The Analytical Solution for Air Monitoring

Volatile and Semi-Volatile Organic Compounds (VOCs and SVOCs) in a Single Air Analysis: The Cost Effective "Green" Solution

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Acknowledgement:
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Formerly from Pace Analytical Services
Stephen Varisco, Technical Manager
Formerly from Caro Analytical Services

Outline

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- Introduction
- Purpose of Study
- Tube Design and Thermal Desorption
- Analytical Data and Performance
- Results from Site Sampling Studies
- Air Monitoring Study Summary

- Focus on two Air Applications
  - Soil Gas: nC3 to nC26
  - Manufacturer Gas Plant Sites: nC4 to nC40

Goals

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- Using the technique of Automated Thermal Desorption to perform both VOCs and SVOCs (up to benzo(g,h,i)Perylene) in one air sample

- Single analysis:
  - more productive
  - more cost effective
  - greener solution

New Sorbent Tubes

- **2010: Soil Vapor Intrusion (SVI) Tube (patented)**
  - C_3 to C_{26}
  - Combines VOC & SVOC from the seven VOC gases to pyrene
  - Developed by PerkinElmer with help from CARO Analytical Services
- **2011: XRO - 640 tube (patent pending)**
  - C_6 to C_{44}
  - Combines VOC & SVOC from BTEX to benzo(g,h,i)perylene
  - Developed by PerkinElmer with help from InnoTech Alberta
- **2013: XRO – 440 (patent pending)**
  - C_4 to C_{44}
  - Combines VOC & SVOC from 1,3-butadiene to benzo(g,h,i)perylene
  - Developed by PerkinElmer with help from Pace Analytical Services

Soil Vapor Intrusion Tube

Importance to develop the

Soil Vapor Intrusion Tube

Why the Soil Vapor Intrusion (*SVI*) Tube was Developed

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- Necessary recoveries of semi-volatiles and diesel which are present in soil gas
- Increase sampling volume while ensuring retention of volatiles
- Automated water management
- Automated sample integrity
  - Internal Standard
  - Surrogate
  - Tube impedance
- Soil vapor differs from other air sampling applications
  - Higher moisture
  - Greater boiling point compound range
  - Wider concentration range
- The SVI tube was developed to handle these challenging samples

XRO – 440 and 640 Tubes

Importance to Development the

Extended Range Organics Tube

Why the XRO-440 Tube was Designed?

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

TO - 13

TO - 15

TO - 17

Two Analysis now ONE

Improve Productivity
Cost Effective
Environmentally Friendly

…. TO – 15 can't go beyond naphthalene

Four Canisters to a box … Yikes!

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… plus hours of cleaning

Hydrophobic adsorbents: XRO-440 and XRO-640 Tubes

Tube	Time for Dry Purge
XRO - 640	nd added moisture on tube
XRO - 440	2 minute Dry Purge

Only slight water retention with 45L sample volume!

TurboMatrix ATD

Clarus SQ8 GC/MS

Introduction to Functioning

How it works?

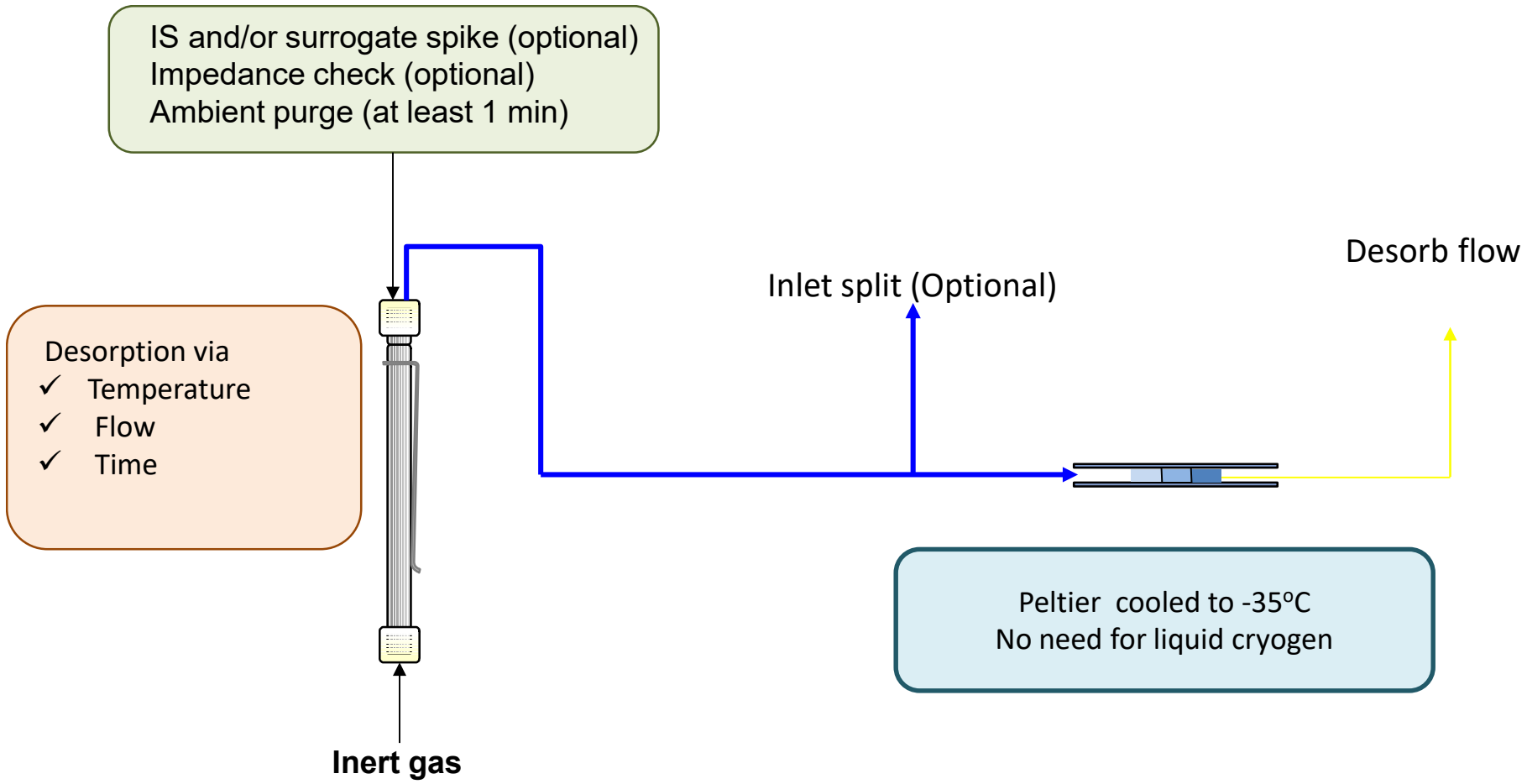
Thermal Desorption Tube

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

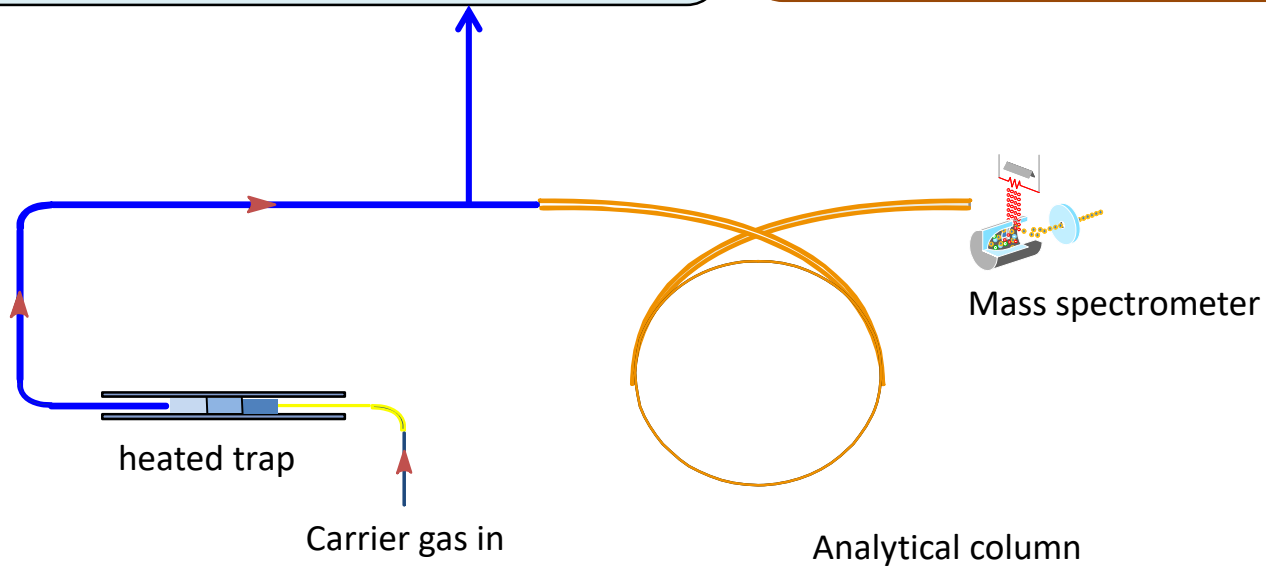
Step 1: Sample Tube (Primary) Desorption



Step 2: Transfer Sample to Analytical Column

Optional outlet split or
Recollect on same tube or new tube

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



Results:

Analytical Performance

SVI and XRO – 440 Tubes

Data was acquired in Simultaneous Full Scan / SIM Mode

Results from Full Scan are reported. Sim was not important to achieve regulatory detection limits

Total Ion Chromatogram: VOC and SVOC: One Analysis

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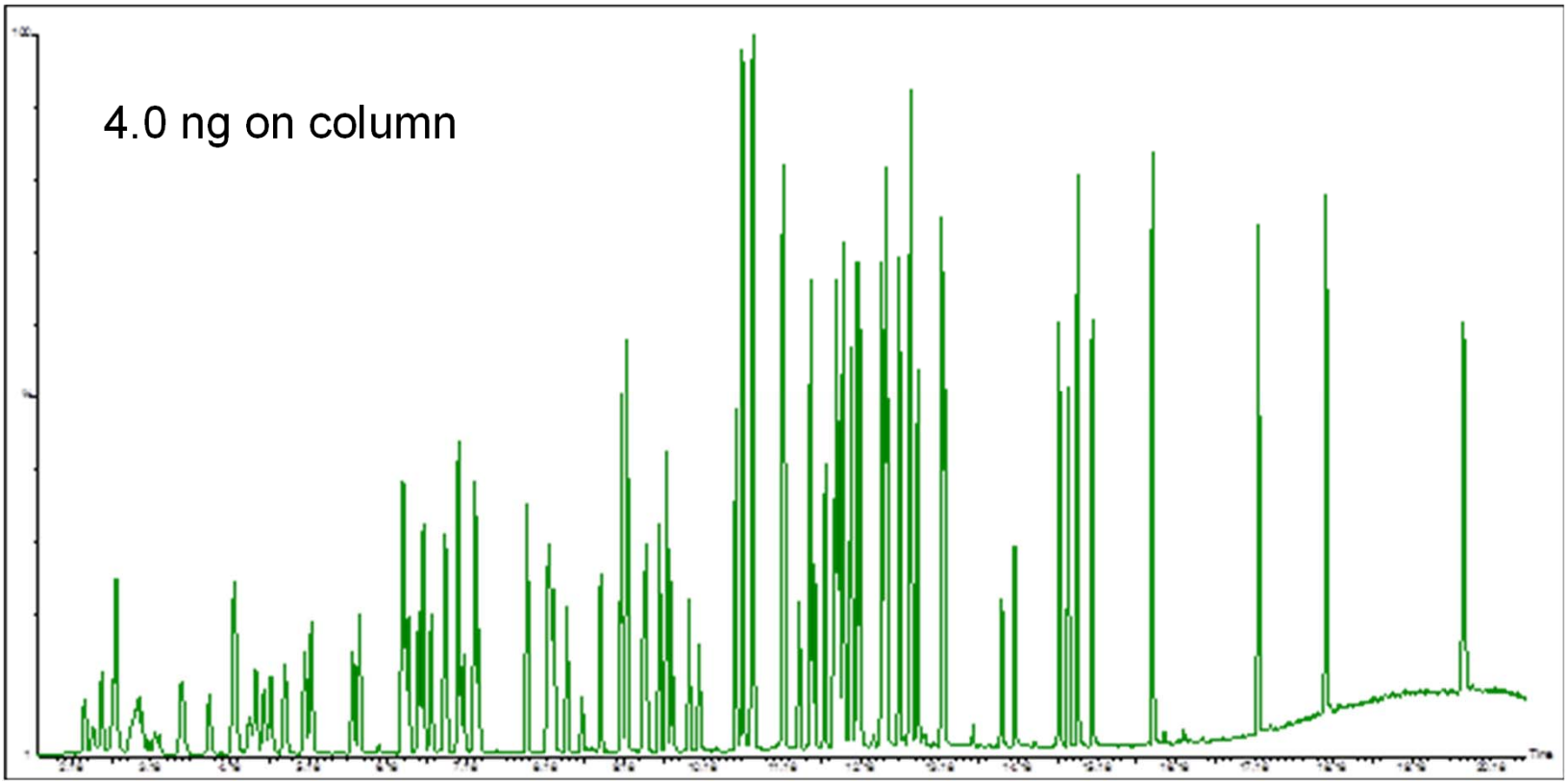
SVI Tube: dichlorodifluoromethane to phenanthrene. Over 90 targets separated



Precision, Linearity, Reporting Limit: SVI Tube

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Reporting limit based on 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)	7	0.9997	8.69	3.56	570:1
others	13	0.9996	9.26	3.19	560:1

Total Ion Chromatogram: VOC and SVOC (XRO - 440 Tube)

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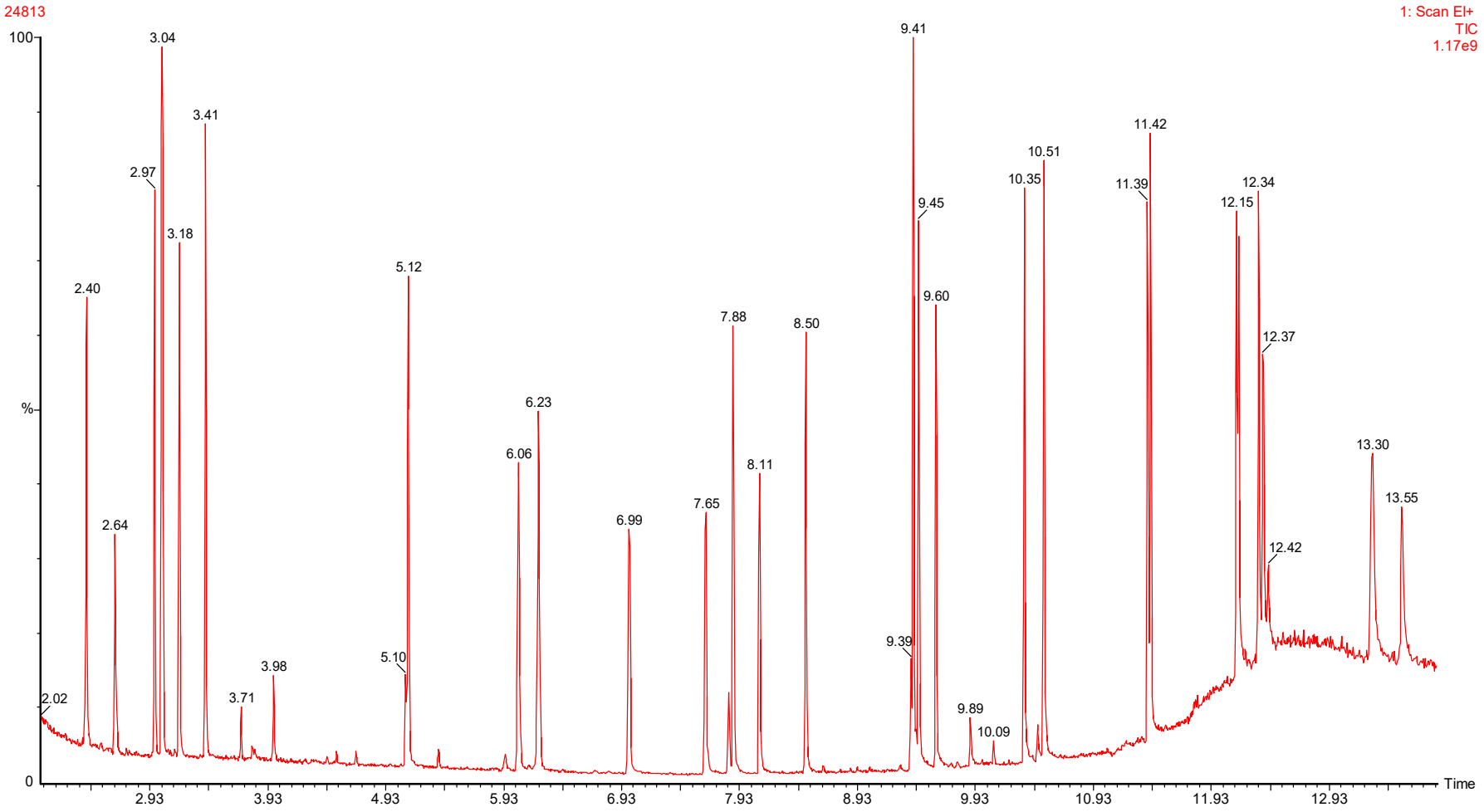
Target Range: 1,3-butadiene to benzo(g,h,i) perylene



Calibration, Precision and Reporting Limit: XRO – 440 Tube

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Compound	Linear (0.2 to 50 µg/m^3)		Precision n = 6	Reporting Limit 1 L sample volume
	r^2	Ave RF %	(%RSD)	S:N @ 0.2 µg/m^3
1,3-Butadiene	0.9991	10.25	1.98	251 : 1
Benzene	0.9998	4.25	0.90	554 : 1
Toluene	0.9999	5.98	0.94	601 : 1
Ethyl Benzene	0.9991	3.89	0.75	598 : 1
m & p - Xylenes	0.9992	5.66	0.91	645 : 1
Styrene	0.9994	7.98	1.20	305 : 1
o - Xylene	0.9995	6.52	1.57	443 : 1
Naphthalene	0.9996	8.90	0.92	402 : 1
2-Methylnaphthalene	0.9996	7.24	0.56	247 : 1
1-Methylnaphthalene	0.9998	6.56	0.62	195 : 1
Acenaphthylene	0.9998	6.88	1.98	104 : 1
Acenaphthene	0.9996	5.29	1.23	199 : 1
Fluorene	1.0000	1.86	0.67	282 : 1
Phenanthrene	0.9994	1.87	1.10	250: 1
Anthracene	0.9995	7.89	1.90	175 : 1
Fluroanthene	0.9997	5.01	0.98	550 : 1
Pyrene	0.9998	4.75	0.96	512 : 1
Benzo[a]anthracene	0.9995	6.32	1.54	480 : 1
Chrysene	1.0000	4.82	0.88	382 : 1
Benzo[b]fluoranthene	0.9998	8.89	1.56	344 : 1
Benzo[k]fluoranthene	0.9992	9.51	2.01	299 : 1
Benzo[e]pyrene	0.9999	6.33	1.75	175 : 1
Benzo[a]pyrene	0.9997	6.58	1.23	150 : 1
Indeno[1,2,3-c,d]pyrene	0.9997	8.26	1.82	198 : 1
Dibenz[a,h]anthracene	0.9991	9.18	1.25	275 : 1
Benzo[g,h,i]perylene	0.9990	10.75	2.01	201 : 1

TurboMatrix ATD

Clarus SQ8 GC/MS

Breakthrough and Recovery Data

SVI and XRO-440 Tubes

What is Breakthrough?

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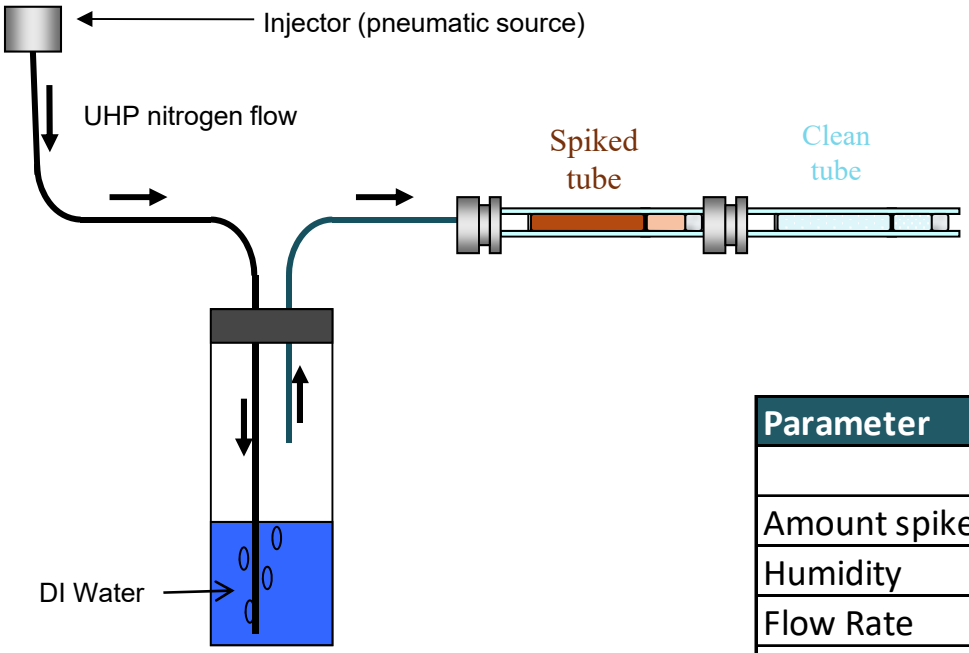
- Occurs when target compounds are not adsorbed by adsorbents
- EPA TO-17 definition: “The volume sampled when the amount of analyte collected in a back-up sorbent tube reaches a certain percentage (typically 5%) of the total amount collected by both sorbent tubes”

Laboratory Breakthrough Experiments

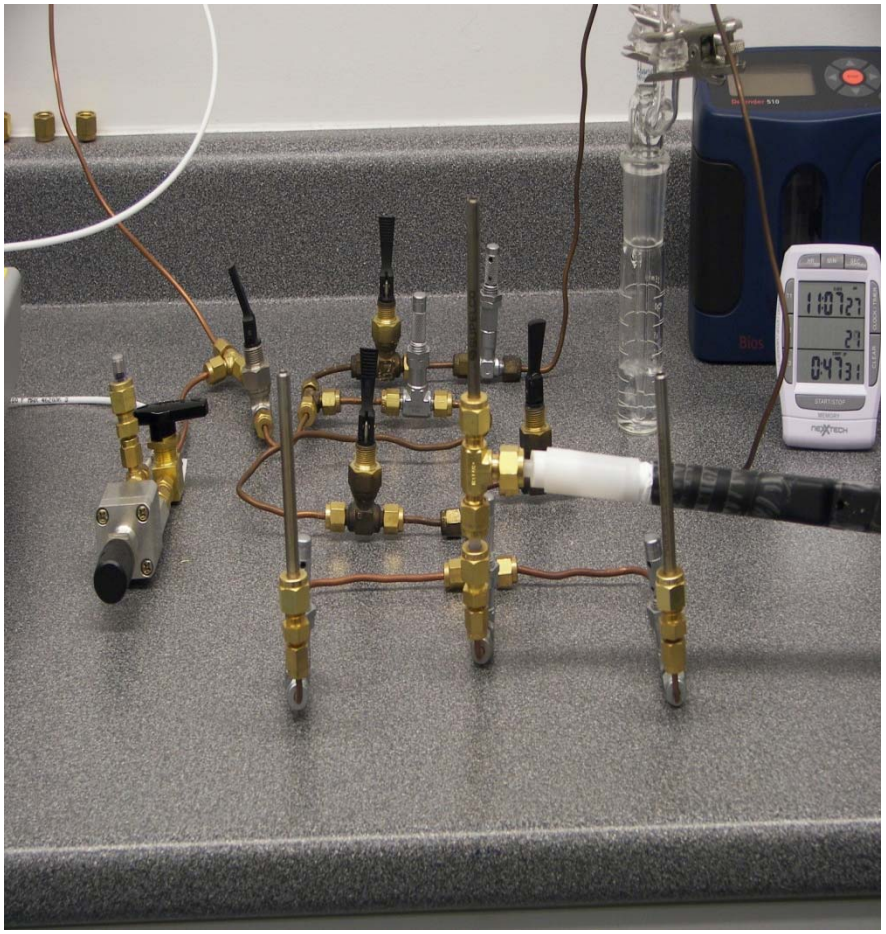


Parameter	SVI Tube	XRO - 440 Tube
Amount spiked on Tube	34.6 ug*	8.0 ug**
Humidity	85%	85%
Flow Rate	100 mL/min	100 mL/min
Time	100 minutes	100 minutes
Total Volume	10 liters	10 liters

*Restek: 300ng 502.2 voa #1; 300ng 1,3-budiene; 300ng 8260 Mega mix; 250 ng 4 PAH; 10ug diesel: Total 34.6 ug components

**custom TO-15 mix and Custom stock mix BTEX and 16 regulated PAHs

Results from Rigorous Laboratory Studies



Results: SVI Tube

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

Results: XRO-440 Tube Tube

non-detectable breakthrough on all compounds first target 1,3-butadiene

SVI Tubes

- Has stood the test of time
- Several field Breakthrough Experiments even with 50 liters without Breakthrough
- Tube with best recoveries for this analysis to date

2nd Experiment on Breakthrough for the XRO – 440

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- 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	
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

Field (real) Breakthrough Studies on XRO – 440 and 640 Tubes

- MGP Study
- Every Site had a BT tube attached to a Primary Tube
- 72 hour sampling in very humid environment
- Non-detect of target compounds in the range from nC4 to nC44 on secondary (BT) Tube
- Site study conducted over six (6) weeks sampling 72 hour intervals

Recovery: SVI Tube
Excellent (freons to phenanthrene)

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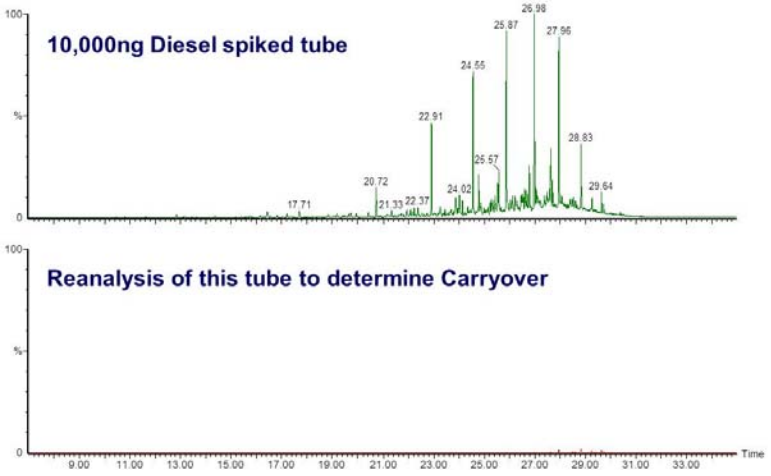
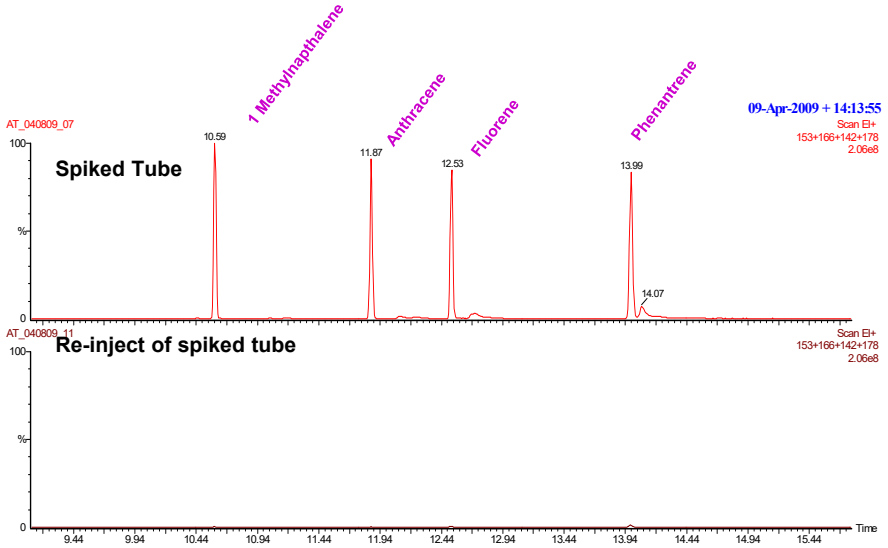
Recovery

- Analyzed spiked tube (shown)
- Analyzed trap
- Analyzed blank tube
- Re-analyzed spiked tube (shown)
- **Non-detectable carryover**

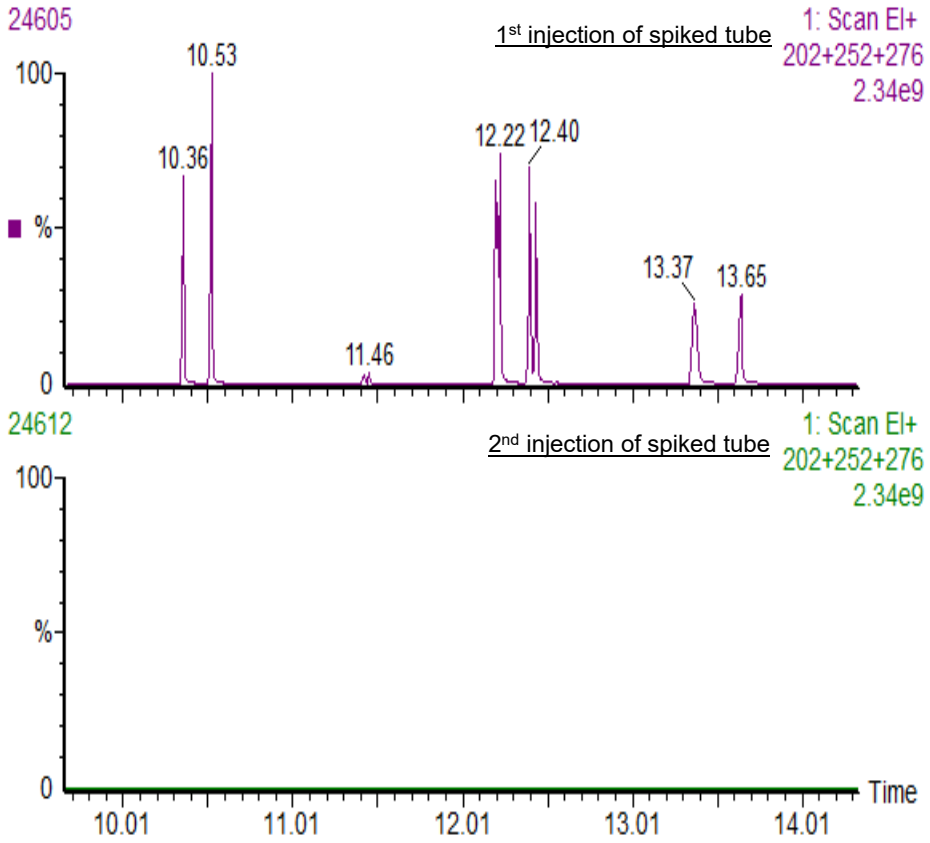
PAH Compounds	% Recovery
1-Methyl Napthalene	99.7
Anthracene	99.8
Fluorene	99.4
Phenanthrene	98.8





Recovery: XRO-440 Tube in nC4 to nC44 Range

- Recovery Experiment
  - Analyzed spiked tube
  - Analyzed trap
  - Analyzed instrument
  - Re-analyzed spiked tube
- Result
  - Non-detectable carryover and excellent recoveries



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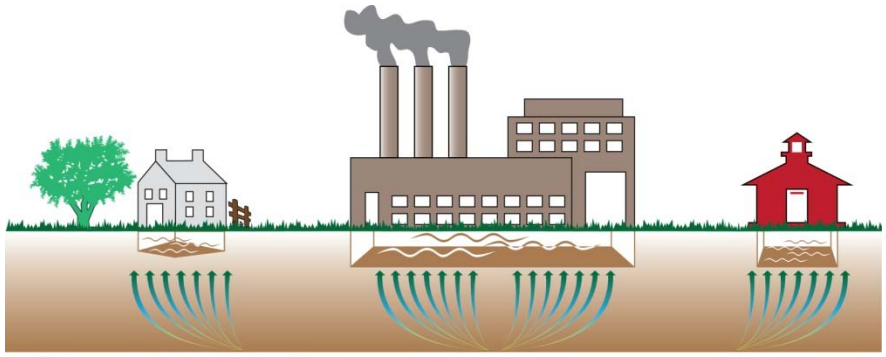
Site Studies

TO-17 data was collected in simultaneous Full Scan/SIM mode only Full Scan data was needed and out performed regulatory requirements by 10 times

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

Site Experiments

Site	Investigating (Research)	Sample Volume
Indoor Air	Comparing PAHs in Sub-Slab to Indoor Air	1 liter
Industrial Sub-Slab (MI)	2-Methyl Naphthalene was the compound of interest comparing recovery using TO-15 to TO-17 (XRO–440 tube)	1 liter
Manufactured Gas Plant (MGP)	Results of naphthalenes from the MPG site comparing TO-15 to TO-17 (XRO-440 tube)	50 liters
Industrial Sub-Slab (IN)	Same site sampling onto SVI tube and XRO-440 tube	1 liter

… acceptable flow rate range is from 10 to 200 mL/min

Indoor Air Site – Soil Vapor Intrusion Concern (conc µg/m³)

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Location	Stock Room		Sewing Room		Maint Room
	Sub-slab	Indoor Air	Sub-slab	Indoor Air	Drain
Target Analyte (SVOC)					
Naphthalene	0.251	3.96	0.286	1.15	1.46
2-Methylnaphthalene	0.345	0.802	0.414	0.252	0.900
1-Methylnaphthalene	0.284	0.408	0.234	0.138	0.529
Acenaphthylene	0.0773	nd	nd	nd	0.180
Acenaphthene	0.157	nd	nd	nd	nd
Fluorene	0.170	0.124	0.166	0.210	0.119
Phenanthrene	0.158	0.111	nd	1.40	0.0794
Anthracene	nd	0.0335	nd	0.240	nd
Fluroanthene	0.0208	nd	0.0336	0.145	nd
Pyrene	0.0286	0.0192	nd	0.238	nd
Benzo[a]anthracene	nd	nd	nd	0.0334	nd
Chrysene	nd	nd	nd	0.0315	nd
Benzo[b]fluoranthene	nd	nd	nd	nd	nd
Benzo[k]fluoranthene	nd	nd	nd	nd	nd
Benzo[e]pyrene	nd	nd	nd	nd	nd
Benzo[a]pyrene	nd	nd	nd	nd	nd
Indeno[1,2,3-c,d]pyrene	nd	nd	nd	nd	nd
Dibenz[a,h]anthracene	nd	nd	nd	nd	nd
Benzo[g,h,i]perylene	nd	nd	nd	nd	nd

Results from Site in Michigan: Soil Gas (XRO-440 Tubes)

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Component	001B	004B	022B	002B	009B	016B
Naphthalene	1.39	1.52	0.81	0.453	0.414	1.1
2-Methylnaphthalene	0.818	0.253	0.189	0.247	0.129	1.2
1-Methylnaphthalene	0.415	0.146	0.116	0.14	0.117	0.631
Acenaphthylene	0.0682	0.0338	0.0458	0.043	0.0232	0.114
Acenaphthene	0.0527	0.0178	0.0246	0.015	0.00897	0
Fluorene	0.0542	0.0162	0.0455	0.0427	0.0312	0.051
Phenanthrene	0.212	0.174	0.214	0.211	0.247	0.546
Anthracene	0.063	0.0416	0.049	0.0455	0.0619	0.0933
Fluoranthene	0.079	0.0873	0.0892	0.116	0.136	0.128
Pyrene	0.0976	0.05	0.0558	0.0638	0.0576	0.057
Benzo(a)anthracene	0.165	0.0465	0.0729	0.0935	0.109	0.103
Chrysene	0.108	0.0623	0.0768	0.0833	0.0682	0.0576
Benzo(b)fluoranthene	0.568	0.547	0.179	0.45	0.435	0.356
Benzo(k)fluoranthene	0.426	0.413	0.164	0.371	0.25	0.13
Benzo(e)pyrene	0.193	0.148	nd	0.23	0.229	0.195
Perylene	nd	0.4	nd	nd	nd	nd
Benzo(a)pyrene	0.247	nd	nd	nd	nd	nd
Ideno(1,2,3-cd)pyrene	nd	nd	nd	nd	nd	nd
Dibenz(a,h)anthracene	nd	nd	nd	nd	nd	nd
Benzo(g,h,i)perylene	nd	nd	nd	nd	nd	nd

… five (5) samples of 28 are shown. All had similar results

Site Map MPG Superfund

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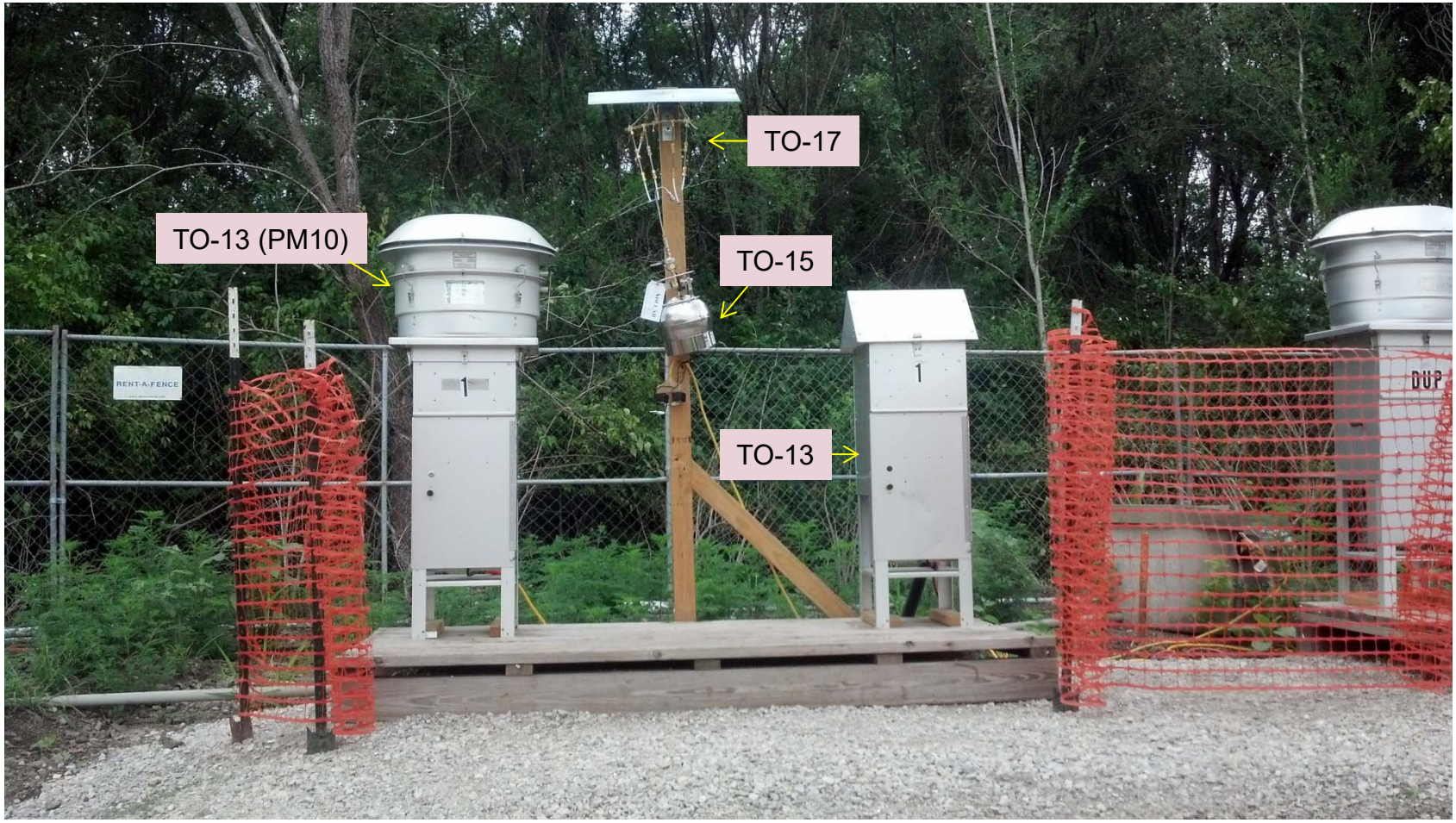
Site Setup: MGP site (fenceline)



Two – 72 Hour Sampling Events: Site #1

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Compound	Site one first 72 hours		Site one third 72 hours	
	TO13 & TO15	TO17	TO13 & TO15	TO17
Benzene	nd (RL 1.9)	0.38	nd (RL 1.9)	0.75
Toluene	15.00	1.30	8.30	1.60
Ethyl Benzene	nd (RL 1.8)	0.15	nd (RL 1.8)	0.66
m & p - Xylenes	nd (RL 3.7)	0.44	nd (RL 3.7)	1.53
o - Xylene	nd (RL 1.8)	0.14	nd (RL 1.8)	0.47
Naphthalene (TO-15)	nd (RL 1.4)	3.10	nd (RL 1.4)	1.1
Naphthalene (TO-13)	0.6800	3.1000	0.0820	1.1000
2-Methylnaphthalene	0.2500	0.6200	0.0440	0.2600
1-Methylnaphthalene	0.1200	0.2600	0.0310	0.2900
Acenaphthylene	0.0058	0.0660	0.0110	0.0650
Acenaphthene	0.1300	0.3000	0.0390	0.4200
Fluorene	0.0700	0.1200	0.0370	0.1600
Phenanthrene	0.0760	0.0550	0.0650	0.1100
Anthracene	0.0039	0.0800	0.0049	0.1700
Fluroanthene	0.0092	0.0040	0.0210	0.0076
Pyrene	0.0050	0.0032	0.0100	0.0088
Benzo[a]anthracene	0.0006	0.0067	nd (0.0005)	nd (0.0044)
Chrysene	0.0009	0.0046	0.0010	nd (0.0044)
Benzo[b]fluoranthene	0.0009	0.0088	nd (0.0005)	nd (0.0044)
Benzo[k]fluoranthene	0.0010	0.0089	nd (0.0005)	nd (0.0044)
Benzo[e]pyrene	nd (0.0005)	0.0044	nd (0.0005)	nd (0.0044)
Benzo[a]pyrene	nd (0.0005)	0.0074	nd (0.0005)	nd (0.0044)
Indeno[1,2,3-c,d]pyrene	nd (0.0005)	nd (.0044)	nd (0.0005)	nd (0.0044)
Dibenz[a,h]anthracene	nd (0.0005)	nd (.0044)	nd (0.0005)	nd (0.0044)
Benzo[g,h,i]perylene	nd (0.0005)	0.0081	nd (0.0005)	nd (0.0044)

Site # 3: Manufactured Gas Plant (MGP): Napthalenes TO-13 versus TO-17

Components	Site One		Site Two		Site Three	
	TO13	TO17	TO13	TO17	TO13	TO17
Naphthalene	0.68	3.1	0.026	1.3	0.082	1.1
2-Methylnaphthalene	0.25	0.62	0.19	0.41	0.044	0.26
1-Methylnaphthalene	0.12	0.26	0.10	0.27	0.031	0.29

Summary

- Analytical performance proves concept
  - Site data suggests targets are being missed using TO-15 and poor recoveries using TO-13
  - Aromatics above boiling point of naphthalene are present in soil gas and other air applications not able to be recovered by TO-15
  - Success: a single analysis method for VOCs and SVOCs

Acknowledgments

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- PerkinElmer
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Thank you

The Analytical Solution for Air Monitoring

Thank You !

Questions please

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