

The Analytical Solution for Air Monitoring



Site Studies in the Analysis of Soil Gas to Determine if Targets are Being Missed?

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Pace Analytical Services*

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

Goal: Determine if Targets Are being missed

- ▶ To determine if semi-volatile (SVOC) polynuclear aromatic hydrocarbons (PAHs) are present in soil gas and not recovered from canisters.

New Sorbent Tubes Investigated

▶ 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 and CARO Analytical Services

▶ 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

▶ 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 and Pace Analytical Services



Why the Soil Vapor Intrusion (SVI) Tube was Developed



- 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

Why the XRO-440 Tube was Designed?

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

Two Analysis now ONE

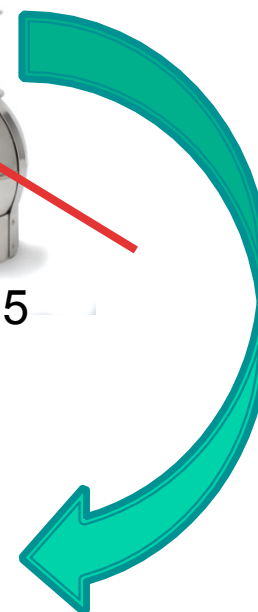
**Improve Productivity
Cost Effective
Environmentally Friendly**

TO - 13



TO - 15

TO - 17



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

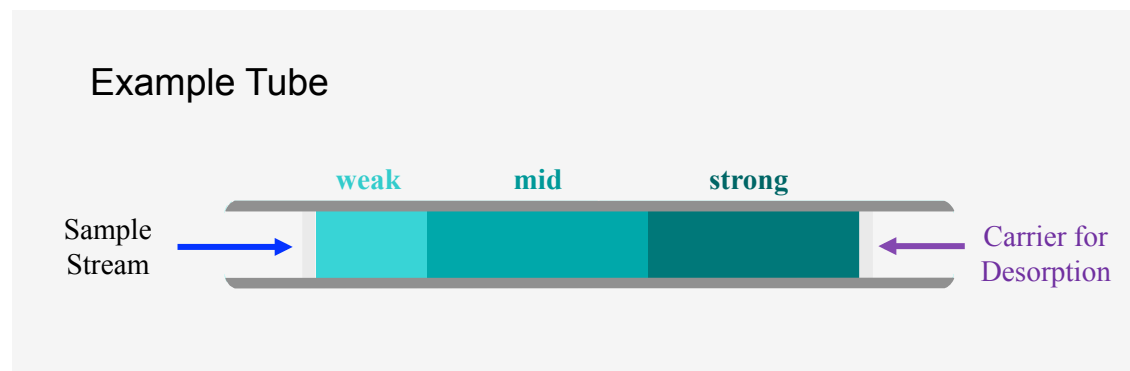
Clarus SQ8 GC/MS



Introduction to Functioning

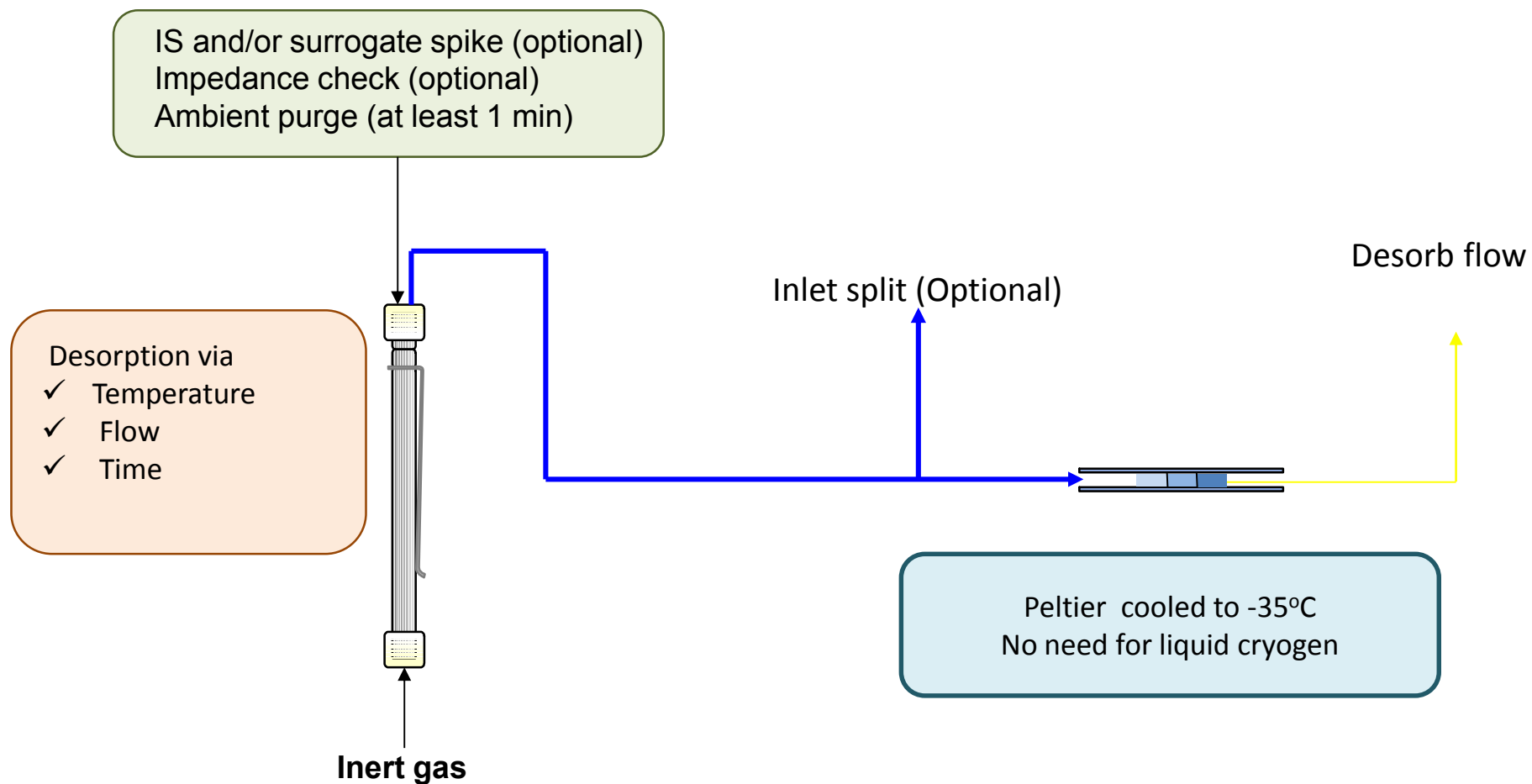
How it works?

Benefits of Multi-Sorbent Tube

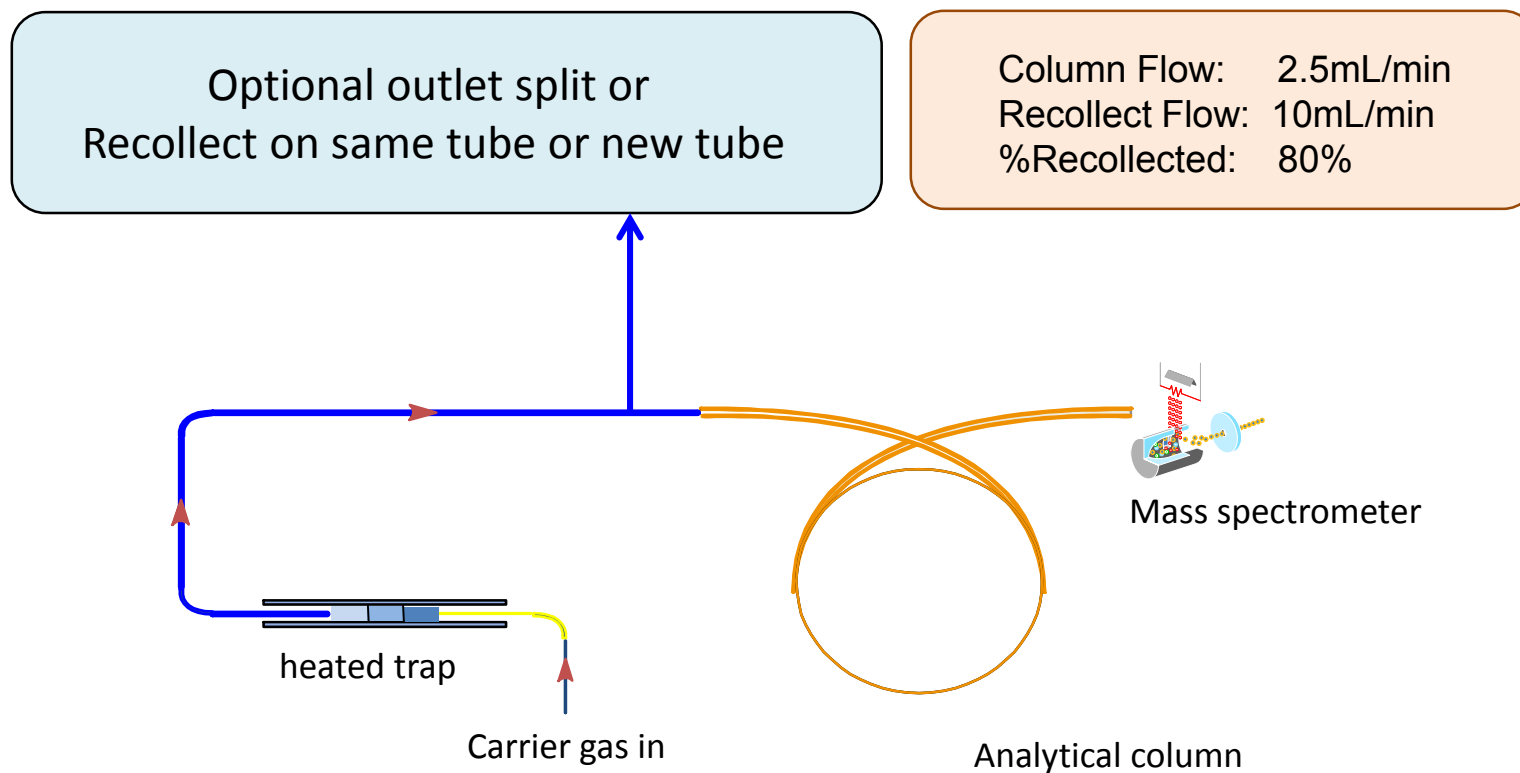


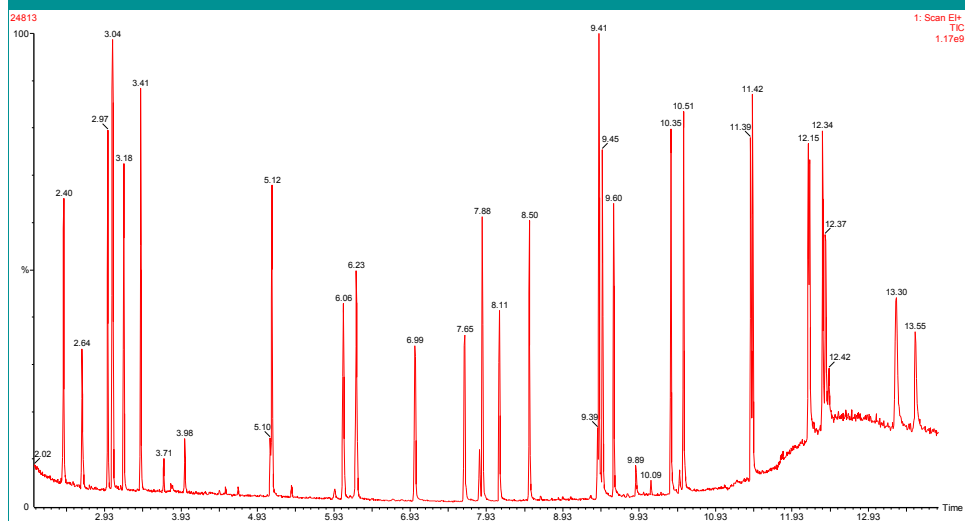
... started with these targets for MGP sites

Step 1: Sample Tube (Primary) Desorption



Step 2: Transfer Sample to Analytical Column

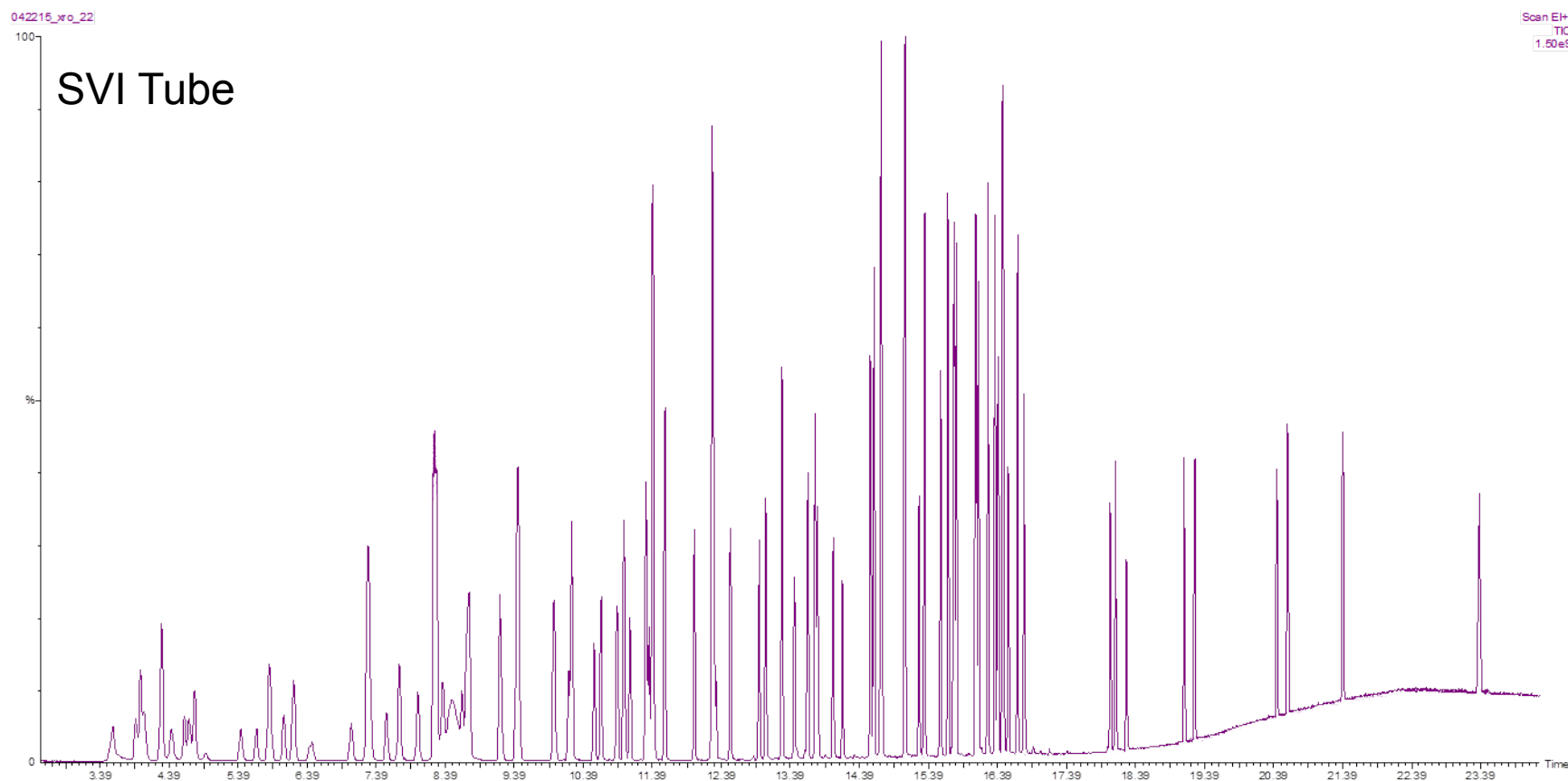




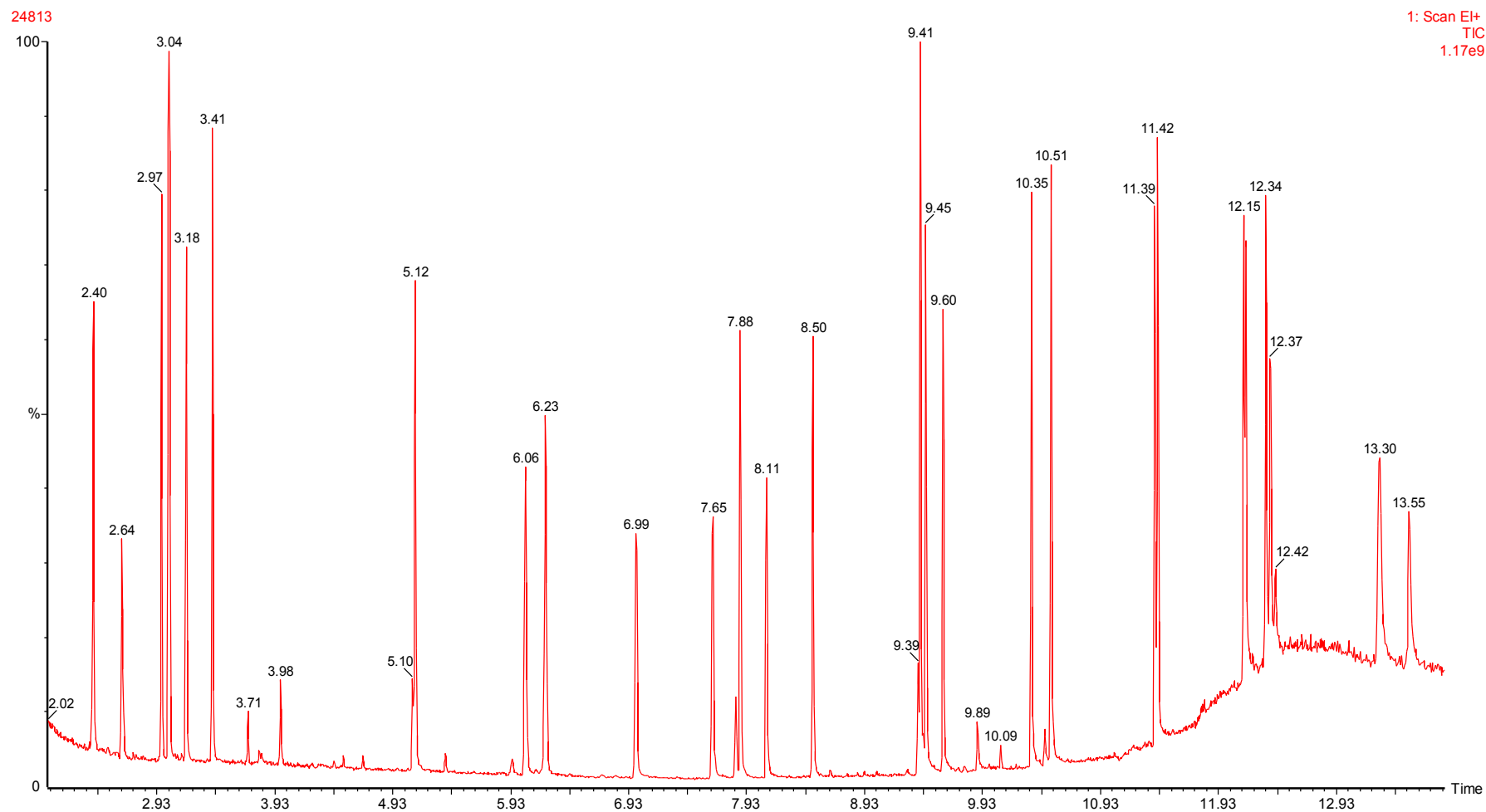
Results of Analytical Performance

Data was acquired in Simultaneous Full Scan/ SIM
Mode. Only results from Full Scan are reported

Total Ion Chromatogram: 8260B mix and a group of PAHs



Total Ion Chromatogram: VOA and SVOA (XRO-440 Tube)



Precision, Linearity, Single to noise (s/n): SVI Tube

1 liter sample volume

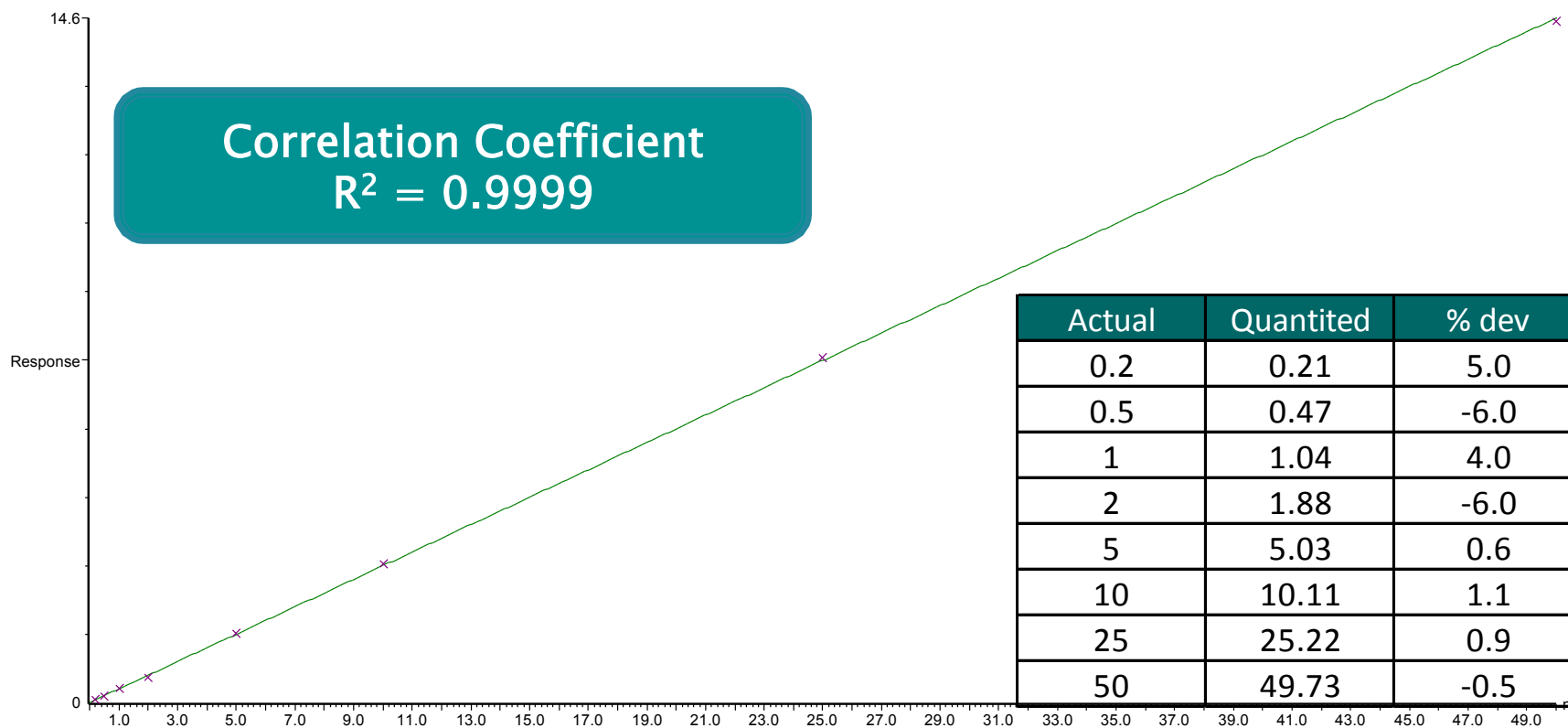
Class of compound	# of analytes per group	Linearity (0.05 to 250 µg/m ³)*		Precision	Reporting Limit
		r ²	Ave RF	(n=10)	S/N at 0.05 µg/m ³
Gases	7	0.9994	9.07	7.39	530:1
Aliphatic Hydrocarbons (halogenated)	35	0.9996	14.00	4.80	560:1
Aromatics (halogenated)	9	0.9997	13.30	2.58	1350:1
Aromatics (non-halogenated)	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

Calibration, Precision and Reporting Limit: XRO – 440 Tube

Target Compound	Range 0.2 to 50ng	Reporting Limit (ug/m ³) 1L sample volume	Precision (%RSD) n=6
1,3-Butadiene	0.9961	0.20	1.89
Benzene	0.9971	0.20	0.90
Toluene	0.9991	0.20	0.94
Ethyl Benzene	0.9989	0.20	0.77
m & p - Xylenes	15.54%	0.20	0.95
o - Xylene	0.9994	0.20	1.57
Naphthalene	25.07%	0.20	0.92
2-Methylnaphthalene	11.79%	0.20	1.69
1-Methylnaphthalene	19.05%	0.20	0.65
Acenaphthylene	11.32%	0.20	1.87
Acenaphthene	14.40%	0.20	1.48
Fluorene	20.96%	0.20	2.27
Phenanthrene	8.13%	0.20	1.67
Anthracene	15.54%	0.20	2.27
Fluroanthene	7.23%	0.20	1.41
Pyrene	22.44%	0.20	1.24
Benzo[a]anthracene	18.93%	0.20	2.04
Chrysene	19.21%	0.20	1.92
Benzo[b&k]fluoranthene	16.21%	0.20	5.96
Benzo[e]pyrene	16.61%	0.20	0.80
Benzo[a]pyrene	10.86%	0.20	0.99
Indeno[1,2,3-c,d]pyrene	20.28%	0.20	1.78
Dibenz[a,h]anthracene	0.9951	0.20	1.21
Benzo[g,h,i]perylene	0.9952	0.20	1.97

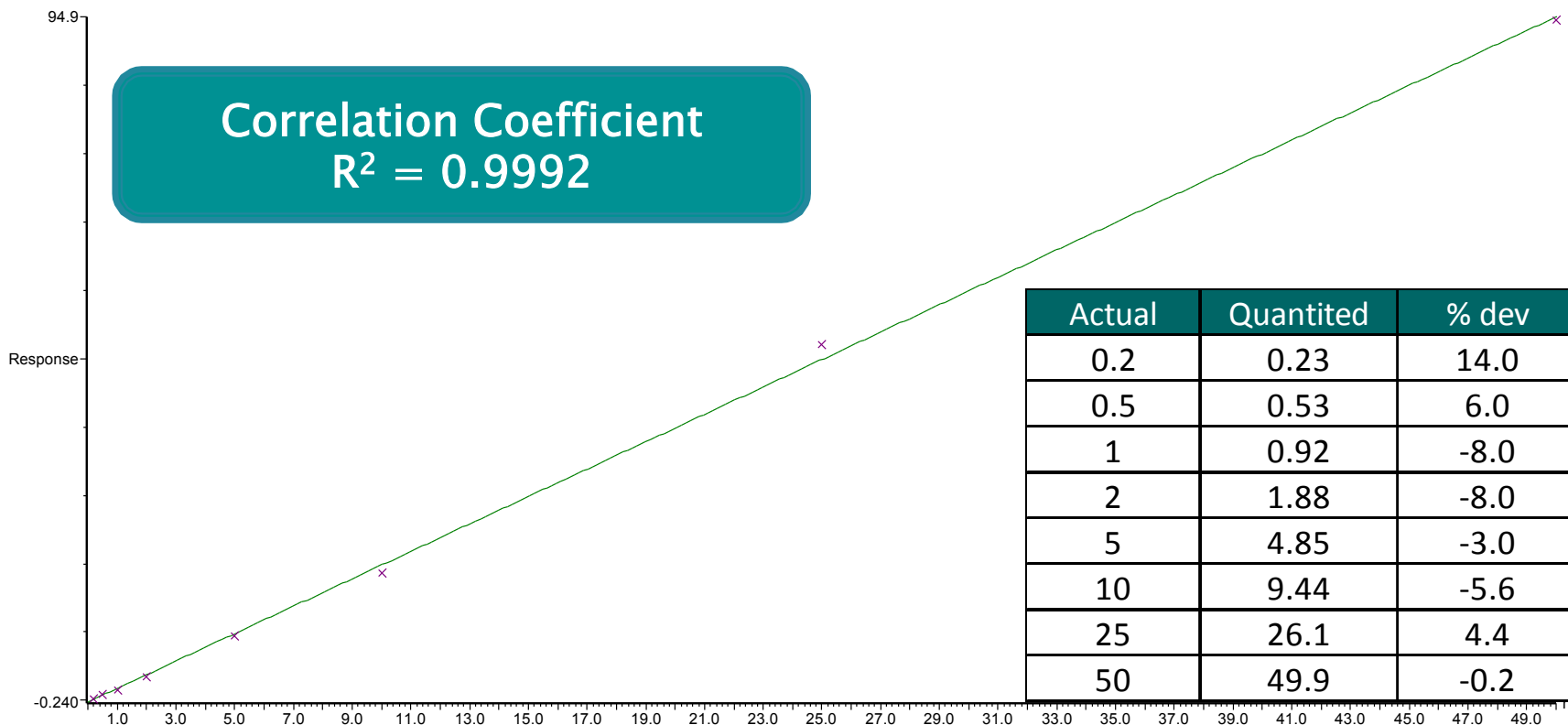
o-Xylene

Compound 12 name: o - Xylene
Coefficient of Determination: 0.999930
Calibration curve: $0.292679 \cdot x + 0.00222540$
Response type: Internal Std (Ref 1), Area * (IS Conc. / IS Area)
Curve type: Linear, Origin: Exclude, Weighting: 1/x, Axis trans: None



Pyrene

Compound 22 name: Pyrene
Coefficient of Determination: 0.999243
Calibration curve: $1.90286 \cdot x + -0.239747$
Response type: Internal Std (Ref 4), Area * (IS Conc. / IS Area)
Curve type: Linear, Origin: Exclude, Weighting: 1/x, Axis trans: None



TurboMatrix ATD Clarus SQ8 GC/MS



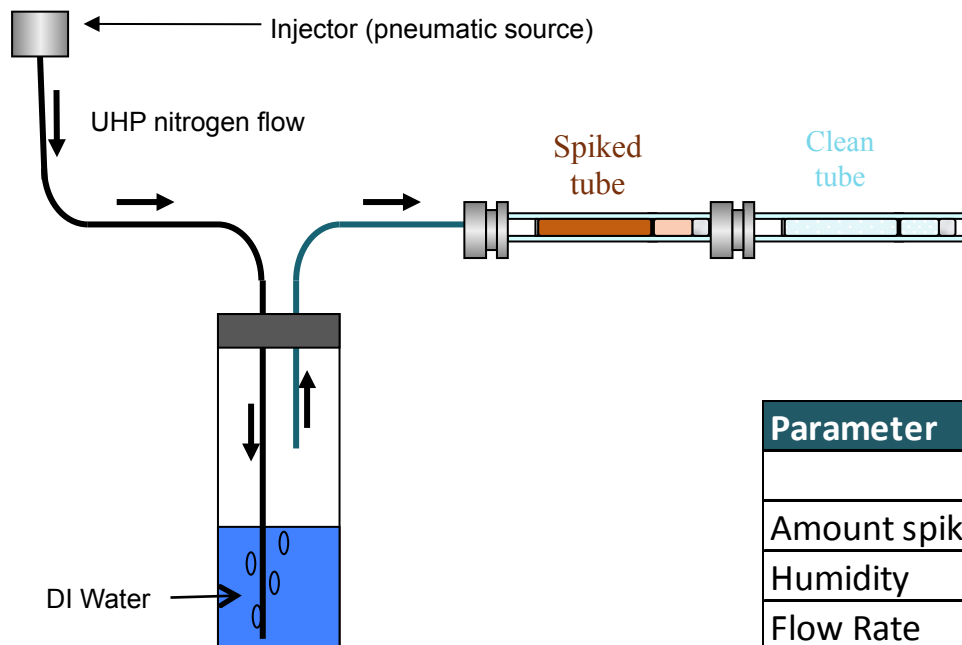
Breakthrough and Recovery Data

SVI and XRO-440 Tubes

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”

Breakthrough experiments

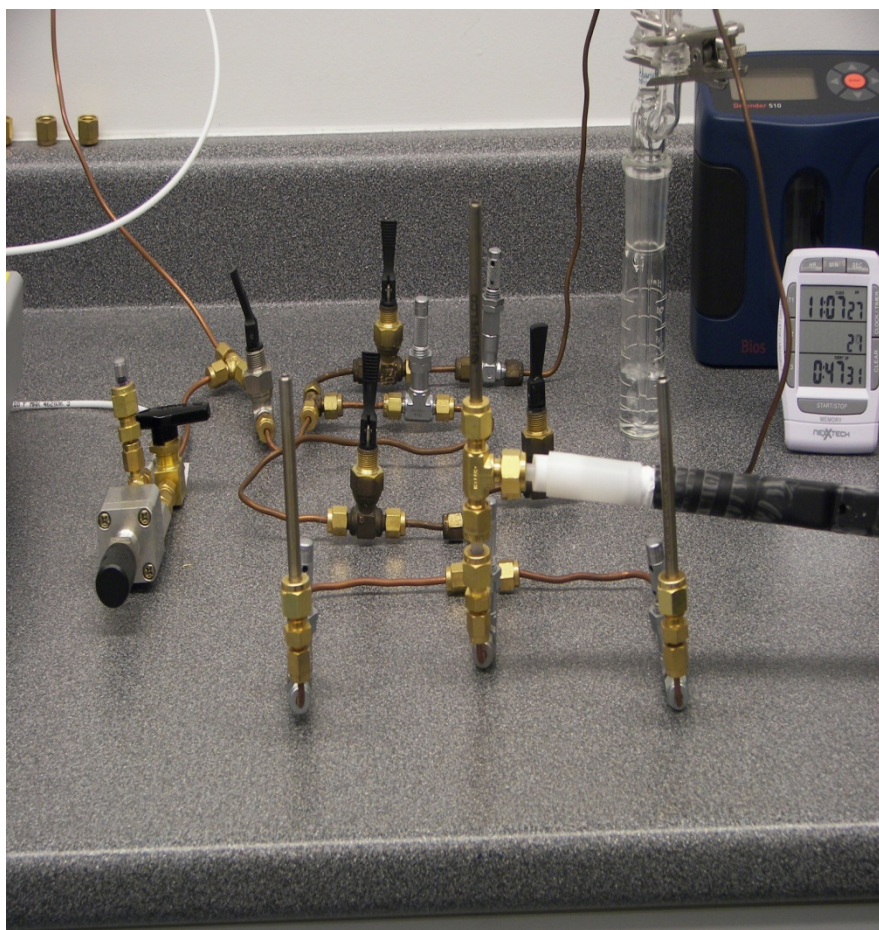


Parameter	SVI Tube	XRO - 440 Tube
Amount spiked on Tube	34.6 ug*	8.0 ug**
Humidity	85%	85%
Flow Rate	100 mL/min	100 mL/min
Time	100 minutes	100 minutes
Total Volume	10 liters	10 liters

*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 breakthrough experiments: SVI Tube



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

2nd Experiment on Breakthrough for the XRO – 440

- ▶ 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

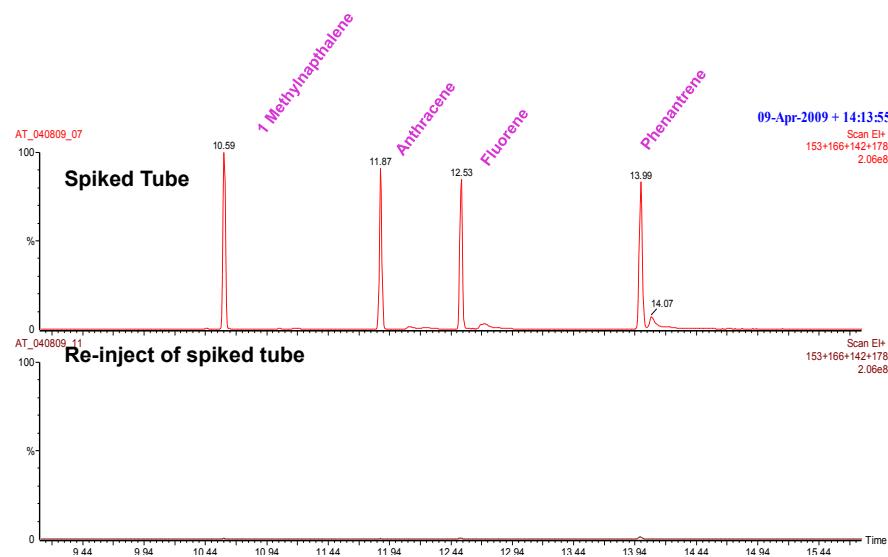
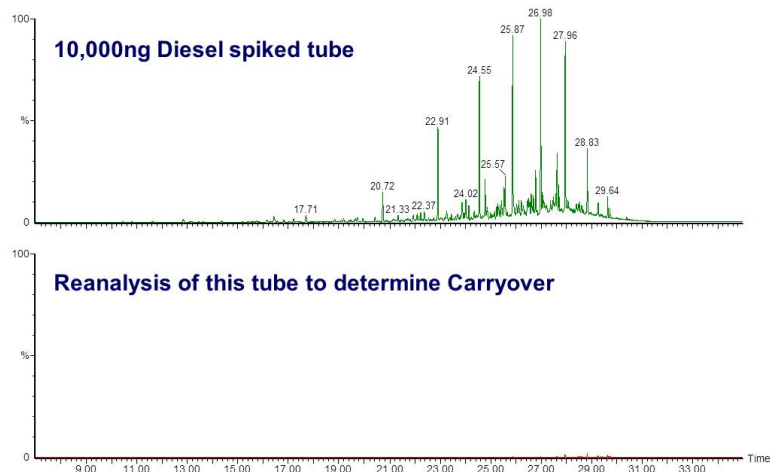
Target Analyte	% BT	% BT	% BT
Benzene	nd	nd	nd
Toluene	nd	nd	nd
Ethyl Benzene	nd	nd	nd
m & p - Xylenes	nd	nd	nd
o - Xylene	nd	nd	nd
Naphthalene	nd	nd	nd
2-Methylnaphthalene	nd	nd	nd
1-Methylnaphthalene	nd	nd	nd
Acenaphthylene	nd	nd	nd
Acenaphthene	nd	nd	nd
Fluorene	nd	nd	nd
Phenanthrene	nd	nd	nd
Anthracene	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

Recovery: SVI Tube Excellent (freons to phenanthrene)

Recovery

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

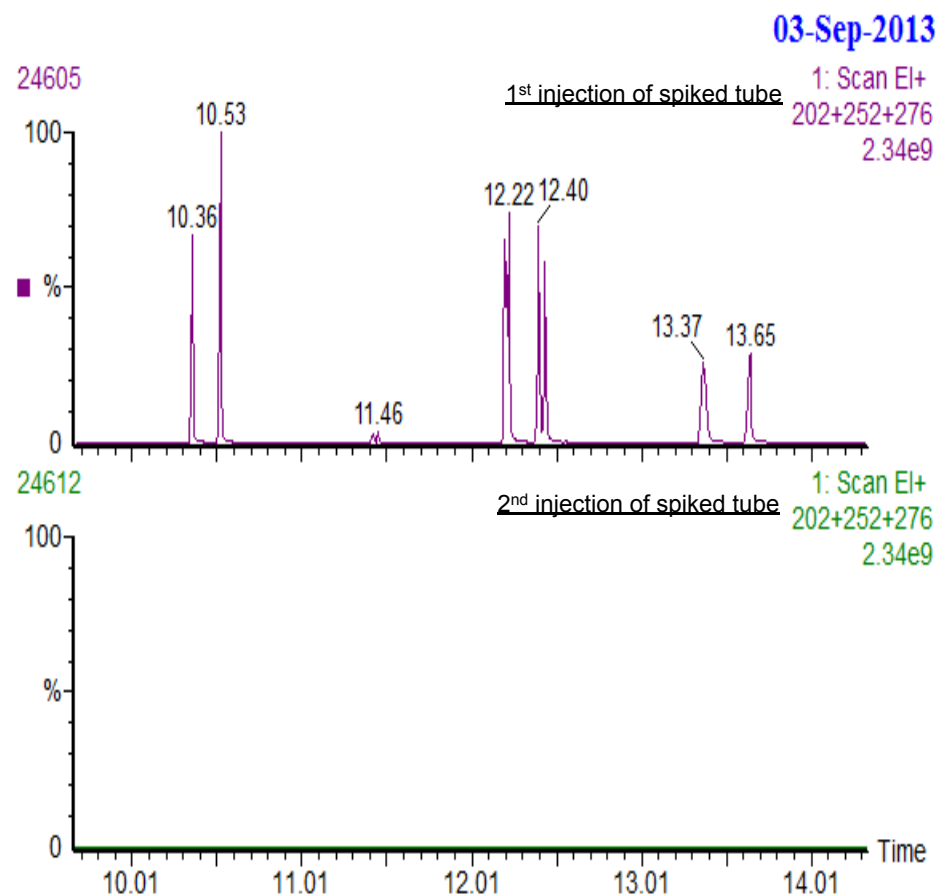
PAH Compounds	% Recovery
1-Methyl Naphthalene	99.7
Anthracene	99.8
Fluorene	99.4
Phenanthrene	98.8



Carryover and Recovery: XRO-440 Tube

- ▶ Carryover Experiment
 - 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



TurboMatrix ATD

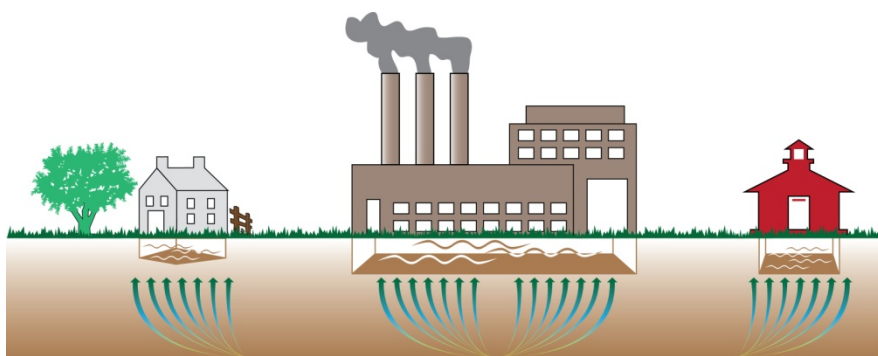
Clarus SQ8 GC/MS



Site Study

TO-17 data was collected in
simultaneous Full Scan/SIM mode
only Full Scan data is presented

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 $\mu\text{g}/\text{m}^3$)

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)

Component	Reporting Limit (RL)	001B	004B	022B	002B	009B	016B
Naphthalene	0.30	1.39	1.52	0.81	0.453	0.414	1.1
2-Methylnaphthalene	0.30	0.818	0.253	0.189	0.247	0.129	1.2
1-Methylnaphthalene	0.30	0.415	0.146	0.116	0.14	0.117	0.631
Acenaphthylene	0.30	0.0682	0.0338	0.0458	0.043	0.0232	0.114
Acenaphthene	0.30	0.0527	0.0178	0.0246	0.015	0.00897	0
Fluorene	0.30	0.0542	0.0162	0.0455	0.0427	0.0312	0.051
Phenanthrene	0.30	0.212	0.174	0.214	0.211	0.247	0.546
Anthracene	0.30	0.063	0.0416	0.049	0.0455	0.0619	0.0933
Fluoranthene	0.30	0.079	0.0873	0.0892	0.116	0.136	0.128
Pyrene	0.30	0.0976	0.05	0.0558	0.0638	0.0576	0.057
Benzo(a)anthracene	0.30	0.165	0.0465	0.0729	0.0935	0.109	0.103
Chrysene	0.30	0.108	0.0623	0.0768	0.0833	0.0682	0.0576
Benzo(b)fluoranthene	0.30	0.568	0.547	0.179	0.45	0.435	0.356
Benzo(k)fluoranthene	0.30	0.426	0.413	0.164	0.371	0.25	0.13
Benzo(e)pyrene	0.30	0.193	0.148	nd	0.23	0.229	0.195
Perylene	0.30	nd	0.4	nd	nd	nd	nd
Benzo(a)pyrene	0.30	0.247	nd	nd	nd	nd	nd
Ideno(1,2,3-cd)pyrene	0.30	nd	nd	nd	nd	nd	nd
Dibenz(a,h)anthracene	0.30	nd	nd	nd	nd	nd	nd
Benzo(g,h,i)perylene	0.30	nd	nd	nd	nd	nd	nd

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

Site: Manufactured Gas Plant (MGP): TO-15 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

Indiana Site: TO-17 (SVI vs XRO-440 Tubes)

Sample			VP - 105		VP - 106		VP - 111		VP - 114		VP - 115	
Compound	SVI RL (ng)	XRO-440 RL (ng)	SVI	XRO - 440	SVI	XRO - 440	SVI	XRO - 440	SVI	XRO - 440	SVI	XRO - 440
Naphthalene	5.0	0.30	2.04	0.999	2.16	1.87	2.25	2.1	2.15	1.1	8.46	6.55
2-Methylnaphthalene	2.0	0.30	1.72	0.439	1.37	1.32	0.612	0.71	0.474	0.742	20.9	20
1-Methylnaphthalene	2.0	0.30	1.11	0.262	1.08	0.78	0.604	0.49	0.38	0.714	12.8	13
Acenaphthylene	2.0	0.30	0.0278	0.0381	0.0327	0.0828	0.0238	0.0514	0.0776	0.0932	1.86	0.704
Acenaphthene	2.0	0.30	0	0.051	0.186	0.118	0.136	0.0382	0.101	0.0465	1.2	0.947
Fluorene	2.0	0.30	0.28	0.0678	0.281	0.106	0.213	0.0676	0.172	0.043	0.795	0.416
Phenanthrene	2.0	0.30	0.249	0.196	0.242	0.347	0.255	0.237	0.179	0.147	0.42	0.358
Anthracene	nd	0.30	nd	nd	nd	0.0622	nd	nd	nd	nd	nd	0.136
Fluoranthene	nd	0.30	nd	0.0576	nd	0.0591	nd	0.0579	nd	0.0539	nd	0.0363
Pyrene	nd	0.30	nd	0.162	nd	0.161	nd	0.15	nd	0.101	nd	0.173
Benzo(a)anthracene	nd	0.30	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Chrysene	nd	0.30	nd	nd	nd	nd	nd	nd	nd	0.0386	nd	nd
Benzo(b)fluoranthene	nd	0.30	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Benzo(k)fluoranthene	nd	0.30	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Benzo(e)pyrene	nd	0.30	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Perylene	nd	0.30	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Benzo(a)pyrene	nd	0.30	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Ideno(1,2,3-cd)pyrene	nd	0.30	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Dibenz(a,h)anthracene	nd	0.30	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Benzo(g,h,i)perylene	nd	0.30	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd

... five (5) samples of 18 are shown. All had similar results

- ▶ Analytical performance proves concept
 - Site data suggests targets are being missed using TO-15
 - Aromatics above boiling point of phenanthrene are present in soil gas

Acknowledgments



- ▶ **Pace Analytical Services**
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Thank you

The Analytical Solution for Air Monitoring



Thank You !

Questions please ????

Tom Mancuso, Product Specialist, PerkinElmer
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Roberta Provost, *Air Method Development Specialist*
Pace Analytical Services