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Single Analysis of Volatile and Semi-Volatile Organics in Air. The Cost Effective Green Solution

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Outline

- Introduction
- Industry Problem/Solution
  - Combining a two analysis solution into one analysis
- EPA Method TO-17 and Thermal Desorption
- Analytical Data and Performance
- Results from Site Sampling (MGP site)
- Air Monitoring Study Summary

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
  - Thank you to CARO Analytical Services for their help
- 2011: XRO-640 (patent pending)
  - (C_6 to C_{44})
  - Residue in Liquefied Petroleum Gas (LPG)
  - Combines VOC & SVOC from BTEX to benzo(g,h,i)perylene
  - Thank you to Alberta Innovates Tech Futures for their help
- 2013: XRO–440 (patent pending)
  - (C_4 to C_{44})
  - Combines VOC & SVOC from 1,3-butadiene to benzo(g,h,i)perylene
  - Thank you to Pace Analytical Services for their help

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Success

Move from a Two Analysis

to One Analysis

The cost effective,

environmentally friendly

Approach

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

PM10 (particulates)

TO-15 (VOCs)

TO-13 (PAHs)

Why the XRO-440 Tube was Designed?

- 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

Only Four Canisters to a Box …. YIKES

… can fit over 500 Tubes!

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The TO-17 Solution for the Analysis of VOCs and SVOCs in air

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

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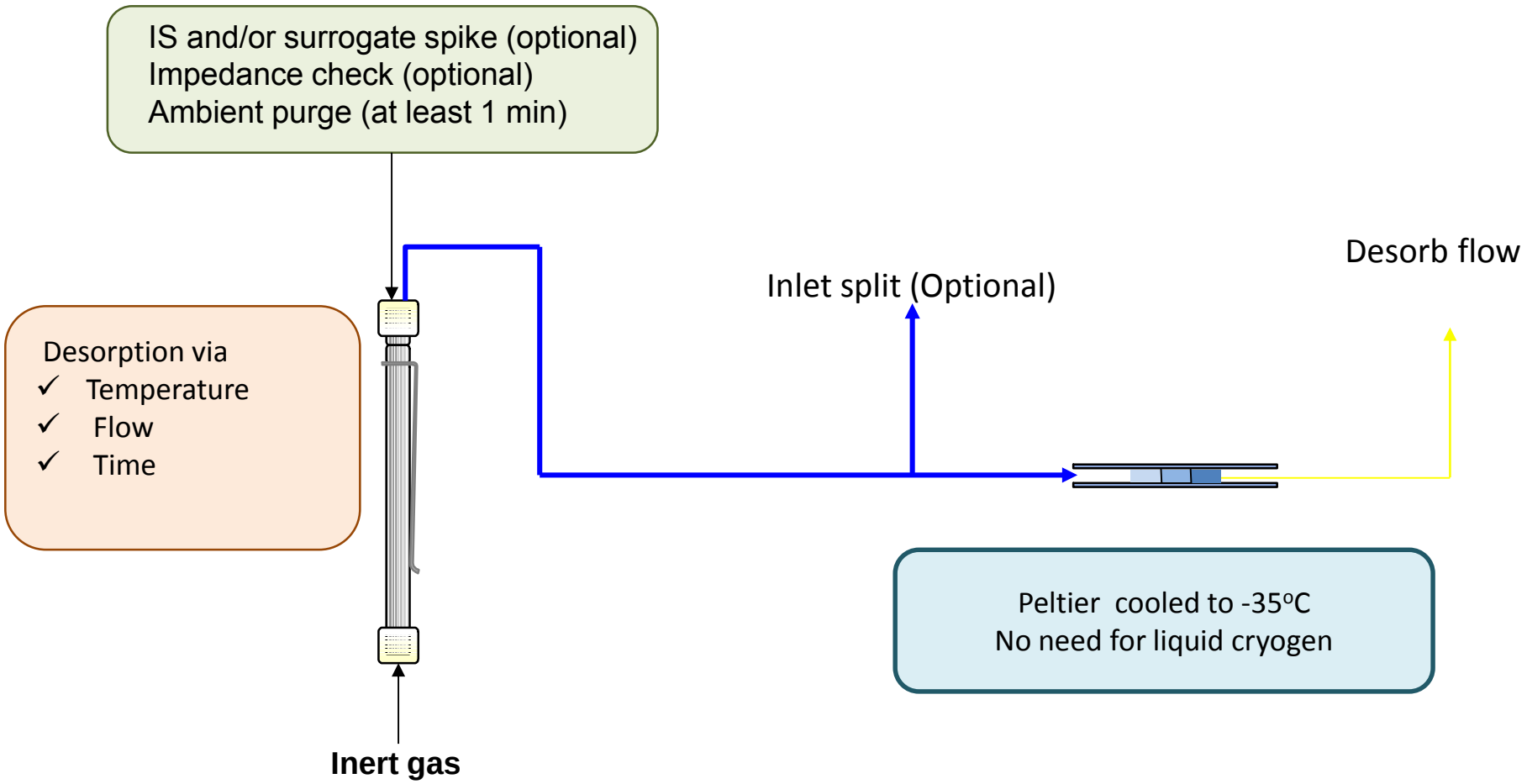
Operation

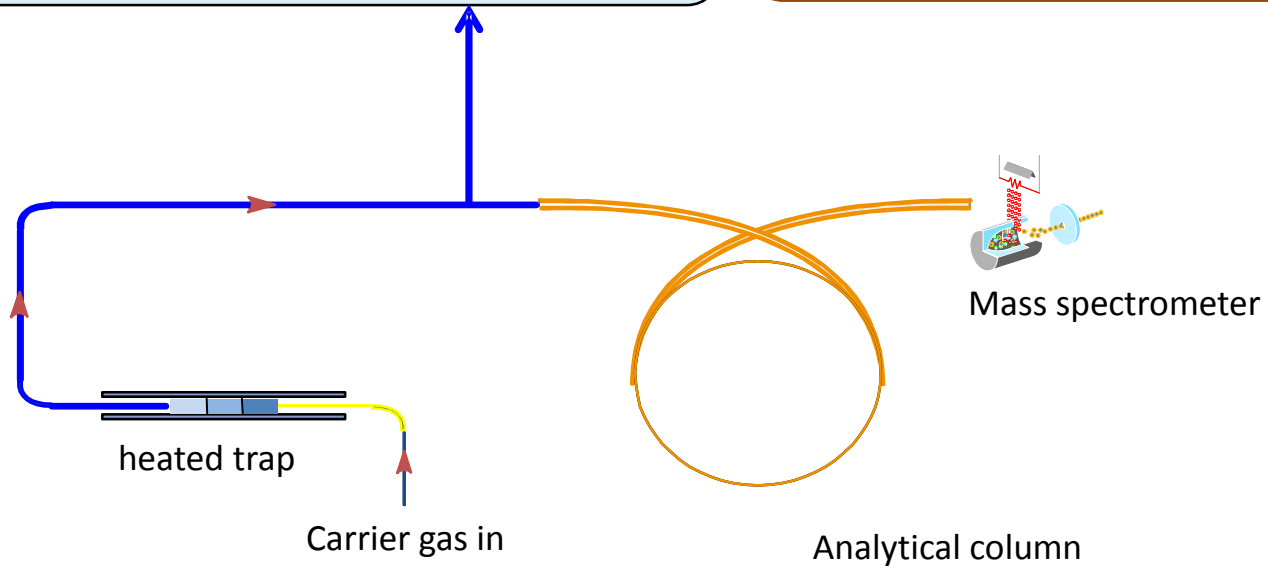
Step 1: Sample Tube (Primary) Desorption



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%



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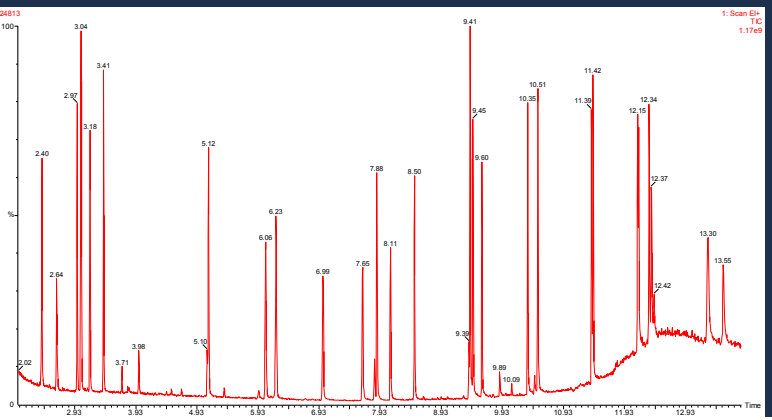
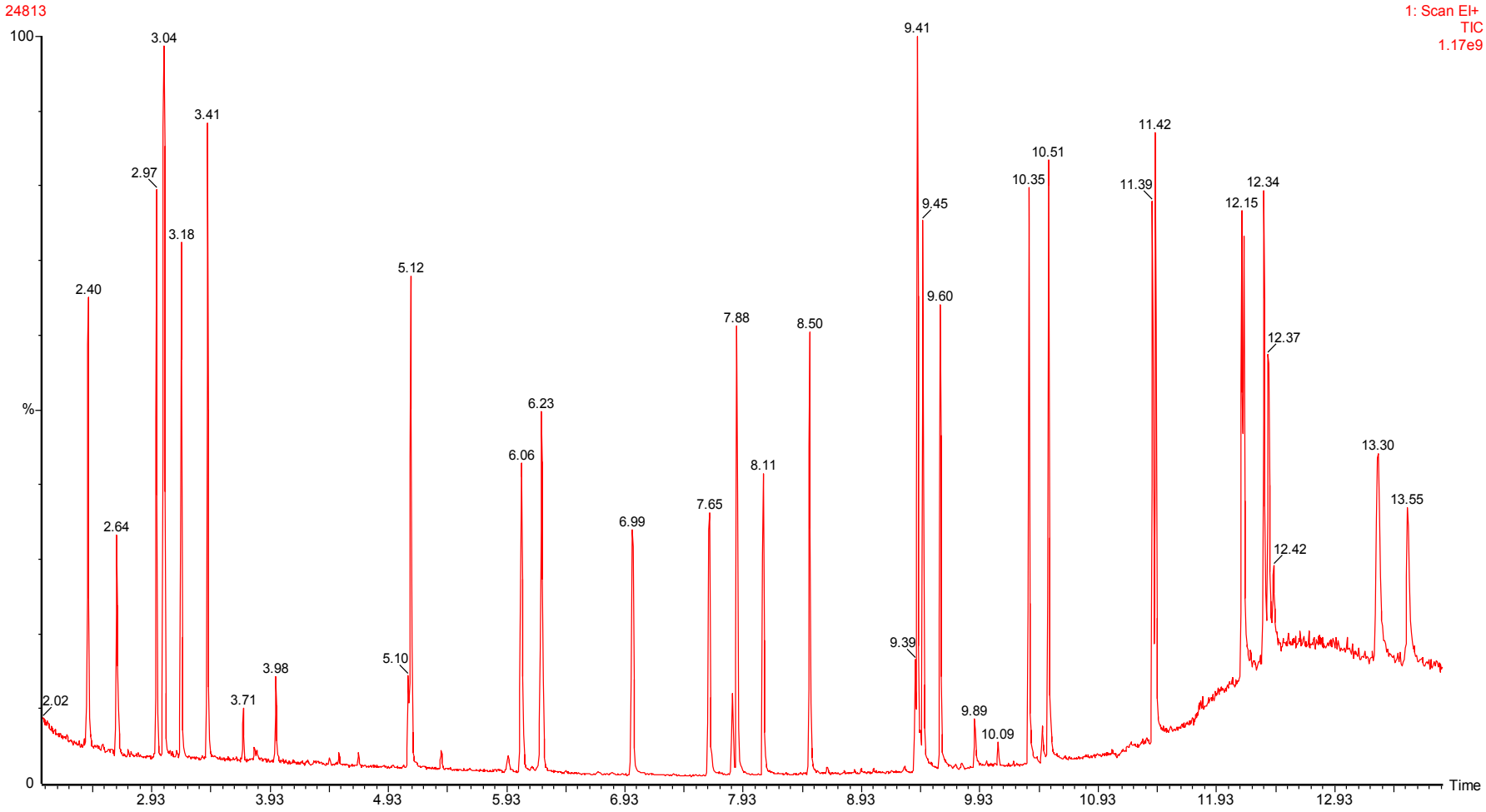


Analytical Performance

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

Total Ion Chromatogram (TIC)

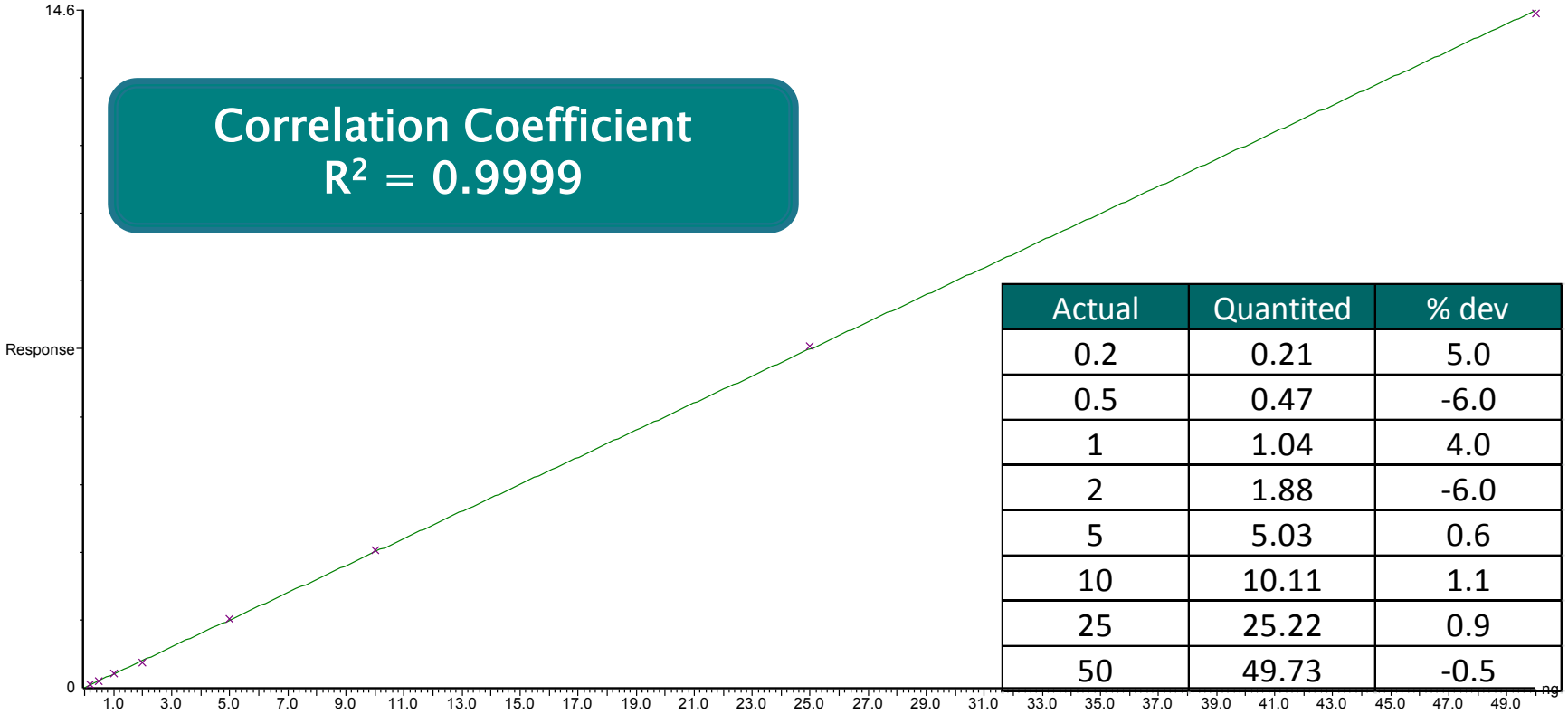


Calibration, Precision and Reporting Limits

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

o-Xylene

Compound 12 name: o - Xylene
Coefficient of Determination: 0.999930
Calibration curve: 0.292679 * 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

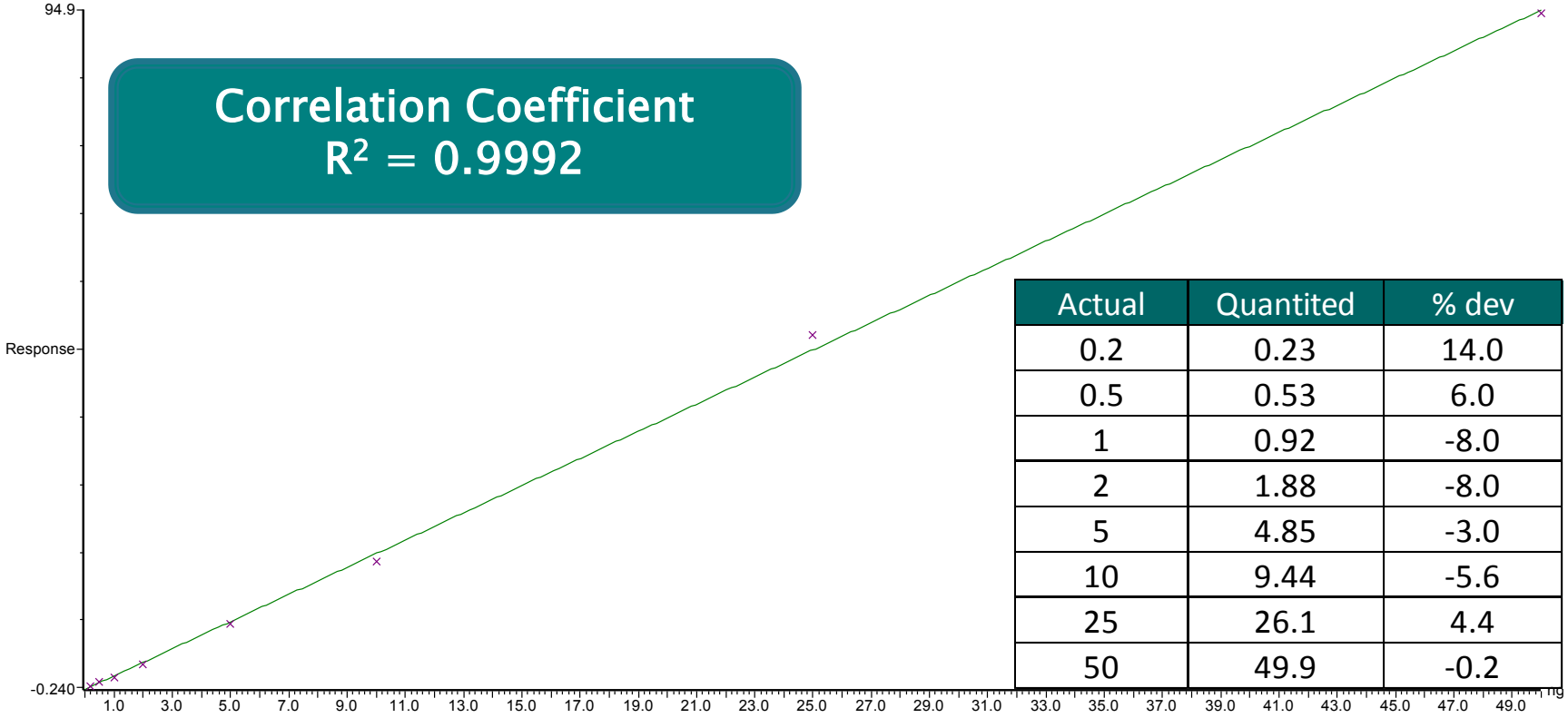


Correlation Coefficient
$R^2 = 0.9999$

Actual	Quantited	% dev
0.2	0.21	5.0
0.5	0.47	-6.0
1	1.04	4.0
2	1.88	-6.0
5	5.03	0.6
10	10.11	1.1
25	25.22	0.9
50	49.73	-0.5

Pyrene

Compound 22 name: Pyrene
Coefficient of Determination: 0.999243
Calibration curve: 1.90286 * 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



Correlation Coefficient
$R^2 = 0.9992$

Actual	Quantited	% dev
0.2	0.23	14.0
0.5	0.53	6.0
1	0.92	-8.0
2	1.88	-8.0
5	4.85	-3.0
10	9.44	-5.6
25	26.1	4.4
50	49.9	-0.2

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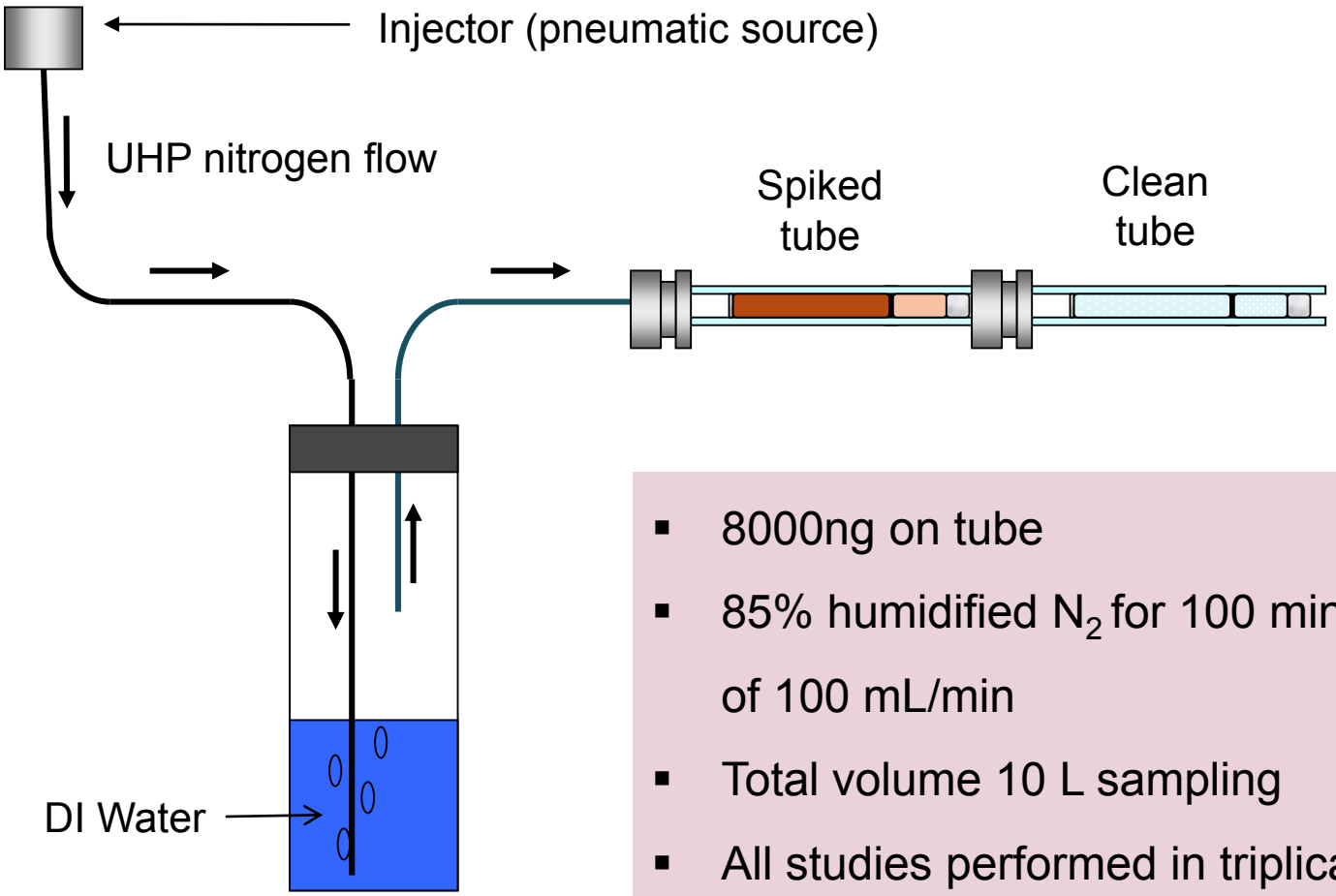
Breakthrough and Recovery

Experiments and Results

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”

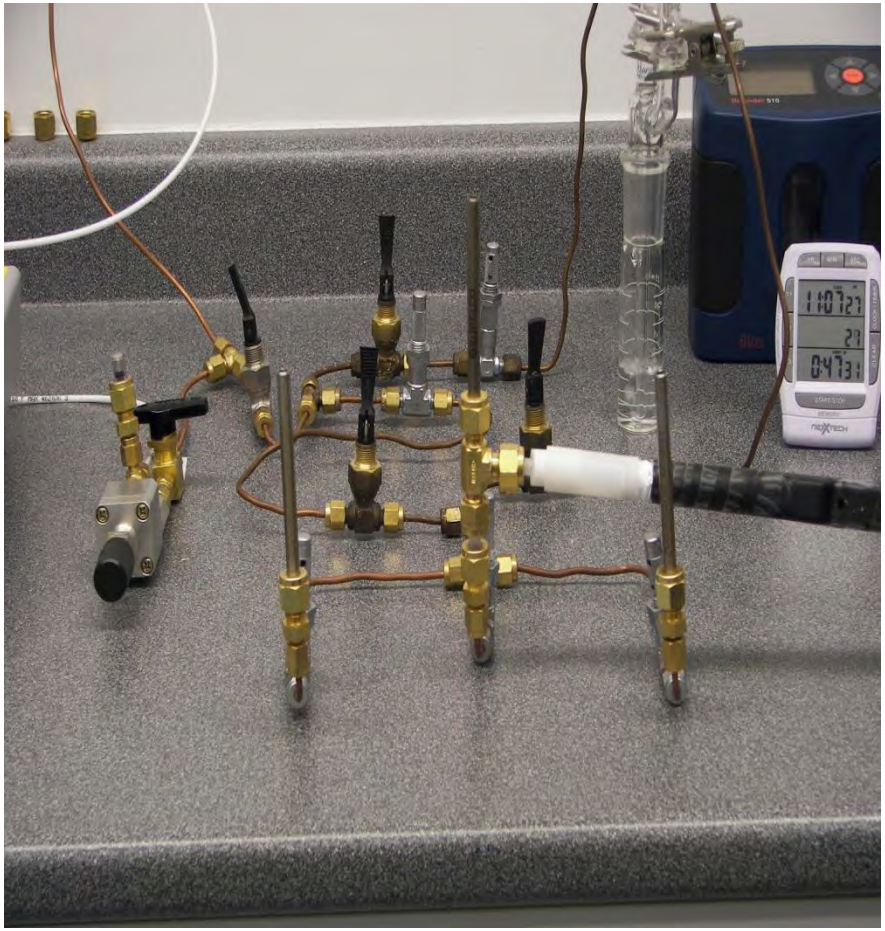
First Breakthrough Experiments



- 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

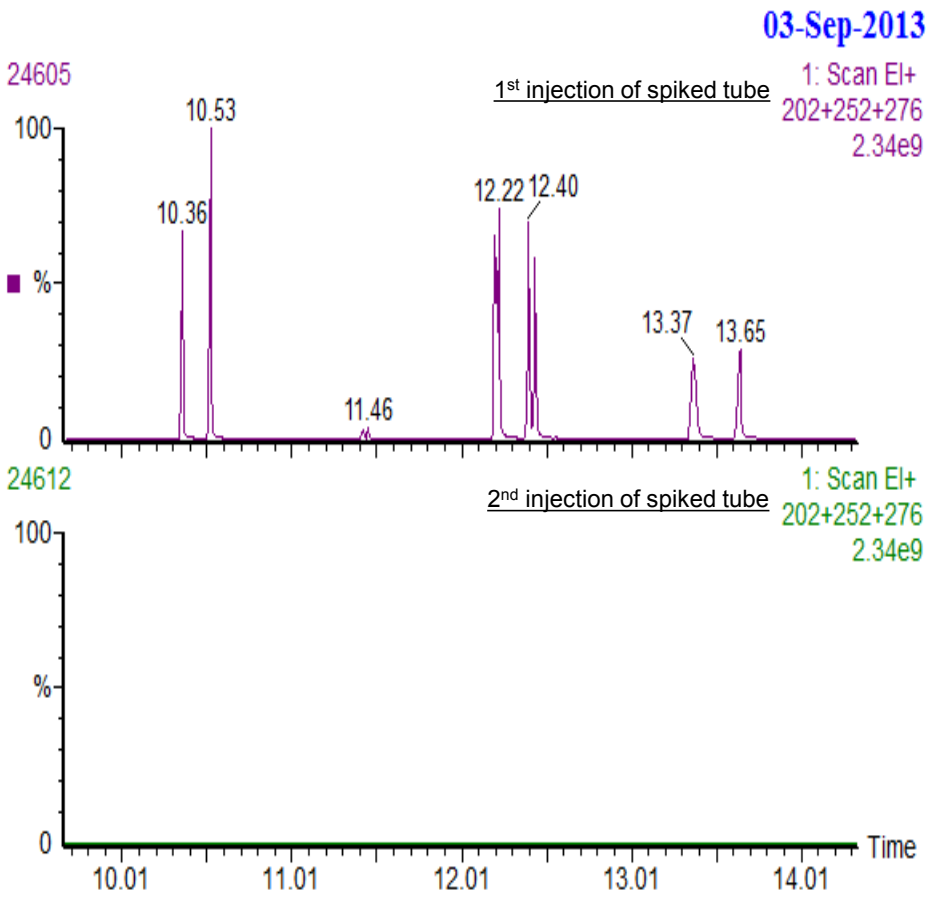


non-detectable breakthrough on all compounds first target 1,3-butadiene

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



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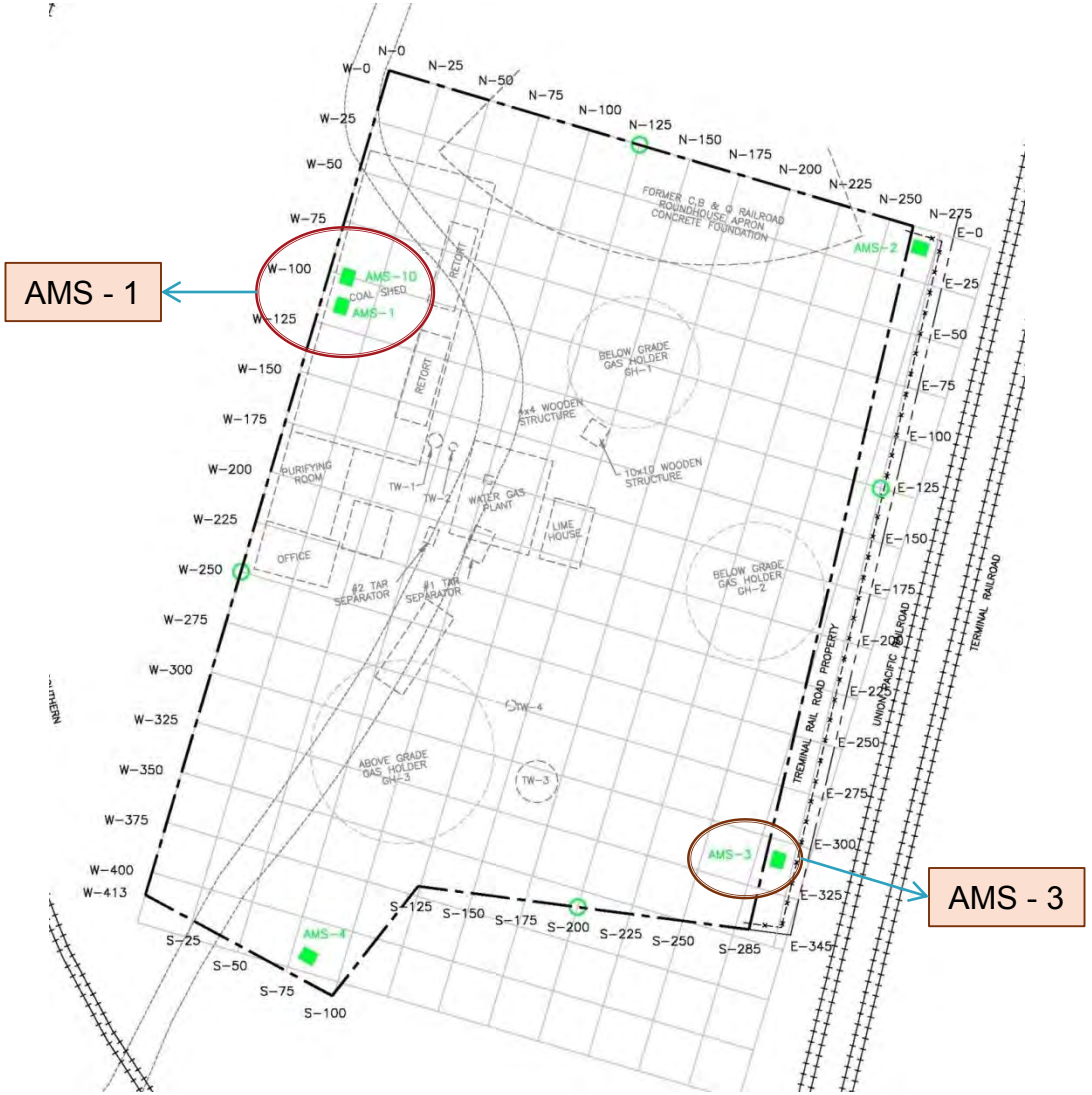
Site Study, 2012-2013

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

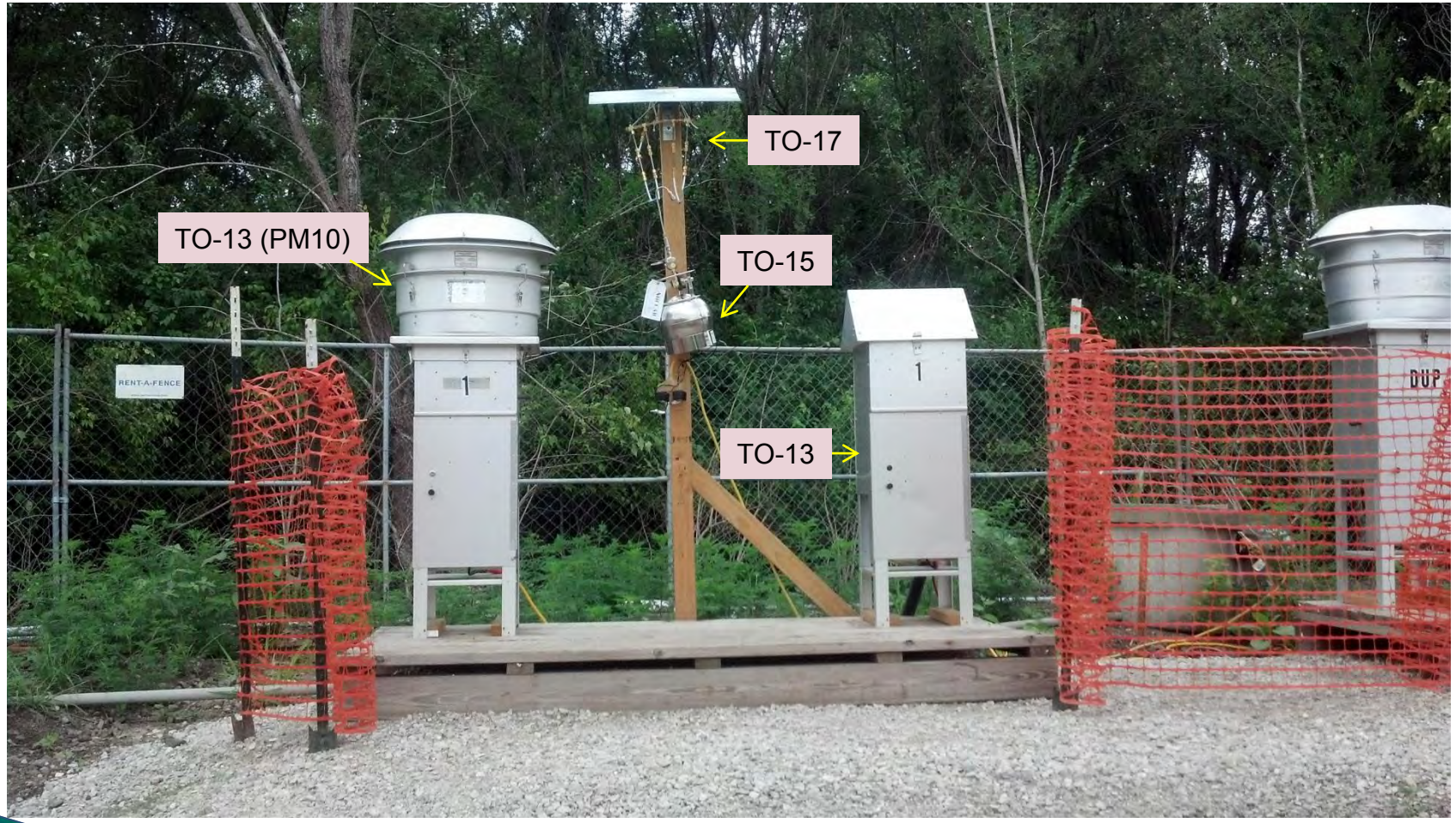
Air Monitoring Study Parameters

- Compare TO-13 / TO-15 to TO-17 from an active MGP remediation site
- 72-hour sample collection
- Continuous sampling for six weeks
- One sample location selected (AMS-03)
- Three 72-hour samples from each site were selected for comparison
- 14 sampling sets

Site Map


AMS - 1
AMS - 3
AMS-10
COAL SHED
AMS-1
AMS-2
AMS-3
AMS-4
RETORT
RETORT
FORMER C.B. & Q. RAILROAD ROUNDHOUSE APRON CONCRETE FOUNDATION
BELOW GRADE GAS HOLDER GH-1
4x4 WOODEN STRUCTURE
10x10 WOODEN STRUCTURE
PURIFYING ROOM
TW-1
TW-2
WATER GAS PLANT
LIME HOUSE
OFFICE
#2 TAR SEPARATOR
#1 TAR SEPARATOR
BELOW GRADE GAS HOLDER GH-2
TW-4
ABOVE GRADE GAS HOLDER GH-3
TW-3
TERMINAL RAIL ROAD PROPERTY
UNION PACIFIC RAILROAD
TERMINAL RAILROAD
N-0
N-25
N-50
N-75
N-100
N-125
N-150
N-175
N-200
N-225
N-250
N-275
E-0
E-25
E-50
E-75
E-100
E-125
E-150
E-175
E-200
E-225
E-250
E-275
E-300
E-325
E-345
W-0
W-25
W-50
W-75
W-100
W-125
W-150
W-175
W-200
W-225
W-250
W-275
W-300
W-325
W-350
W-375
W-400
W-413
S-25
S-50
S-75
S-100
S-125
S-150
S-175
S-200
S-225
S-250
S-285

Site Setup



TO-17 Site Study expanded view

- Two types of tubes investigated (XRO-440 and XRO-640)
- Each type of tube was sampled in duplicate
- One of the duplicates had filter attached and analyzed
- A breakthrough tube was attached to every tube sampled

Sample Volumes

72 Hour Sampling Duration

- TO-13 = ~1,000,000 Liters (1000 m^3)
- TO-15 = 6 Liters
- TO-17 = ~45 Liters

Moisture: Hydrophobic adsorbents

Tube	Time for Dry Purge
Sample Tube Type 1	nd added moisture on tube
Sample Tube Type 2	2 minute Dry Purge

Only slight water retention with 45L sample volume!

Breakthrough Results from Site Studies

- There was non-detectable targets on the breakthrough tubes from the site studies with an average of 45 liter sample volume

Duplicates from Site Study

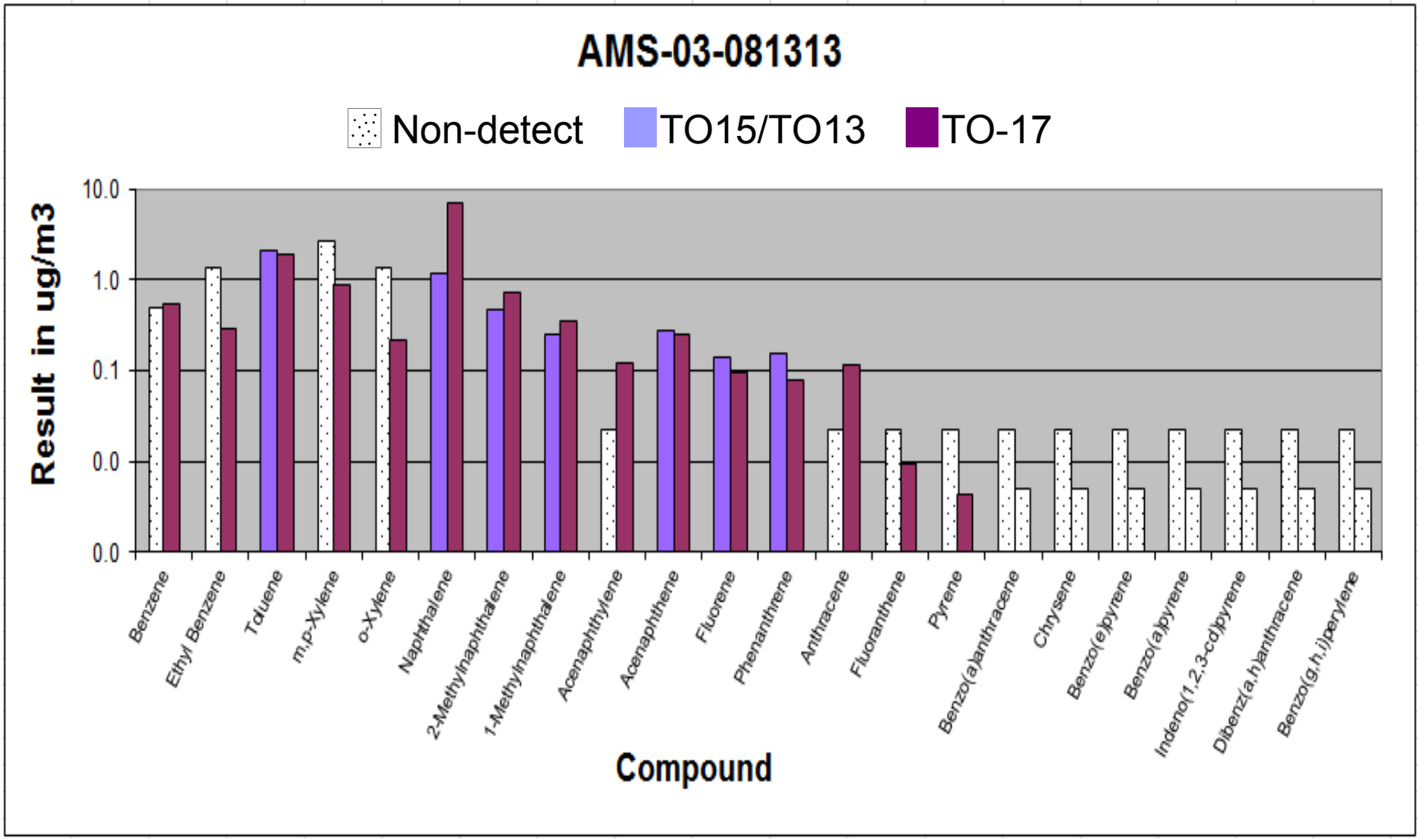
Target Analyte	ug/m3 (first tube)	ug/m3 (second tube)	equates to ng on tube	% relative dif
1,3-Butadiene	0.0193	0.0200	0.87	3.6
Benzene	0.3827	0.4090	17.2	6.6
Toluene	1.3329	9.7246	60.0	152
Ethyl Benzene	0.1543	0.2136	6.94	32.2
m & p - Xylenes	0.4413	0.6081	19.9	31.8
o - Xylene	0.1434	0.1586	6.45	10.1
Naphthalene	3.1182	3.4084	140	8.9
2-Methylnaphthalene	0.6185	0.6083	27.8	1.7
1-Methylnaphthalene	0.2647	0.3138	11.9	17.0
Acenaphthylene	0.0656	0.0492	2.95	28.6
Acenaphthene	0.3022	0.2660	13.6	12.8
Fluorene	0.1238	0.1768	5.57	35.3
Phenanthrene	0.0547	0.0931	2.46	52.0
Anthracene	0.0803	0.0915	3.61	13.1
Fluroanthene	0.0040	0.0050	0.18	21.7
Pyrene	0.0032	0.0050	0.14	45.4
Benzo[a]anthracene	0.0067	0.0054	0.30	21.0
Chrysene	0.0046	0.0033	0.21	32.7
Benzo[b&k]fluoranthene	0.0044	nd	0.20	
Benzo[e]pyrene	0.0044	nd	0.20	
Benzo[a]pyrene	0.0074	nd	0.33	
Indeno[1,2,3-c,d]pyrene	nd	nd		
Dibenz[a,h]anthracene	nd	nd		
Benzo[g,h,i]perylene	nd	nd		

Results from Study: AMS-03

Sample ID	AMS-03-081313		AMS-03-081613		AMS-03-082213	
Analyte	TO13 & TO15	TO17	TO13 & 15	TO17	TO13 & 15	TO17
Benzene	0.52	0.54	1.20	0.56	1.2	0.48
Ethyl Benzene	1.4	0.29	1.4	0.29	3.2	0.78
Toluene	2	1.9	1.6	1.1	4.4	0.86
m,p-Xylene	2.8	0.87	2.8	0.83	6.5	0.91
o-Xylene	1.4	0.22	1.4	0.24	3.2	0.26
Naphthalene (TO15)	3.2	6.9	3.3	1.1	3.9	2.4
Naphthalene (TO13)	1.2	6.9	0.95	1.3	0.18	2.4
2-Methylnaphthalene	0.48	0.74	0.51	0.41	0.10	0.67
1-Methylnaphthalene	0.25	0.36	0.26	0.25	0.088	1.2
Acenaphthylene	0.023	0.12	0.0094	0.047	0.17	0.40
Acenaphthene	0.27	0.25	0.30	0.21	0.17	1.7
Fluorene	0.14	0.10	0.17	0.081	0.13	0.45
Phenanthrene	0.16	0.077	0.17	0.019	0.24	0.24
Anthracene	0.023	0.11	0.0061	0.0258	0.016	0.36
Fluoranthene	0.023	0.0092	0.017	0.0047	0.13	0.013
Pyrene	0.023	0.0043	0.0088	0.0047	0.027	0.0018
Benzo(a)anthracene	0.023	0.0051	0.0011	0.0047	0.00074	0.00029
Chrysene	0.023	0.0051	0.0016	0.0047	0.0014	0.0046
Benzo(b+k)fluoranthene	0.046	0.010	0.0027	0.0094	0.00091	0.0092
Benzo(e)pyrene	0.023	0.0051	0.0011	0.0047	0.00050	0.0046
Benzo(a)pyrene	0.023	0.0051	0.0010	0.0066	0.00050	0.0046
Indeno(1,2,3-cd)pyrene	0.023	0.0051	0.0009	0.0065	0.00050	0.0046
Dibenz(a,h)anthracene	0.023	0.0051	0.00050	0.0140	0.00050	0.0046
Benzo(g,h,i)perylene	0.023	0.0051	0.0013	0.0220	0.00050	0.015

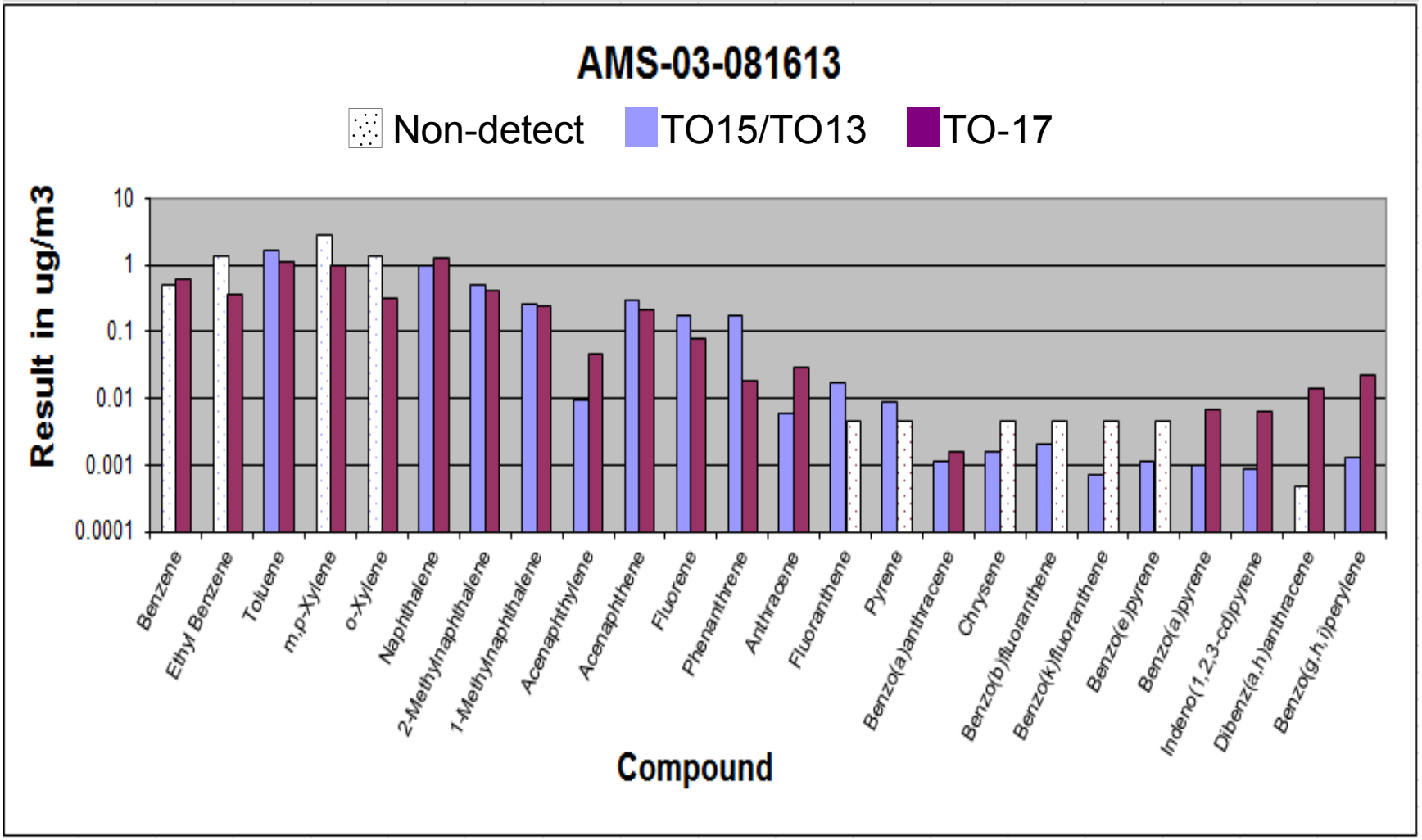
Note: yellow cells are non-detect with the reporting limit value for that target in the cell

Chart for Site AMS-03-081313



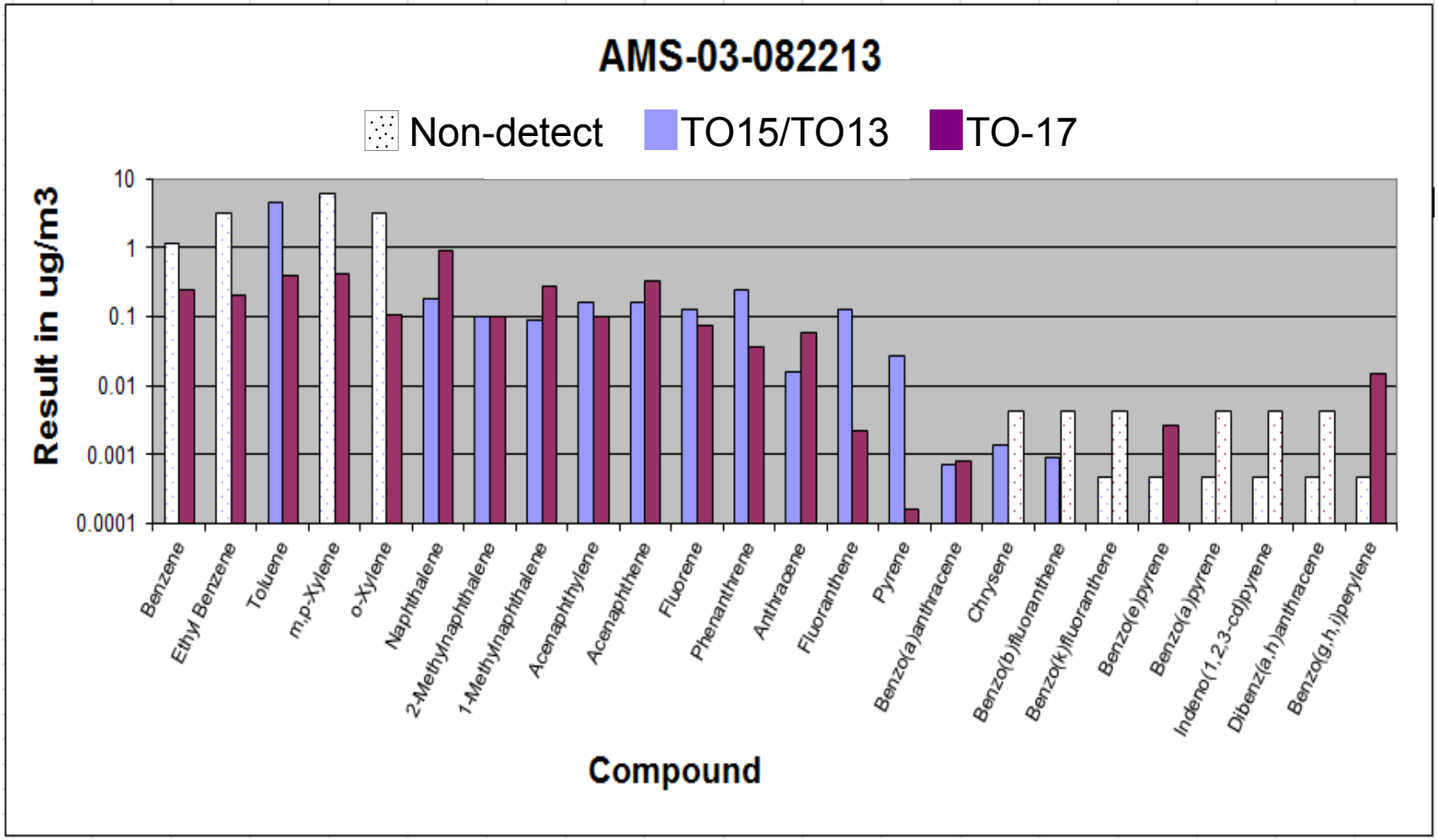
Note: dotted, unfilled bars are non-detects. Value represents reporting limit.

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.

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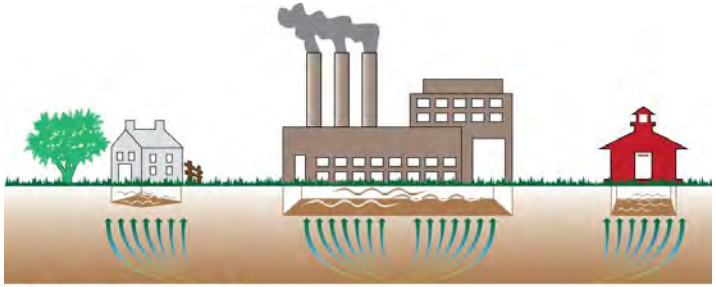
Other Projects and Site Studies

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
Industrial Sub-Slab (IN)	Same site sampling onto SVI tube and XRO-440 tube	1 liter



Soil Vapor Intrusion™ Tubes

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

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

EPA Acceptance for SVOC by TO-17

- 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

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- PerkinElmer Instruments
  - James Day, Sr Service Engineer

The Analytical Solution for Air Monitoring

… efficient, environmentally friendly and cost effective approach

Questions please ????

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