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

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PerkinElmer Instruments

Working Together to Protect Our Environment and Improve Our Health

Outline

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

About Pace Analytical Services

- Pace is the largest, privately owned, full service environmental and analytical testing firm in the Unites States
- Pace provides organic, inorganic, radiochemistry and specialty analytical capabilities that include the analysis of trace level contaminants in air, water, soil, waste and biota.
- Headquarters located in Minneapolis, MN
- The Pace Air Lab has over 2,500 summa canisters in its inventory and supports the remediation, vapor intrusion, landfill gas, and stationary source testing markets

Typical Air Methods Overview

PM10 (particulates)

TO-15 (VOCs)

TO-13 (PAHs)

Goal: one analysis instead of two

- **Eliminate liquid extractions**
  - Save time and money
  - More productive and efficient
  - Enhance recoveries
  - A Greener Analysis

TO - 13

TO - 17

Four Canisters to a box … Yikes!

… can fit over 500 Tubes!

Automated Thermal Desorption/ GC/MS

Modified EPA Method TO-17

to include SVOC

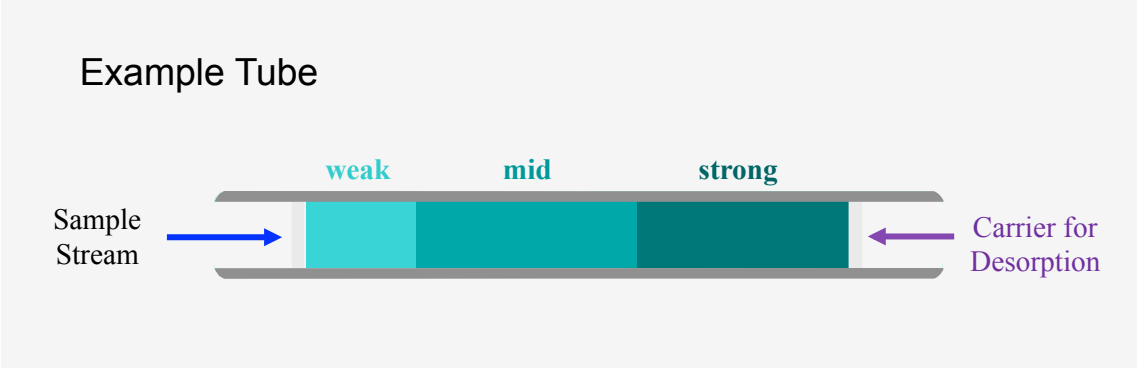
(specifically 16 regulated PAH)

What is Thermal Desorption?

- Thermal desorption (TD) is the process of collection and desorption of analytes from solid sorbents using heat and a flow of inert gas, rather than solvent extraction.
- Analytes are then focused onto a cold trap prior to entering the analytical column, resulting in higher responses and narrow, more symmetric peaks
- TD is highly sensitive and can significantly lower detection limits, by as much as 10^3

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

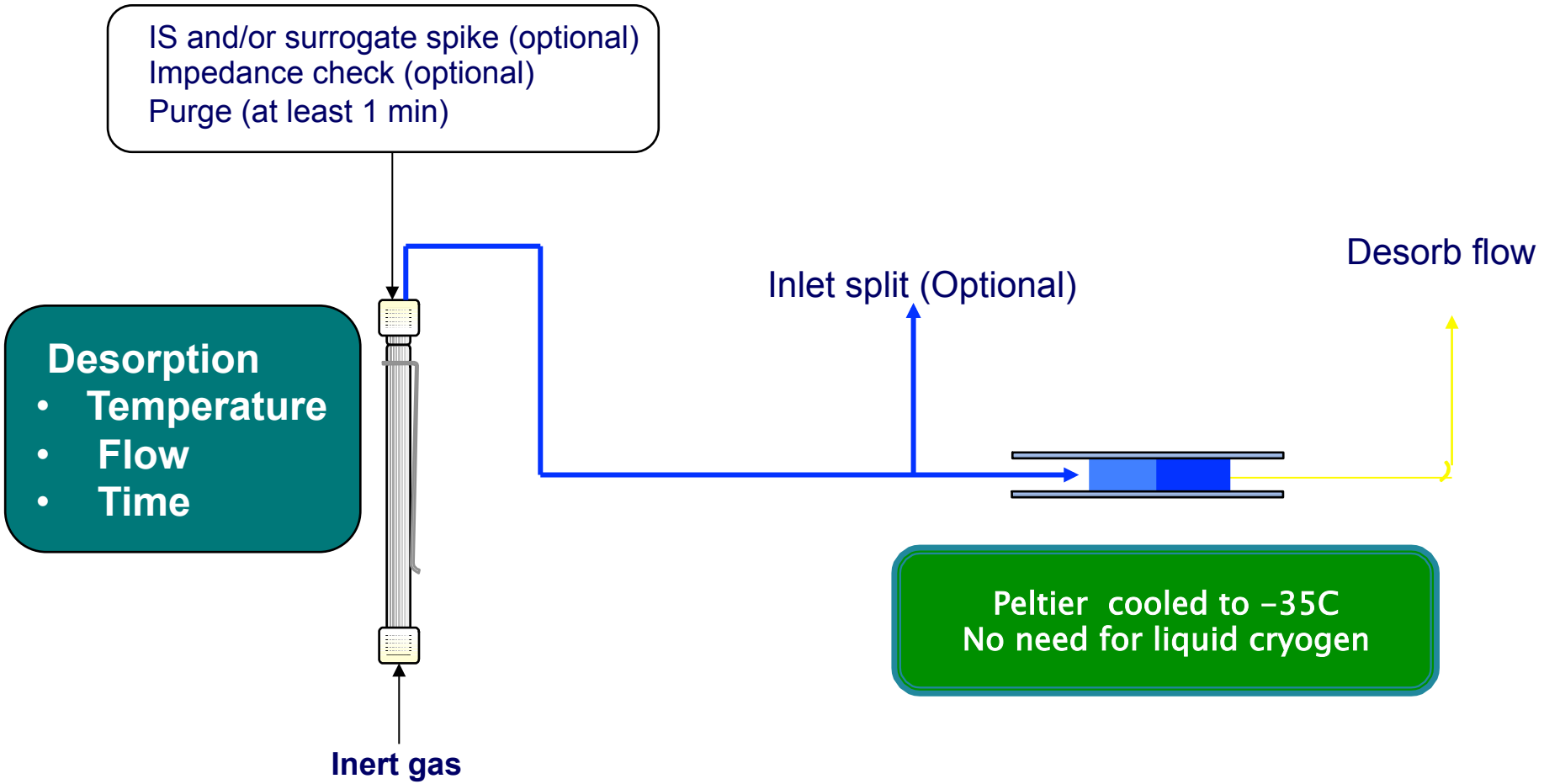


Automated Thermal Desorption

Introduction to Functioning

How it works?

Step 1: Sample Tube (Primary) Desorption

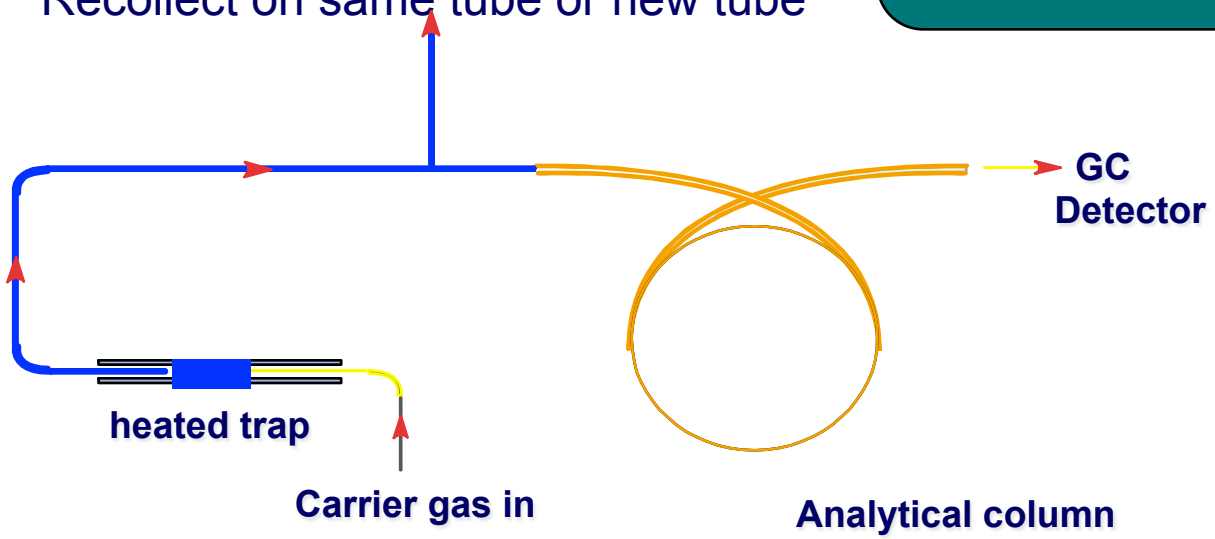


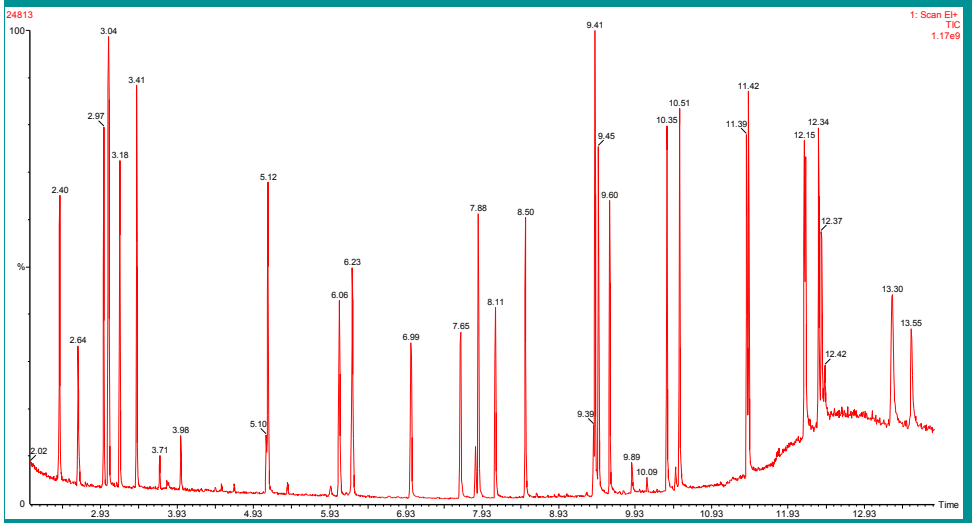
Step 2: Transfer of Sample to Analytical Column

Pace Analytical®

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

Optional 'outlet' split or
Recollect on same tube or new tube



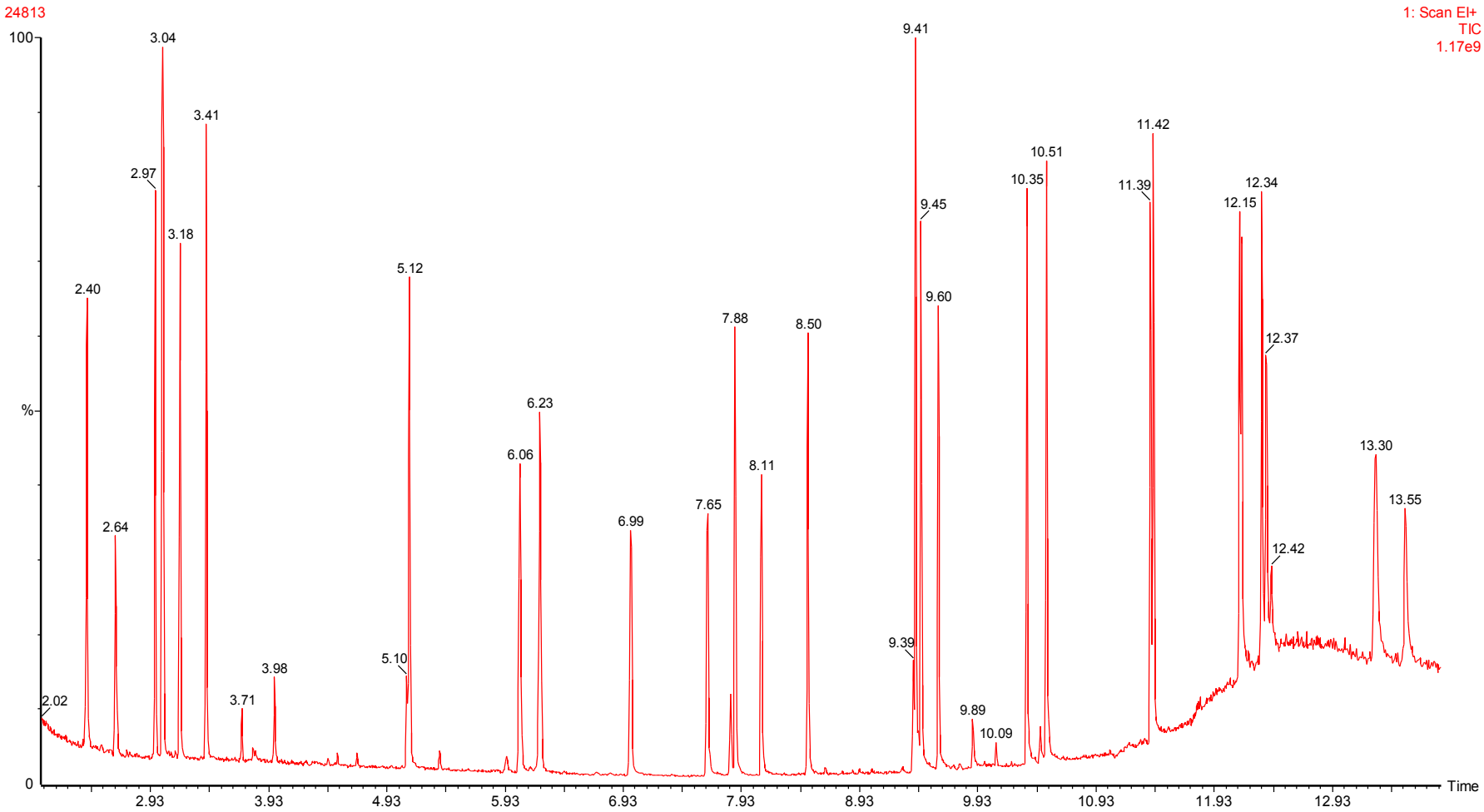


Note: Data was acquired in Simultaneous Full Scan/ SIM Mode. Only results from Full Scan are reported

Results of

Analytical Performance

Total Ion Chromatogram (TIC)

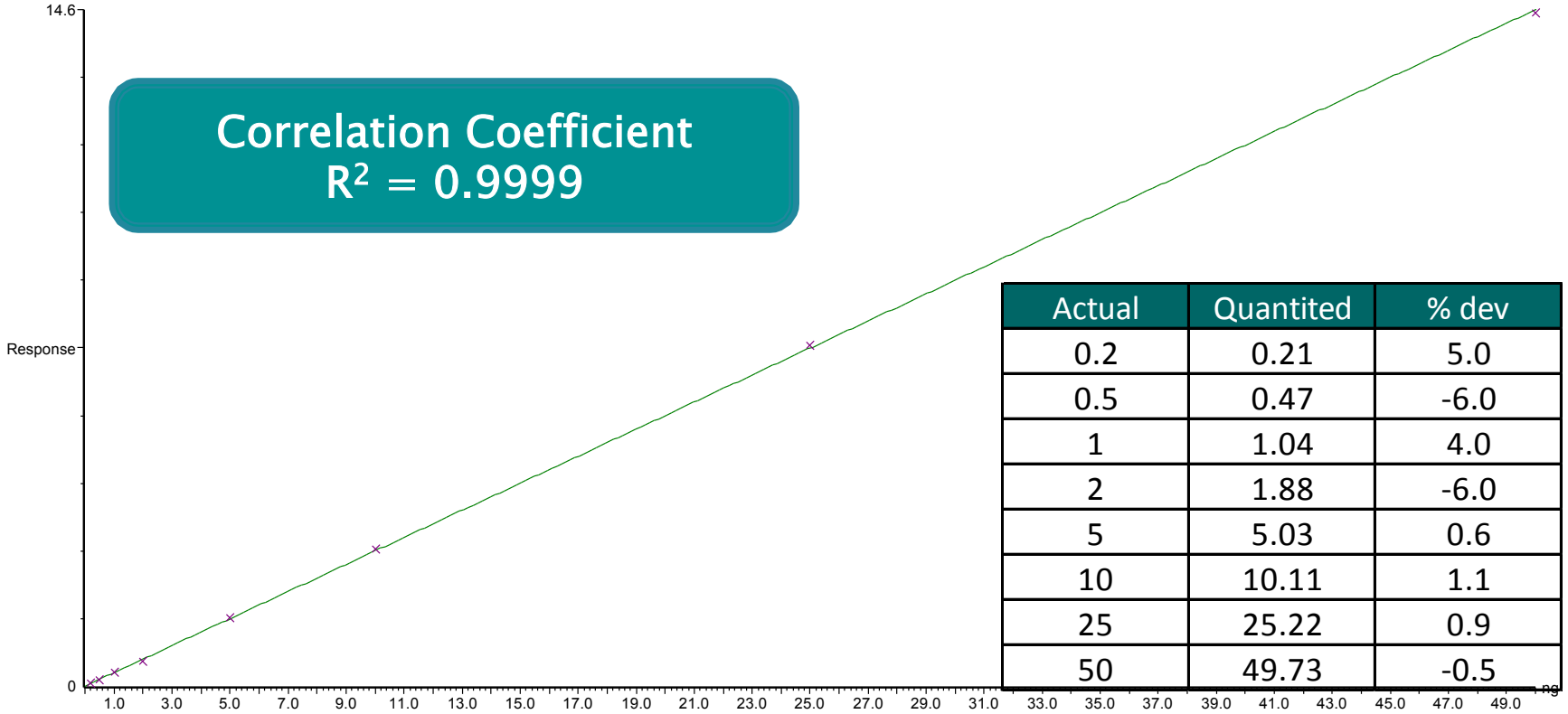


Calibration, Precision and Reporting Limit

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

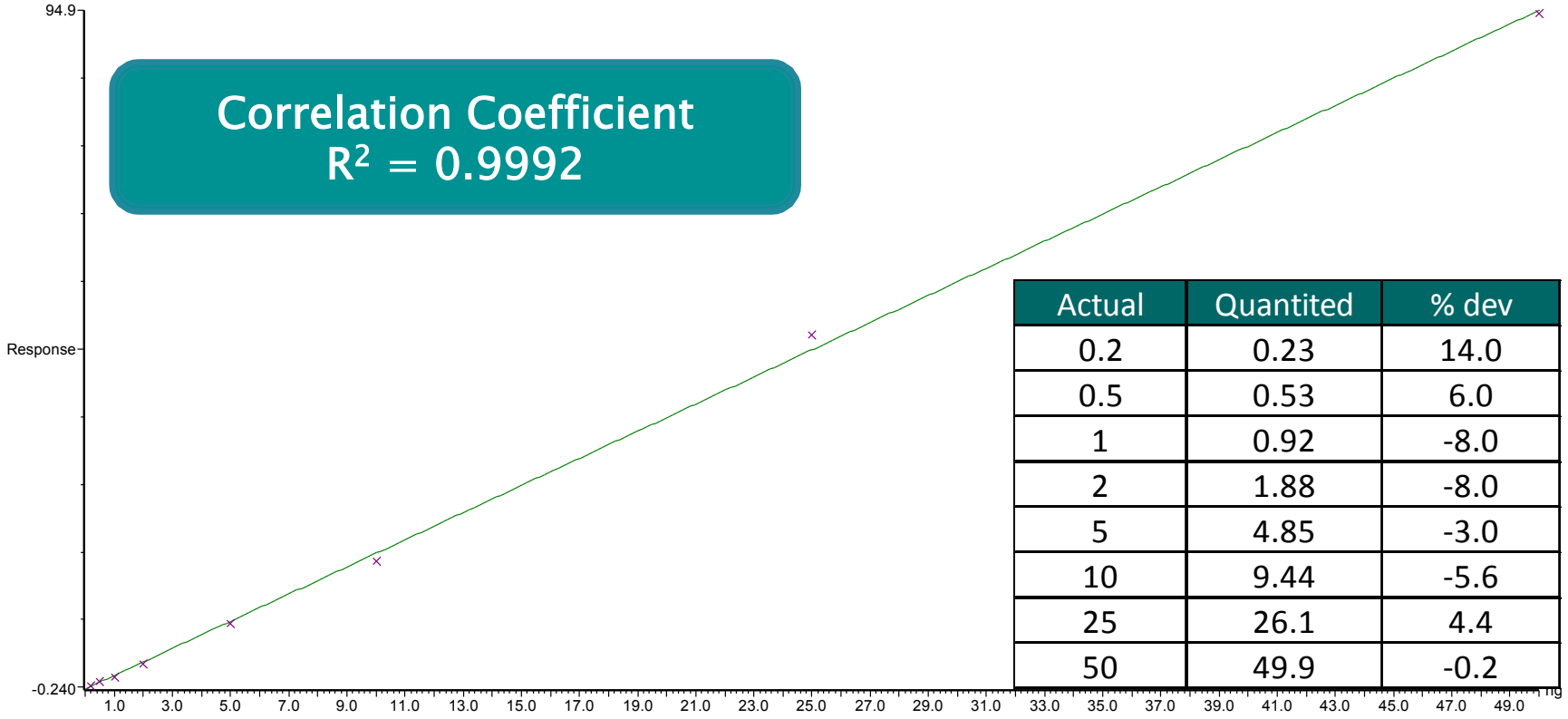


Correlation Coefficient
$R^2 = 0.9999$

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

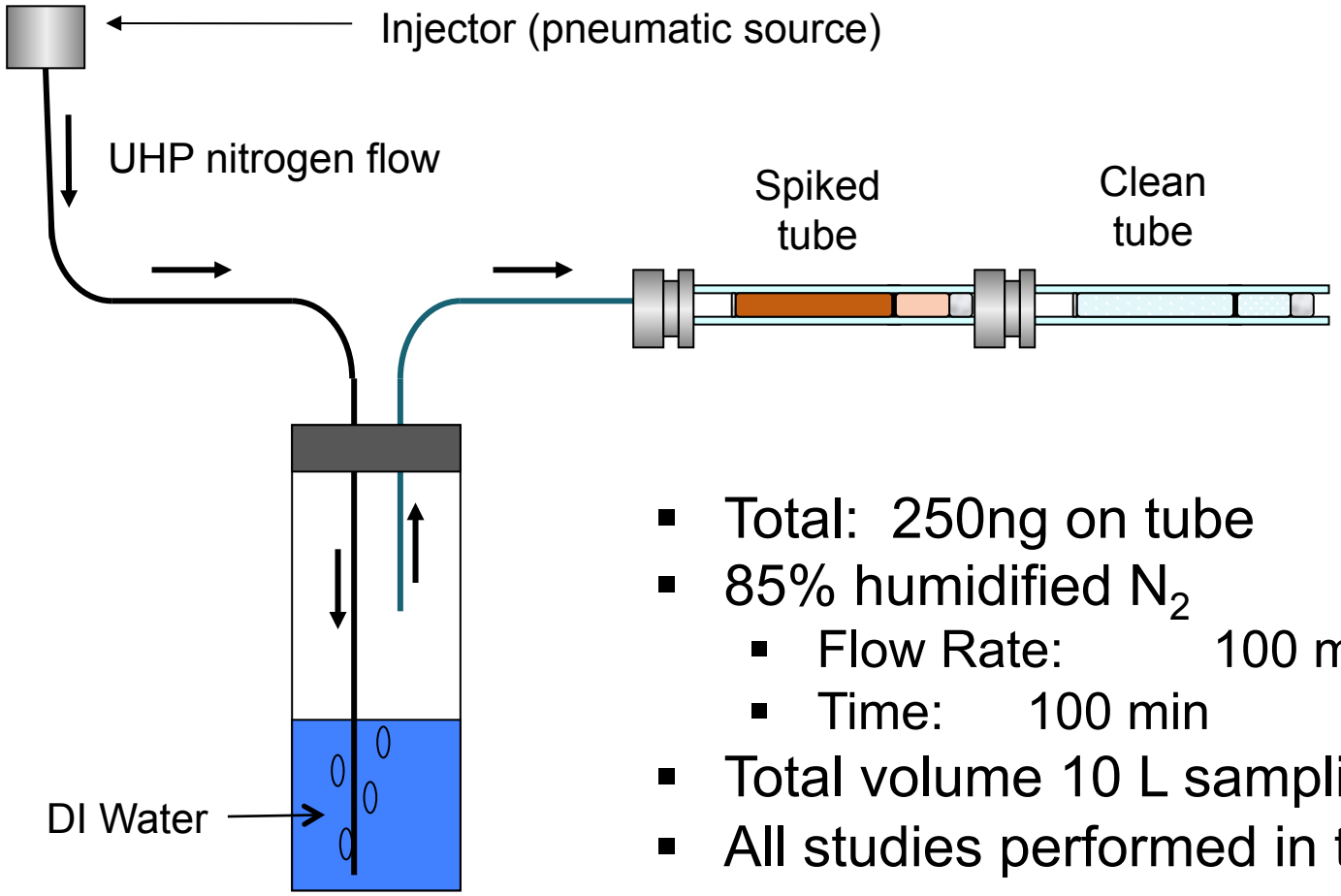
Automated Thermal Desportion

Breakthrough and Recovery Data

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



- Total: 250ng on tube
- 85% humidified N_2
  - Flow Rate: 100 mL/min
  - Time: 100 min
- Total volume 10 L sampling
- All studies performed in triplicate

Results of Laboratory Breakthrough

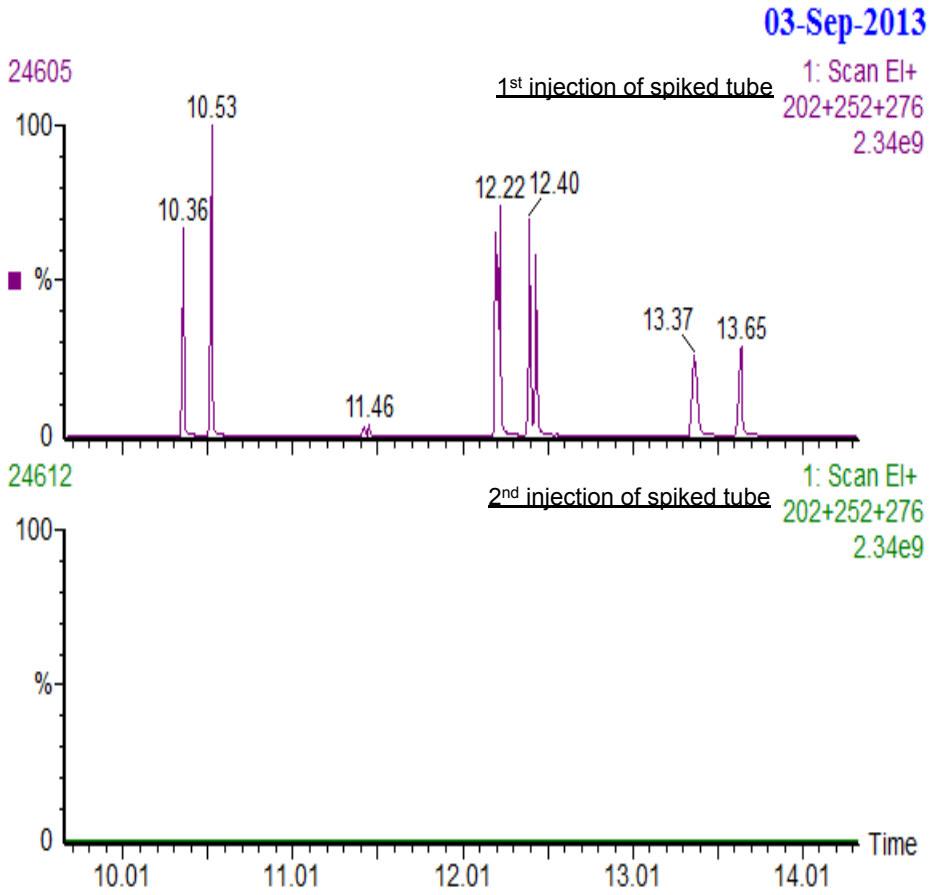
- A primary TD tube was attached to a gaseous standard to continuously deliver target compounds (mimics a real-world sampling event)
- A BT tube was attached and monitored on a regular basis
- Ultimately, the primary tube was loaded with >200mg analyte with no detectable breakthrough

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

Carryover and Recovery

- 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



… Minimal carryover of high boilers

Automated Thermal Desportion

Site Study

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

Air Monitoring Study Parameters

- Compare TO-13, TO-15, and TO-17 results from an active MGP remediation site
- 72-hour sample collection periods over a six week period
- Two sample locations selected (AMS-01 and AMS-03)
- Three 72-hour samples from each site were selected for comparison

Site Map


N–0
N–25
N–50
N–75
N–100
N–125
N–150
N–175
N–200
N–225
N–250
N–275
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
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
S–25
S–50
S–75
S–100
S–125
S–150
S–175
S–200
S–225
S–250
S–285
AMS–1D
COAL SHED
AMS–1
AMS–2
AMS–3
AMS–4
FORMER C.B. & Q. RAILROAD ROUNDHOUSE APRON CONCRETE FOUNDATION
RETORT
RETORT
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

Site Setup

TO-17 PAH Sample Configuration

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

Duplicate Concentrations and On-Tube Values

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 the Study – AMS-01

Sample ID	AMS-01-081313		AMS-01-081613		AMS-01-082213	
Analyte	TO13 & 15	TO17	TO13 & 15	TO17	TO13 & 15	TO17
Benzene	0.68*	0.38	0.50	0.56	1.9	0.75
Ethyl Benzene	1.8	0.15	1.4	0.29	5.1	0.66
Toluene	15	1.3	1.6	1.1	8.3	1.6
m,p-Xylene	3.7	0.44	2.8	0.83	10	1.53
o-Xylene	1.80	0.14	1.4	0.24	5.1	0.47
Naphthalene (TO15)	1.4	3.1	2.9	1.1	6.2	1.10
Naphthalene (TO13)	0.68	3.1	0.68	1.1	0.082	1.10
2-Methylnaphthalene	0.25	0.62	0.33	0.26	0.044	0.26
1-Methylnaphthalene	0.12	0.26	0.17	0.16	0.031	0.29
Acenaphthylene	0.0058	0.066	0.0073	0.045	0.011	0.065
Acenaphthene	0.13	0.30	0.18	0.14	0.039	0.42
Fluorene	0.070	0.12	0.10	0.042	0.037	0.16
Phenanthrene	0.076	0.055	0.11	0.015	0.065	0.11
Anthracene	0.0039	0.080	0.0039	0.0040	0.0049	0.17
Fluoranthene	0.0092	0.0040	0.014	0.0047	0.021	0.0076
Pyrene	0.0050	0.0032	0.0073	0.0047	0.010	0.0044
Benzo(a)anthracene	0.0006	0.0067	0.0013	0.0047	0.00051	0.0044
Chrysene	0.00089	0.0046	0.0017	0.0047	0.0010	0.0044
Benzo(b+k)fluoranthene	0.00092	0.0088	0.0033	0.014	0.00062	0.0094
Benzo(e)pyrene	0.00051	0.0044	0.0013	0.0084	0.00050	0.0044
Benzo(a)pyrene	0.00048	0.0074	0.0013	0.0047	0.00050	0.0044
Indeno(1,2,3-cd)pyrene	0.00046	0.0044	0.0011	0.0047	0.00050	0.0044
Dibenz(a,h)anthracene	0.00046	0.0044	0.00050	0.0075	0.00050	0.0044
Benzo(g,h,i)perylene	0.00050	0.0081	0.0016	0.0047	0.00050	0.0044

*yellow cells are non-detect with the reporting limit for that target

Chart for Site AMS-01-081313

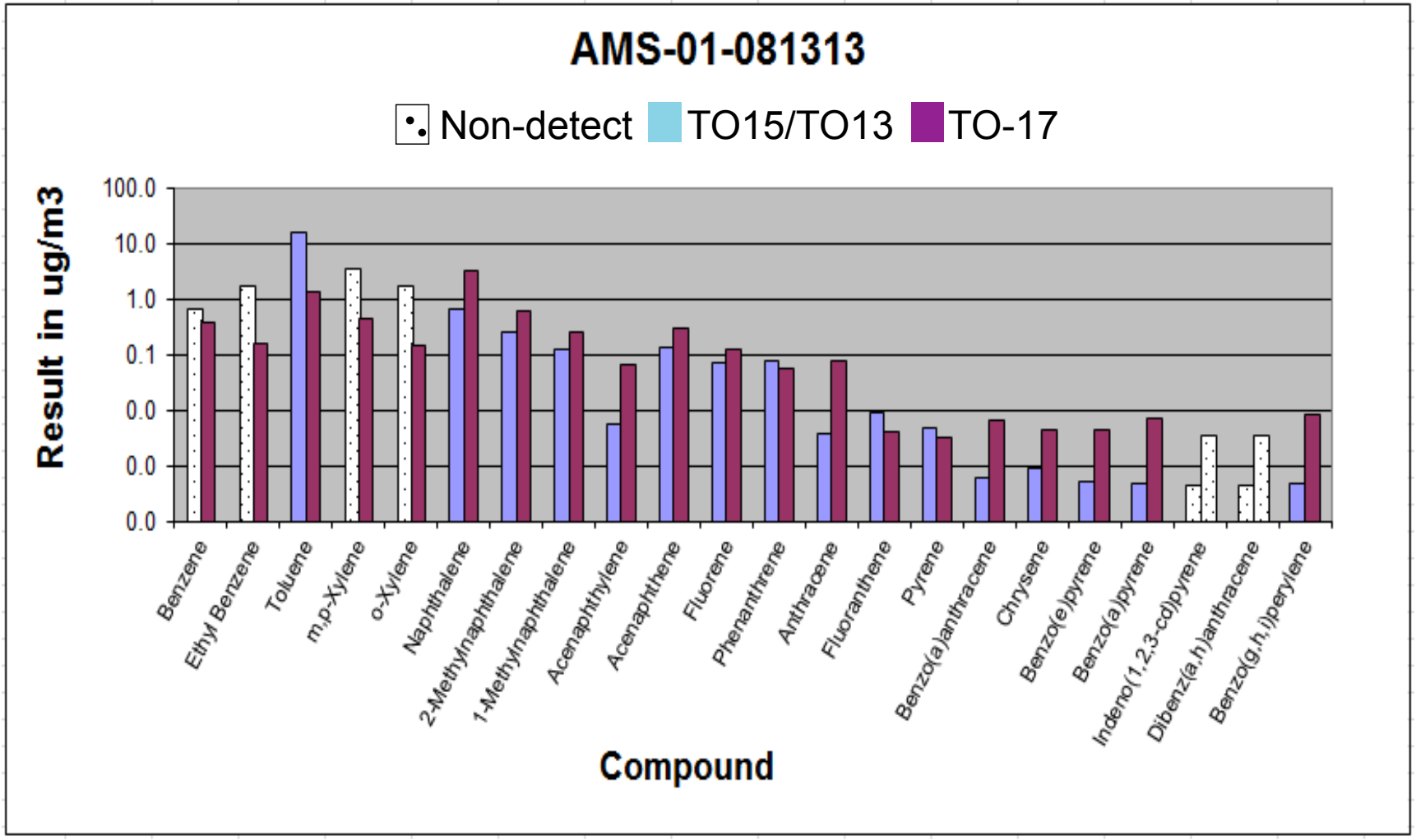


Chart for Site AMS-01-081613

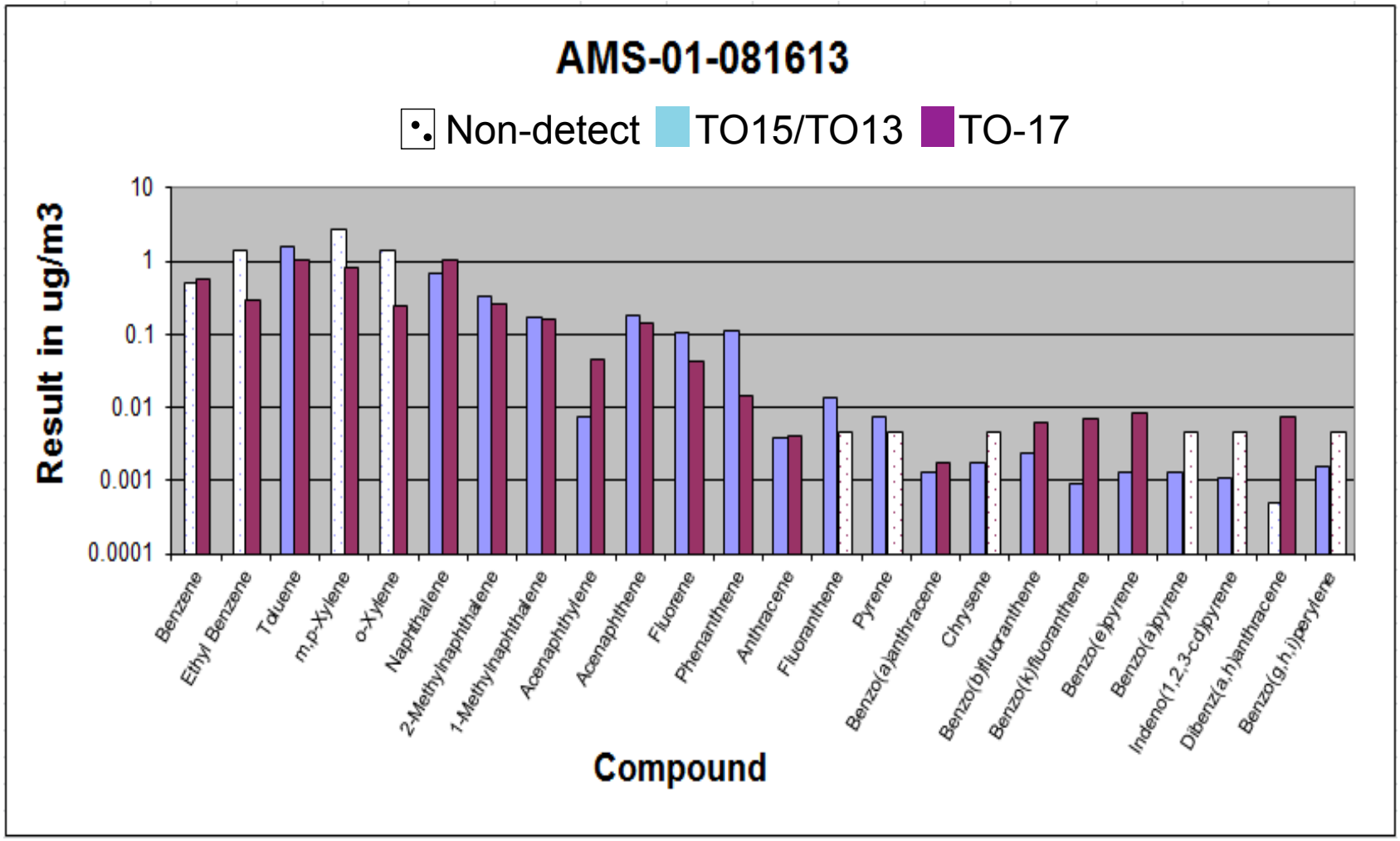
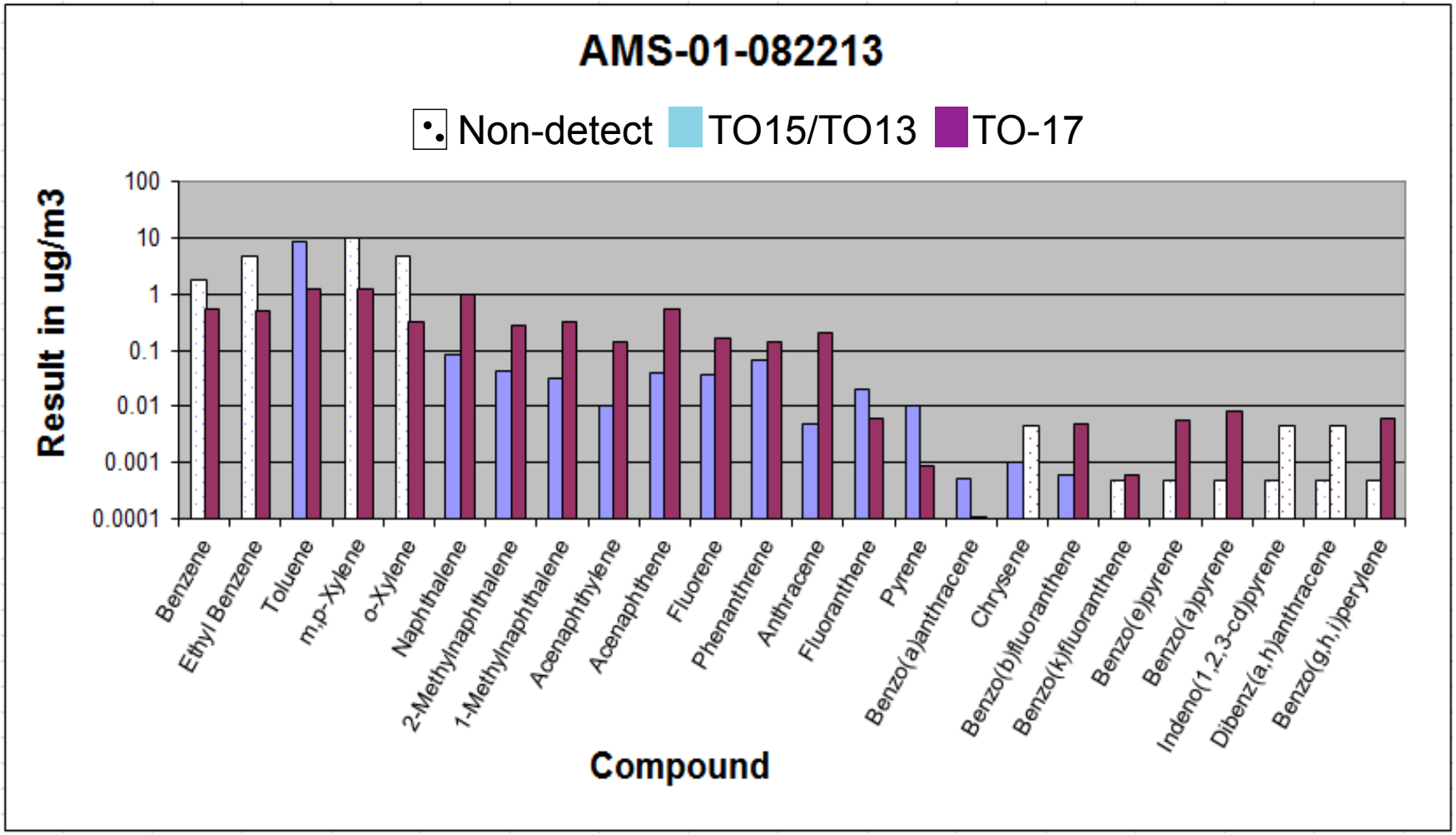


Chart for Site AMS-01-082213



Results from the 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

*yellow cells are non-detect with the reporting limit for that target

Chart for Site AMS-03-081313

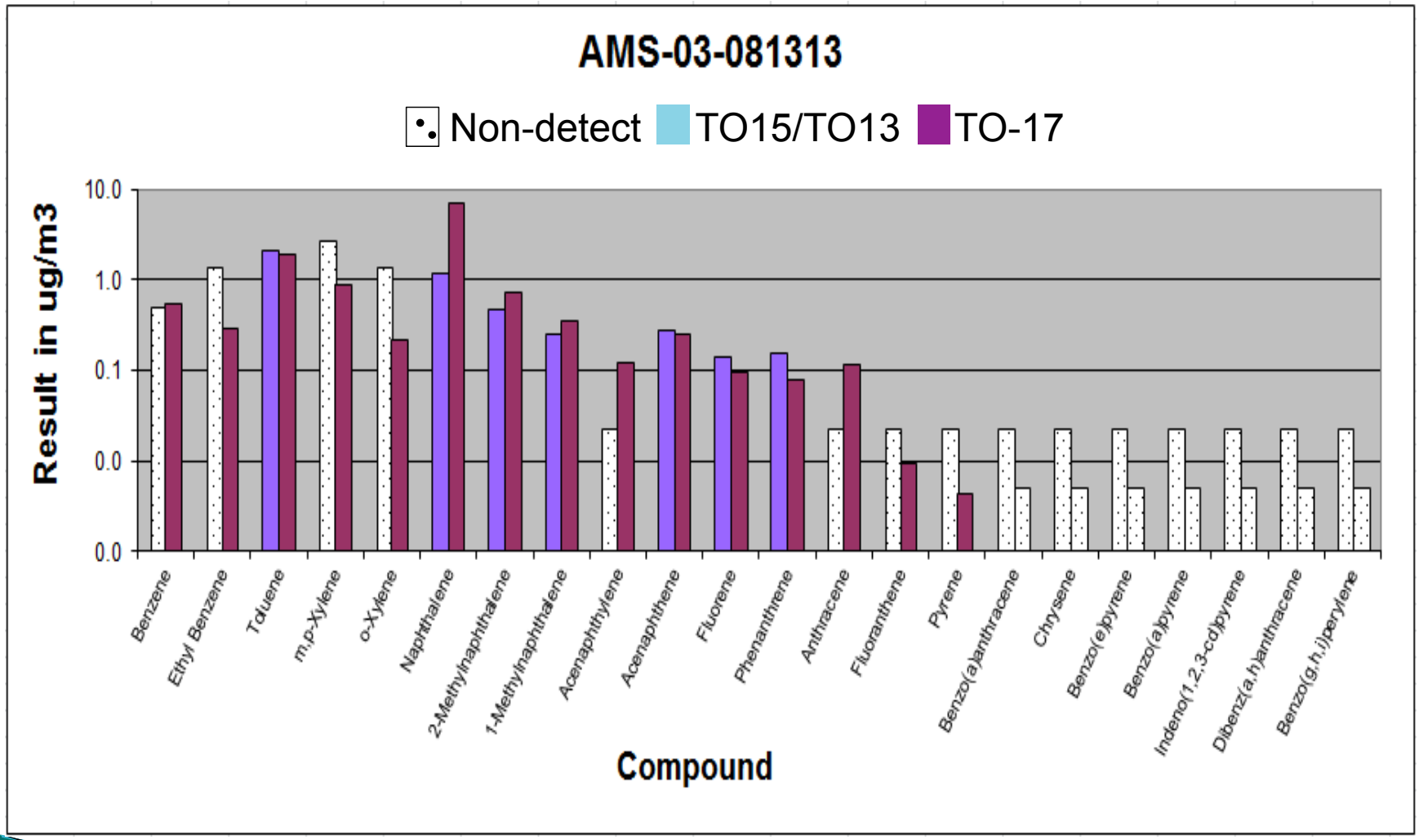


Chart for Site AMS-03-081613

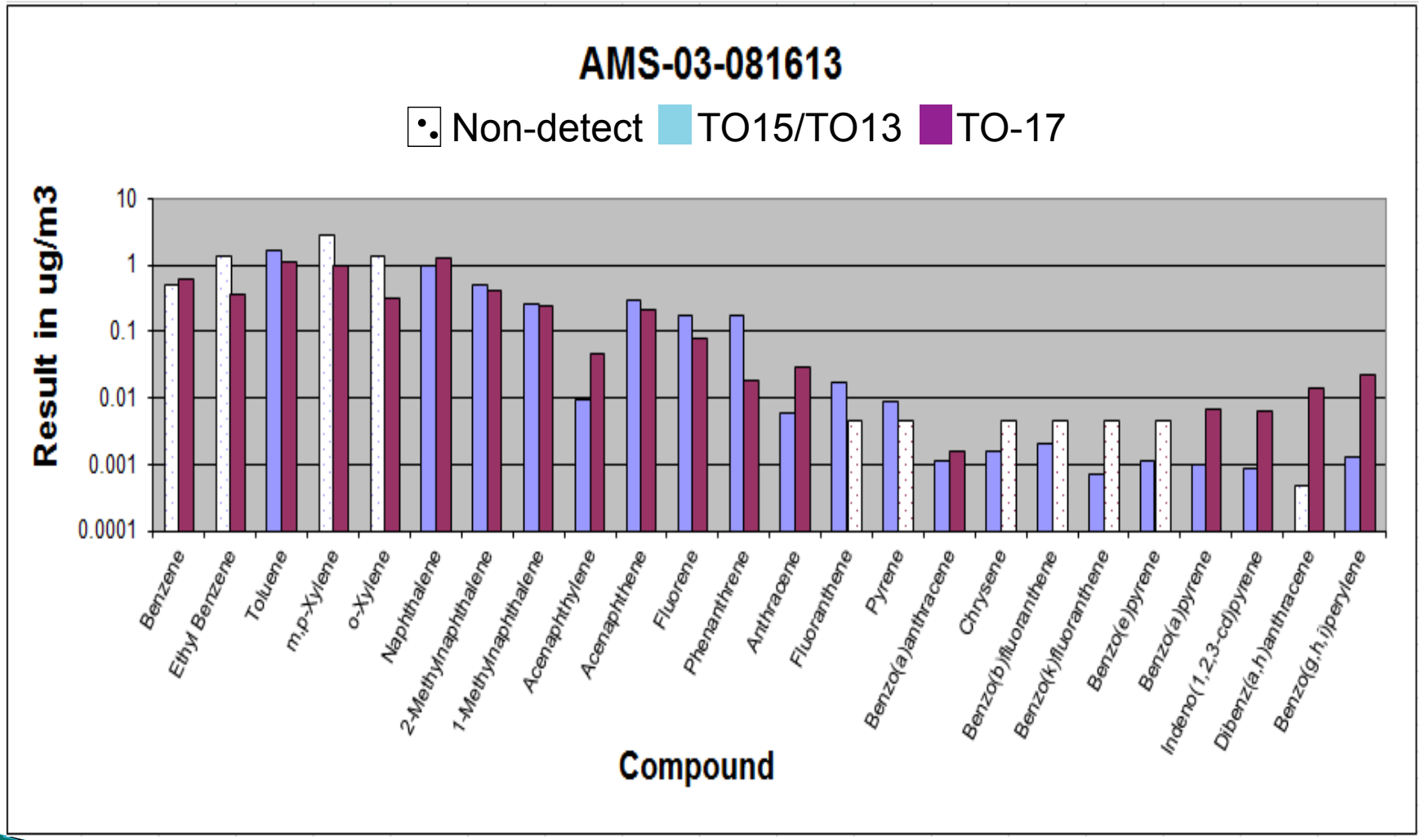
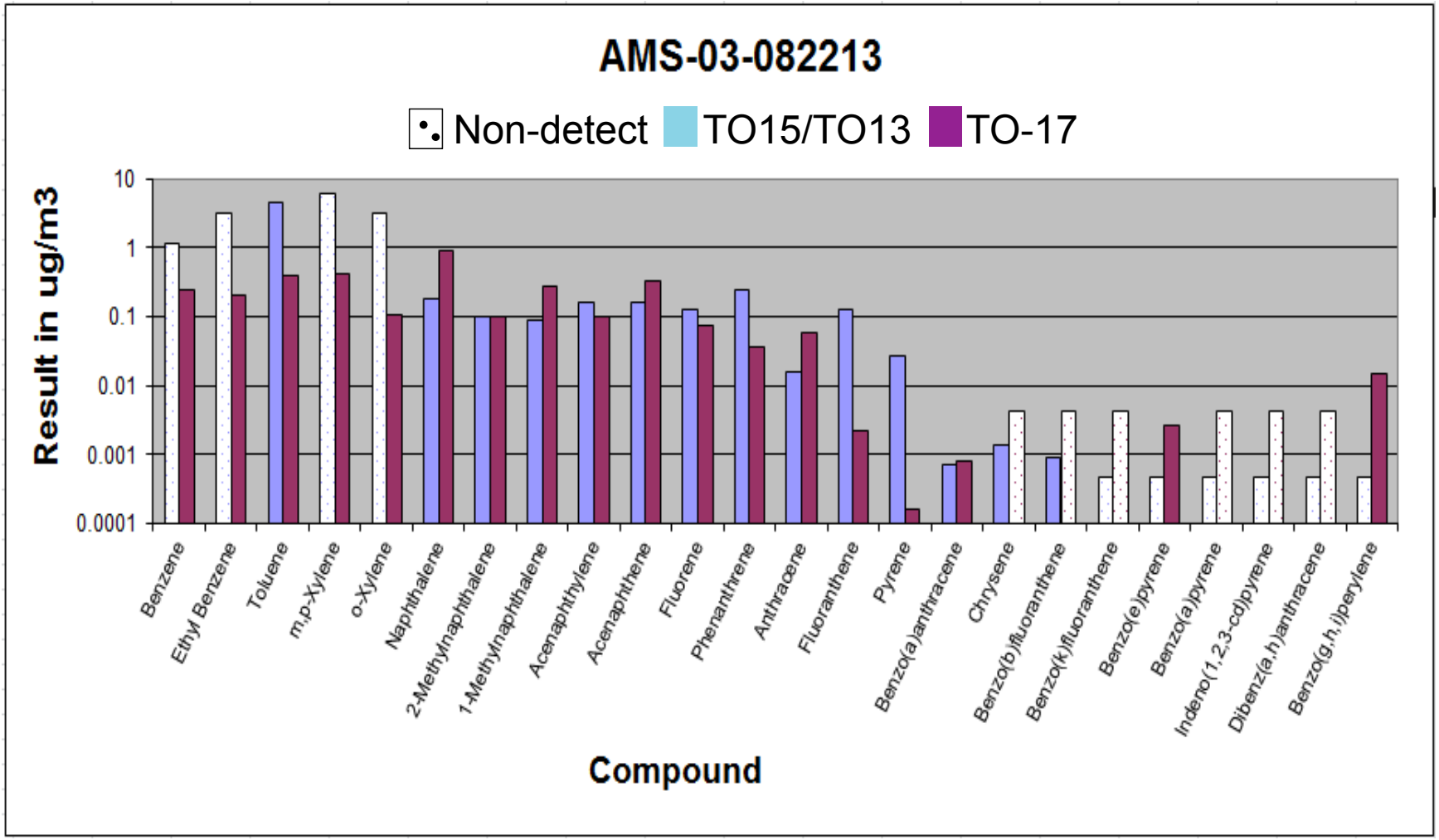


Chart for Site AMS-03-082213



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 our data and given verbal acceptance
  - 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

Acknowledgments

- Amy Jacobson, Specialty Analytical Services Manager, Pace Analytical Services
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- James Day, Service Engineer, PerkinElmer

Thank you!

Questions Please ????

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