

# Complete Fractionation of Extractable Petroleum Hydrocarbons Using Newly Developed EPH SPE Cartridges

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# Outline

- Background
- EPA Method Requirements
- Background and Recovery
- PAHs in Used Motor Oil

# What is EPH?

- Extractable Petroleum Hydrocarbons
- Means to separate Aliphatic and Aromatic compounds
- Clean up step for environmental samples
- Typical cartridge format for MA and NJ methods: 5g irregular silica gel fritted in 25 mL syringe tube

# Importance of EPH:

- Multiple states follow EPH Methods
  - MA, NJDEP, Texas, WA, Atlantic RBCA
- Used to assess impact of environmental samples
  - Separates target aliphatic components from target aromatic components
- Allows separation of EPA priority 16 PAHs
  - Higher proportion of aromatics have more hazardous designation relative to samples consisting of primarily aliphatic hydrocarbons

# How does a EPH cartridge work?

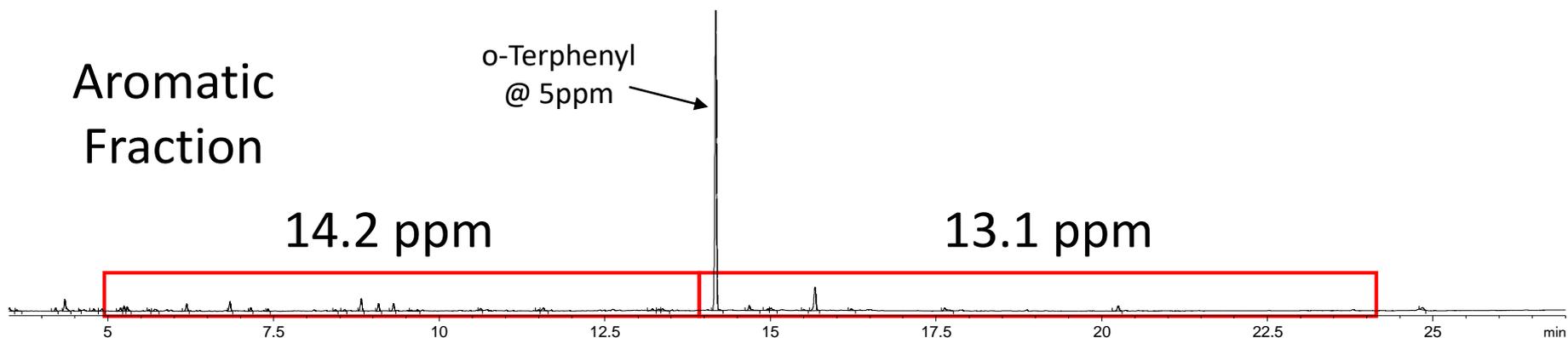
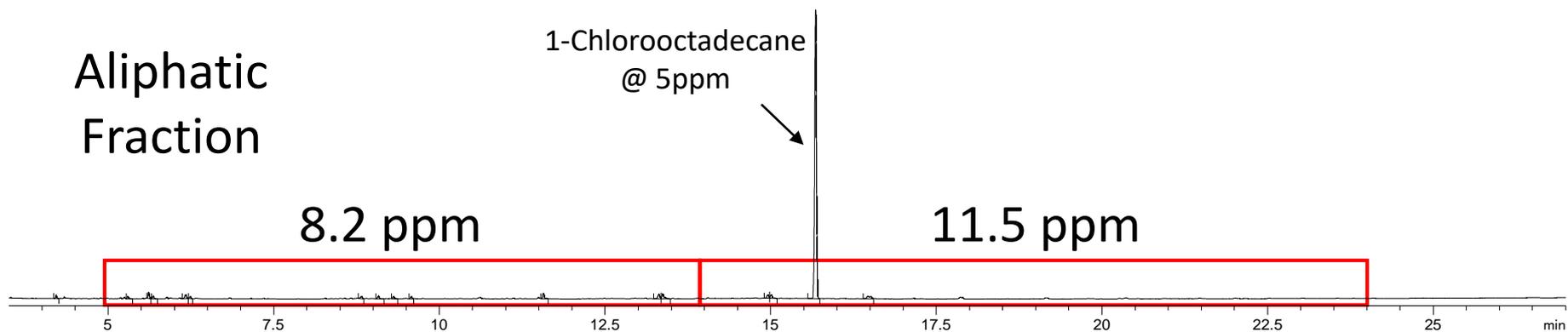
- Normal Phase
- Dried Silica Gel (Activated) is Polar
  - Non-polar compounds will elute first
- Hexane pulls off non-polar aliphatic compounds
- Dichloromethane pulls off more polar aromatic compounds
  - Compared to Hexane, DCM is moderately polar

# EPH Method Requirements:

- MA EPH Method
  - 40 – 140% Recovery for Analytes and Surrogates
  - < 5% Breakthrough for Naphthalene and 2-Methylnaphthalene
- NJ EPH Method
  - Based off MA EPH Method
  - Requires monitoring of additional analytes
- Texas EPH Method
  - Uses Pentane instead of Hexane
  - 60 – 140% Recovery for Analytes, 70 – 130% Recovery for Surrogates
  - < 10 – 20% Crossover

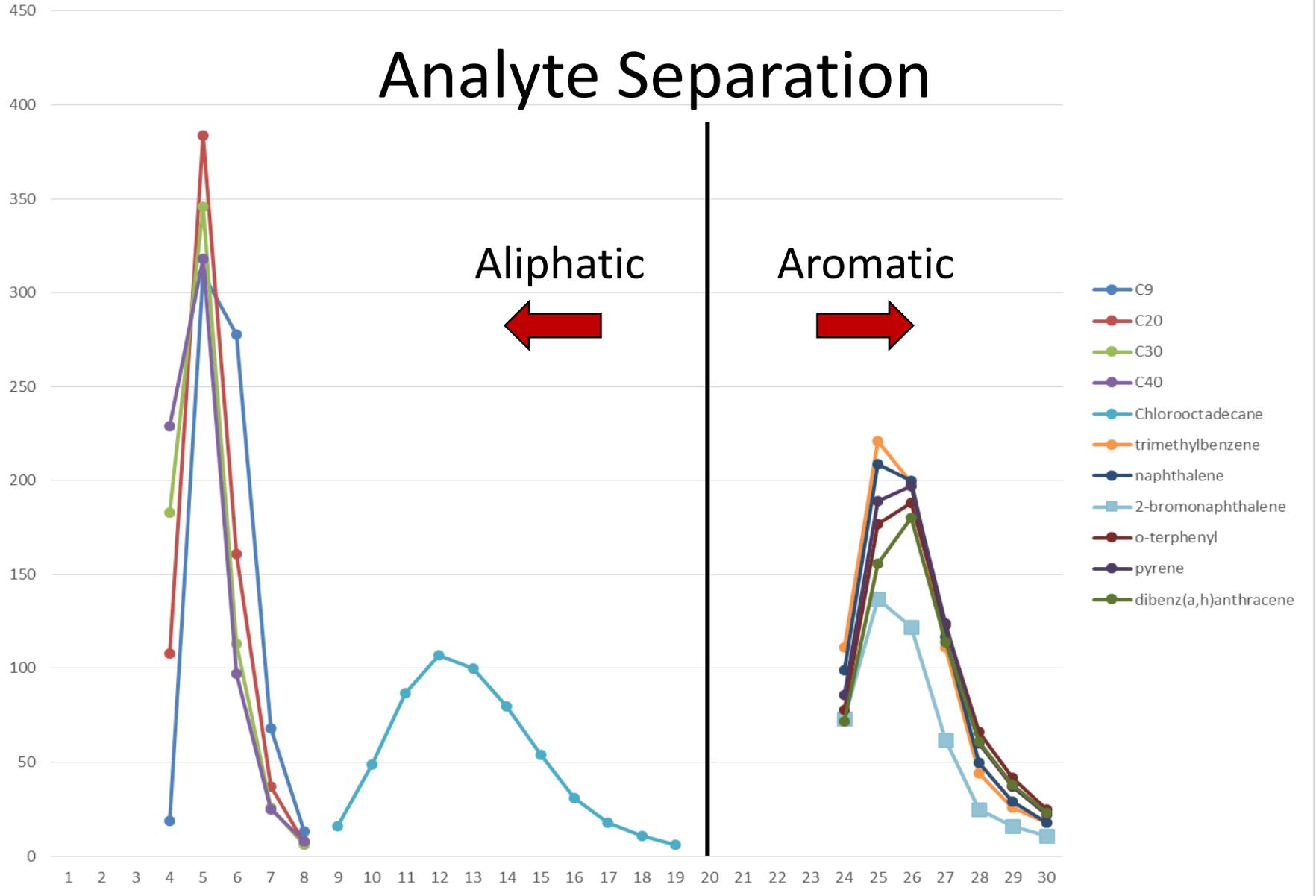
# Extractable Background

- < 30 ng of background contamination on-column



ng on-column = ppm

# Analyte Separation



# Recovery – MA and NJDEP

- EPH Cartridge:
  - Resprep EPH Fractionation SPE Cartridge – Restek Cat # 25859
- Reference Standards:
  - MA Fractionation Surrogate Spike Mix – Restek Cat # 31480
  - MA Surrogate Spike Mix – Restek Cat # 31479
  - NJDEP Aliphatic Calibration Standard – Restek Cat # 30544
  - NJDEP Aromatic Calibration Standard – Restek Cat # 30545
  - Naphthalene Standard – Restek Cat # 31280
  - 2-Methylnaphthalene Standard – Restek Cat # 31285

# Recovery – MA and NJDEP

- Sample Preparation:
  - Condition Cartridge with 15 mL Hexane
  - Addition of 1 mL of Sample
  - Elute with 19 mL of Hexane (Aliphatic Fraction), followed by 20 mL of dichloromethane (Aromatic Fraction)
  - Concentration to a final volume of 1 mL
- Analysis:
  - Agilent 7890 GC-FID
  - Column: Rxi-5Sil MS – 30m x 0.32mm x 0.25 $\mu$ m – Restek Cat # 13624
  - Oven Program: 40°C (1.5 min.) → 300°C @12°C/min → 350°C (7 min.) @ 6°C/min
  - Injection temperature: 300°C; Injection volume: 1.0  $\mu$ L, Carrier: Helium, constant flow @ 3 mL/min.
  - Injection mode: splitless, purge flow: 50 mL/min. @ 1min.
  - Detector Temp: 350°C

# Recovery – MA and NJDEP

Average of 3 Replicates of 3 Different Lots @ 35 ppm

Aliphatic Fraction:	% Rec.	Std.Dev.	% RSD	Aromatic Fraction:	% Rec.	Std.Dev.	% RSD
n-Nonane (C9)	85.8	1.42	1.65	1,2,3-Trimethylbenzene	91.0	1.85	2.03
n-Decane (C10)	87.7	1.59	1.82	Naphthalene	92.8	4.22	4.55
n-Dodecane (C12)	92.2	1.85	2.01	2-Methylnaphthalene	94.1	4.17	4.43
n-Tetradecane (C14)	93.6	2.07	2.22	2-Fluorobiphenyl	95.1	3.98	4.19
n-Hexadecane (C16)	97.0	2.26	2.33	Acenaphthylene	95.4	3.92	4.11
n-Octadecane (C18)	99.2	2.03	2.05	2-Bromonaphthalene	96.4	3.98	4.13
n-Nonadecane (C19)	103.0	2.15	2.08	Acenaphthene	95.9	4.02	4.19
n-Eicosane (C20)	101.5	2.22	2.19	Fluorene	97.2	4.03	4.14
1-Chlorooctadecane	94.1	2.71	2.88	Phenanthrene	99.5	4.09	4.11
n-Heneicosane (C21)	91.0	0.78	0.86	Anthracene	98.6	4.02	4.07
n-Docosane (C22)	100.3	2.59	2.59	o-Terphenyl	96.6	3.94	4.08
n-Tetracosane (C24)	99.9	2.15	2.15	Fluoranthene	98.6	4.15	4.21
n-Hexacosane (C26)	99.6	1.76	1.77	Pyrene	99.5	4.20	4.22
n-Octacosane (C28)	99.5	1.85	1.86	Benzo(a)anthracene	99.2	4.45	4.49
n-Triacontane (C30)	98.9	2.09	2.12	Chrysene	99.6	4.55	4.56
n-Hexatriacontane (C36)	98.2	2.90	2.96	Benzo(b) fluoranthene	100.7	4.69	4.66
n-Octatriacontane (C38)	92.5	0.92	1.00	Benzo(k)fluoranthene	100.0	4.65	4.65
Tetracontane (C40)	91.7	0.85	0.92	Benzo(a)pyrene	98.8	4.62	4.67
				Indeno(1,2,3-cd)pyrene	99.3	4.66	4.69
				Dibenzo(a,h)anthracene	98.7	4.64	4.70
				Benzo(g,h,i)perylene	99.4	4.66	4.69

40 – 140% Analyte Recovery

# Recovery – Texas

- EPH Cartridge:
  - Resprep EPH Fractionation SPE Cartridge – Restek Cat # 25859
- Reference Standards:
  - MA EPH Surrogate Spike Mix – Restek Cat # 31479
  - 1-Chlorooctane – Restek Cat # 30084
  - 8270 Calibration Mix #5, Revised – Restek Cat # 31995
  - BTEX Standard – Restek Cat # 30213
  - TNRCC 1006 Retention Time Marker Mix – Restek Cat # 31814
  - Custom 1,2,3-Trimethylbenzene and Benzo(e)pyrene Mix

# Recovery – Texas

- Sample Preparation:
  - Condition Cartridge with 15 mL Pentane
  - Addition of 1 mL of Sample
  - Elute with 40 mL of Pentane (Aliphatic Fraction), followed by 20 mL of Dichloromethane (Aromatic Fraction)
  - Concentration to a final volume of 1 mL
- Analysis:
  - Agilent 7890 GC-FID
  - Column: Rxi-5Sil MS – 30m x 0.25mm x 0.25 $\mu$ m – Restek Cat # 13623
  - Oven Program: 35°C (4 min.)  $\rightarrow$  200°C @10°C/min  $\rightarrow$  260°C @ 4°C/min  $\rightarrow$  330°C @20°C/min
  - Injection temperature: 300°C; Injection volume: 1.0  $\mu$ L, Carrier: He, constant flow 2 mL/min
  - Inj. mode: pulsed splitless, 30 psi until 0.5 min, 75 mL/min at 0.6 min
  - Detector Temp: 330°C

# Recovery – Texas

Average (n = 3) @ 5ppm

Aliphatic Fraction:	% Rec.	Std.Dev.	% RSD
n-Hexane (C6)	76.7	1.17	1.52
n-Heptane (C7)	75.1	1.69	2.25
n-Octane (C8)	74.8	1.46	1.96
n-Decane (C10)	78.8	1.62	2.06
1-Chlorooctane	78.9	1.13	1.44
n-Dodecane (C12)	79.9	2.70	3.38
n-Hexadecane (C16)	86.8	0.86	0.99
1-Chlorooctadecane	83.7	1.12	1.34
n-Heneicosane (C21)	85.3	1.02	1.20
n-Octacosane (C28)	86.4	0.76	0.88
n-Pentatriacontane (C35)	83.3	0.98	1.18

Aromatic Fraction:	% Rec.	Std.Dev.	% RSD
Benzene	86.6	0.21	0.24
Toluene	127.5	1.45	1.13
Ethylbenzene	87.3	0.67	0.77
p-Xylene	100.1	1.10	1.10
m-Xylene	102.4	1.05	1.03
o-Xylene	102.8	0.95	0.92
1,2,3-Trimethylbenzene	78.4	2.67	3.40
Naphthalene	80.3	5.94	7.40
2-Methylnaphthalene	81.2	0.75	0.92
1-Methylnaphthalene	79.7	0.49	0.61
Acenaphthylene	76.0	1.10	1.45
Acenaphthene	79.9	0.14	0.17
Fluorene	82.7	3.22	3.89
Phenanthrene	81.8	0.89	1.09
Anthracene	76.7	1.38	1.79
o-Terphenyl	80.2	1.40	1.74
Fluoranthene	79.2	1.47	1.85
Pyrene	78.9	4.16	5.27
Benz(a)anthracene	82.4	1.06	1.29
Chrysene	82.6	1.19	1.44
Benzo(b)fluoranthene	81.8	1.04	1.27
Benzo(k)fluoranthene	81.5	1.15	1.41
Benzo( e)pyrene	81.9	0.96	1.18
Benzo(a)pyrene	81.1	1.22	1.50
Indeno(1,2,3-cd)pyrene	80.7	1.13	1.40
Dibenz(a,h)anthracene	77.9	3.49	4.48
Benzo(g,h,i)perylene	75.2	5.94	7.91

60 – 140% Analyte Recovery  
70 – 130% Surrogate Recovery

# Matrix Overview:

- Motor oil loading at a range of concentrations
- Evaluation of breakthrough of Naphthalene and 2-Methylnaphthalene
- Breakthrough of used motor oil samples at 20 mg/mL
- PAH levels

# Cartridge Loading Capacity

- MADEP recommends maximum of 25 mg/mL
  - Saturation of silica could lead to breakthrough of early eluting aromatics
- The separation is typically one of a delicate balance as it is without additional encumbrances
  - Complex matrices
- A range of concentrations of motor oil were prepared
- Breakthrough of naphthalene and 2-methylnaphthalene monitored in hexane fraction

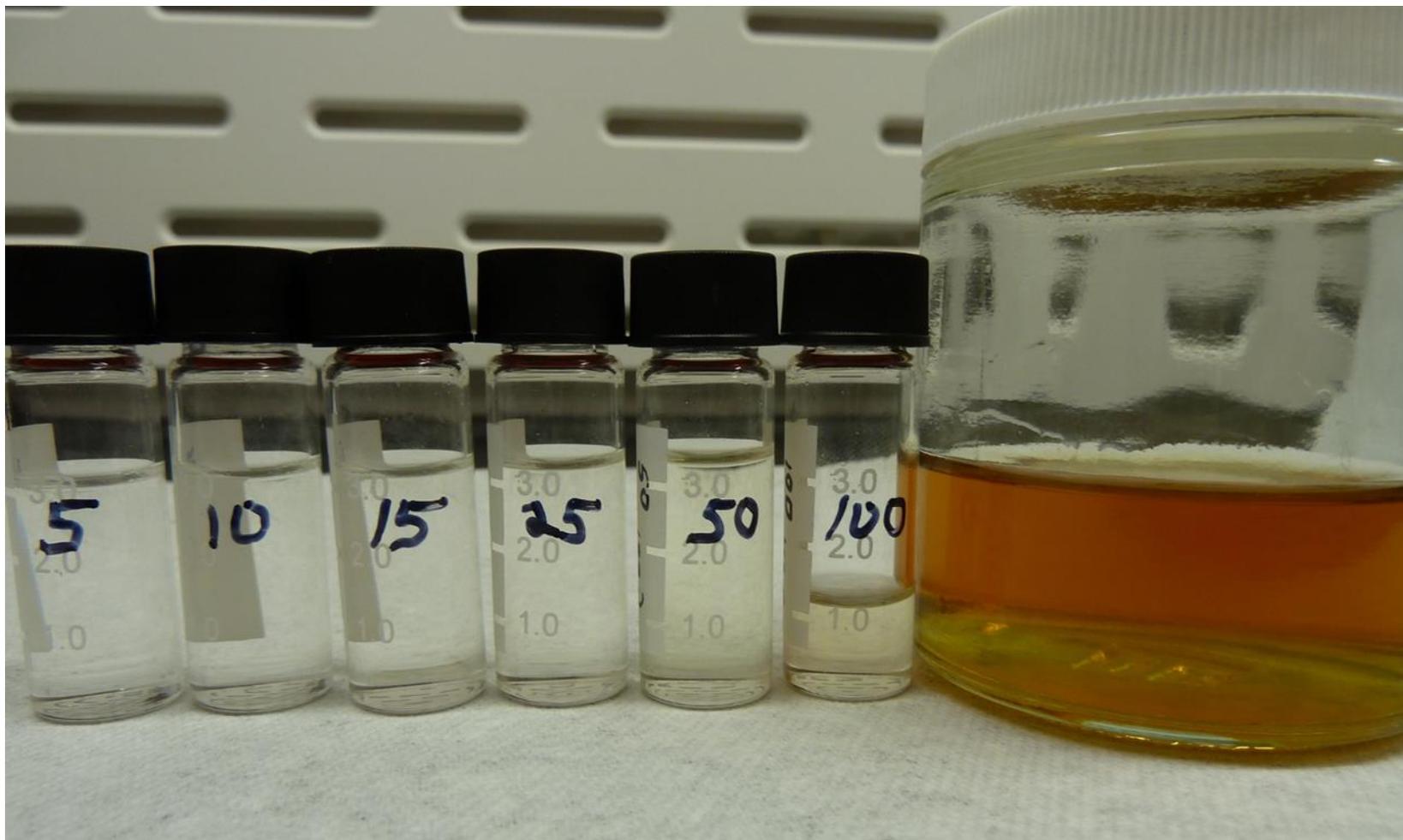
# Sample Preparation – Loading Capacity

- 5W/20 conventional motor oil was diluted into hexane to produce each target concentration
- Each sample was spiked with naphthalene and 2-methylnaphthalene at 10 ppm
- Surrogates 1-chlorooctadecane, o-Terphenyl and fractionation surrogates, 2-bromonaphthlene and 2-fluorobiphenyl, were spiked at 20 ppm
- 6 levels of motor oil were prepared in hexane
  - 5 mg/mL to 100 mg/mL

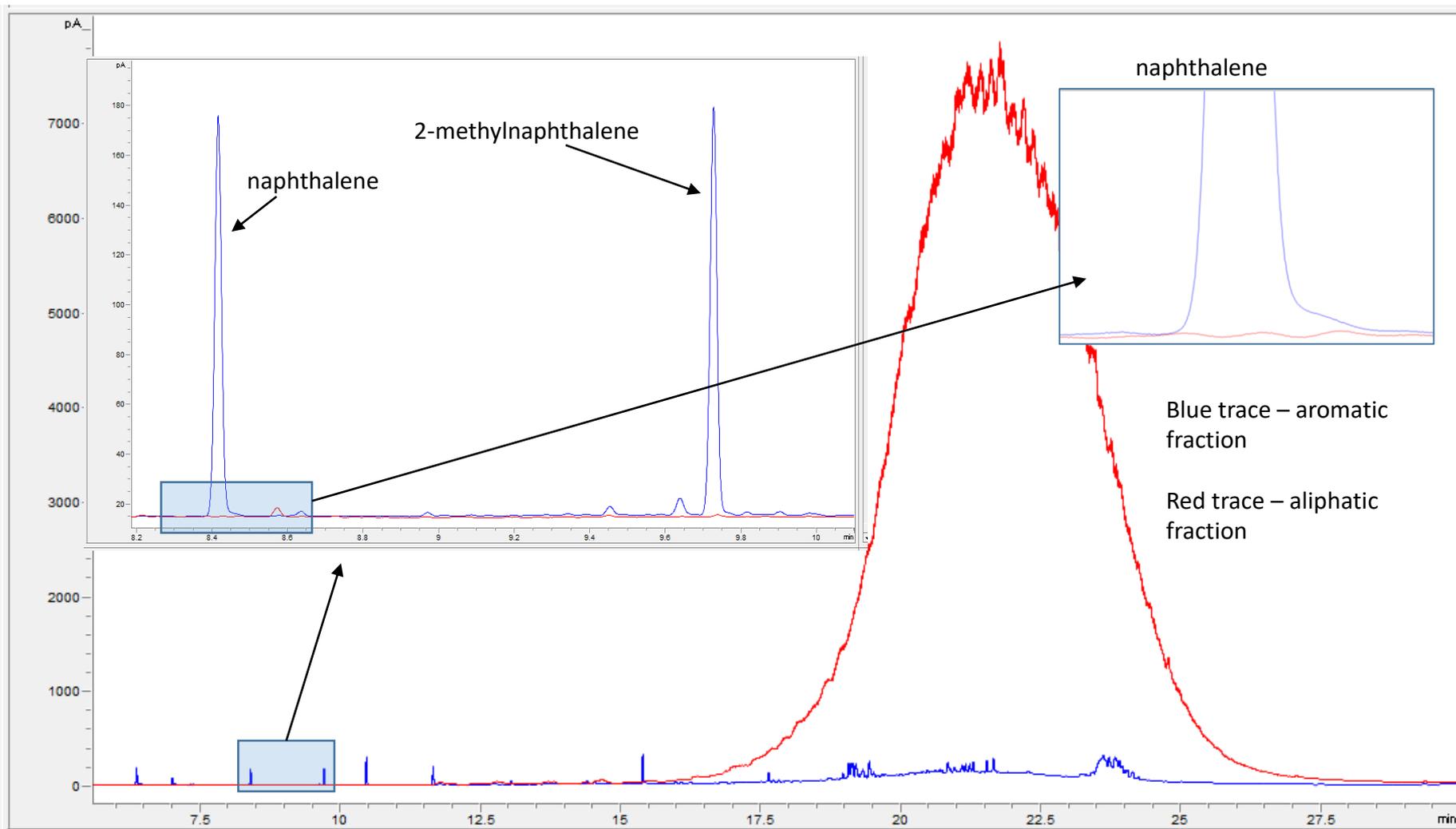
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- Analysis:
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  - Oven Program: 40°C (1.5 min.) → 300°C @12°C/min → 350°C (7 min.) @ 6°C/min
  - Injection temperature: 300°C; Injection volume: 1.0  $\mu$ L, Carrier: Helium, constant flow @ 3 mL/min.
  - Injection mode: splitless, purge flow: 50 mL/min. @ 1min.
  - Detector Temp: 350°C

# Sample Preparation – Loading Capacity



# Loading Capacity Results (100 mg/mL)

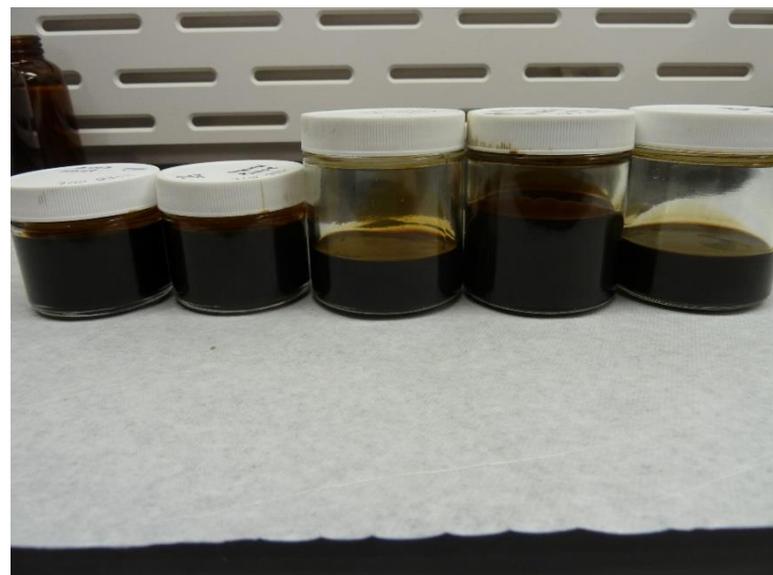


# PAHs in Used Motor Oil

- PAH is a result of incomplete combustion produced by internal combustion engines
- Can accumulate in motor oil through blow-by
- Would be expected in higher concentrations with increasing engine age and mileage
  - Older technology and declining engine performance produce more PAH
  - Deterioration of compression rings due to age and wear from high mileage increases blow-by
- Diesel vehicles produce more PAH during combustion

# PAHs in Used Motor Oil

- Because of PAH content (as well as metals and other contaminants) used motor oil is more of a concern than new oil
- Wrecking yards, storage tanks



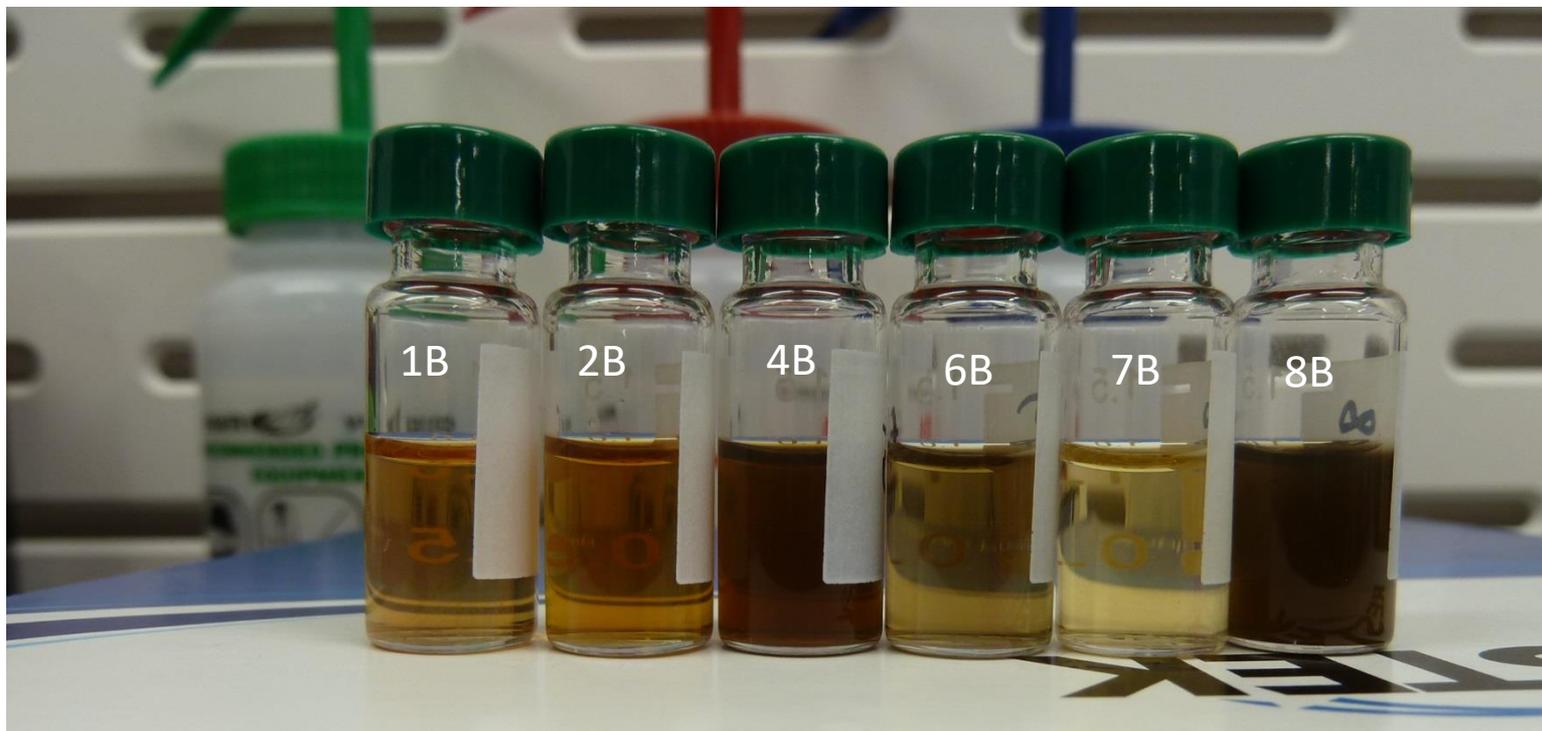
# PAHs in Used Motor Oil

- Samples were collected from vehicles with a range of ages and mileage

Sample ID	Vehicle	Year	Car Mileage	Oil Mileage	Oil Wt
1B	Ford Taurus Limited	2013	41,862	9,756	5w/20
2B	Honda Pilot EX	2008	73,000	5,000	5w/20
3B	Ford Taurus Limited	2013	53,500	6,000	5w/20
4B	Chevy Camaro IROC-Z	1986	172,659	3,000	20w/50
5B	Ford F-250 Ranger XLT	1971	103,000	2,000	20w/50
6B	Ford F-250 Ranger XLT	2005	95,418	3,200	15w/40
7B	Chevy Camaro Z-ZB	1994	105,464	728	5w/20
8B	Chevy Camaro Z-ZB	1980	178,000	NA	20w/50

# PAHs in Used Motor Oil

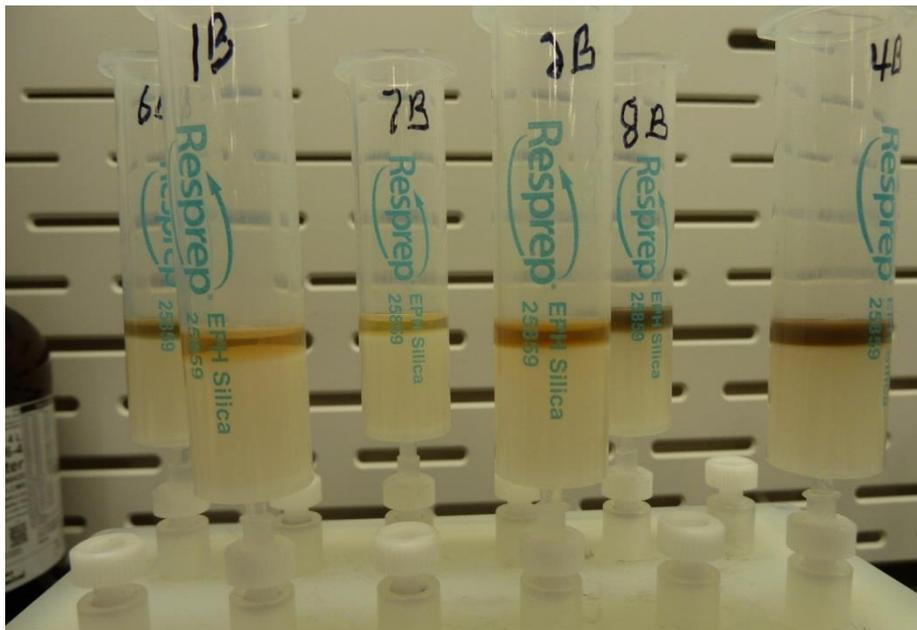
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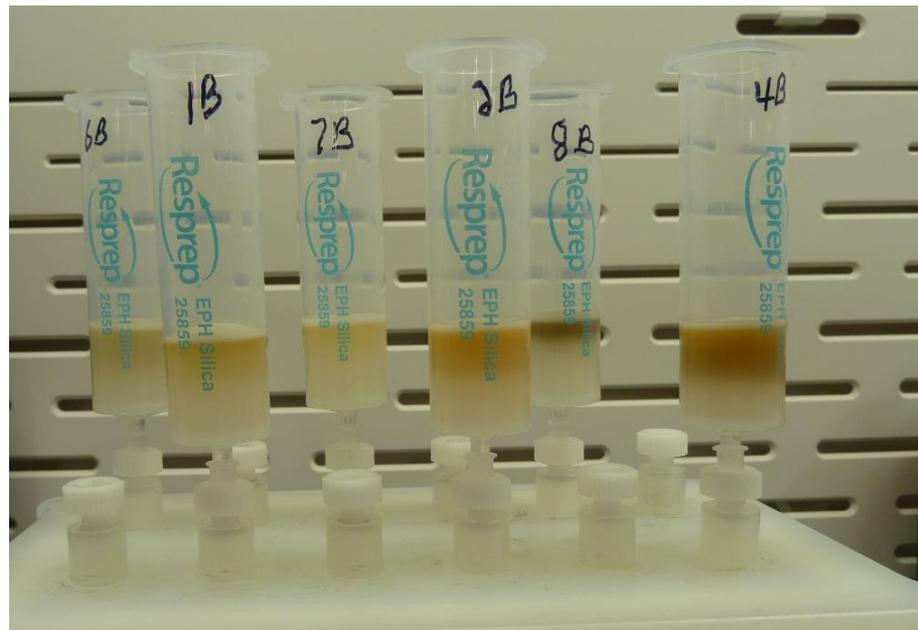
# PAHs in Used Motor Oil

- Extent of migration of color band during elution

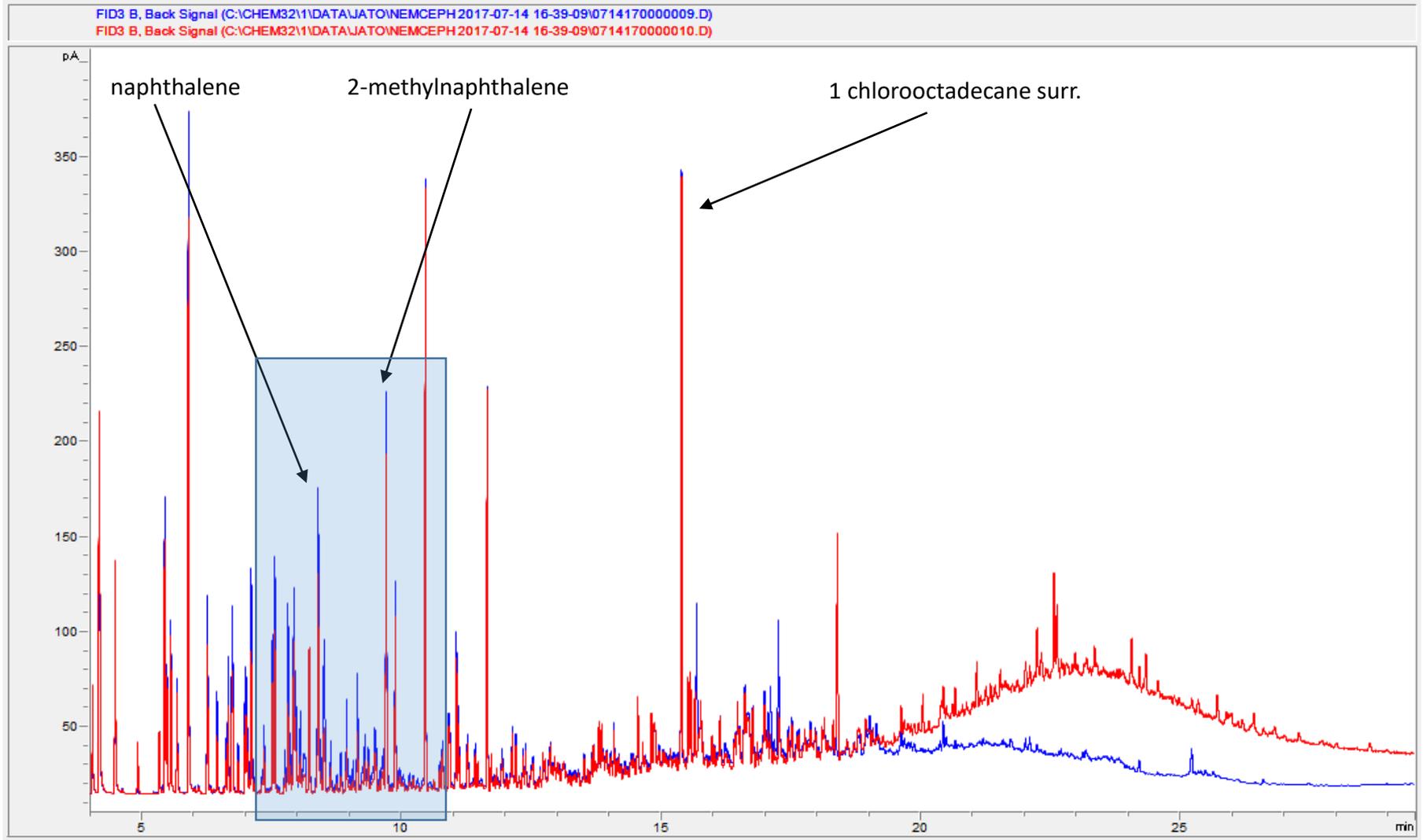
Sample Loading



After Extraction



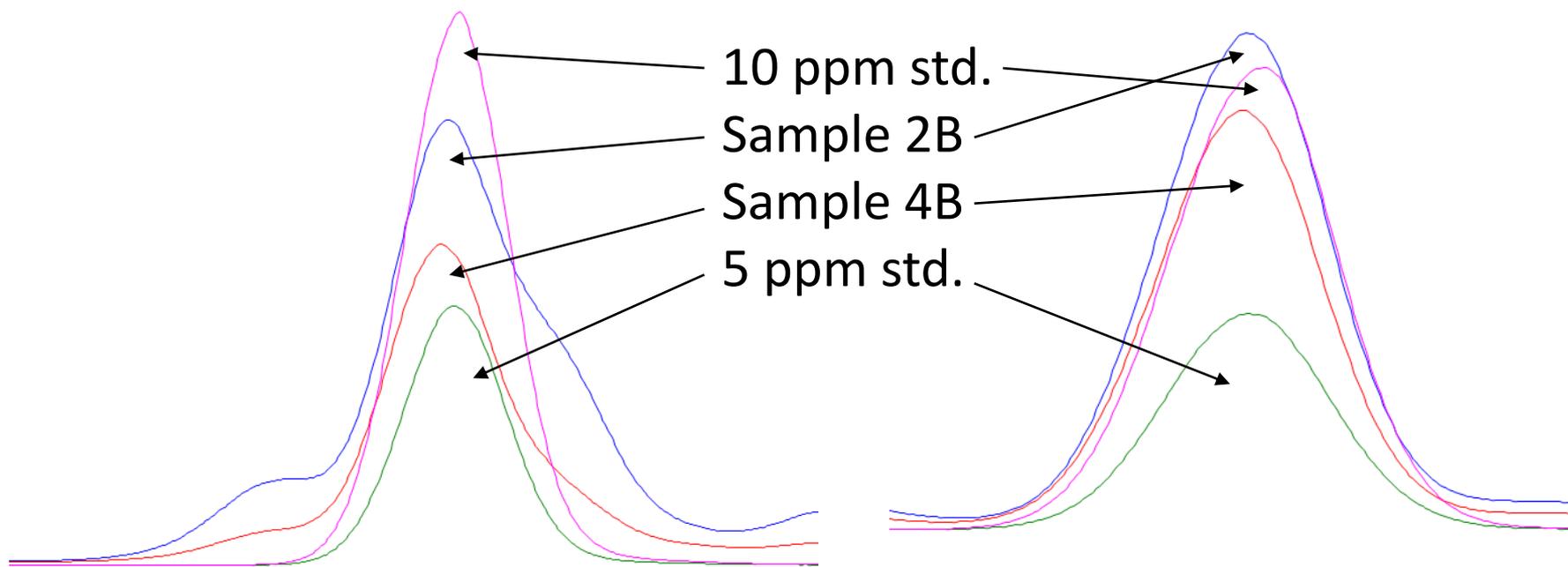
# PAHs in Used Motor Oil (Breakthrough)



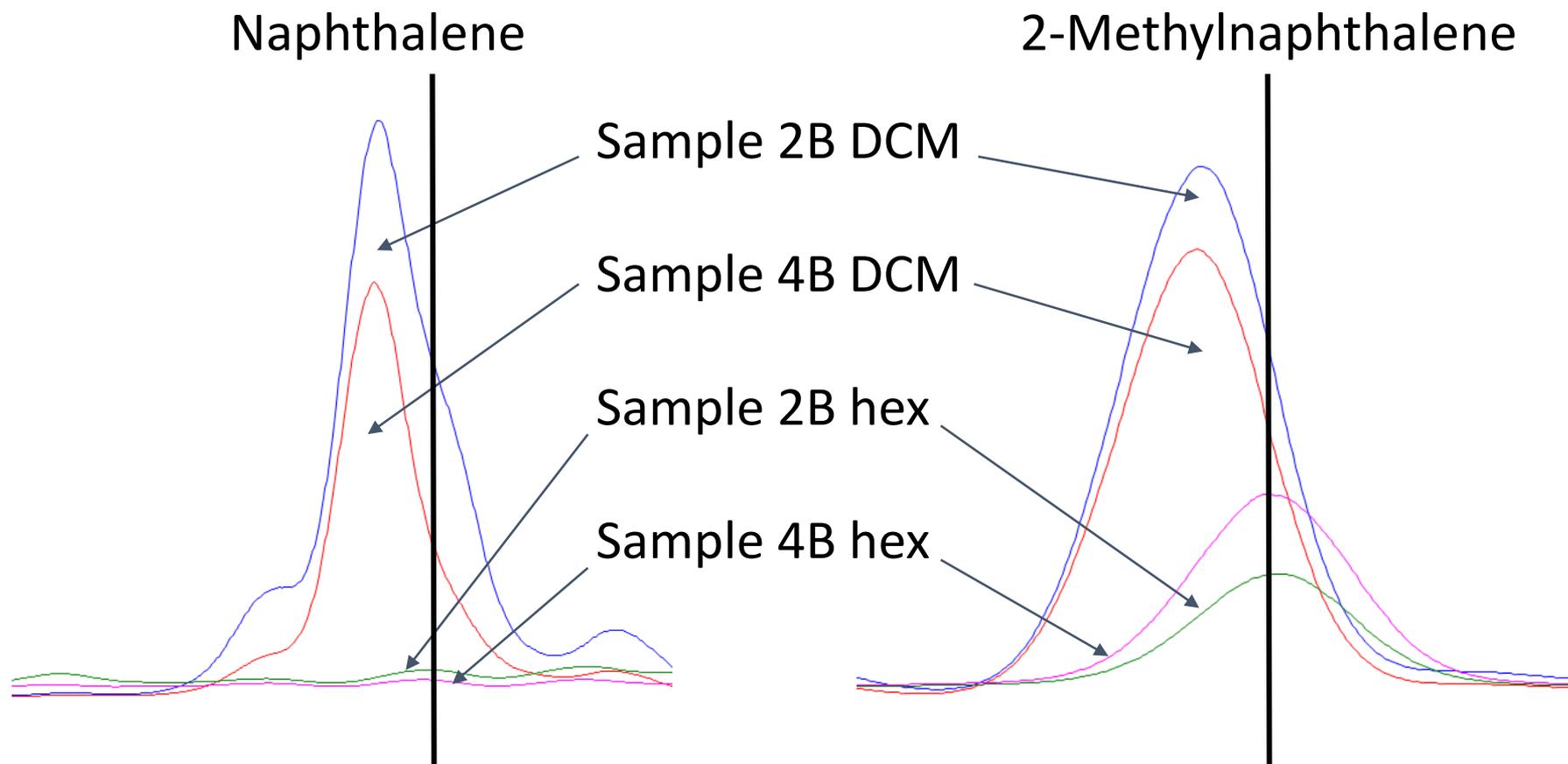
# PAHs in Used Motor Oil (Breakthrough-Aromatic Fraction)

Naphthalene

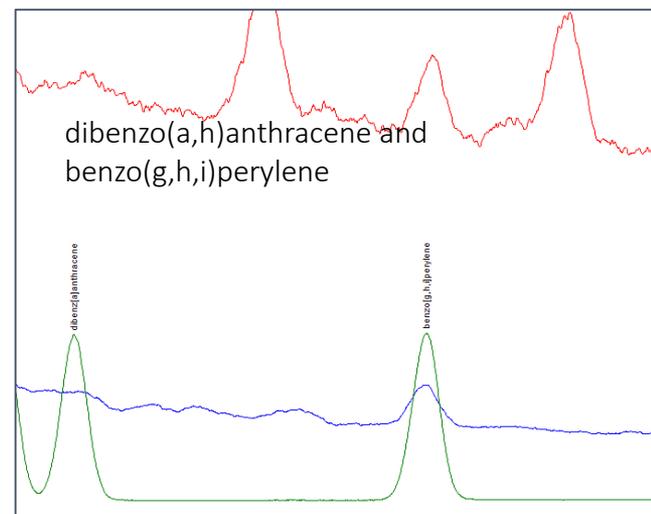
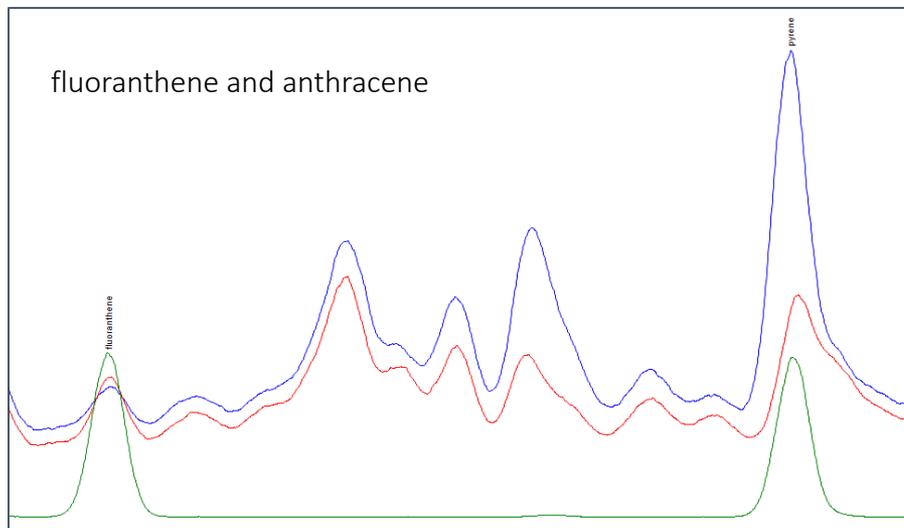
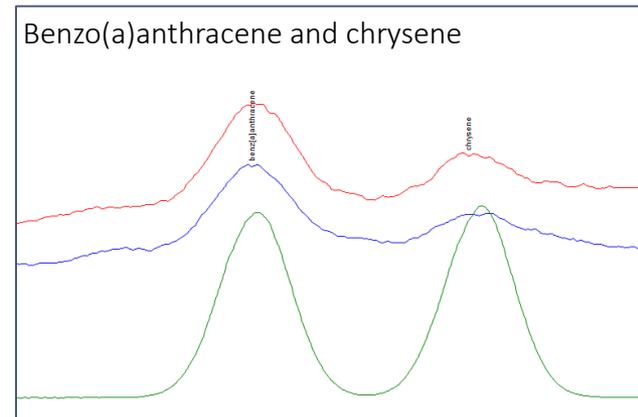
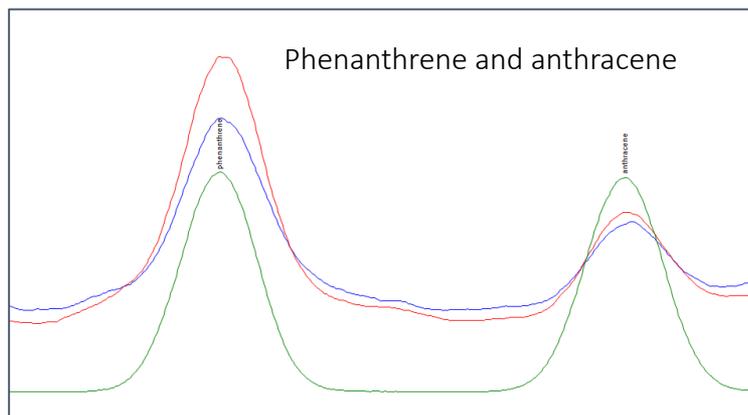
2-Methylnaphthalene



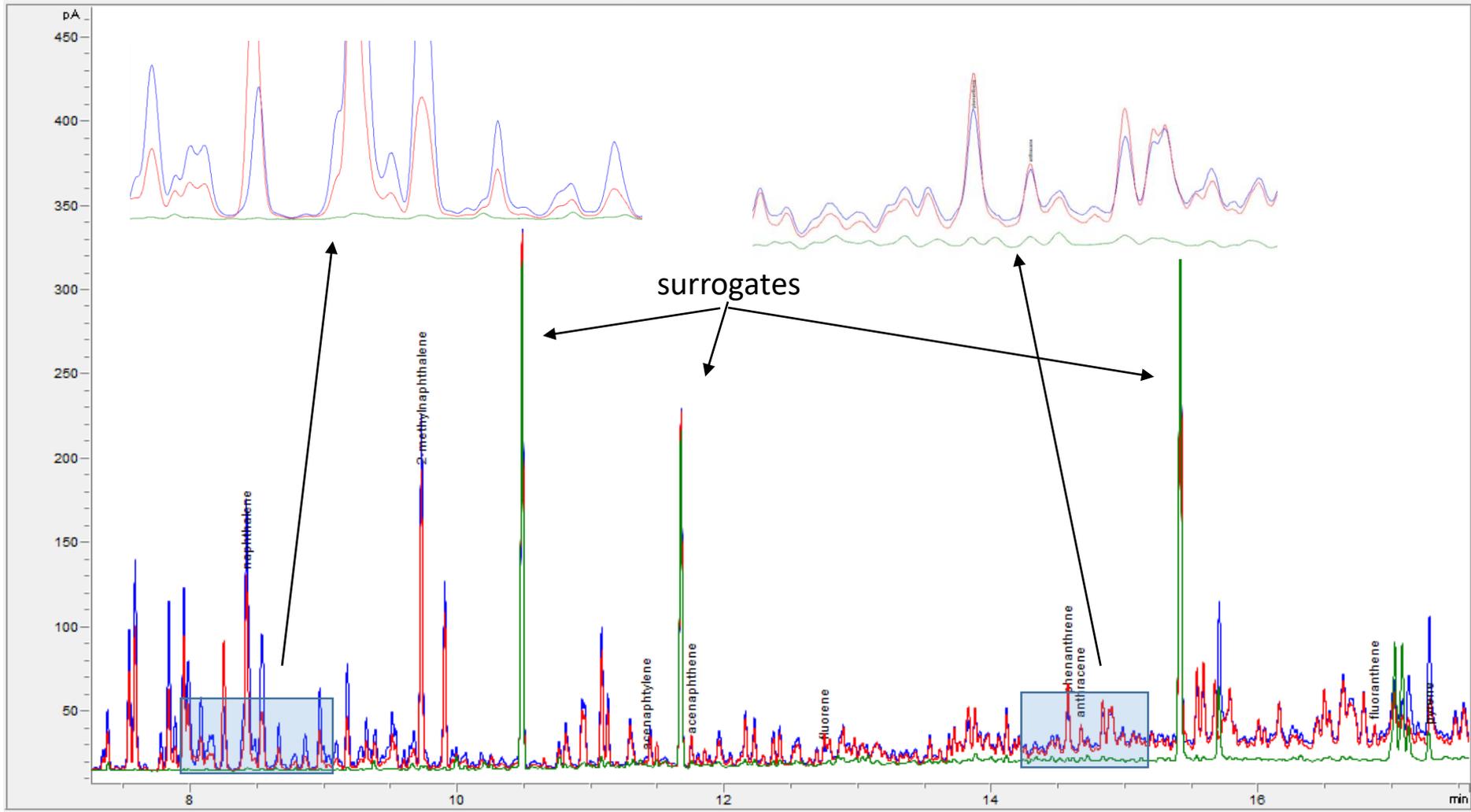
# PAHs in Used Motor Oil (Breakthrough-Aliphatic Fraction)



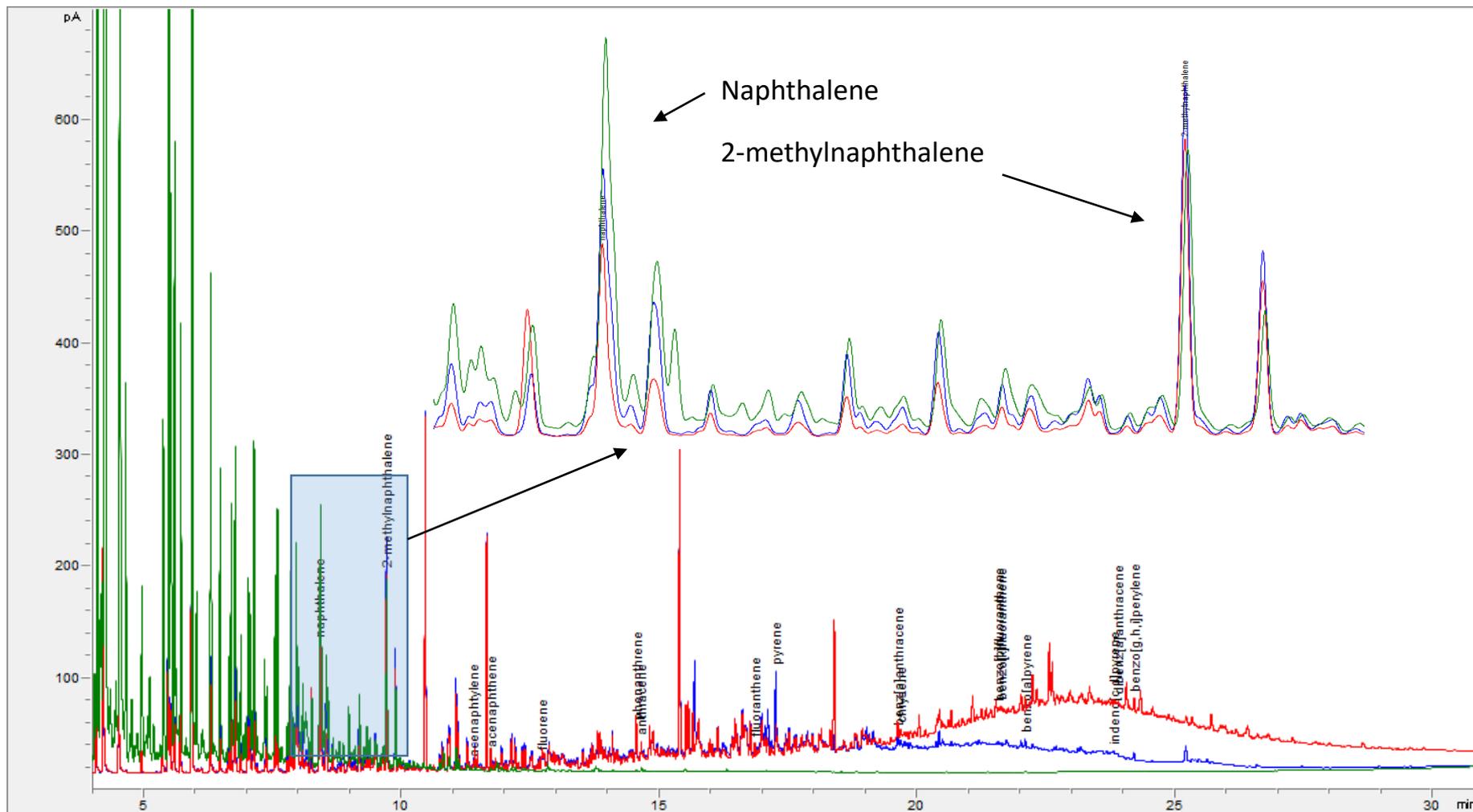
# PAHs in Used Motor Oil (Heavier PAHs)



# PAHs in Used Motor Oil (Diesel compared to gasoline powered vehicle)



# Likely Source of Lighter PAHs in Used Motor Oil (Diluted gasoline sample)



# Conclusions

- A method specific Silica gel cartridge provides excellent fractionation and cleanup properties even under heavy loading and with complex matrices
- PAHs were found in used motor oil samples but not necessarily correlated to vehicle age and mileage
- Likely reason for lack of correlation is that lighter PAHs are likely a result of concentrated gasoline in the oil rather than from blow-by

# Questions?

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