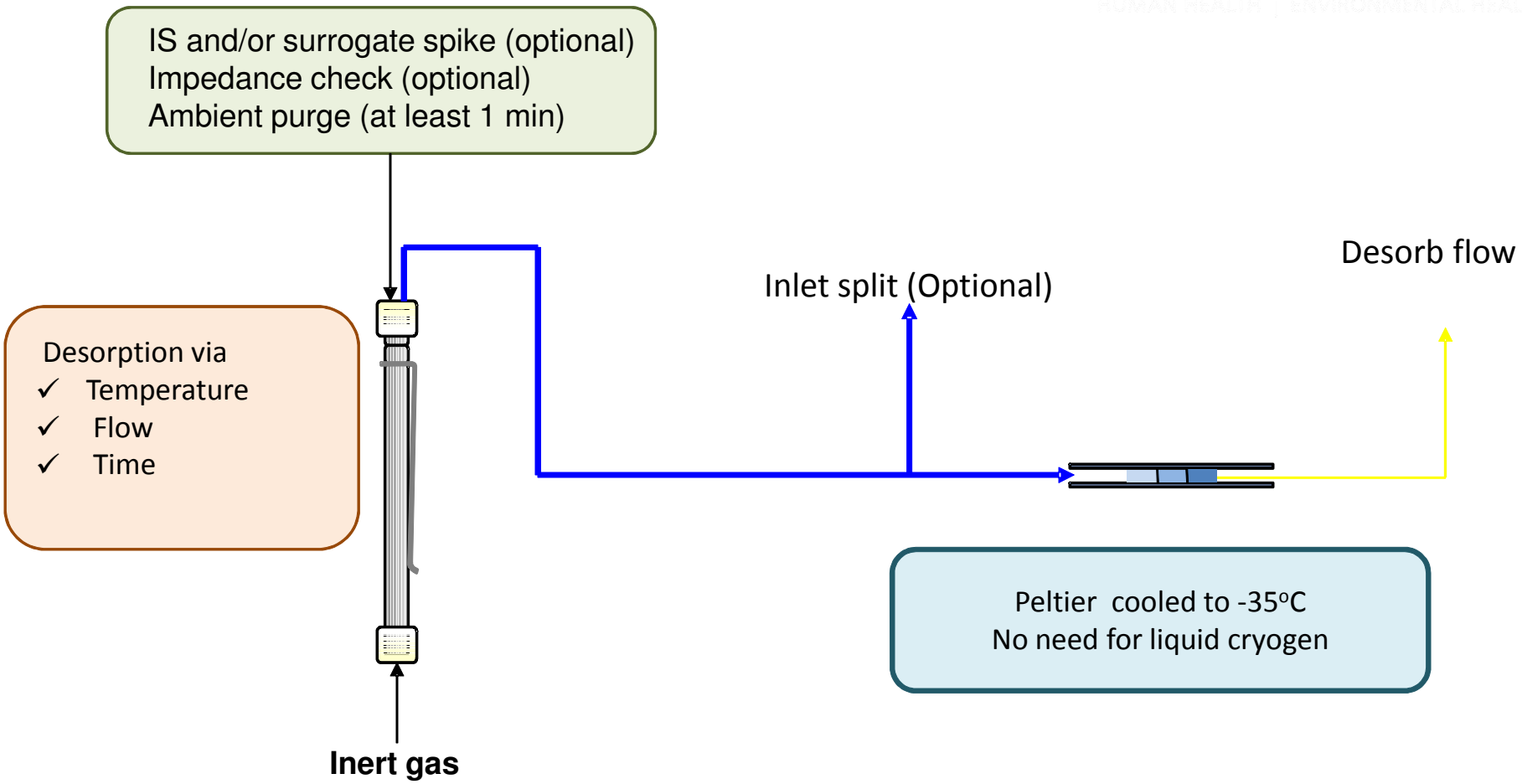
Operation of ATD

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

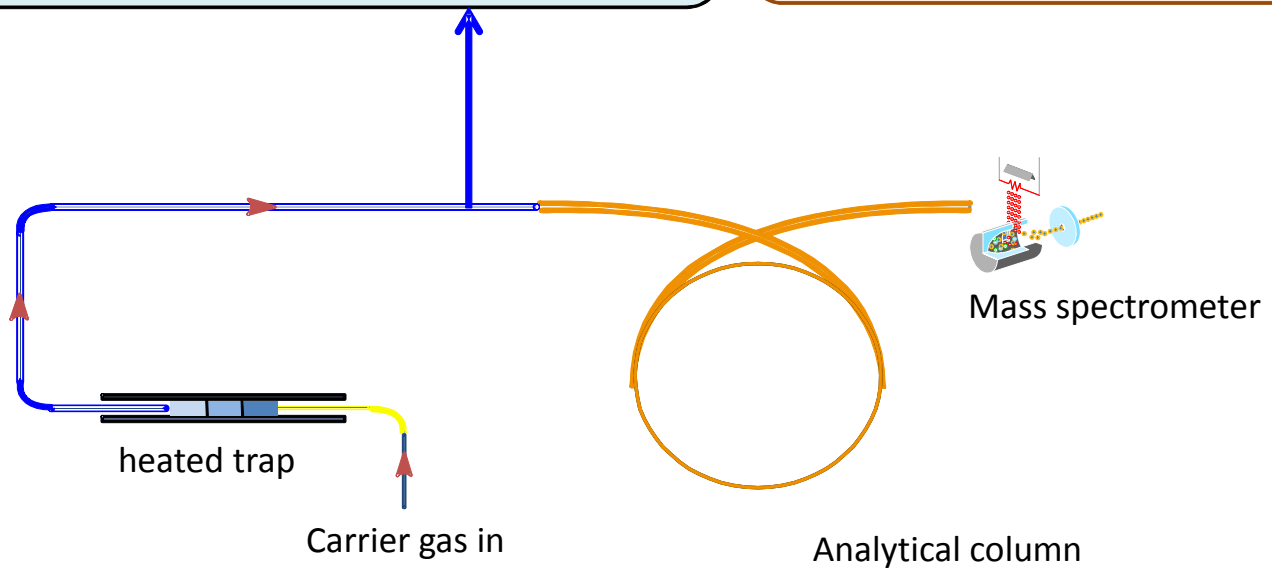
State 1: Sample Tube Desorption



Stage 2: Transfer of Sample to Instrument

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

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



Thermal Desorption Tube

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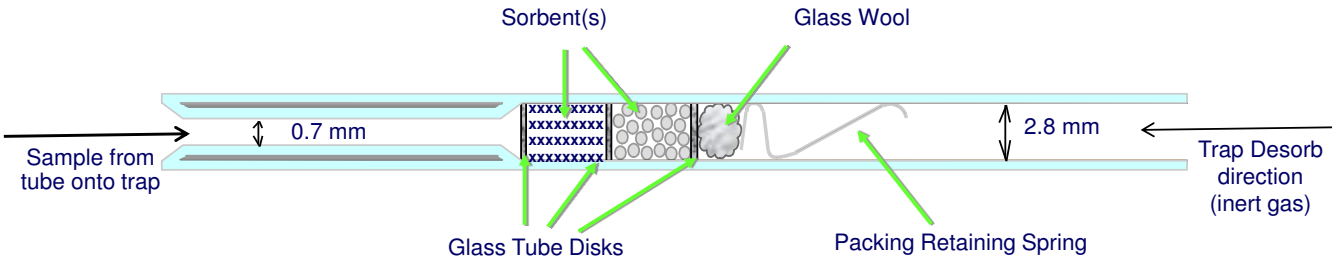
Multiple Adsorbents: *accommodate wide boiling point analyte range*

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

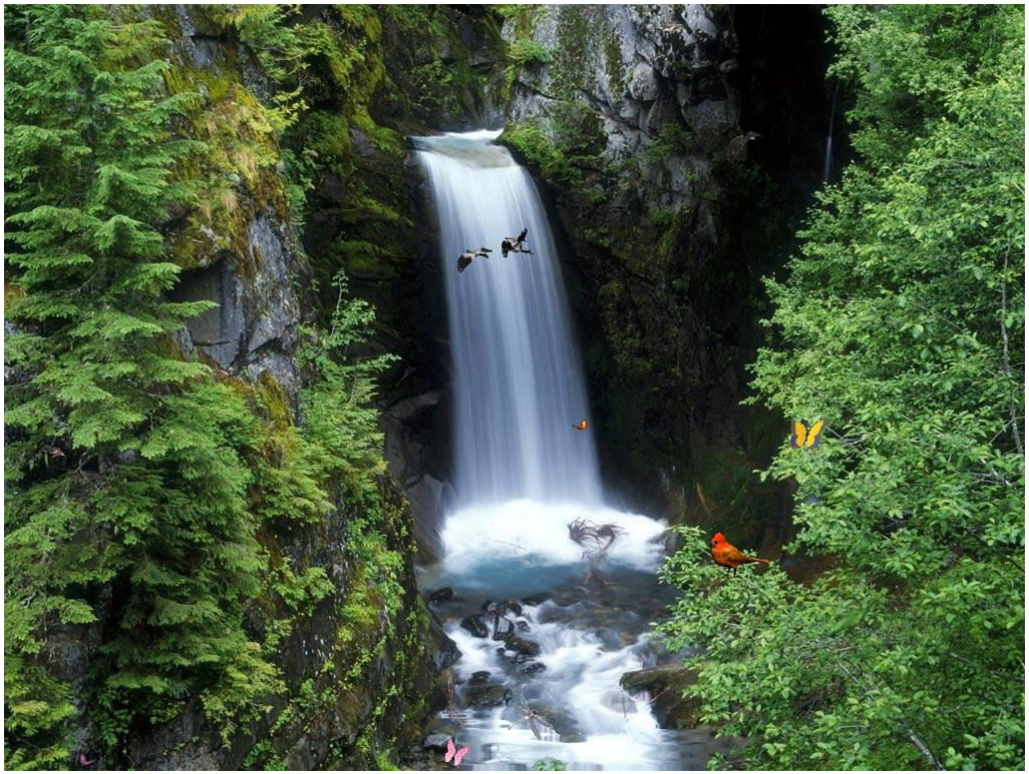
← Desorb the tube in the direction of strong adsorbent to weak adsorbent

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



Water Management

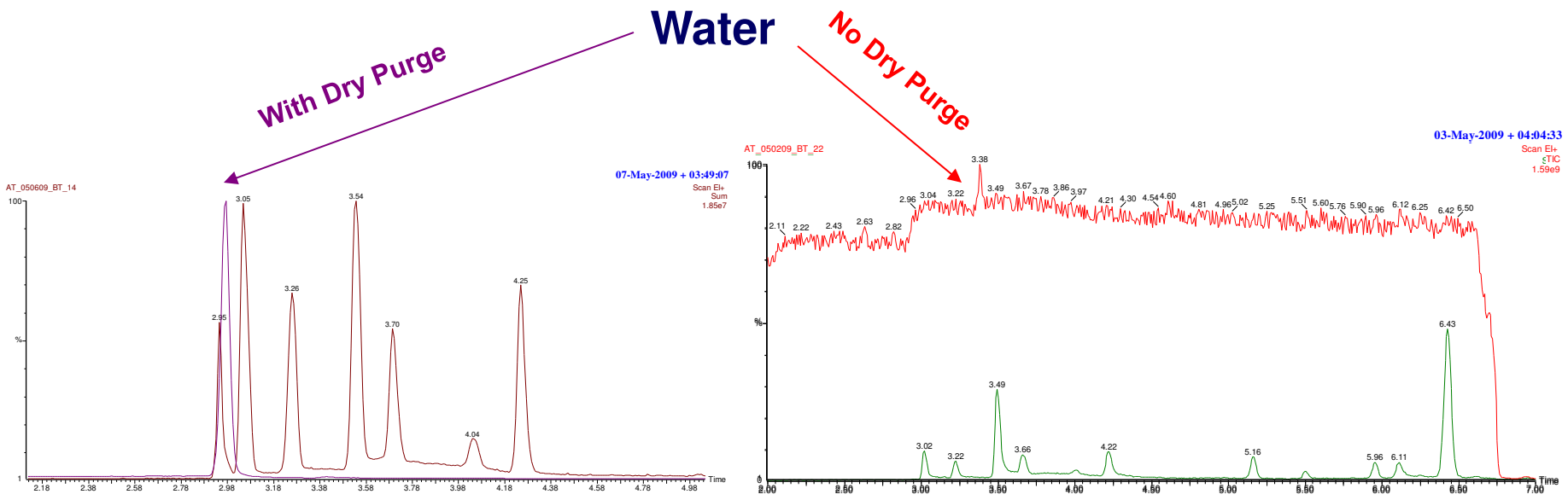


Methods of Water Removal

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

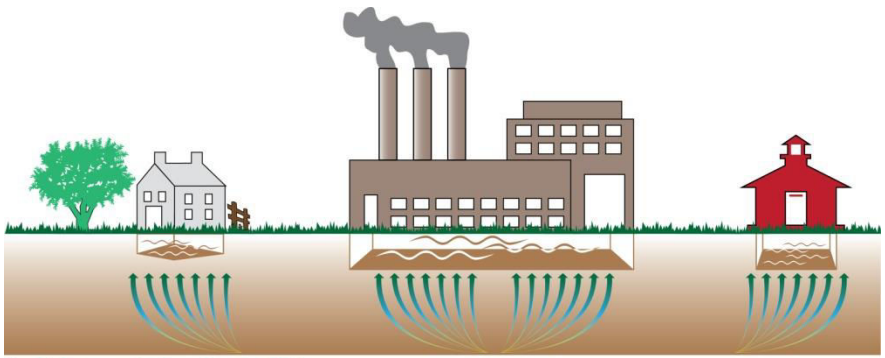
Why Remove Moisture?

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



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

Optimize a Tube for the Most Challenging Vapor - Soil Gas

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- Soil vapor differs from other air sampling applications

  - Higher moisture
  - Greater analyte range
  - Wider concentration range

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

Total Ion Chromatogram

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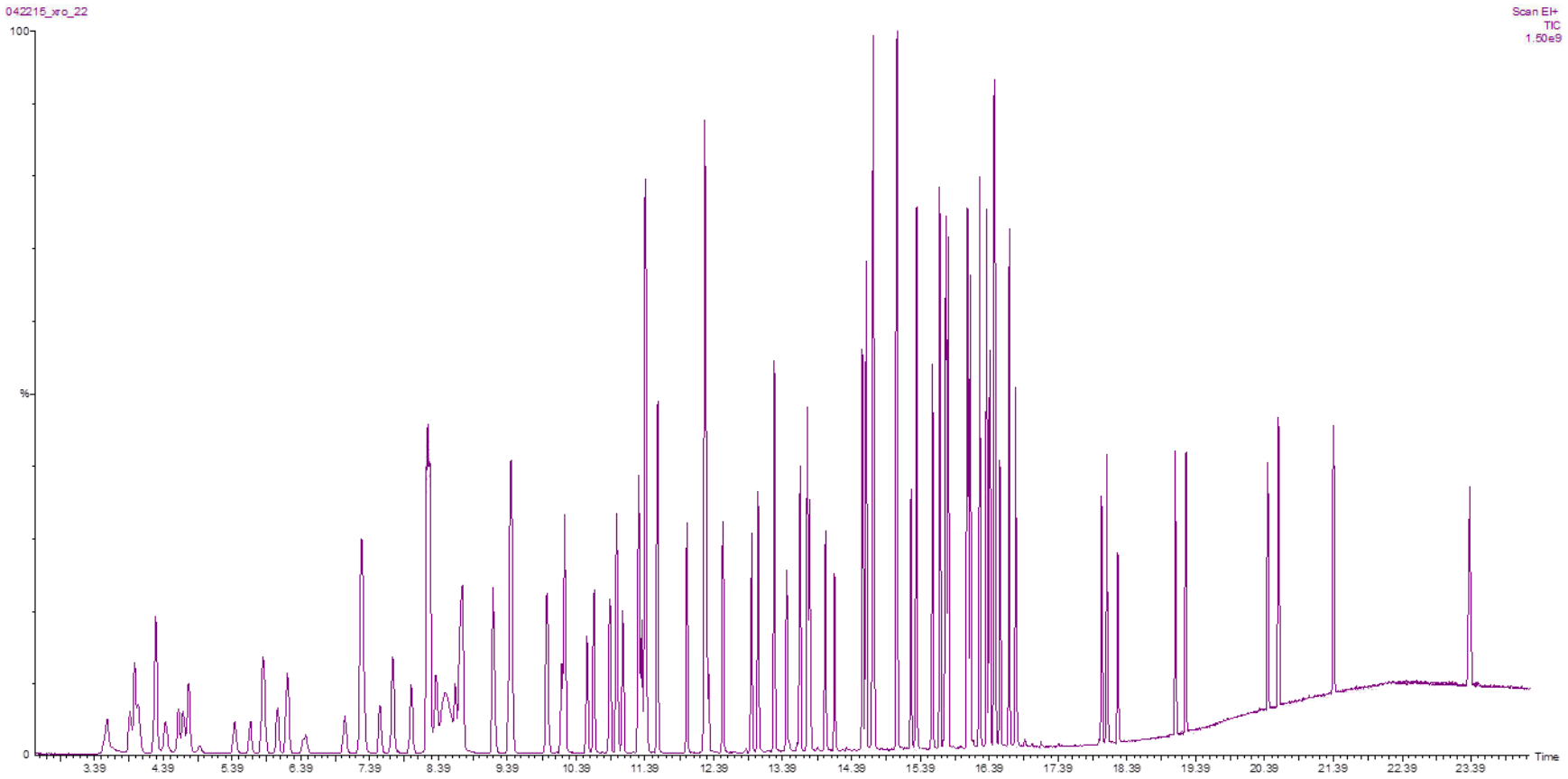
Mass Range: 35 to 300 AMU

Conc: 4ng on Column

Broad Boiling Point Range: Chloromethane to Naphthalene



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

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1 Liter sample volume

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

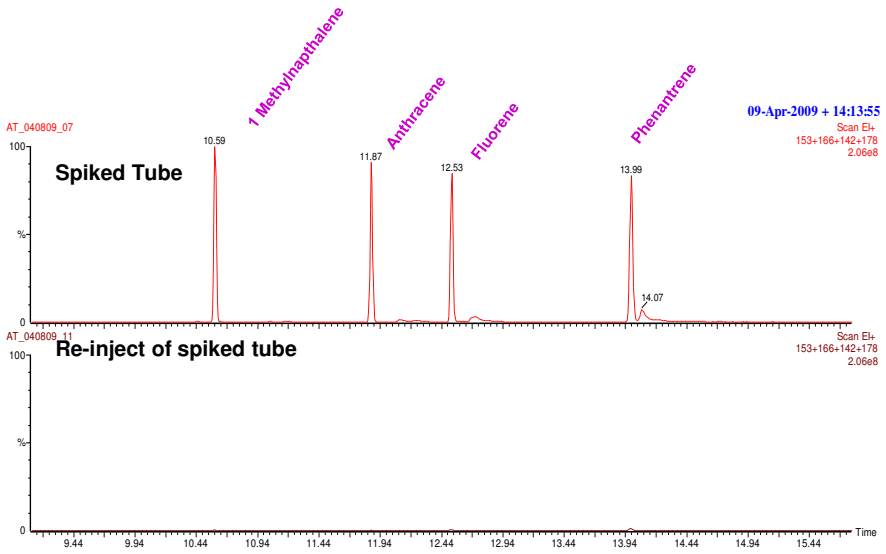
… better than method criteria

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)

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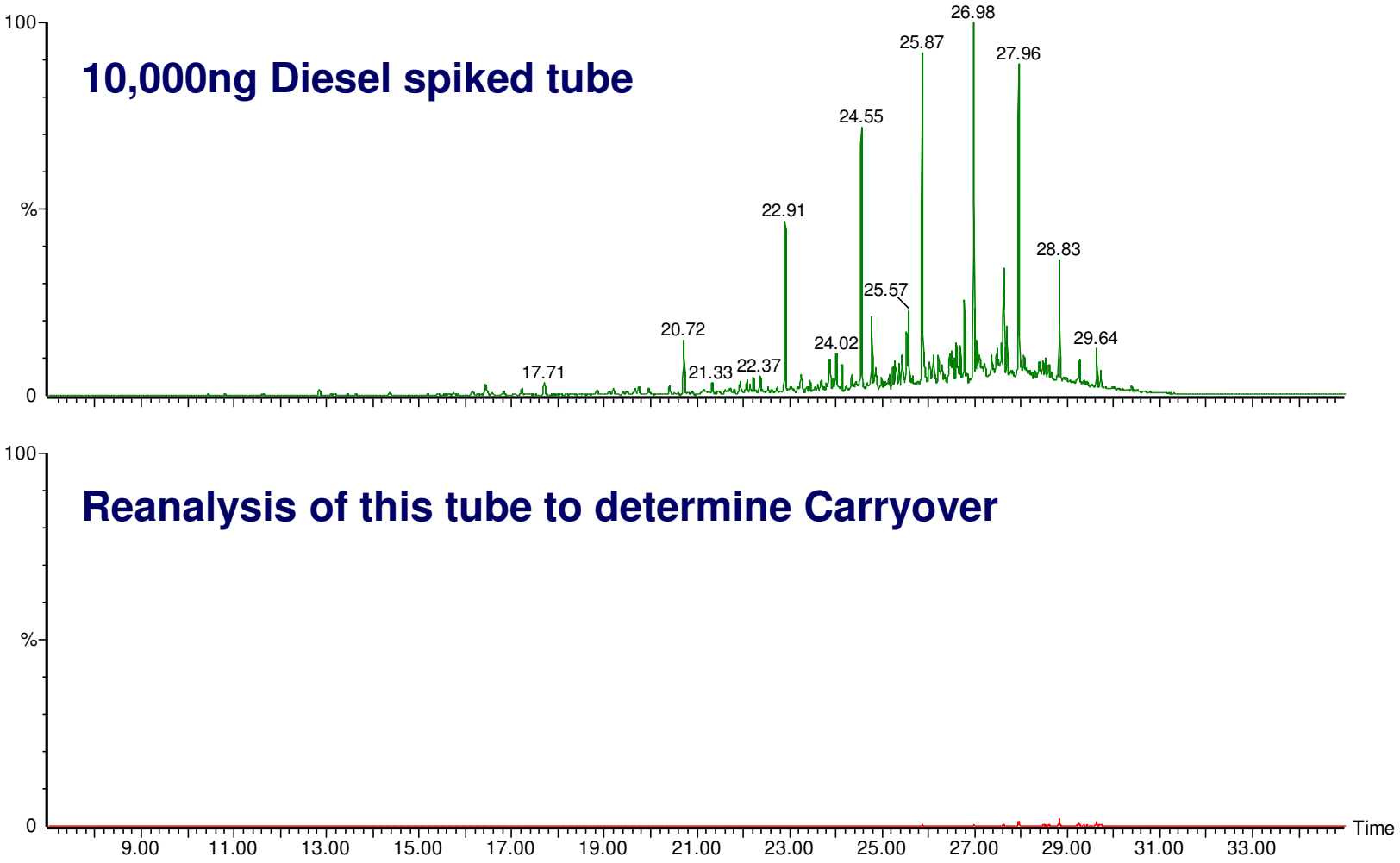
Carryover <1%

Masses 57 + 69



EPA Method TO-17: To Include 1- regulated PAH

Single Tube Sampling: Analysis of Volatile and Semi-Volatile Organics in Air.

The Cost Effective

Green Solution

New Sorbent Tubes designed by PerkinElmer

- 2010: Soil Vapor Intrusion (SVI) Tube (patented)
  - (C_3 to C_{26})
  - Combines VOC & SVOC from the seven VOA gases to pyrene
- 2011: XRO-644 (patent pending)
  - (C_6 to C_{44})
  - Residue in Liquefied Petroleum Gas (LPG)
  - Combines VOC & SVOC from BTEX to benzo(g,h,i)perylene
- 2013: XRO–444 (patent pending)
  - (C_4 to C_{44})
  - Combines VOC & SVOC from 1,3-butadiene to benzo(g,h,i)perylene

TO-15 (VOA) and TO-13 (SVOA)

PM10 (particulates)

TO-15 (VOCs)

TO-13 (PAHs)

Goal: one analysis instead of two

- **Eliminate liquid extractions using TO-17**
  - **Save time and $$$**
  - **Improve productivity and efficiency**
  - **Enhance recoveries**
  - **A Greener analysis**

TO - 13

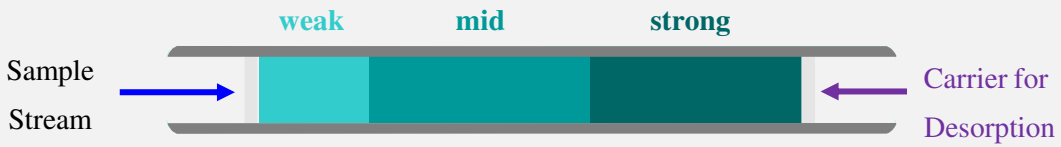
TO - 15

TO - 17

Research required *NEW* TD Tube Design

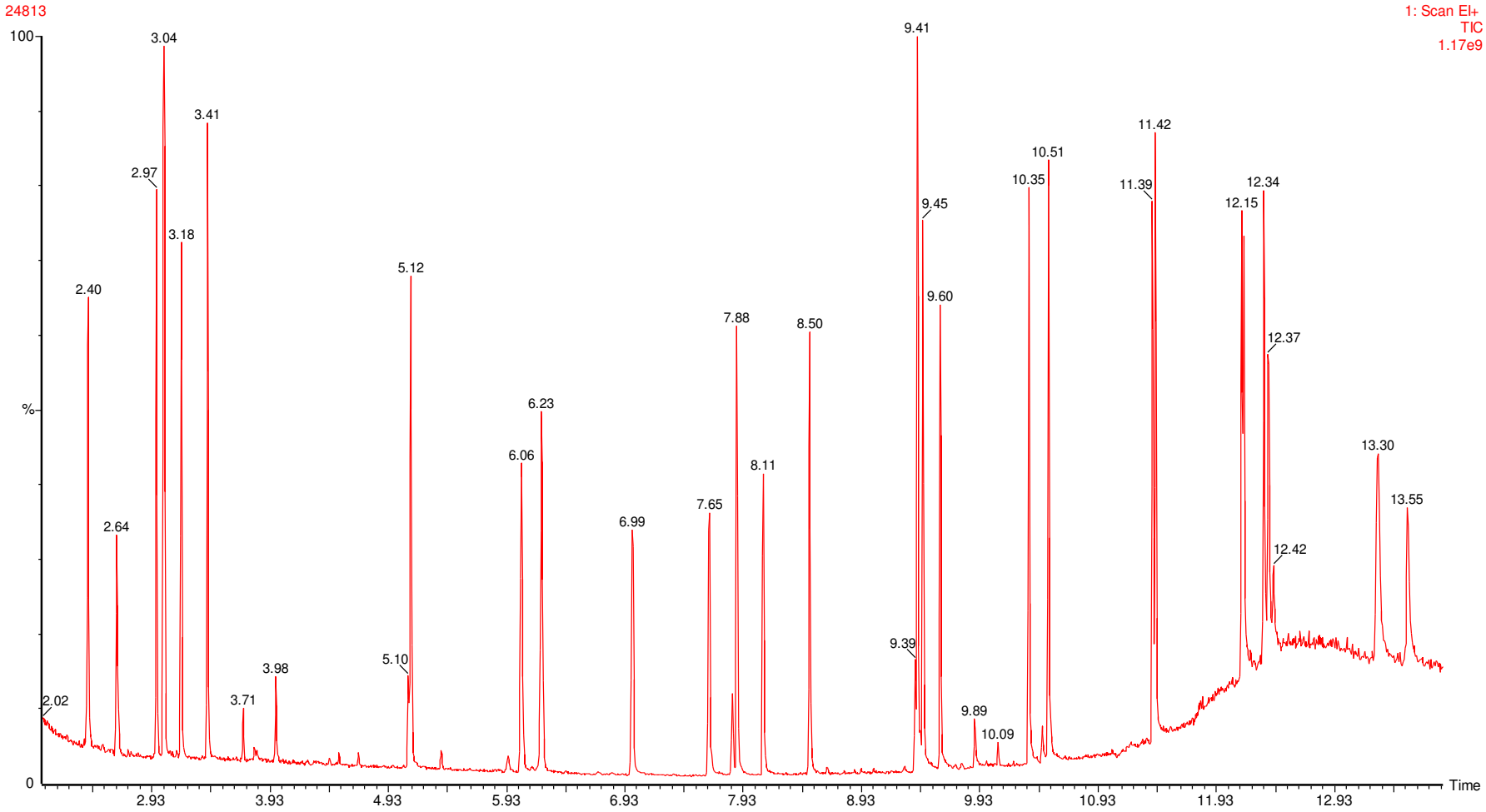
Volatiles	Semi-volatiles
1,3-Butadiene	Napthalene
Benzene	2-Methylnapthalene
Toluene	1-Methylnapthalene
Ethyl Benzene	Acenaphthylene
Xylenes	Acenaphthene
	Fluorene
	Phenathrene
	Acenapthene
	Fluoranthene
	Pyrene
	Benzo(a)anthracene
	Chrysene
	Benzo(b)fluoranthene
	Benzo(k)fluoranthene
	Benzo(e)pyrene
	Benzo(a)pyrene
	Indeno(1,2,3-c,d)pyrene
	Dibenz(a,h)anthracene
	Benzo(g,h,i)perylene

Example Tube



… Started with these targets for MGP sites

Total Ion Chromatogram (TIC)



Calibration, Precision and Reporting Limit

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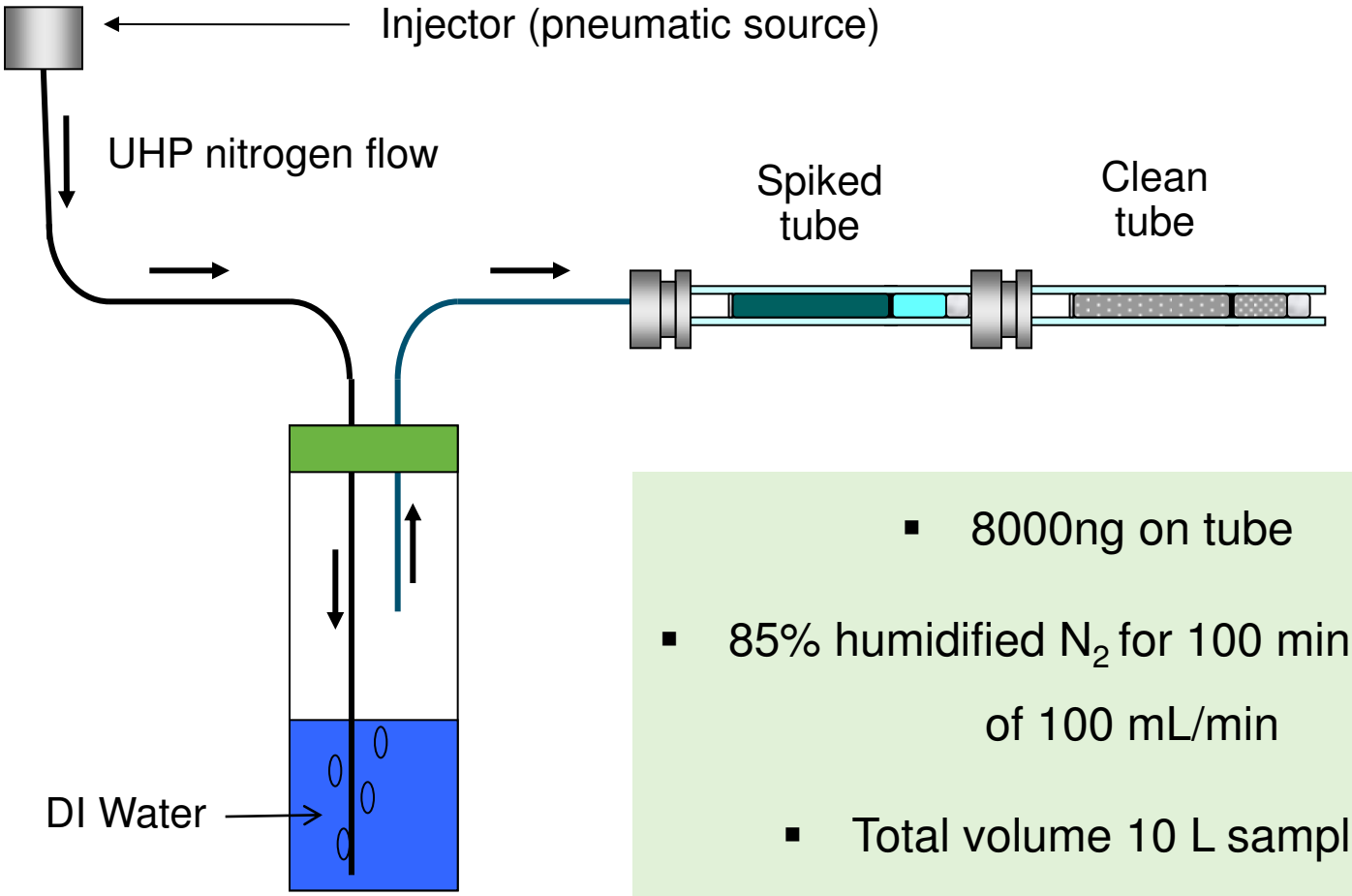
Target Compound	Range 0.2 to 50ng	Reporting Limit (ug/m^3) 45L sample volume	Precision (%RSD) n=6
1,3-Butadiene	0.9961	0.0111*	1.89
Benzene	0.9971	0.0044	0.90
Toluene	0.9991	0.0044	0.94
Ethyl Benzene	0.9989	0.0044	0.77
m & p - Xylenes	15.54%	0.0044	0.95
o - Xylene	0.9994	0.0044	1.57
Naphthalene	25.07%	0.0044	0.92
2-Methylnaphthalene	11.79%	0.0044	1.69
1-Methylnaphthalene	19.05%	0.0044	0.65
Acenaphthylene	11.32%	0.0044	1.87
Acenaphthene	14.40%	0.0044	1.48
Fluorene	20.96%	0.0044	2.27
Phenanthrene	8.13%	0.0044	1.67
Anthracene	15.54%	0.0044	2.27
Fluroanthene	7.23%	0.0044	1.41
Pyrene	22.44%	0.0044	1.24
Benzo[a]anthracene	18.93%	0.0044	2.04
Chrysene	19.21%	0.0044	1.92
Benzo[b&k]fluoranthene	16.21%	0.0044	5.96
Benzo[e]pyrene	16.61%	0.0044	0.80
Benzo[a]pyrene	10.86%	0.0044	0.99
Indeno[1,2,3-c,d]pyrene	20.28%	0.0044	1.78
Dibenz[a,h]anthracene	0.9951	0.0044	1.21
Benzo[g,h,i]perylene	0.9952	0.0044	1.97

What is Breakthrough?

- Occurs when target compounds are not adsorbed by adsorbents
- EPA TO-17 definition: “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”

First Breakthrough Experiments



- 8000ng on tube
- 85% humidified N_2 for 100 min at a flow of 100 mL/min
- Total volume 10 L sampling

- All studies performed in triplicate

2nd Breakthrough Experiment and Results

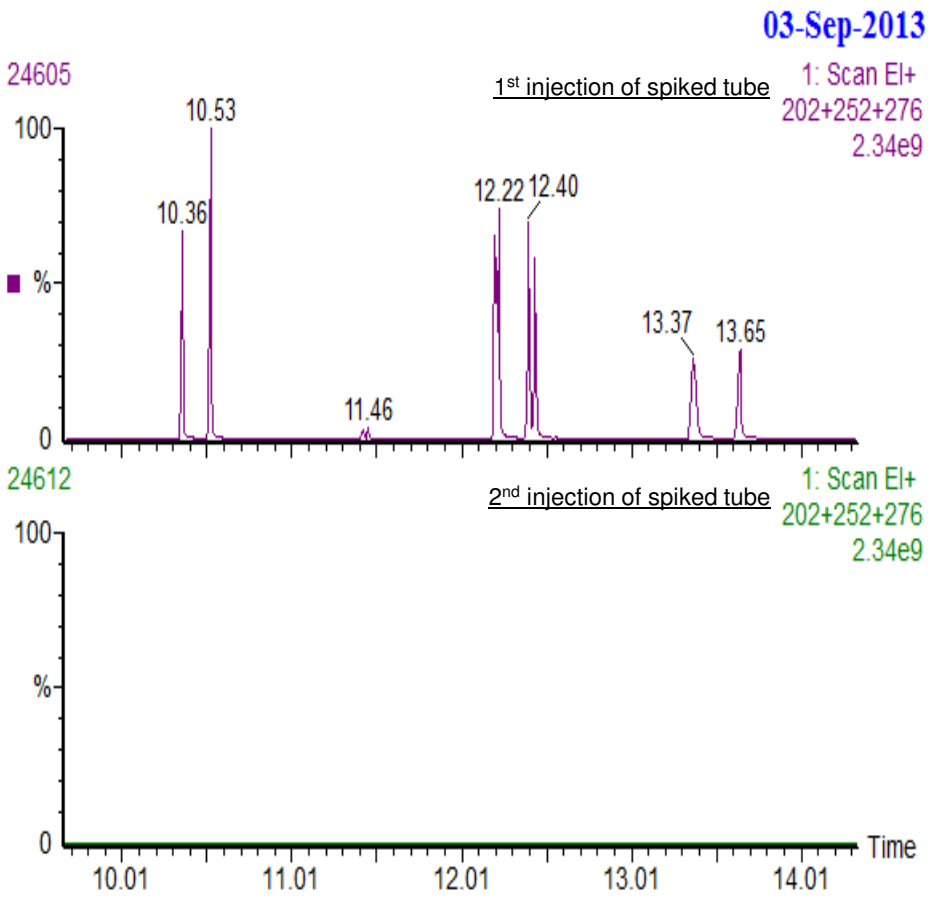
- A primary TD tube was attached to a gaseous standard to continuously deliver target compounds (mimics a real-world sampling event)
- A BT tube was attached and monitored on a regular basis
- Ultimately, the primary tube was loaded with >200mg analyte with no detectable breakthrough

Target Analyte	% BT	% BT	% BT
1,3-Butadiene	nd	nd	nd
Benzene	nd	nd	nd
Toluene	nd	nd	nd
Ethyl Benzene	nd	nd	nd
m & p - Xylenes	nd	nd	nd
o - Xylene	nd	nd	nd
Naphthalene	nd	nd	nd
2-Methylnaphthalene	nd	nd	nd
1-Methylnaphthalene	nd	nd	nd
Acenaphthylene	nd	nd	nd
Acenaphthene	nd	nd	nd
Fluorene	nd	nd	nd
Phenanthrene	nd	nd	nd
Anthracene	nd	nd	nd
Fluroanthene	nd	nd	nd
Pyrene	nd	nd	nd
Benzo[a]anthracene	nd	nd	nd
Chrysene	nd	nd	nd
Benzo[b&k]fluoranthene	nd	nd	nd
Benzo[e]pyrene	nd	nd	nd
Benzo[a]pyrene	nd	nd	nd
Indeno[1,2,3-c,d]pyrene	nd	nd	nd
Dibenz[a,h]anthracene	nd	nd	nd
Benzo[g,h,i]perylene	nd	nd	nd

Carryover and Recovery

- Recovery/Carryover Experiments
  - Analyzed spiked tube (50ng)
  - Analyzed trap
  - Analyzed valve
  - Re-analyzed spiked tube

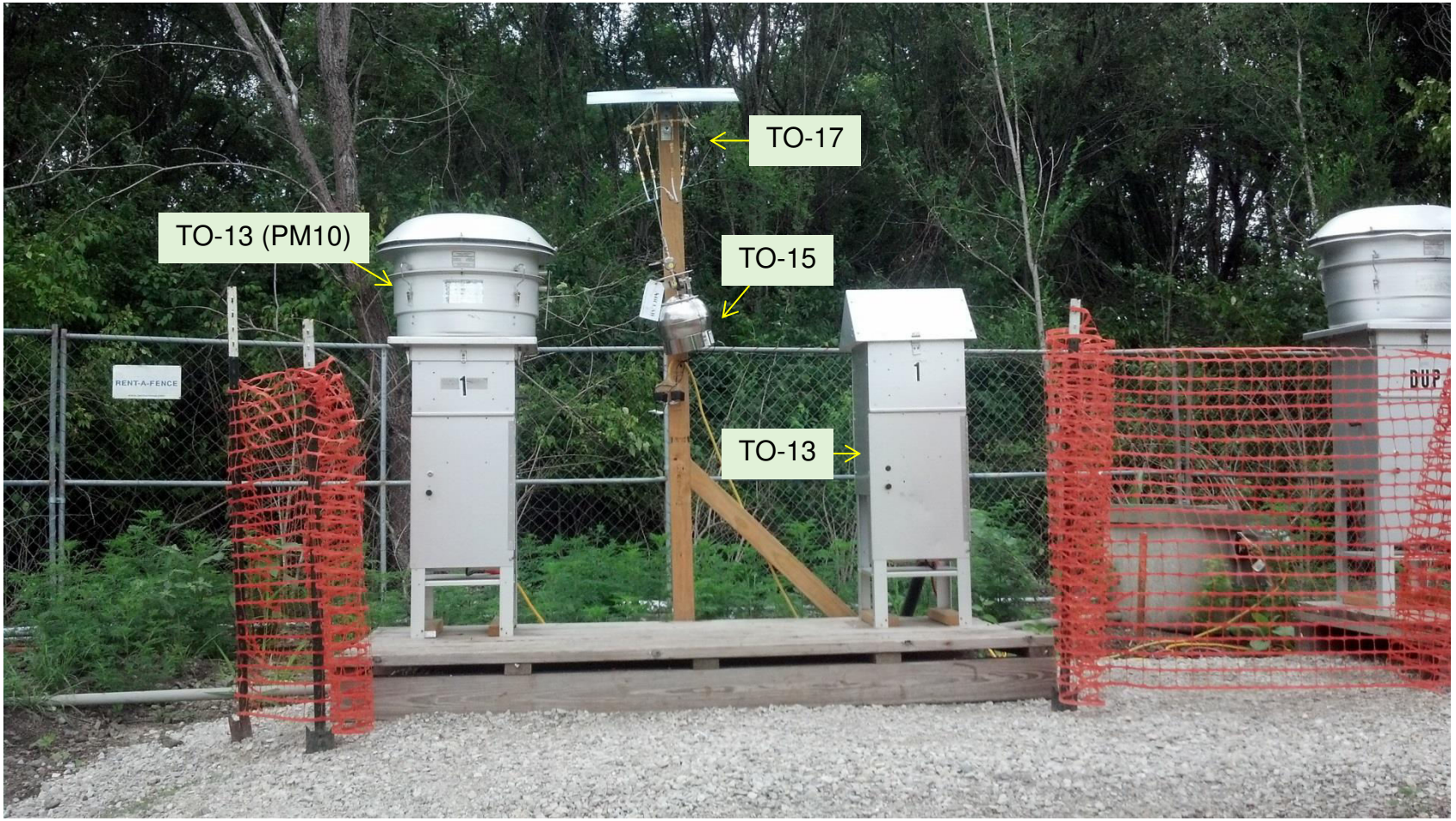
Target Analyte	Trap Test	Tube Test	Valve Test
Benzene	nd	nd	nd
Toluene	nd	nd	nd
Ethylbenzene	nd	nd	nd
m&p-Xylene	nd	nd	nd
o-Xylene	nd	nd	nd
Naphthalene	nd	nd	nd
2-Methylnaphthalene	nd	nd	nd
Acenaphthylene	nd	nd	nd
Acenaphthene	nd	nd	nd
Fluorene	nd	nd	nd
Phenanthrene	nd	nd	nd
Fluoranthene	nd	nd	nd
Chrysene	nd	nd	nd
Benzo[a]pyrene	nd	nd	nd
Indeno[1,2,3-cd]pyrene	nd	nd	nd
Benzo[g,h,i]perylene	nd	nd	nd



Air Monitoring Study Parameters : Site Study

- Compare TO-13 / TO-15 to TO-17: results from an active MGP remediation site
- 72-hour sample collection
- Continuous sampling for six weeks
- Two sample locations selected (AMS-01 and AMS-03)
- Three 72-hour samples from each site were selected for comparison

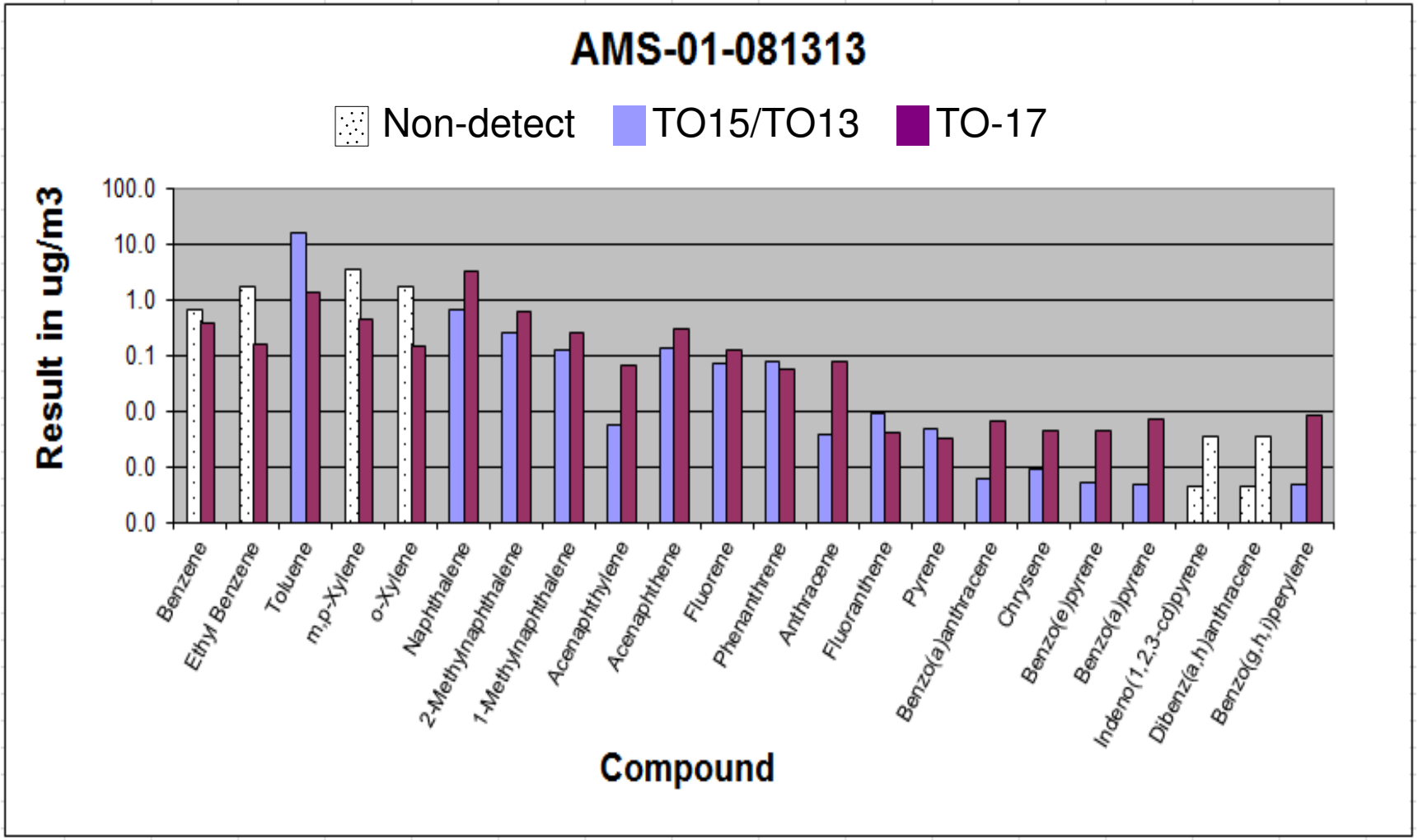
Site Setup



TO-17 Site Study expanded view

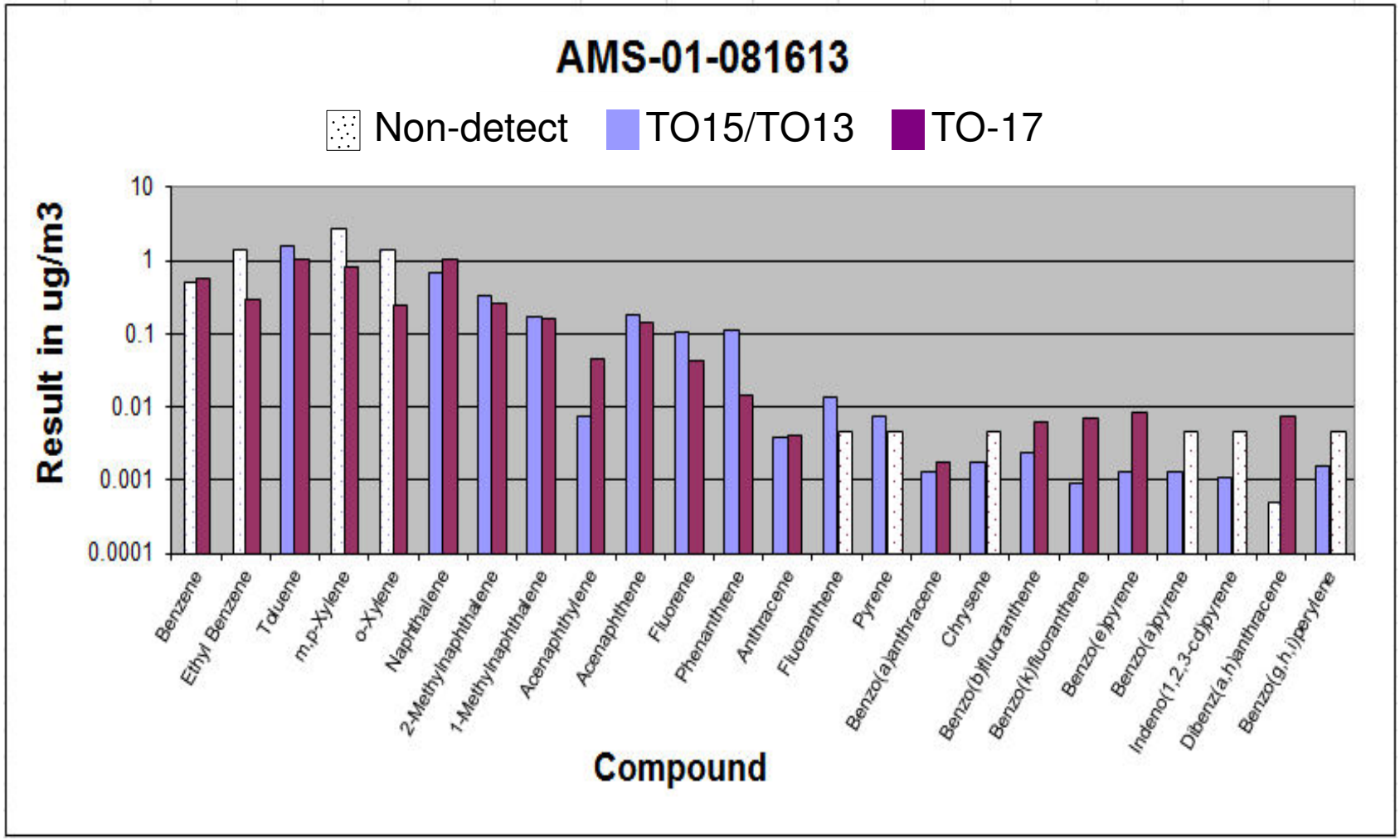
- Two types of tubes investigated (XRO-444 and XRO-644)
- Each type was sampled in duplicate
- One of the duplicates had filter attached and analyzed
- A breakthrough tube was attached to every tube sampled

Chart for Site AMS-01-081313



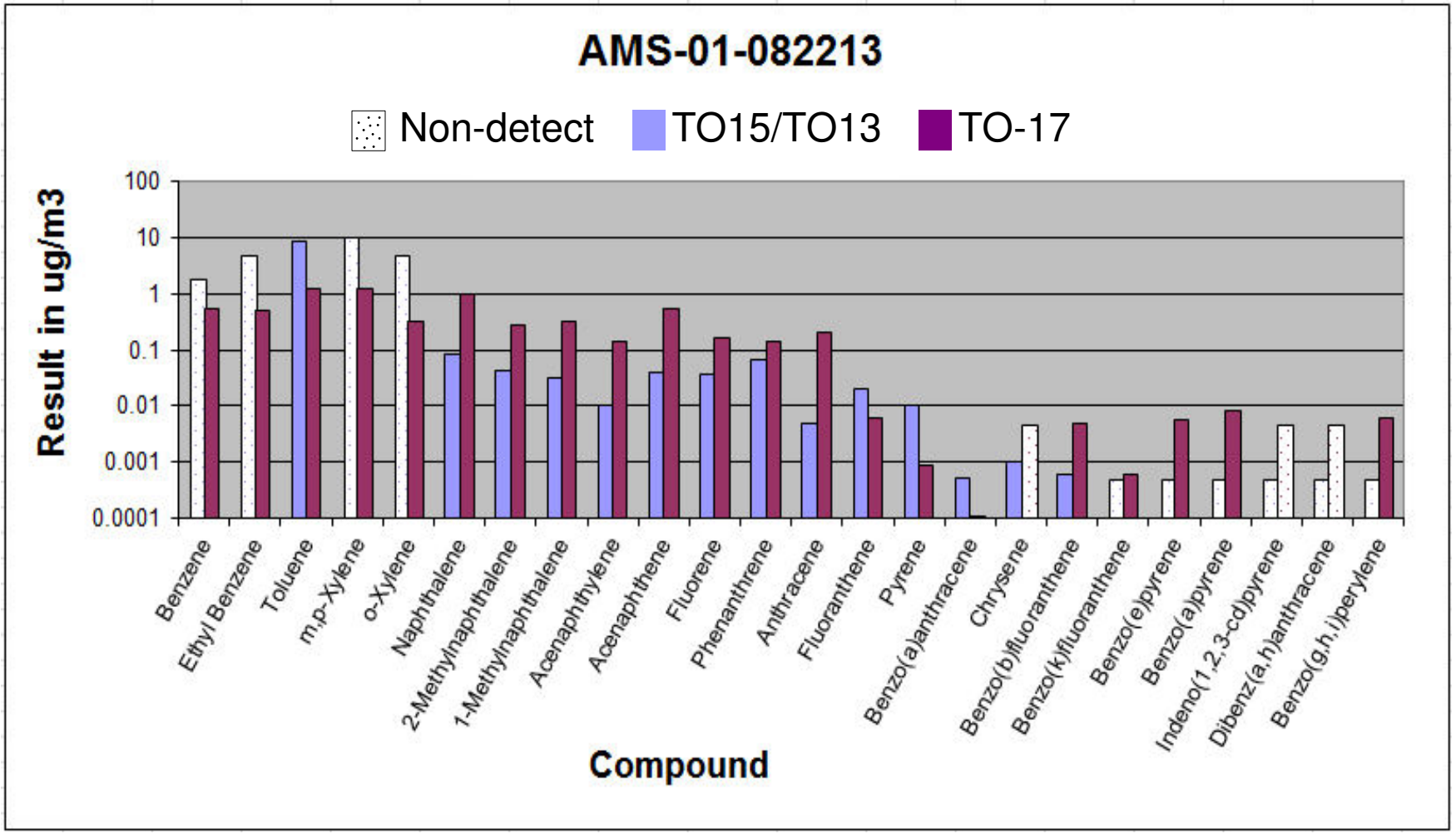
Note: dotted, unfilled bars are non-detects. Value represents reporting limit.

Chart for Site AMS-01-081613



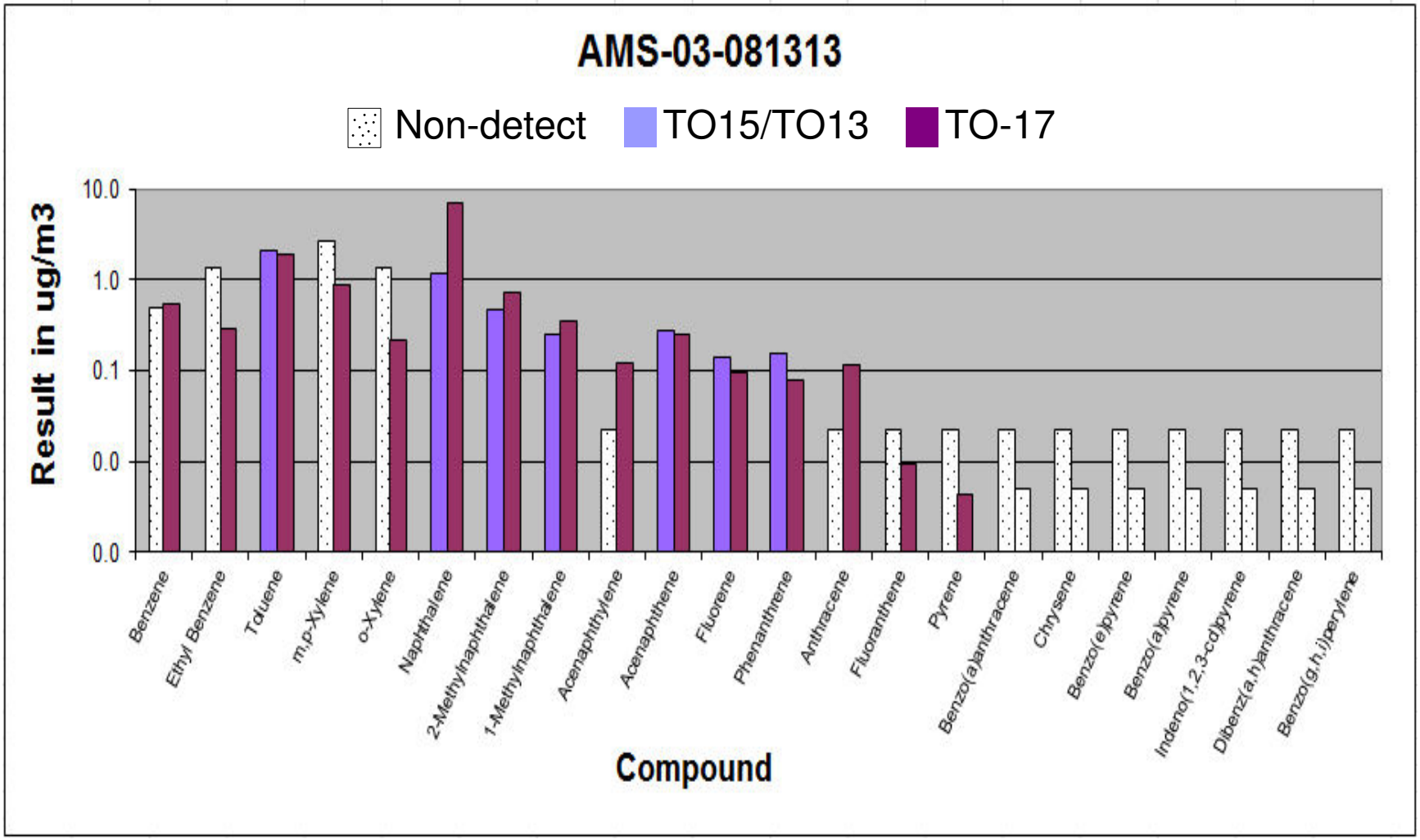
Note: dotted, unfilled bars are non-detects. Value represents reporting limit.

Chart for Site AMS-01-082213



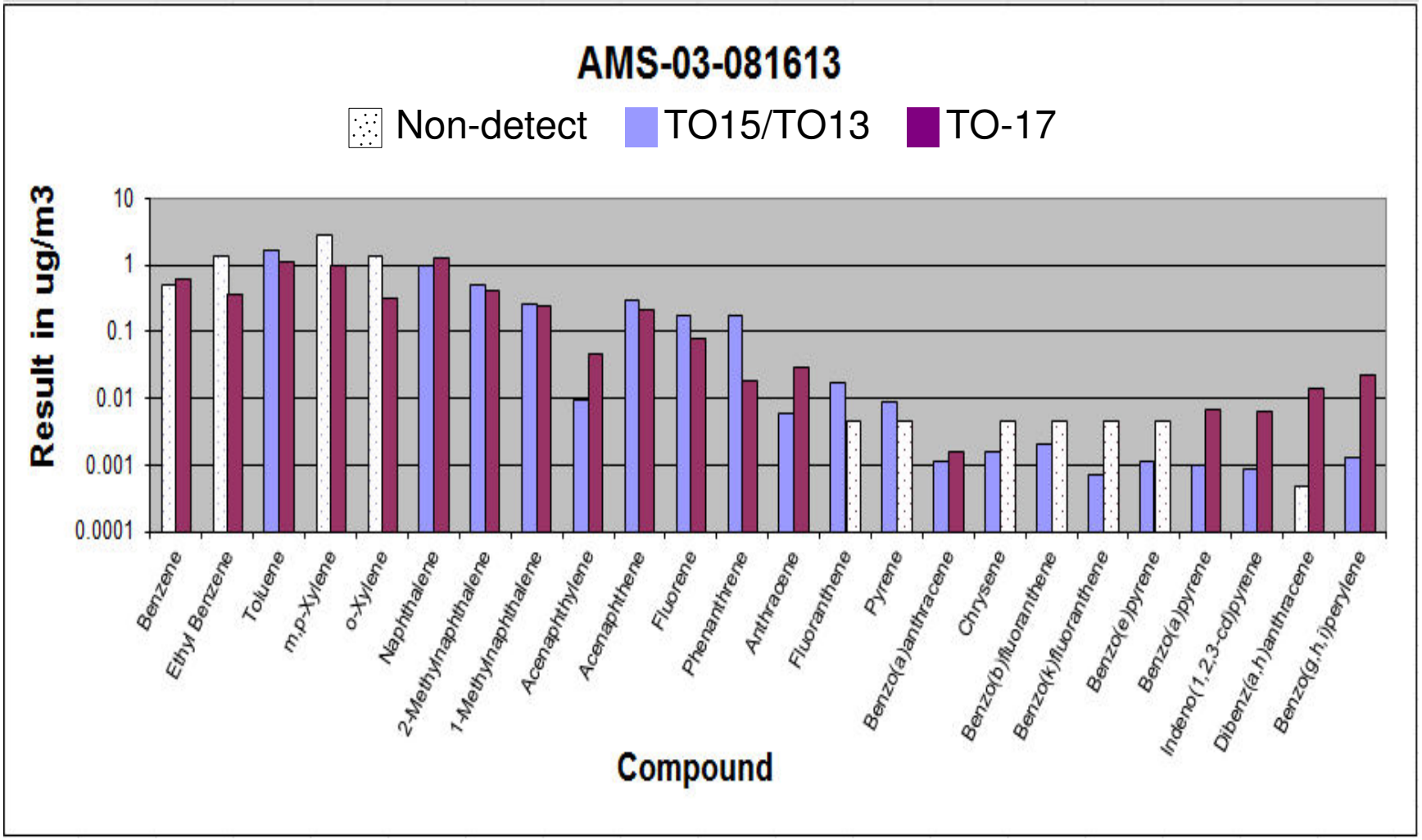
Note: dotted, unfilled bars are non-detects. Value represents reporting limit.

Chart for Site AMS-03-081313



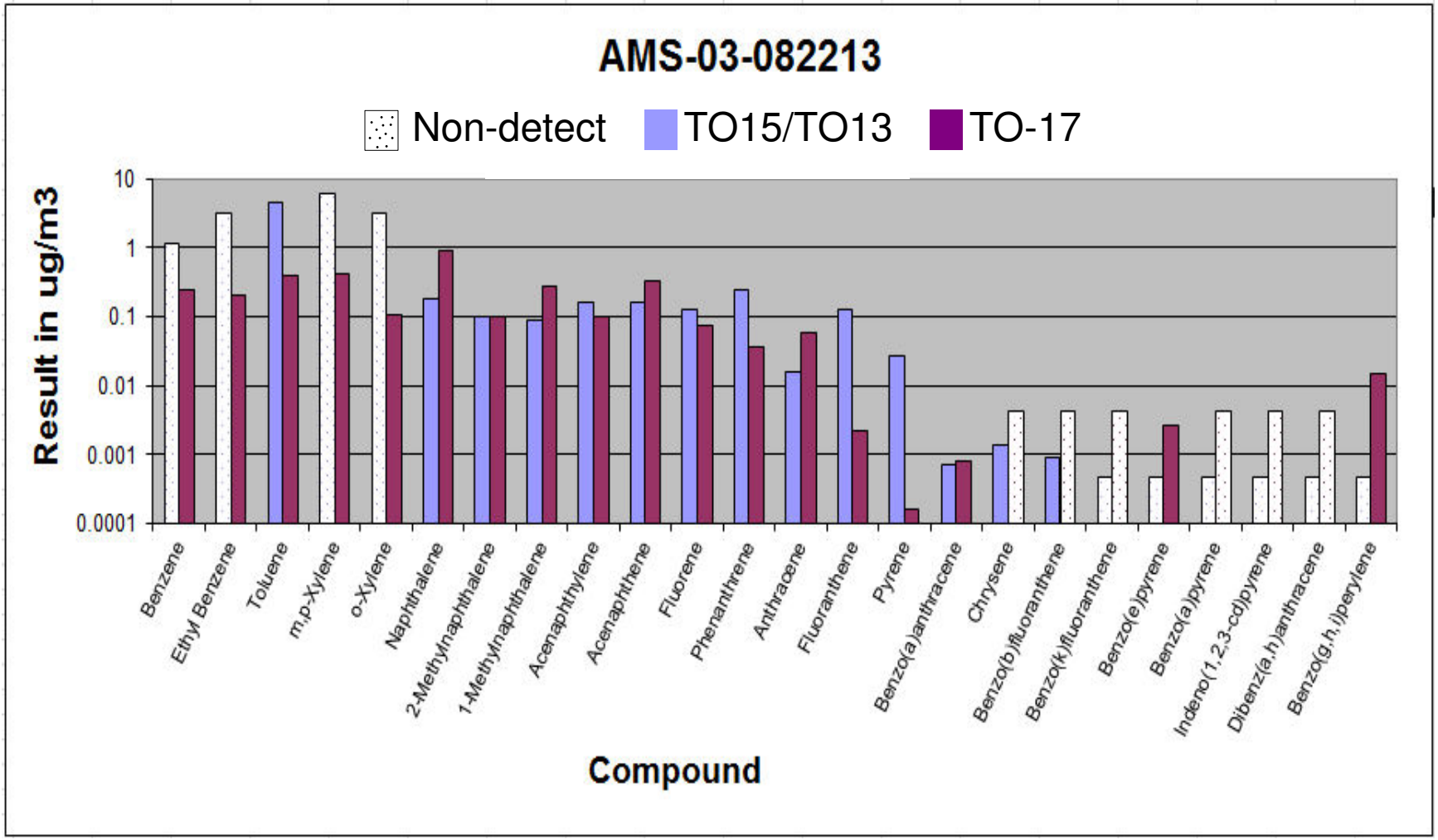
Note: dotted, unfilled bars are non-detects. Value represents reporting limit.

Chart for Site AMS-03-081613



Note: dotted, unfilled bars are non-detects. Value represents reporting limit.

Chart for Site AMS-03-082213



Note: dotted, unfilled bars are non-detects. Value represents reporting limit.

Will the EPA accept PAHs by TO17?

- EPA Method TO-17 is performance-based, guidance method
  - Section 2.5 states: "…This method provides performance criteria to demonstrate acceptable performance of the method ***(or modifications of the method)*** for monitoring a compound or set of compounds."

- EPA has seen this data and has given verbal acceptance stating that TO-17 is performance based so targets may be included as long as criteria is met
  - U.S. Environmental Protection Agency
    Office of Air Quality Planning and Standards
    Ambient Air Monitoring Group C304-06
    Research Triangle Park, NC 27711

Summary

- Analytical performance proves concept
- Site data suggests this is a better alternative
- One analysis instead of two:
  - Reduce sampling and analytical costs and disposal
  - Save on shipping and labor costs
  - Enhance productivity and efficiency
  - Increase profits
  - Better for our environment … A Greener analysis
- More data is available

Summary

- Thermal Desorption Technology
  - Tubes well-suited for vapor intrusion investigations and Air Toxic applications
  - 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

PerkinElmer TurboMatrix 650 Thermal Desorber / SQ 8 GC/MS …

Thank you

… Air Toxic Analyzer

Special thanks to :

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Miles Snow, Research Scientist, PerkinElmer

Tom Kwoka, Sr Product Specialist, PerkinElmer

Stephen Varisco, CARO Analytical Laboratories

Roberta Provost, *Air Method Development Specialist Pace Analytical Services*

For their valuable contribution to this work