Development of a Semi-Volatile Column Optimized for the Analysis of Hazardous Waste

Chris English, Christopher Rattray, Corby Hilliard, Kristi Sellers, Jason Herrington, Whitney Dudek-Salisbury, Brian Salisbury.

Restek Corporation, 110 Benner Circle, Bellefonte, PA 16823, United States

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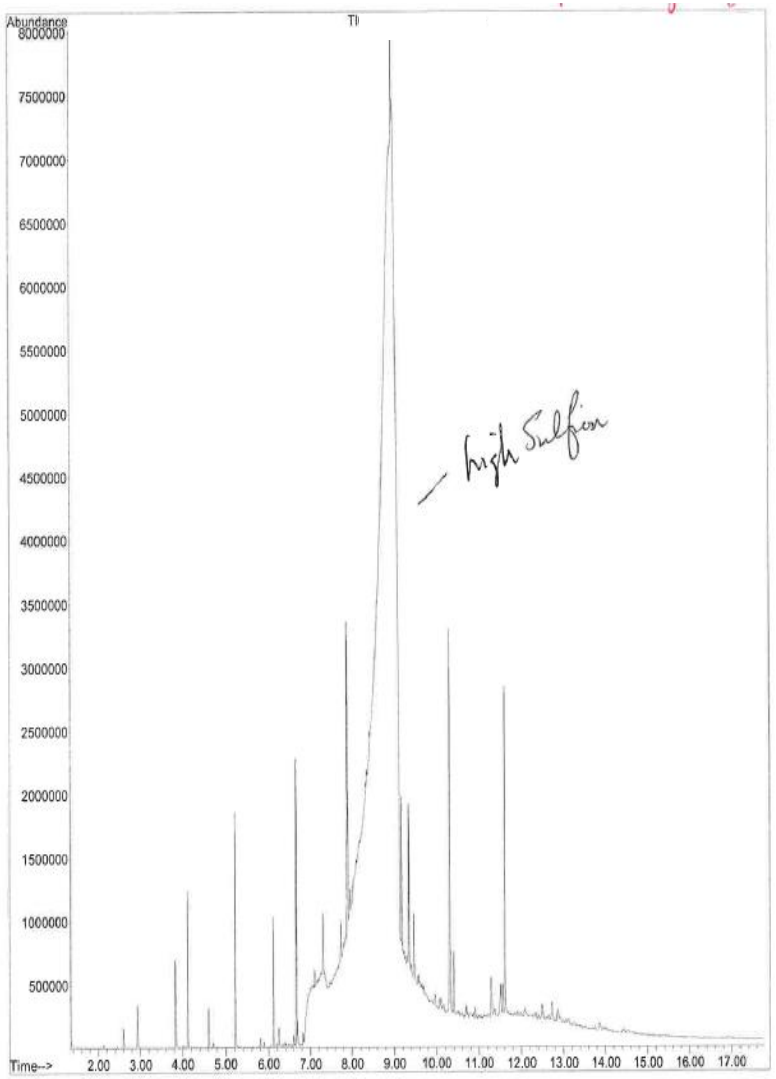
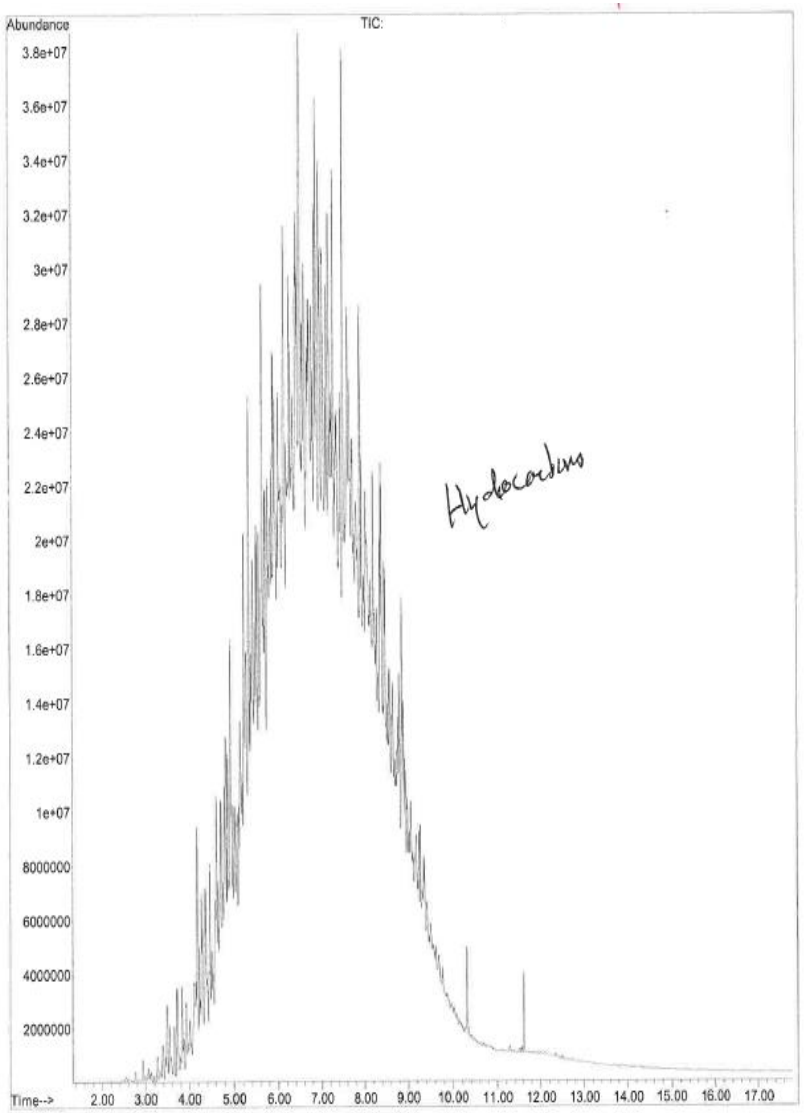
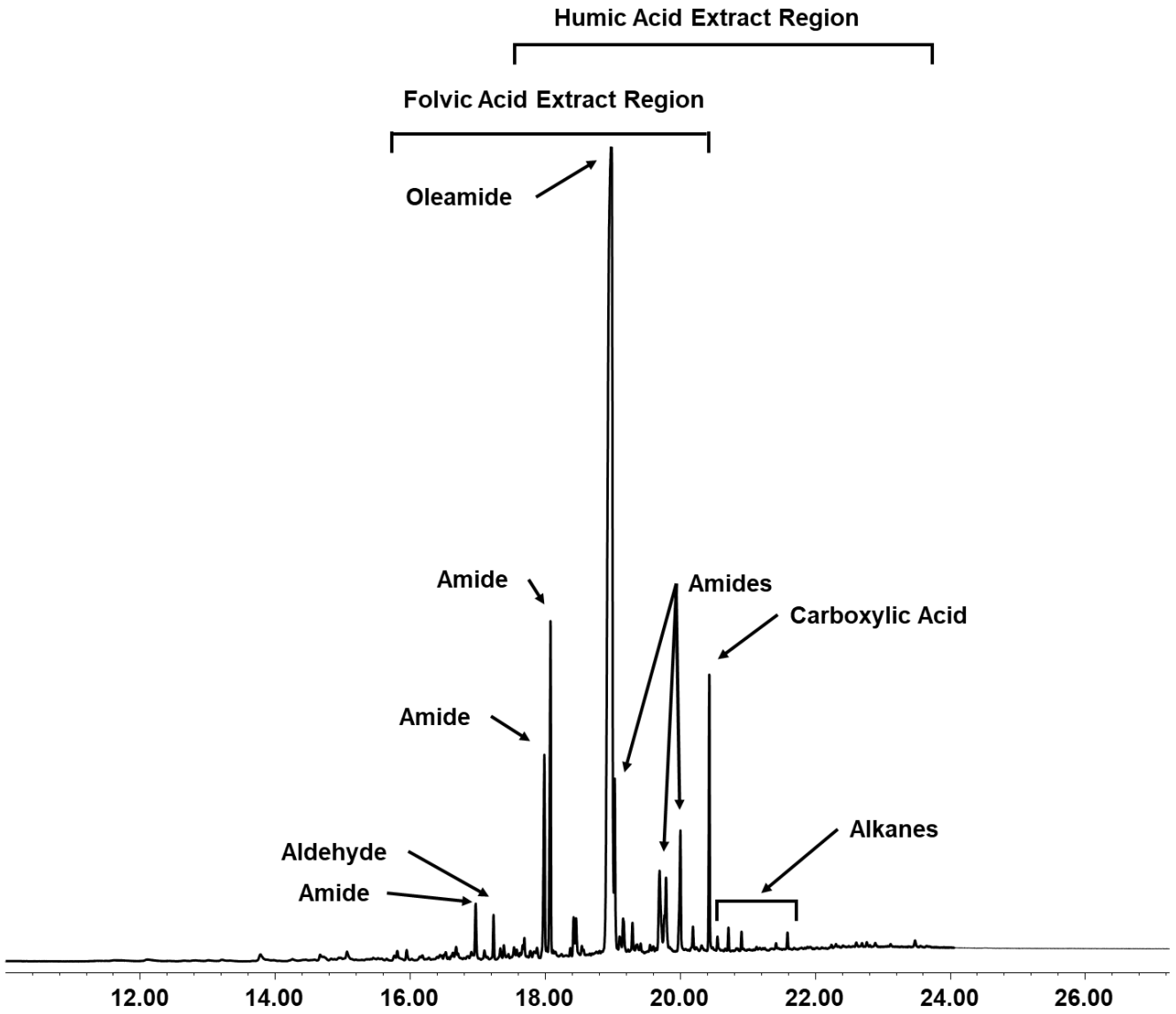
Review Details of the Lifetime Study Results Using Contaminated Extracts

Highly Contaminated Samples: Sulfur & Hydrocarbons



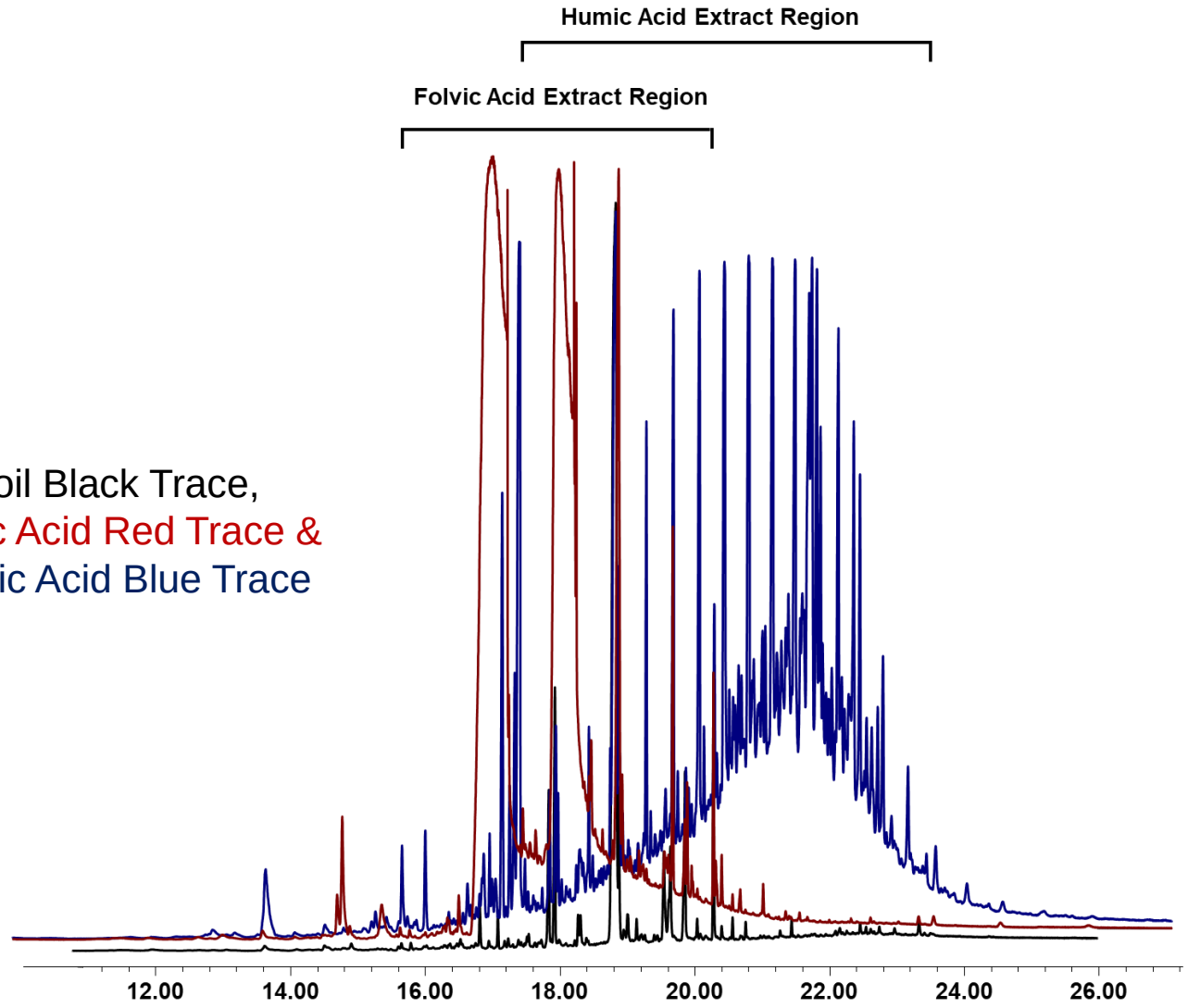


What is Dirt?


Humic Acid Extract Region
Folvic Acid Extract Region
Oleamide
Amide
Amide
Aldehyde
Amide
Amides
Carboxylic Acid
Alkanes
12.00
14.00
16.00
18.00
20.00
22.00
24.00
26.00

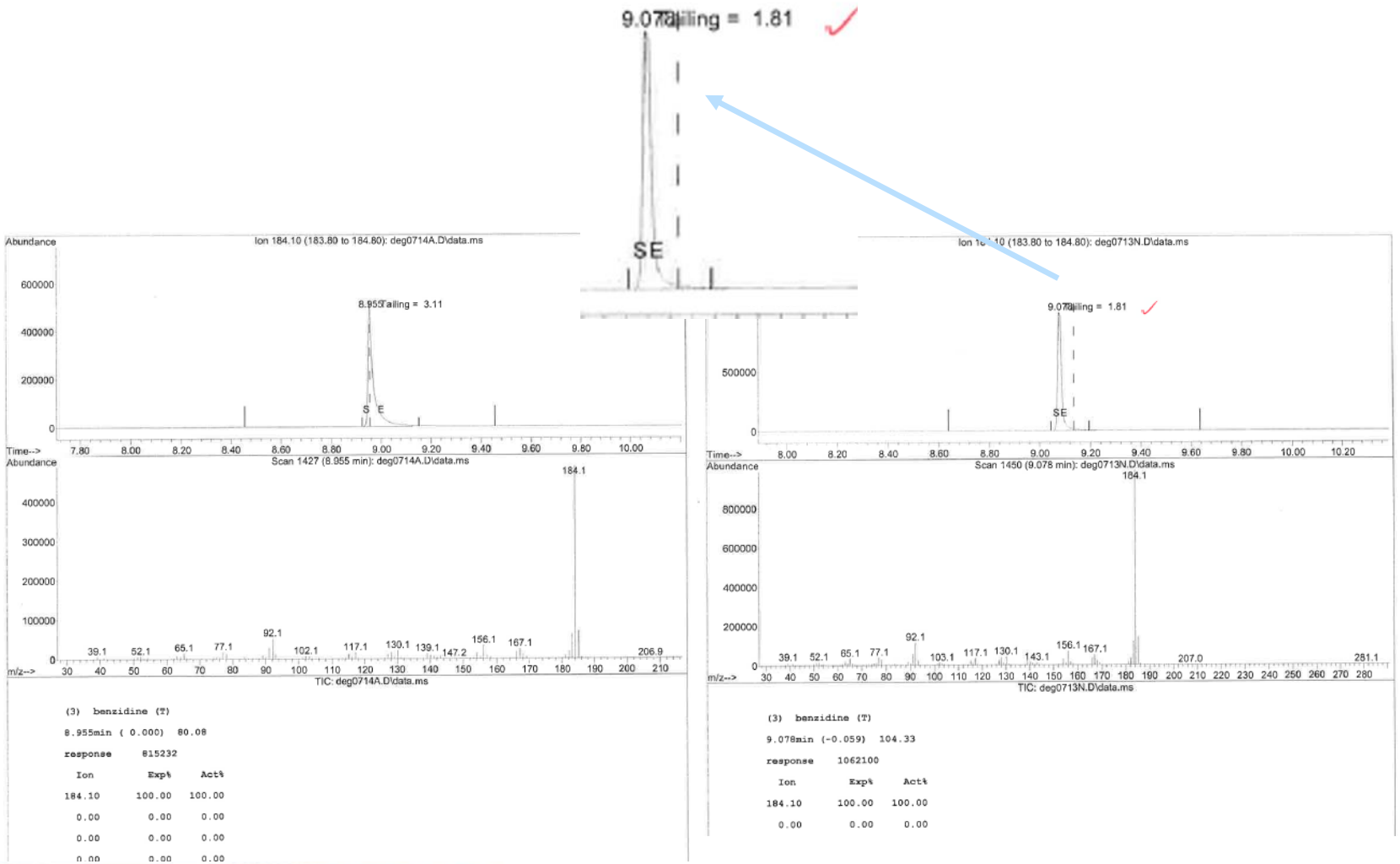

Humic Acid
Tannic Acid
Bentonite

What is Dirt?



Soil Black Trace,
Folvic Acid Red Trace &
Humic Acid Blue Trace

GC/MS Tune Check Solution: DFTPP, DDT, PCP & Benzidine



https://www.epa.gov/sites/production/files/2017-04/documents/method_8260d_update_vi_final_03-13-2017_0.pdf

Sources of activity in the sample pathway

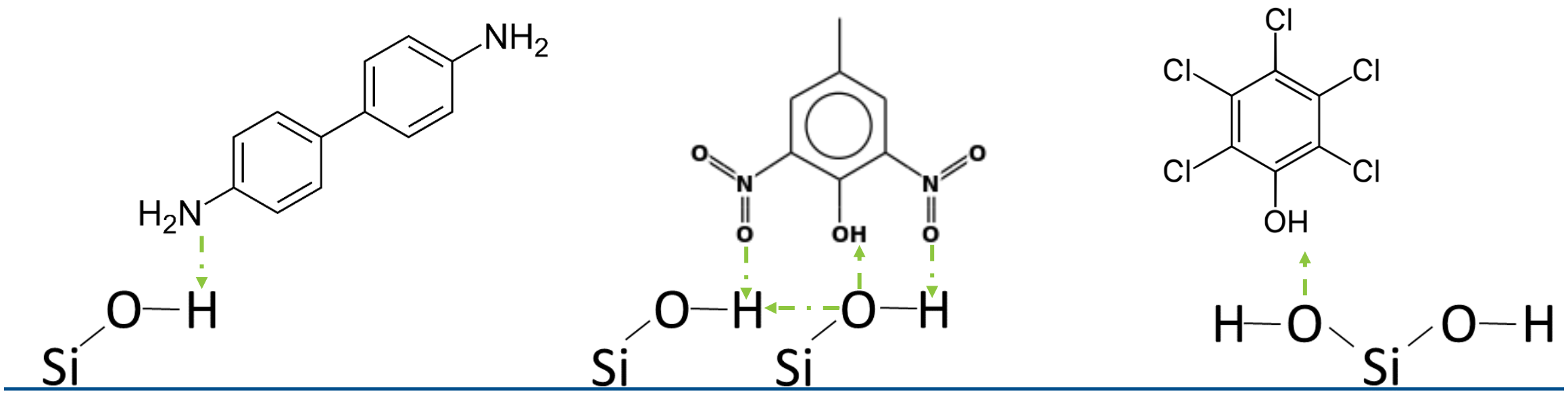
Inlet liner surface: 4.4 cm^2

Glass wool plug: 30 cm^2

Inlet seal surface: 1.0 cm^2

30 m x 0.25 mm ID GC column surface area: 236 cm^2

What causes activity in the column?



Isolated Silanol

Vicinal Silanol (H-bond)

Geminal Silanol

Increasing silanol acidity

Shifting retention times

Activity in the column will act as a 2nd retention mechanism

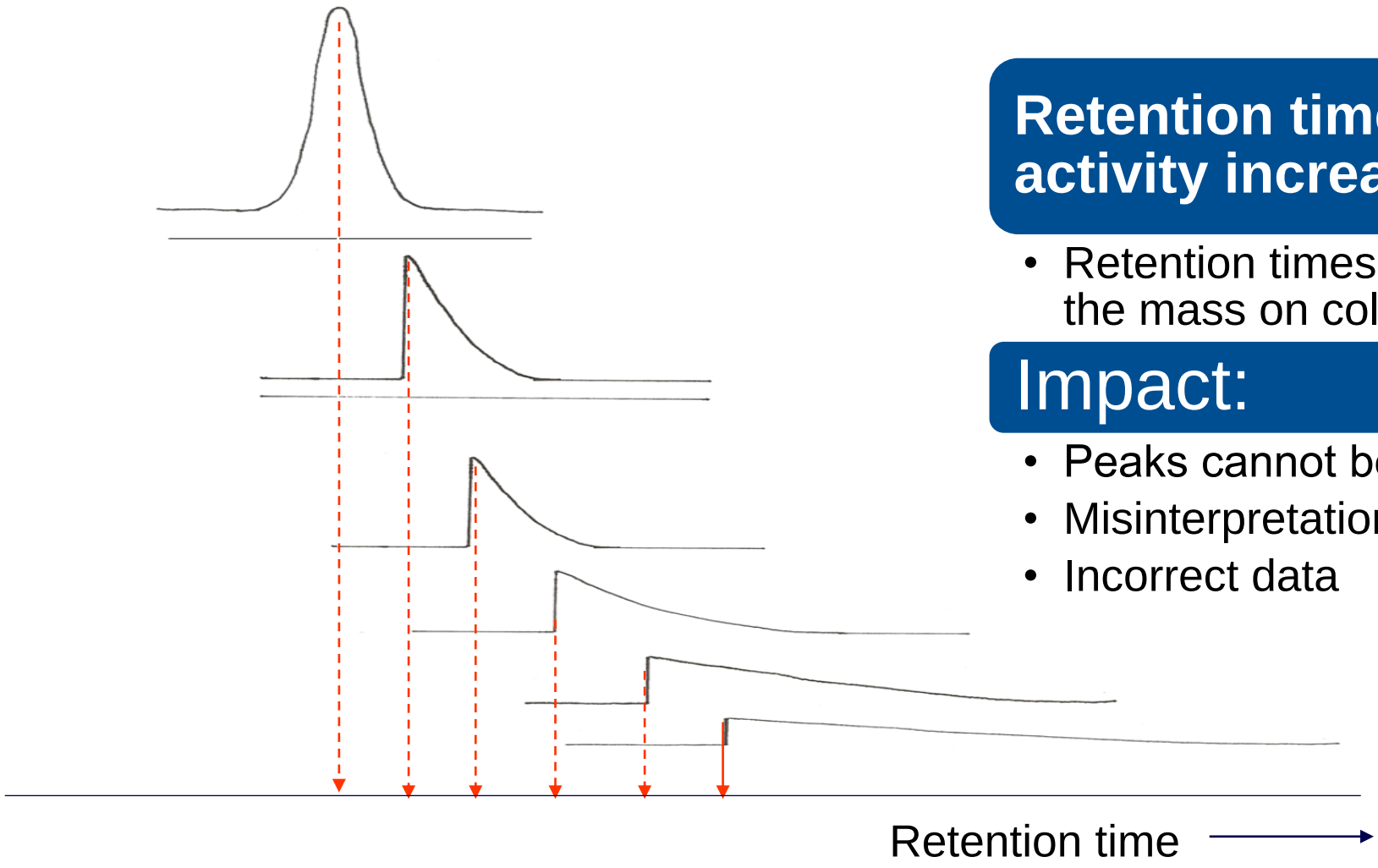
- *Retention (and RI) depend on degree of activity*
- *If not carefully controlled, each column can show a different RI*

Impact:
- Retention time increases Peak start to tail
- Peakheight reduces

Retention time becomes a function of mass injected on the column: Lower levels elute later

Impact:
- Retention time increases Peak start to tail
- Peakheight reduces

The consequence of strong interactions with active sites



Retention times shift as column activity increases

- Retention times can shift on active columns as the mass on column drops

Impact:

- Peaks cannot be “found”
- Misinterpretation
- Incorrect data

Other Options: Extract and Analyze Dirt

National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 1622e

Sulfur in Residual Fuel Oil
(Nominal Mass Fraction 2 %)

Lifetime test w/ Sulfurs

Other Possible Standards

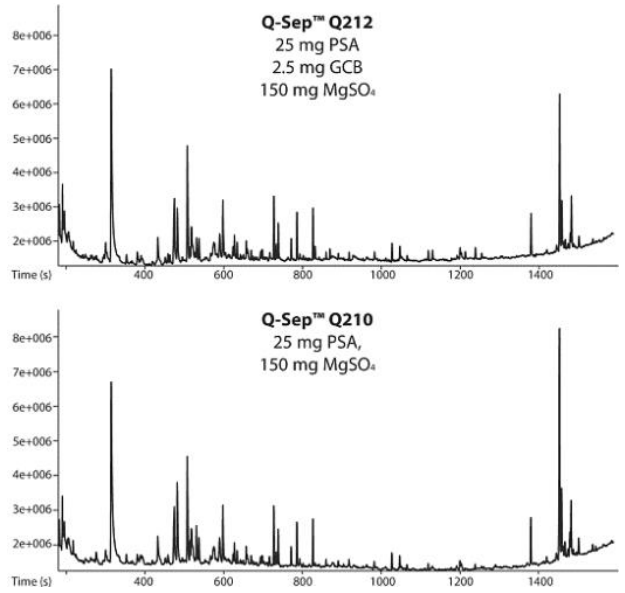
National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 1991

Mixed Coal Tar/Petroleum Extract in Methylene Chloride

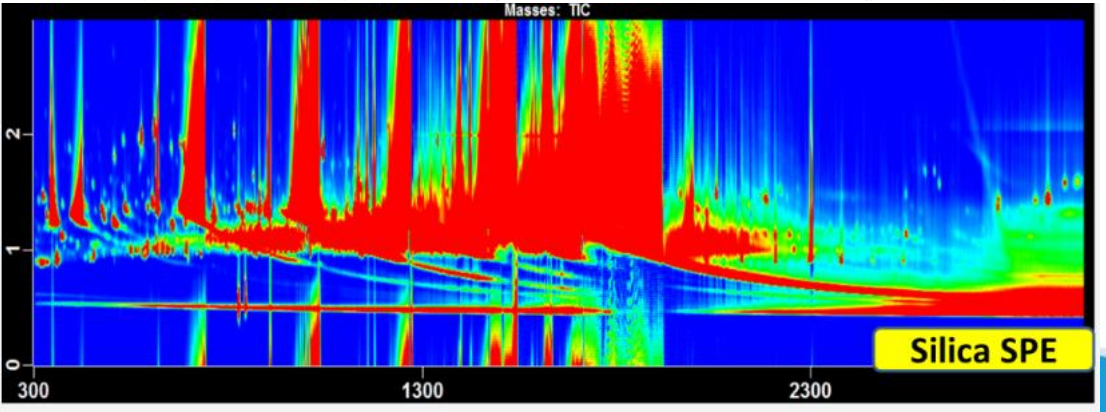
This Standard Reference Material (SRM) is intended for use in evaluating analytical methods for the determination of selected polycyclic aromatic hydrocarbons (PAHs), particularly in determining relative response factors for ASTM Method D7363-11 "Standard Test Method for Determination of Parent and Alkyl Polycyclic Aromatics in Sediment Pore Water Using Solid-Phase Microextraction and Gas Chromatography/Mass Spectrometry in Selected Ion Monitoring Mode" [1]. All of the constituents for which certified, reference, and information values are provided are naturally present in the extract. A unit of SRM 1991 consists of five ampoules each containing 1.2 mL of a methylene chloride solution.

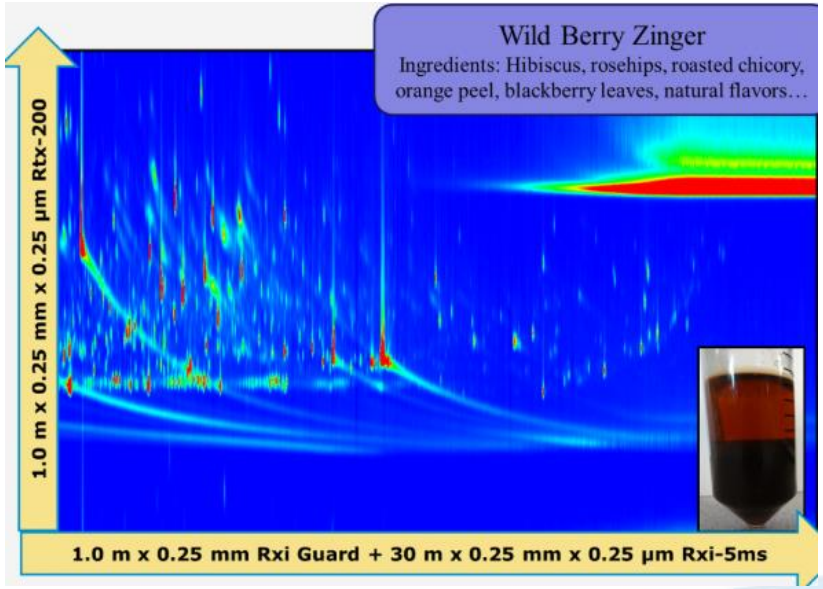


Are fatty acids overwhelming your QuEChERS dSPE PSA cleanup and causing issues in your GC analysis? Get more cleanup capacity with cartridge SPE cleanup!

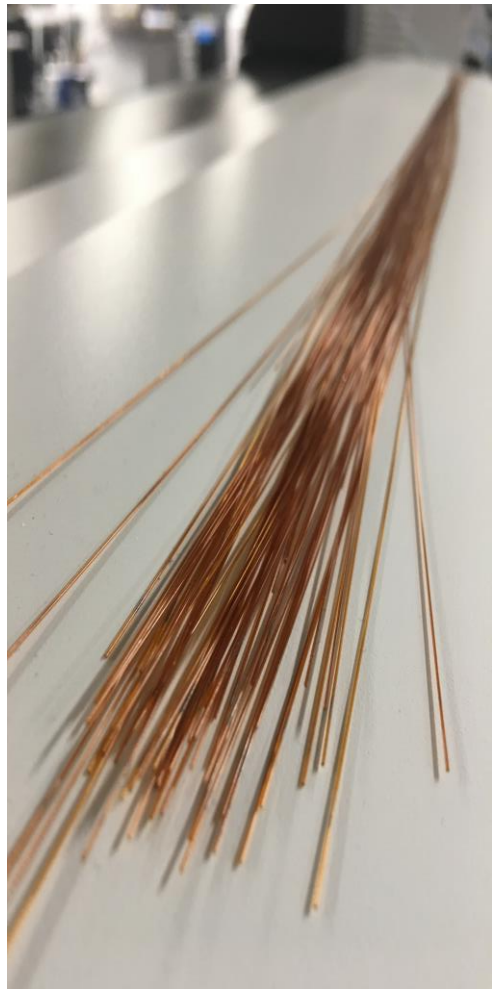
March 4th, 2014 by Michelle Misselwitz

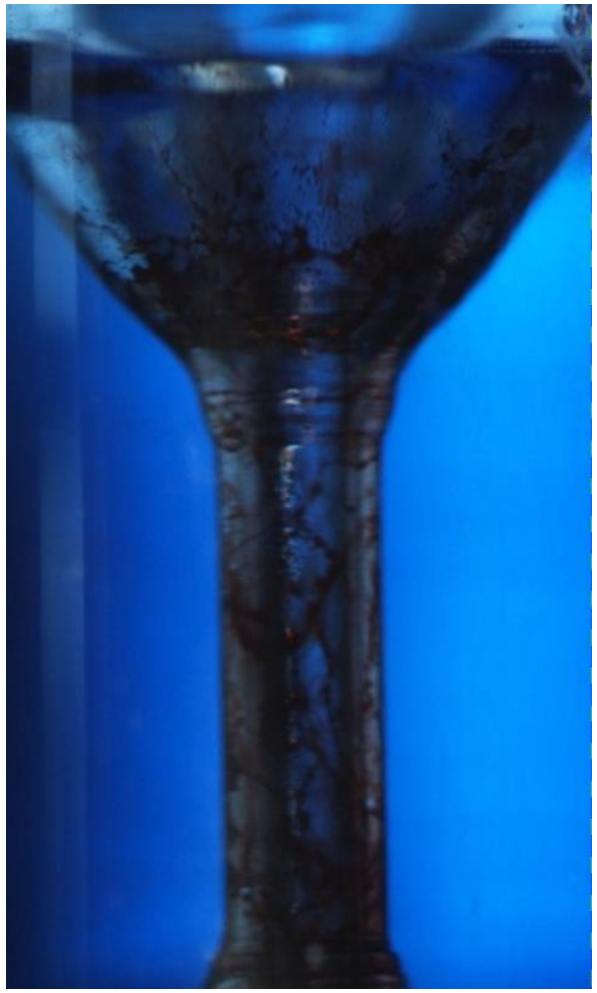
Fatty acids are important molecules in the human body because they are used as a source of fuel. There are many food sources of both "healthy" and "unhealthy" fatty acids. Many sources of dietary fatty acids come from fruits, vegetables, seeds, nuts, and animal fats. The QuEChERS methodology was developed to analyze





Testing Contamination in Columns *and Liners*





National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 1975

Diesel Particulate Extract

This Standard Reference Material (SRM) is intended for use in evaluating analytical methods for the determination of selected polycyclic aromatic hydrocarbons (PAHs) and nitro-substituted PAHs in diesel particulate extracts and similar matrices. In addition to certified, reference, and information values for selected PAHs and nitro-subsituted

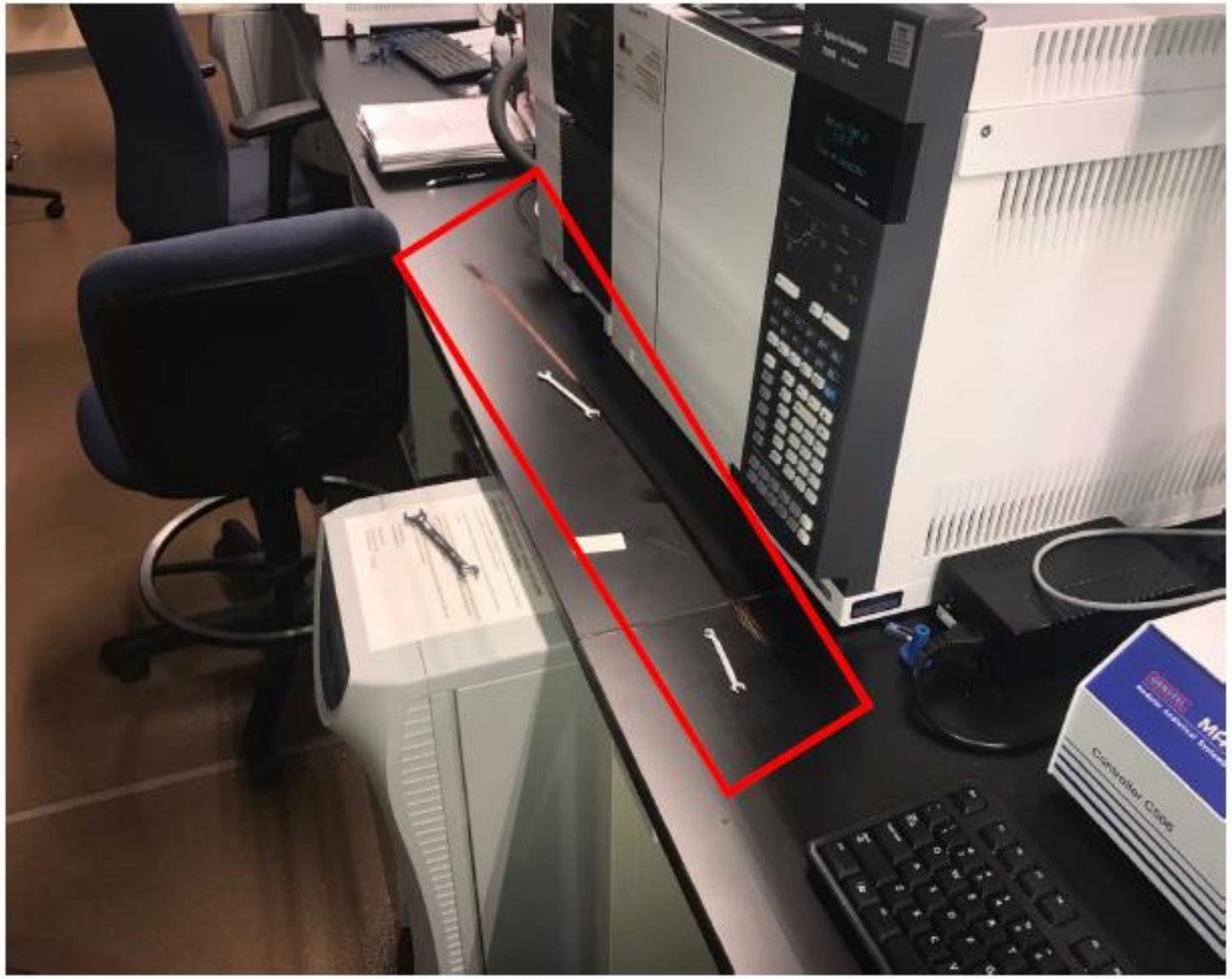
https://www-s.nist.gov/srmors/view_cert.cfm?srm=1975

https://www-s.nist.gov/srmors/certificates/1975.pdf

SRM 1975 Lifetime Test

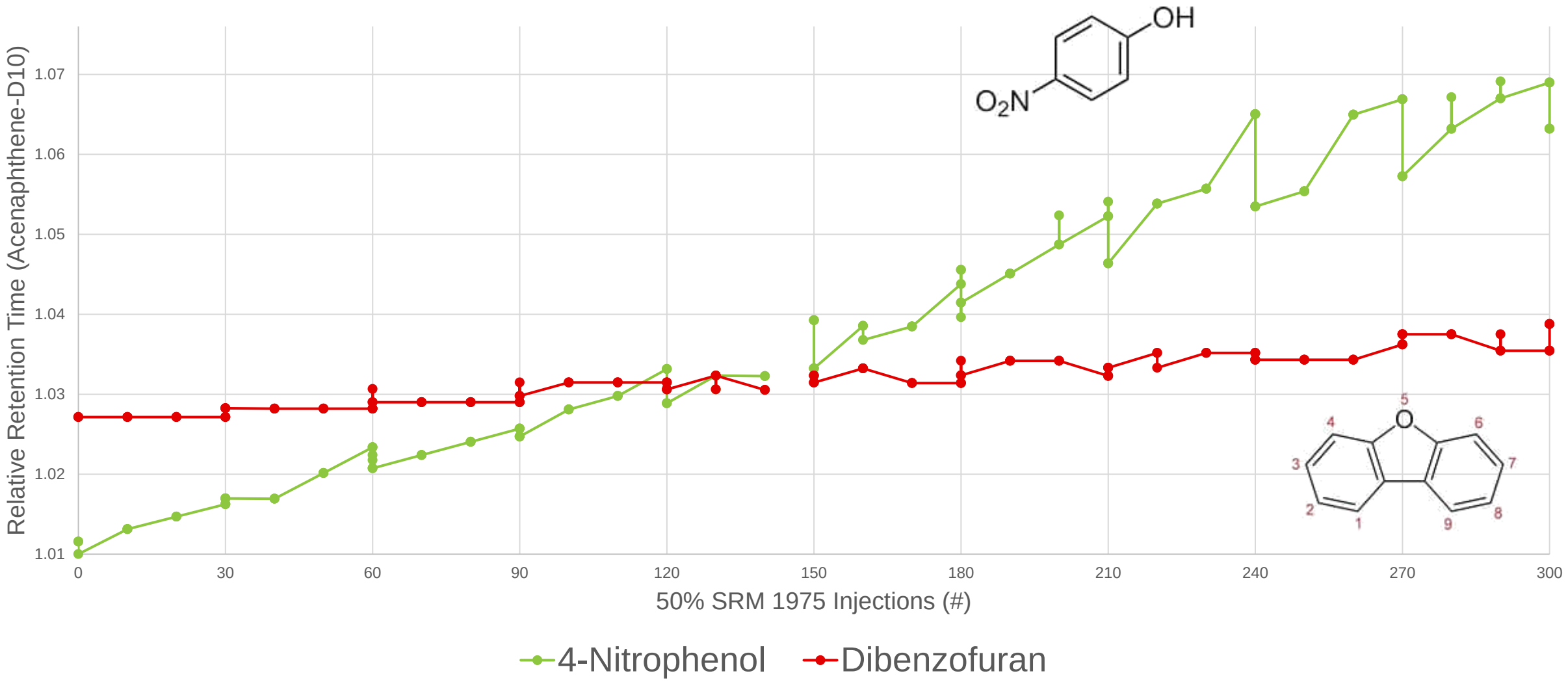
GC Inlet Maintenance

- After the 30 SRM Injections, a segment of column was cut from the head of the column (highlighted on the right), and the liner, septum, and gold seal was replaced
  - We've been saving the segments to ensure that the same length is removed each day
- Ideally, the column performance should be restored by these maintenance actions.

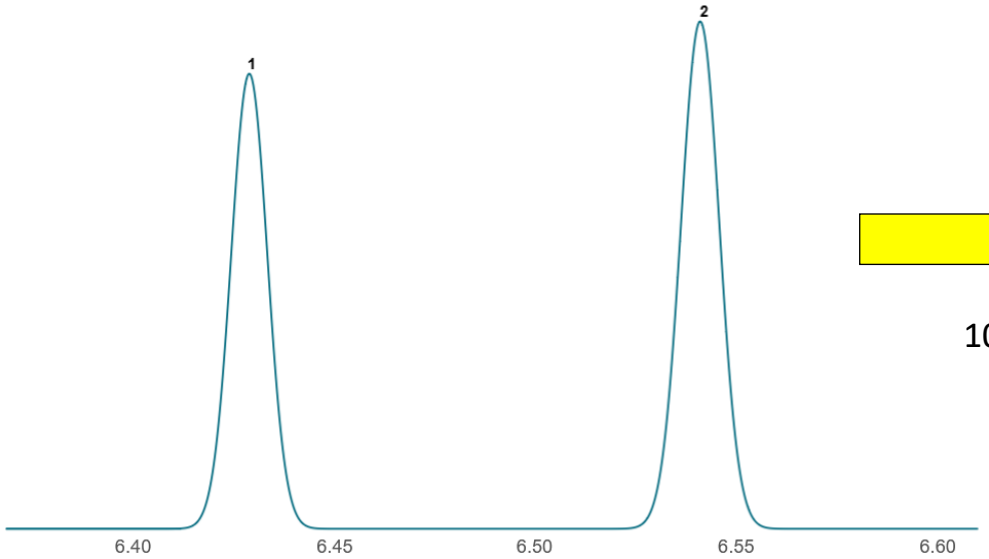


Slide Courtesy Christopher Rattray

The ageing process during routine analysis of challenging samples is normal



Trimming alone shouldn’t cause the elution order switch

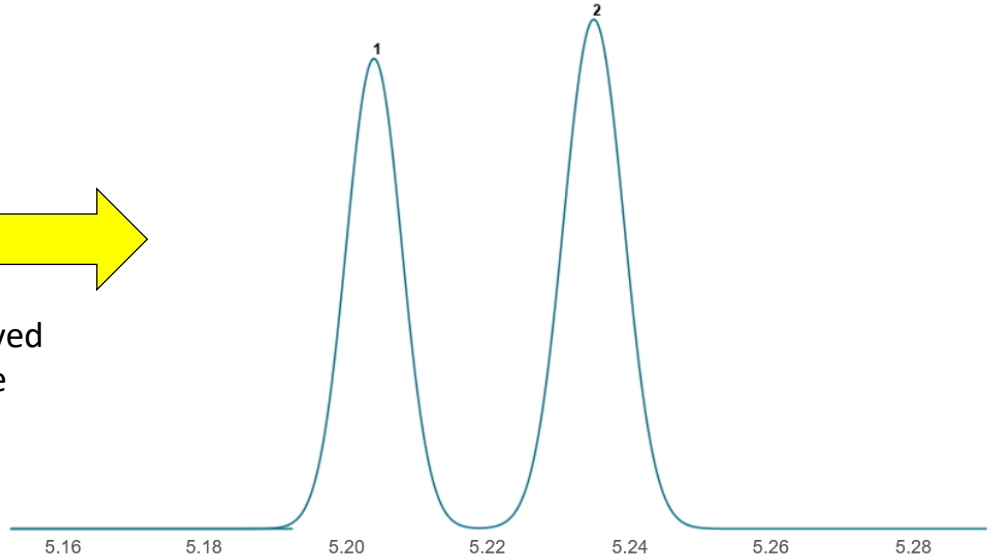


Click and drag to zoom; double-click to reset.

Column: **Rxi-SVOCms**, 30.00 m, 0.25 mm ID, 0.25 µm (cat.# 16623)
Carrier Gas: Helium, Constant Flow @ 1.20 mL/min
Average Velocity: 39.95 cm/sec
Outlet Pressure (abs): 0.00 psi (Vacuum)
Oven Temp.: 60 °C (hold 0.5 min) to 285 °C @ 25 °C/min

Peaks	t_R (min)	R_S	Peak Width (min)	T_{peak} (°C)
1. **4-Nitrophenol**	6.43	5.4	0.021	208.2
2. **Dibenzofuran**	6.54	5.4	0.022	211.0

10 m of column removed
Same head pressure



Click and drag to zoom; double-click to reset.

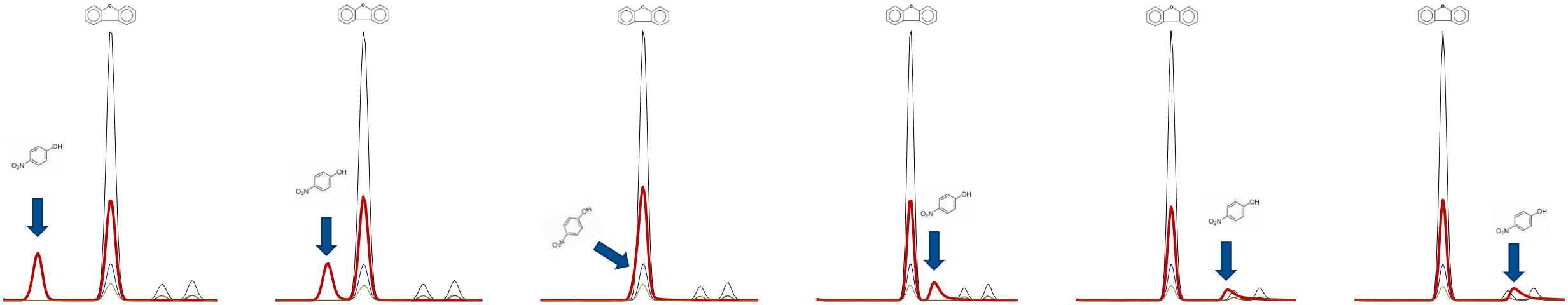
Column: **Rxi-SVOCms**, 20.00 m, 0.25 mm ID, 0.25 µm
Carrier Gas: Helium, Constant Flow @ 1.80 mL/min
Average Velocity: 59.92 cm/sec
Outlet Pressure (abs): 0.00 psi (Vacuum)
Oven Temp.: 60 °C (hold 0.5 min) to 285 °C @ 25 °C/min

Peaks	t_R (min)	R_S	Peak Width (min)	T_{peak} (°C)
1. **4-Nitrophenol**	5.20	1.7	0.018	177.6
2. **Dibenzofuran**	5.24	1.7	0.019	178.4

4-Nitrophenol is a good example of how column activity can change relative retention times.

Adsorption at active sites

- Peak height reduces (sensitivity)
- Peaks become broader (separation)

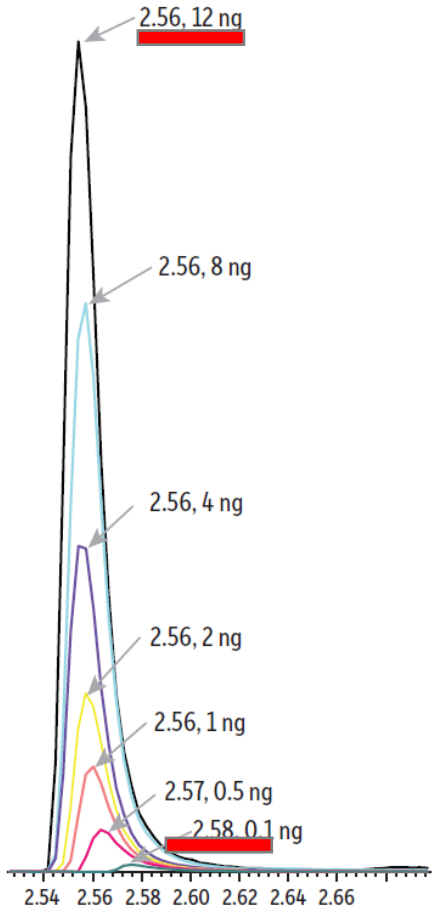


0 SRM	60 SRM	120 SRM	180 SRM	240 SRM	300 SRM
Day 1	Day 3	Day 5	Day 7	Day 9	Day 11
30 m	28 m	26 m	24 m	22 m	20 m

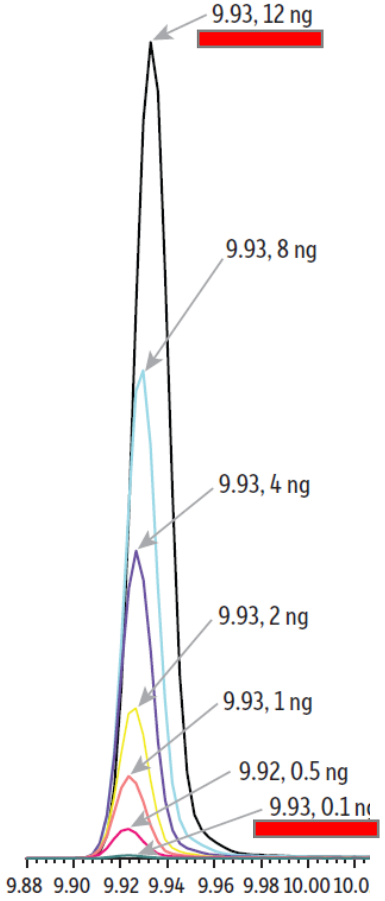
New Column Inertness Performance

Injection of 12, 8, 4, 2, 1, 0.5 and 0.1 ng on the column

Pyridine



Pentachlorophenol



Inertness Facilitates Linear Calibrations

Average %RSDs for 6 Rxi-SVOCms columns (16623) calibrated from 1 ng/µL to 120 ng/µL

Compound	Calibration Range (µg/mL)	Average %RSD of Response Factors
N-Nitrosodimethylamine	1 - 120	4.70%
Pyridine	1 - 120	6.10%
(SS) 2-Fluorophenol	1 - 120	1.70%
(SS) Phenol-d6	1 - 120	2.10%
Phenol	1 - 120	3.20%
Aniline	1 - 120	3.10%
Bis(2-chloroethyl)ether	1 - 120	2.40%
2-chlorophenol	1 - 120	2.80%
1,3-dichlorobenzene	1 - 120	2.60%
1,4-Dichlorobenzene	1 - 120	2.10%
Benzyl alcohol	1 - 120	3.30%
1,2-Dichlorobenzene	1 - 120	2.70%
2-Methylphenol	1 - 120	3.30%
Bis(2-chloroisopropyl)ether	1 - 120	2.40%
4-Methylphenol/3-methylphenol	1 - 120	3.30%
N-nitroso-di-*n*-propylamine	1 - 120	3.80%
Hexachloroethane	1 - 120	3.00%
(SS) Nitrobenzene-D5	1 - 120	1.60%
Nitrobenzene	1 - 120	2.60%
Isophorone	1 - 120	3.40%
2-Nitrophenol	1 - 120	7.00%
2,4-Dimethylphenol	1 - 120	3.70%
Benzoic acid	2.5 - 120	25.00%

Benzoic Acid is the only compound > 20% RSD

Compound	Calibration Range (µg/mL)	Average %RSD of Response Factors
Bis(2-chloroethoxy)methane	1 - 120	3.60%
2,4-Dichlorophenol	1 - 120	4.10%
1,2,4-Trichlorobenzene	1 - 120	2.80%
Naphthalene	1 - 120	3.20%
4-Chloroaniline	1 - 120	3.90%
Hexachlorobutadiene	1 - 120	3.70%
4-Chloro-3-methylphenol	1 - 120	4.40%
2-Methylnaphthalene	1 - 120	3.40%
1-Methylnaphthalene	1 - 120	3.60%
Hexachlorocyclopentadiene	1 - 120	6
2,4,6-Trichlorophenol	1 - 120	5
2,4,5-Trichlorophenol	1 - 120	6
(SS) 2-Fluorobiphenyl	1 - 120	1
2-Chloronaphthalene	1 - 120	2.80%
2-Nitroaniline	1 - 120	7.80%
1,4-Dinitrobenzene	1 - 120	11.10%
Dimethyl phthalate	1 - 120	3.40%
1,3-Dinitrobenzene	1 - 120	10.80%

Compound	Calibration Range (µg/mL)	Average %RSD of Response Factors
2,6-Dinitrotoluene	1 - 120	7.80%
Acenaphthylene	1 - 120	4.10%
1,2-Dinitrobenzene	1 - 120	8.10%
3-Nitroaniline	1 - 120	5.80%
Acenaphthene	1 - 120	3.30%
2,4-Dinitrophenol	2.5 - 120	17.30%
4-Nitrophenol	1 - 120	7.90%
Dibenzofuran	1 - 120	3.50%
2,4-Dinitrotoluene	1 - 120	11.60%
Benzo[ghi]perylene	1 - 120	6.40%
	Average %RSD:	6.00%
Fluorene	1 - 120	4.40%
4-Nitroaniline	1 - 120	9.10%
4,6-Dinitro-2-methylphenol	2.5 -120	15.10%
N-nitrosodiphenylamine	1 - 120	4.60%
Diphenylhydrazine	1 - 120	4.60%
(SS) 2,4,6-Tribromophenol	1 - 120	5.50%
4-Bromophenyl phenyl ether	1 - 120	5.50%
Hexachlorobenzene	1 - 120	4.30%
Pentachlorophenol	1 - 120	10.60%
Phenanthrene	1 - 120	3.70%

Compound	Calibration Range (µg/mL)	Average %RSD of Response Factors
Anthracene	1 - 120	4.80%
Carbazole	1 - 120	5.30%
di-*n*-Butyl phthalate	1 - 120	7.90%
Fluoranthene	1 - 120	5.10%
Benzidine	1 - 120	9.30%
(SS) Pyrene-D10	1 - 120	1.50%
Pyrene	1 - 120	4.30%
(SS) *p*-Terphenyl-d14	1 - 120	1.80%
3,3'-Dimethylbenzidine	1 - 120	9.50%
Butyl benzyl phthalate	1 - 120	8.60%
Bis(2-ethylhexyl)adipate	1 - 120	10.50%
3,3'-Dichlorobenzidine	1 - 120	8.50%
Benz[a]anthracene	1 - 120	3.20%
Chrysene	1 - 120	3.70%
Bis(2-ethylhexyl)phthalate	1 - 120	10.40%
Di-*n*-octyl phthalate	1 - 120	13.20%
Benzo[b]fluoranthene	1 - 120	5.60%
Benzo[k]fluoranthene	1 - 120	4.90%
Benzo[a]pyrene	1 - 120	6.30%
Indeno[123-cd]pyrene	1 - 120	7.20%
Dibenz[a,h]anthracene	1 - 120	7.50%
Benzo[ghi]perylene	1 - 120	6.40%
	Average %RSD:	6.00%

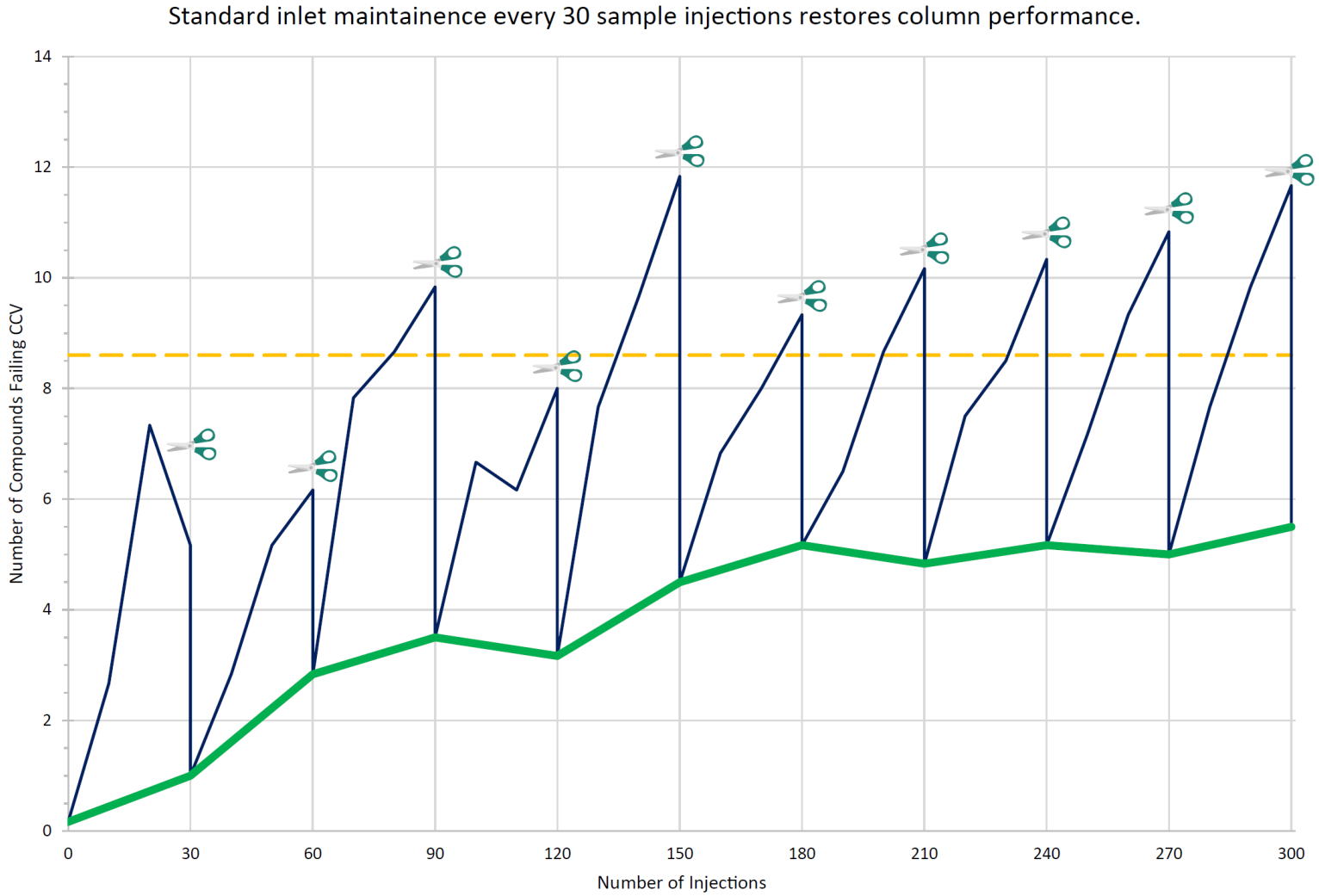
New Surface Deactivation: Rugged Enough for the Harshest Matrices

300 injections of a diesel particulate extract (NIST SRM 1975)

- Calibration Verification (CCV) performed every 10 SRM injections
- Maintenance (2 loops removed, new liner, new seal) every 30 SRMinjections

After 300 injections, CCV still meets expected peformance targets

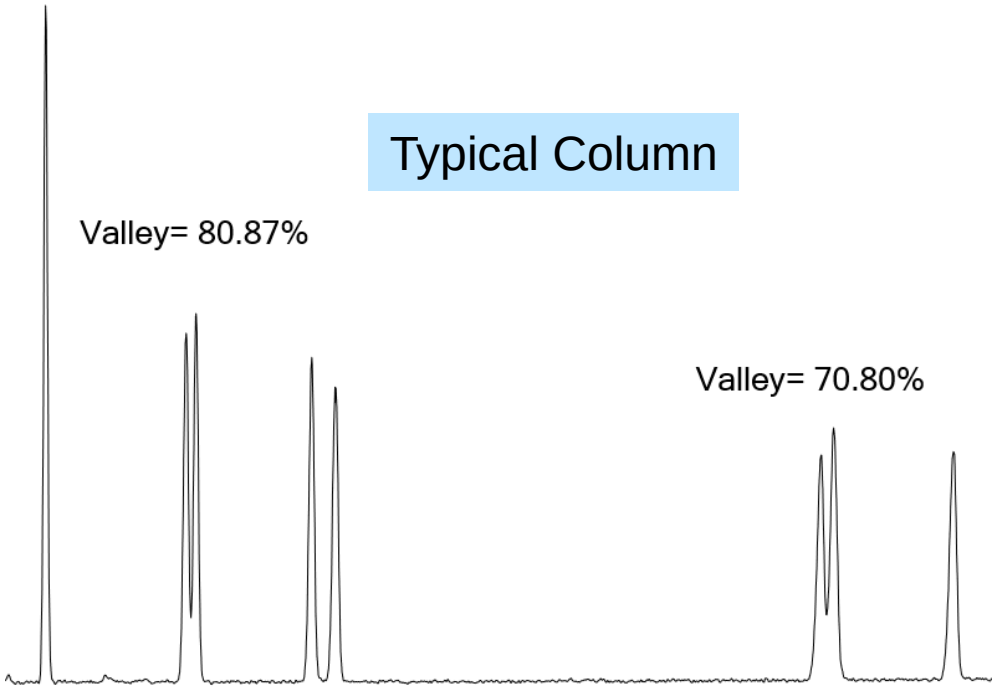
- 6.4% of targets analytes fall outside the ± 20% recovery window



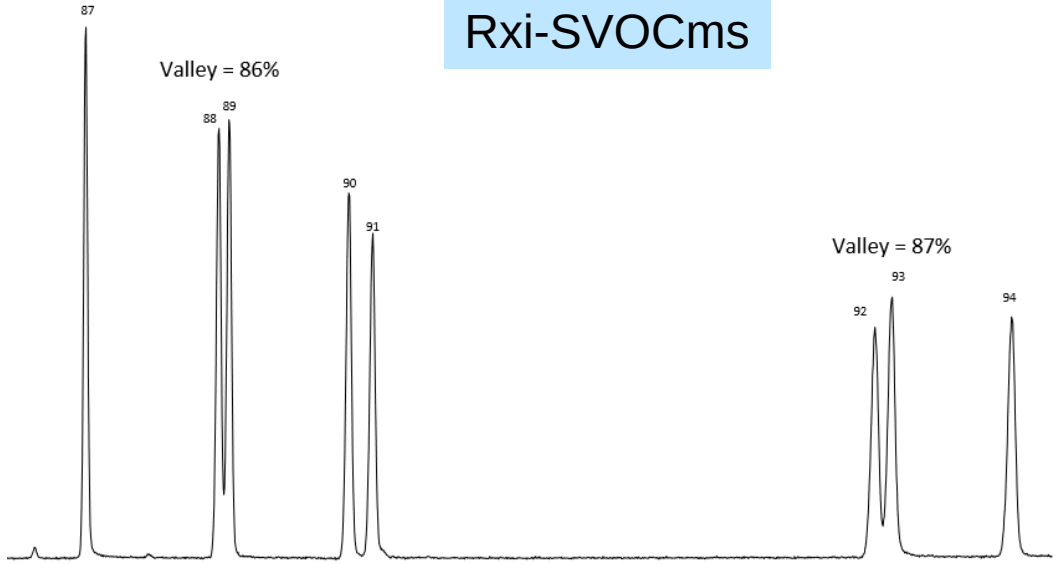
New Polymer, Optimized PAH Selectivity

Improved Benzofluoranthene and Indeno[123-cd]pyrene – Dibenz[ah]anthracene Separations

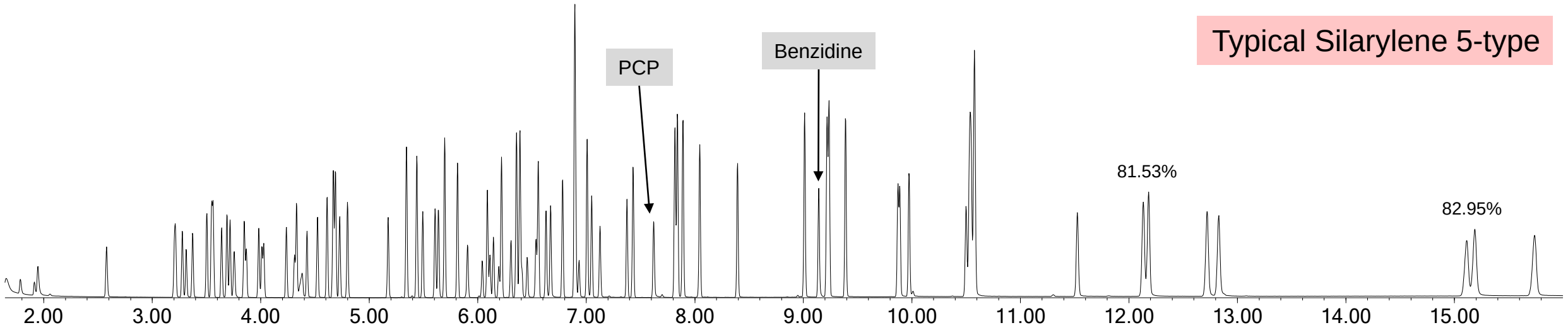
Typical Column

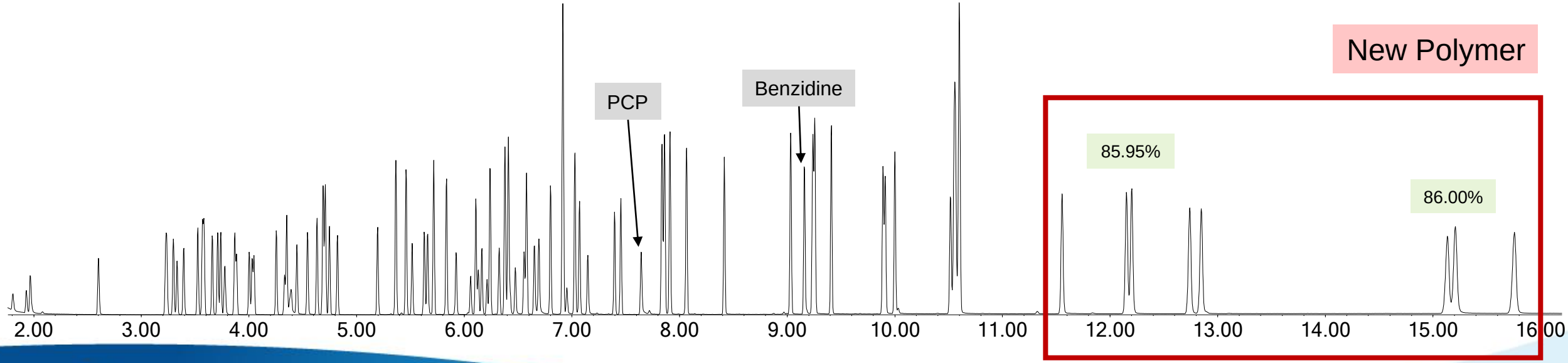


Rxi-SVOCms

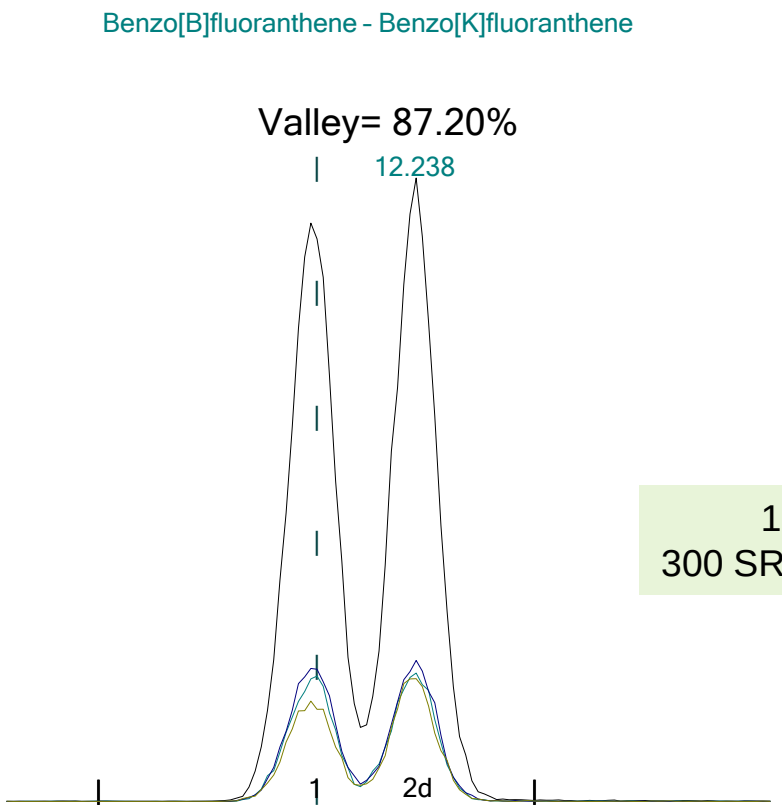


New Polymer, Same Chromatogram

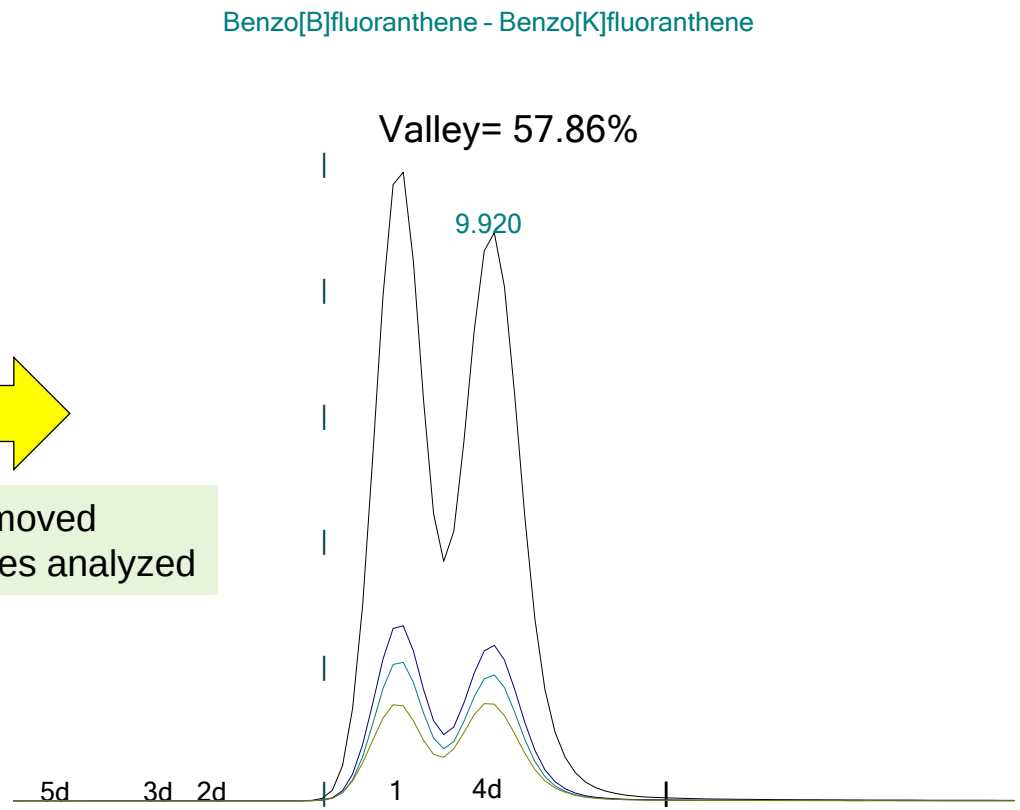




Benzofluoranthene isomers are still sufficiently resolved after removing ten meters of from a 30 m x 0.25 mm x 0.25 µm

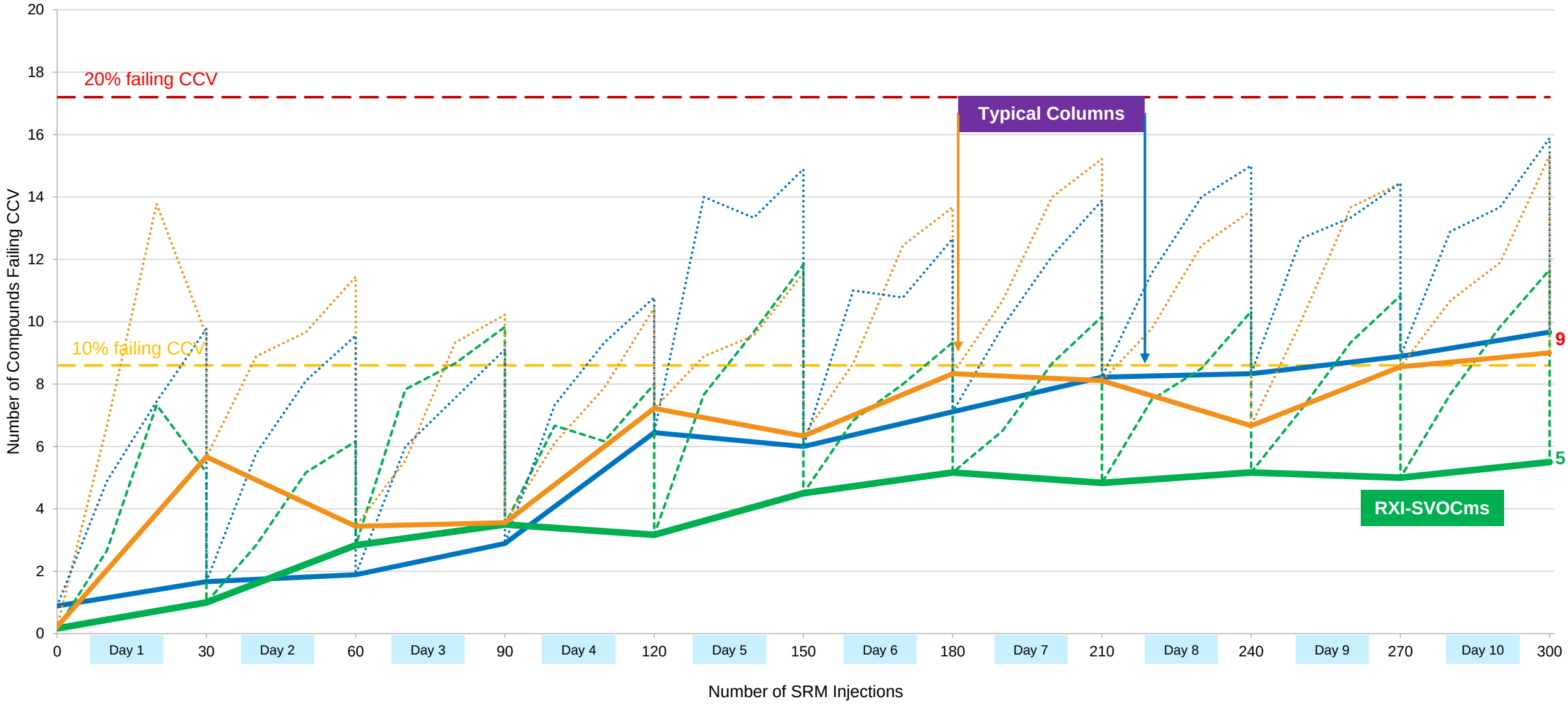


10m column removed
300 SRM 1975 samples analyzed

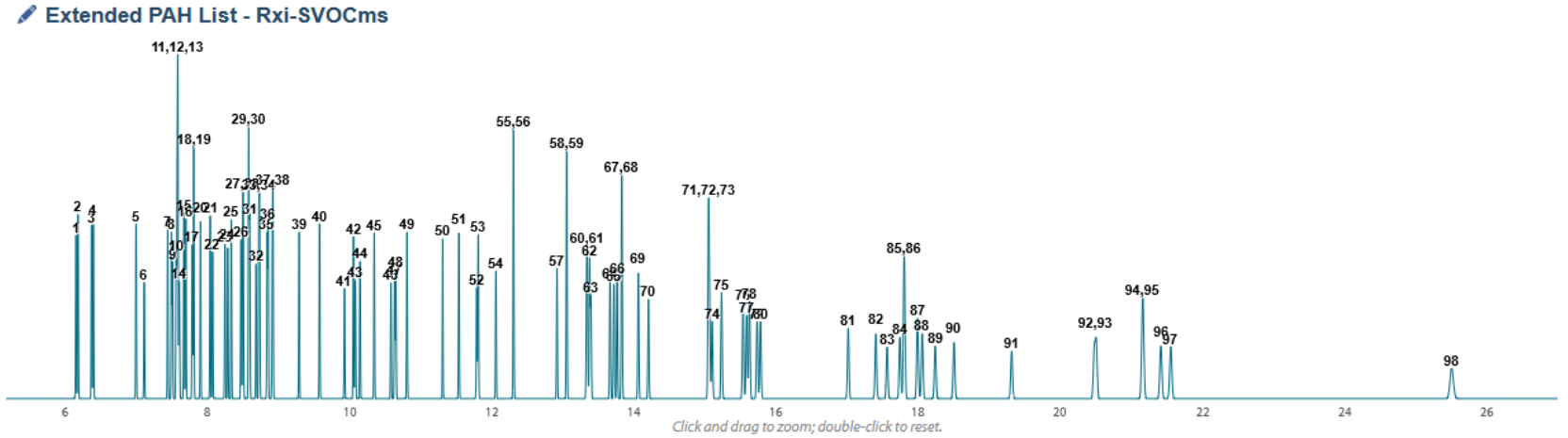


No Changes to temperature program or flow rate

Calibration Stability Compared to the Typical Columns



There is an extensive PAH library in *EZ*GC



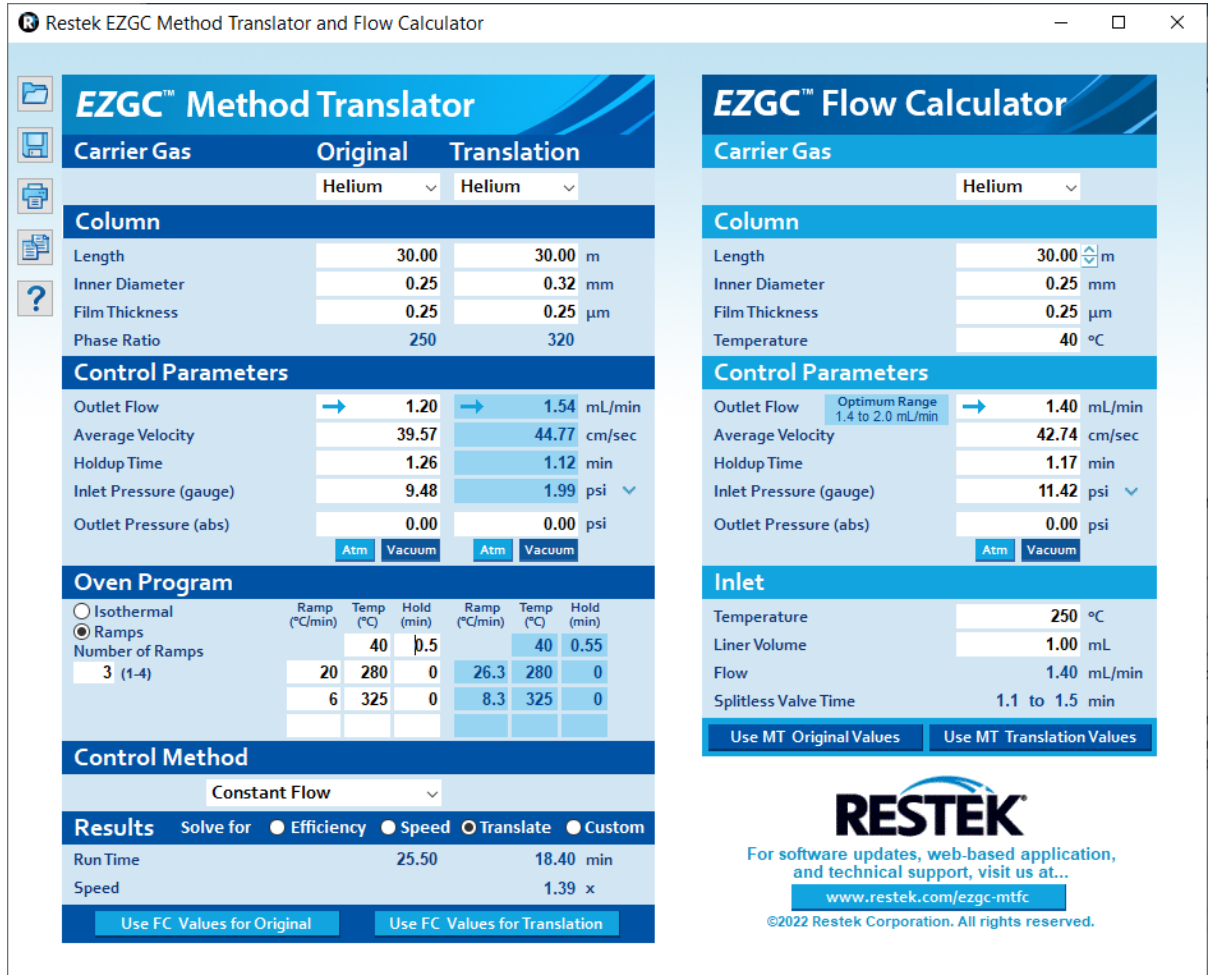
Column: **Rxi-SVOCms**, 30.00 m, 0.25 mm ID, 0.25 µm (cat.# 16623)
Carrier Gas: Helium, Constant Flow @ 1.40 mL/min
Average Velocity: 42.74 cm/sec
Outlet Pressure (abs): 0.00 psi
Oven Temp.: 40 °C (hold 0.5 min) to 280 °C @ 20 °C/min to 330 °C @ 6 °C/min (hold 6 min)

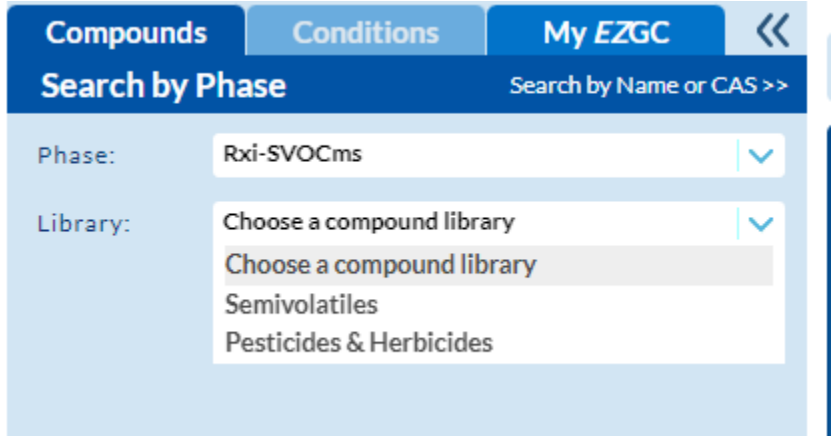
https://ez.restek.com/proezgc/en

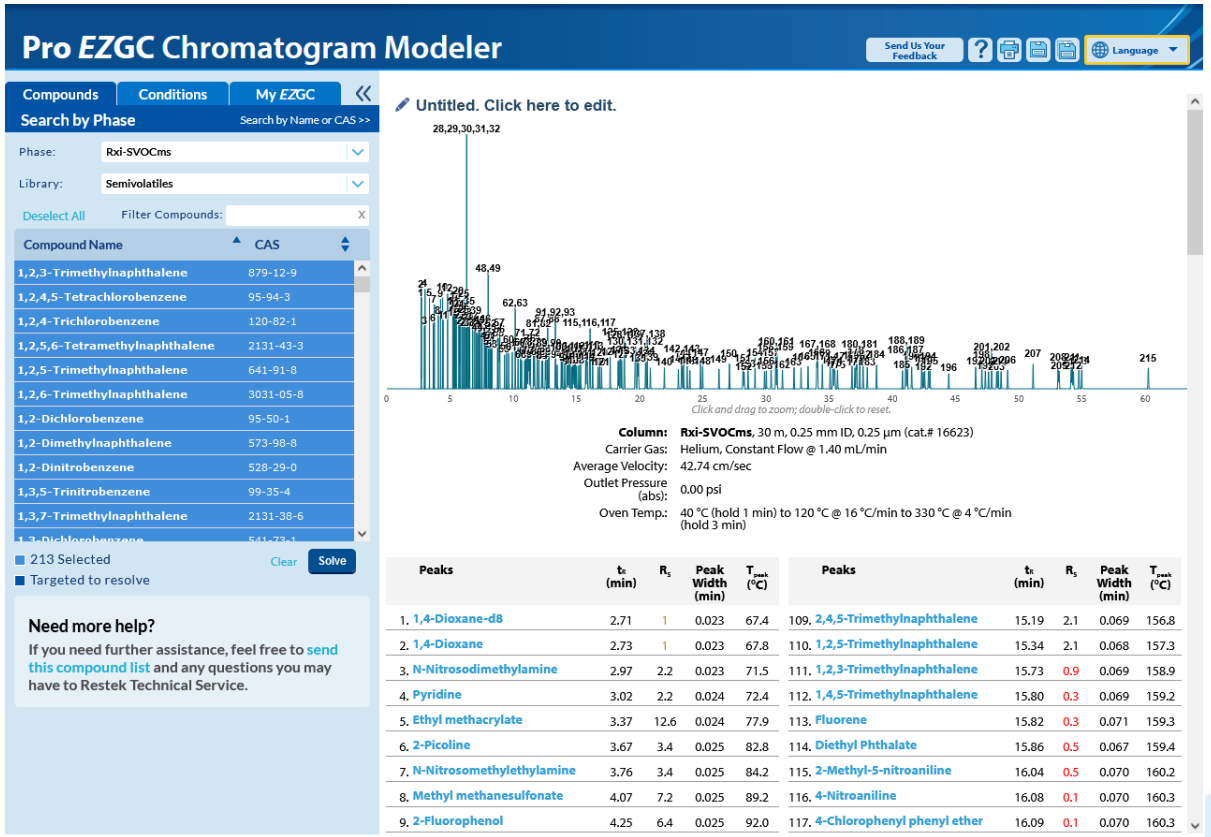
Peaks	t_R (min)	R_s	Peak Width (min)	T_{peak} (°C)
1. Naphthalene-D8	6.15	1.2	0.023	153.0
2. Naphthalene	6.18	1.2	0.023	153.6
3. Quinoline-d7	6.37	1.1	0.023	157.4
4. Quinoline	6.40	1.1	0.023	157.9
5. 2-Methylnaphthalene	7.00	4.9	0.023	169.9
6. 1-Methylnaphthalene	7.11	4.9	0.024	172.3
7. 2-Fluorobiphenyl	7.44	2.3	0.023	178.8
8. 2-Ethylnaphthalene	7.50	0.6	0.023	179.9
9. 1-Ethylnaphthalene	7.51	0.6	0.023	180.2
10. Biphenyl	7.56	0.5	0.023	181.2
11. 2,6-Dimethylnaphthalene	7.58	0.3	0.023	181.5
12. 2-Chloronaphthalene	7.58	0.1	0.024	181.7
13. 2,7-Dimethylnaphthalene	7.59	0.1	0.023	181.8
14. 1-Chloronaphthalene	7.61	0.8	0.024	182.1
15. 1,3-Dimethylnaphthalene	7.67	1.1	0.023	183.4
16. 1,6-Dimethylnaphthalene	7.70	1.1	0.023	184.0
17. 1,4-Naphthoquinone	7.79	0.9	0.023	185.8
18. 1,4-Dimethylnaphthalene	7.81	--	0.023	186.2
19. 2,3-Dimethylnaphthalene	7.81	--	0.023	186.2
20. 1,2-Dimethylnaphthalene	7.90	4.1	0.023	188.1
21. 1,8-Dimethylnaphthalene	8.04	1.4	0.023	190.8
22. Acenaphthylene	8.07	1.4	0.024	191.5
23. Acenaphthene-d10	8.25	1.6	0.024	195.0
24. Acenaphthene	8.29	1.6	0.024	195.8
25. 1,3,7-Trimethylnaphthalene	8.34	2	0.023	196.7
26. 1,4,6-Trimethylnaphthalene	8.47	1	0.023	199.5
27. Dibenzofuran	8.50	0.3	0.024	200.0
28. 2,3,6-Trimethylnaphthalene	8.51	0.3	0.023	200.1
29. 2,3,5-Trimethylnaphthalene	8.58	0.1	0.023	201.6
30. 1-Naphthalamine	8.58	0.1	0.024	201.7
31. 1,2,6-Trimethylnaphthalene	8.60	0.5	0.023	201.9
32. 2-Naphthalamine	8.69	1.6	0.024	203.7
33. 2,4,5-Trimethylnaphthalene	8.72	0.4	0.024	204.5
34. 1,2,5-Trimethylnaphthalene	8.74	0.4	0.023	204.7
35. 1,2,3-Trimethylnaphthalene	8.84	0.6	0.023	206.8
36. 1,4,5-Trimethylnaphthalene	8.86	0.6	0.023	207.1
37. Fluorene	8.92	0.4	0.024	208.3
38. 2-Methyl-5-nitroaniline	8.93	0.4	0.023	208.5
39. 1,4,6,7-Tetramethylnaphthalene	9.29	12.4	0.023	215.8
40. 1,2,5,6-Tetramethylnaphthalene	9.58	12.4	0.024	221.6
41. Dibenzothiophene	9.93	5.1	0.025	228.6
42. Phenanthrene-D10	10.06	1.1	0.025	231.1
43. Phenanthrene	10.08	1.1	0.025	231.7
44. Anthracene	10.15	2.6	0.025	233.0
45. Carbazole	10.35	8.1	0.024	237.0
46. 2-Methylanthracene	10.58	2.1	0.024	241.7
47. 1-Methylanthracene	10.63	0.7	0.024	242.7
48. 1-Methylphenanthrene	10.65	0.7	0.024	243.1
49. 4H-Cyclopenta[def]phenanthrene	10.81	6.4	0.025	246.2

Peaks	t_R (min)	R_s	Peak Width (min)	T_{peak} (°C)
50. 2-Methylfluoranthene	11.31	11.6	0.019	256.3
51. Fluoranthene	11.54	9.8	0.025	260.8
52. Pyrene-d10	11.79	0.8	0.026	265.8
53. Pyrene	11.81	0.8	0.025	266.2
54. p-Terphenyl	12.06	9.8	0.024	271.2
55. 1-Methylpyrene	12.31	0.1	0.025	276.1
56. Benzo[c]fluorene	12.31	0.1	0.025	276.2
57. 2-(Acetylamino)fluorene	12.92	5.1	0.027	282.5
58. Benzo[ghi]fluoranthene	13.06	--	0.028	283.3
59. Benzo[c]phenanthrene	13.06	--	0.029	283.4
60. Cyclopenta[cd]pyrene	13.34	0.3	0.030	285.0
61. Benz[a]anthracene	13.35	0.3	0.030	285.1
62. Triphenylene	13.38	0.5	0.030	285.3
63. Chrysene	13.40	0.5	0.030	285.4
64. 1-Methylbenz[a]anthracene	13.67	1.7	0.031	287.0
65. 3-Methylchrysene	13.72	1.4	0.032	287.3
66. 2-Methylchrysene	13.77	1.4	0.032	287.6
67. 4-Methylchrysene	13.83	--	0.032	288.0
68. 6-Methylchrysene	13.83	--	0.032	288.0
69. 5-Methylchrysene	14.06	4.1	0.034	289.4
70. Benz(A)anthracene-7,12-dione	14.21	4.1	0.034	290.3
71. 7,12-Dimethylbenzo[a]anthracene	15.05	--	0.040	295.3
72. Benzo[b]fluoranthene	15.05	--	0.040	295.3
73. Benzo[j]fluoranthene	15.07	0.3	0.040	295.4
74. Benzo[k]fluoranthene	15.10	0.9	0.040	295.6
75. Benzo(a)fluoranthene	15.24	3.2	0.041	296.4
76. Benzo[e]pyrene	15.54	1.2	0.043	298.2
77. Benzo[a]pyrene-d12	15.59	0.9	0.043	298.5
78. Benzo[a]pyrene	15.63	0.9	0.043	298.8
79. Perylene-D12	15.74	1.1	0.044	299.4
80. Perylene	15.78	1.1	0.044	299.7
81. p-Quaterphenyl	17.02	8	0.048	307.1
82. Dibenz[a,j]acridine	17.41	3	0.051	309.4
83. Dibenzo(a,j)anthracene	17.57	3	0.052	310.4
84. Indeno[1,2,3-cd]pyrene	17.75	1.1	0.053	311.5
85. Dibenz[a,h]anthracene	17.81	--	0.053	311.8
86. Dibenz[a,c]anthracene	17.81	--	0.053	311.8
87. Benzo[b]chrysene	17.99	1.2	0.053	313.0
88. Picene	18.06	1.2	0.054	313.4
89. Benzo[ghi]perylene	18.24	3.4	0.055	314.5
90. Anthanthrene	18.51	4.7	0.056	316.0
91. 6,13-Pentacenedione	19.32	14.4	0.057	320.9
92. Dibenzo[a,l]pyrene	20.48	0.4	0.060	327.9
93. Dibenzo[b,k]fluoranthene	20.51	0.4	0.060	328.1
94. Dibenzo[a,e]pyrene	21.16	0.1	0.064	330.0
95. Coronene	21.17	0.1	0.065	330.0
96. Dibenzo(a,i)pyrene	21.42	2	0.067	330.0
97. Dibenzo(a,h)pyrene	21.56	2	0.069	330.0
98. p-Quinquephenyl	25.51	57.4	0.109	330.0

Method Development Tools







1 ng 8270 MegaMix on the Rxi-SVOCms 20 m x 0.15 mm x 0.15 µm

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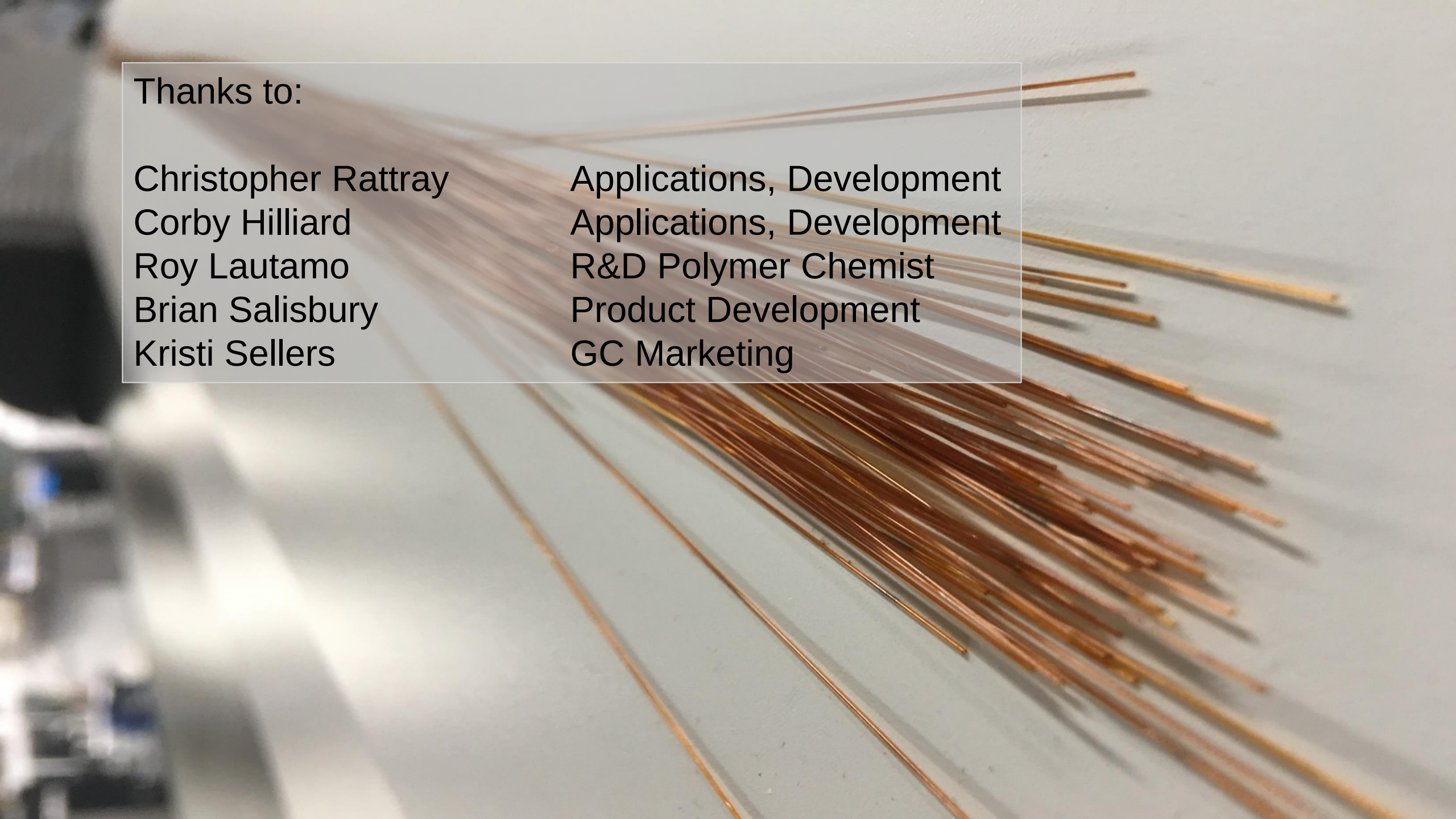

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Christopher Rattray	Applications, Development
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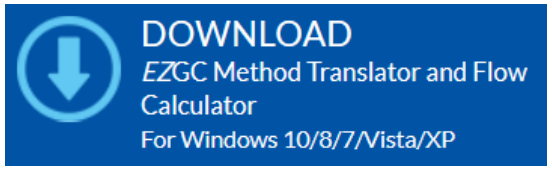
Brian Salisbury	Product Development
Kristi Sellers	GC Marketing

1. **Phase for semivolatiles developed with unique characteristics**
2. **Designed for improved lifetime based on testing using NIST SRM 1975**
3. **Targeted for PAH resolutions**

- *Each column is tested with semivolatiles at 1 ng level & 340°C*

Pro *EZ*GC Chromatogram Modeler

ChromaBLOGraphy



Questions?