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GC-MS analysis of polycyclic aromatic hydrocarbons in multiple matrices using a single calibration curve following EPA method 8270E

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Product Marketing Manager – Americas

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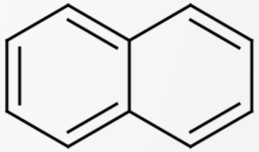
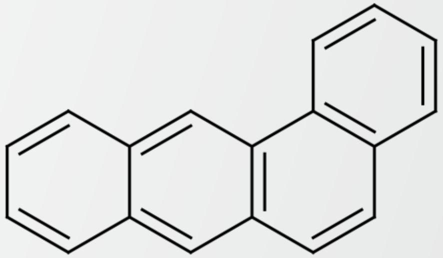
Agenda

Introduction – Polycyclic Aromatic Hydrocarbons (PAHs)

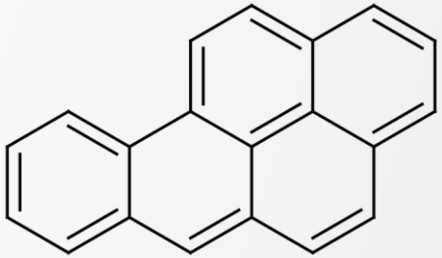
- Organic compounds consisting of 2 or more aromatic rings
- Sources:
  - Naturally occurring in fossil fuels
  - Anthropogenically produced form the incomplete combustion of organic matter (i.e., fossil fuels, wood, garbage)
- Over 100 PAH compounds identified in environmental samples



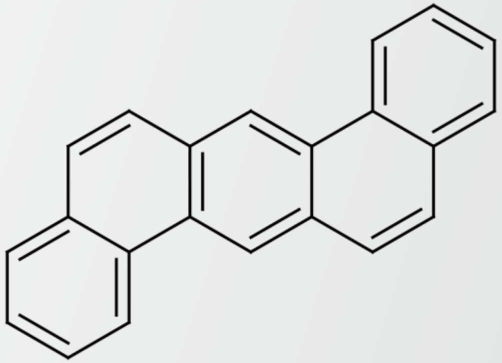
Napthalene



Benz[*a*]anthracene



Benzo[*a*]pyrene



Dibenz[*a*,*h*]anthracene

Polycyclic Aromatic Hydrocarbons (PAHs)

- **Wide environmental distribution**
  - Physical/Chemical properties allow for partitioning between various environmental media (air, water, soil)
- **Bioaccumulate in living organisms**
  - Exposure increases up the food chain
- **Toxic**
  - Carcinogenic
  - Genotoxicity
  - Endocrine disruptors

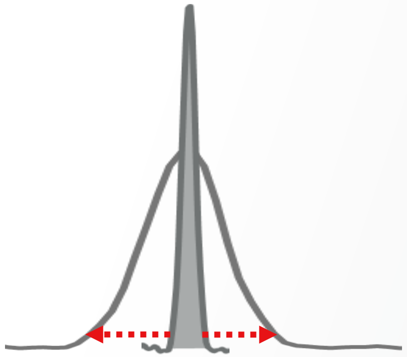
Environment and Human health hazard

Gas Chromatography Mass spectrometry (GC-MS)

Semi-volatile nature of PAHs makes GC-MS an ideal tool for sample introduction and analysis

Challenges

- Sufficient chromatographic separation between PAH isomers needed to avoid isobaric interferences

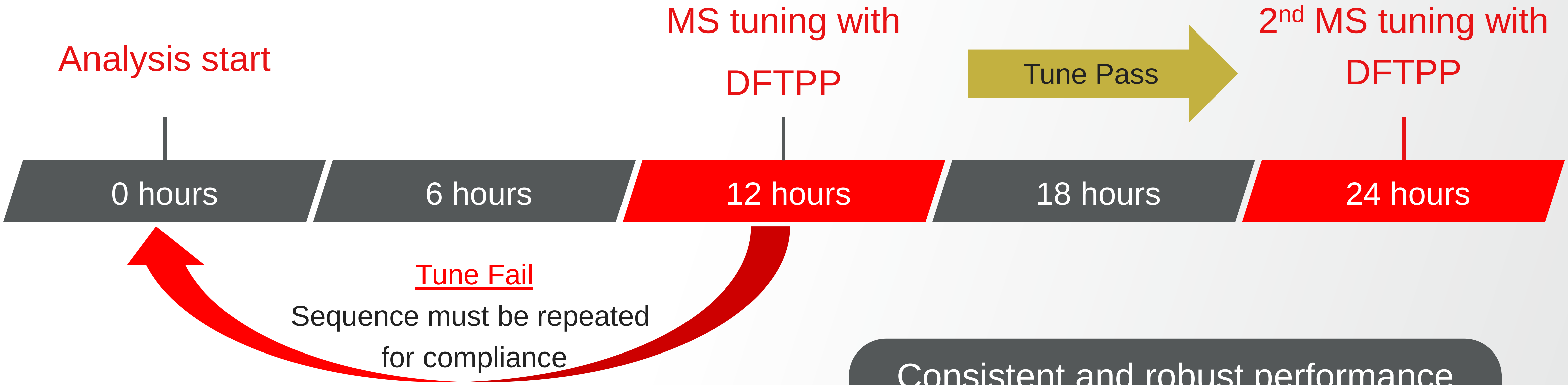


- Compounds with high boiling points prone to peak broadening and carryover between injections

- Multiple calibration curves needed to accurately quantify concentration range present in various sample matrices

Additional challenges with EPA Method 8270E

- In sequence MS tuning with 50 ng decafluorotriphenylphosphine (DFTPP) required after every 12 hours of analysis



Consistent and robust performance from GC-MS desirable for extended run times with maintenance interruptions minimized for extended up time

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Analytical Configuration

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Injection parameters	
Inlet module and mode	SSL, split
Liner	P/N 453A1925-UI
Liner type and size	Thermo Scientific™ LinerGOLD™, 4 mm i.d. × 78.5 mm
Injection volume (µL)	1
Inlet temperature (˚C)	300
Split flow (mL/min)	15
Carrier gas, carrier flow (mL/min), carrier mode	He, 1.5, constant flow
Split ratio	10:1
Purge flow (mL/min)	5
Pre-injection needle wash	5 times, with DCM
Post-injection needle wash	10 times with DCM, 10 times with MeOH

Chromatographic column	
Thermo Scientific™ TraceGOLD™ TG-PAH	P/N 26055-0470
Column dimensions	30 m × 0.25 mm i.d. × 0.10 µm

Oven temperature program	
Temperature 1 (˚C)	40
Hold time (min)	1
Temperature 2 (˚C)	285
Rate (˚C/min)	35
Temperature 3 (˚C)	295
Rate (˚C/min)	3
Temperature 4 (˚C)	350
Rate (˚C/min)	30
Hold time (min)	2
Total GC run time (min):	15.2

MS parameters	
Ion source	ExtractaBrite
Transfer line temperature (˚C)	350
Ion source temperature (˚C)	350
Ionization type	EI
Electron energy (eV)	70
Emission current (µA)	10
Acquisition mode	SIM, 2 ions/compound

Compound name	Rt (min)	MS quantifier ion (*m/z*)	MS confirmatory ion (*m/z*)
Naphthalene-d_8	4.7	136	108
Naphthalene	4.8	128	129
2 - methyl Naphthalene	5.2	142	141
1 - methyl Naphthalene	5.3	142	141
Acenaphthylene	5.9	152	151
Acenaphthene	6.0	153	154
Acenaphthene-d_{10}	6.0	162	164
Dibenzofuran	6.1	168	139
Fluorene	6.4	165	166
Phenanthrene-d_{10}	7.2	188	184
Phenanthrene	7.2	178	176
Anthracene	7.2	178	176
Fluoranthene	8.1	202	200
Terphenyl-d_{14}	8.3	244	122
Pyrene	8.4	202	200
Benz[*a*]anthracene	9.5	228	226
Chrysene-d_{12}	9.7	240	236
Chrysene	9.7	228	226
Benzo[*b*]fluoranthene	11.3	252	250
Benzo[*k*]fluoranthene	11.4	252	250
Benzo[*a*]pyrene	12.1	252	250
Perylene-d_{12}	12.2	264	260
Dibenzo[*a,h*]anthracene	13.5	278	139
Indeno[1,2,3-*cd*]pyrene	13.5	276	138
Benzo[*g,h,i*]perylene	13.9	276	138

Chromatographic separation and isomer resolution

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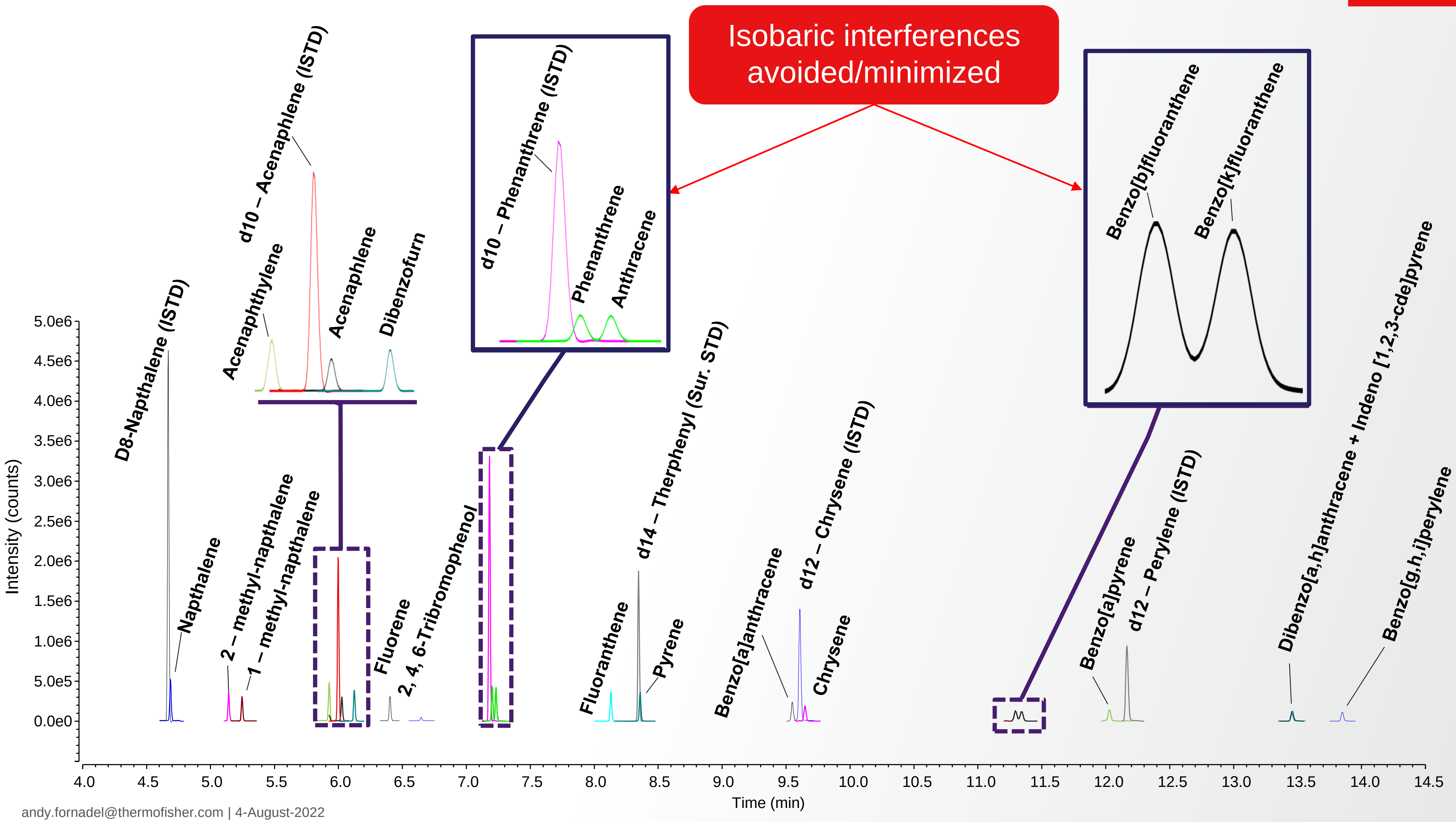

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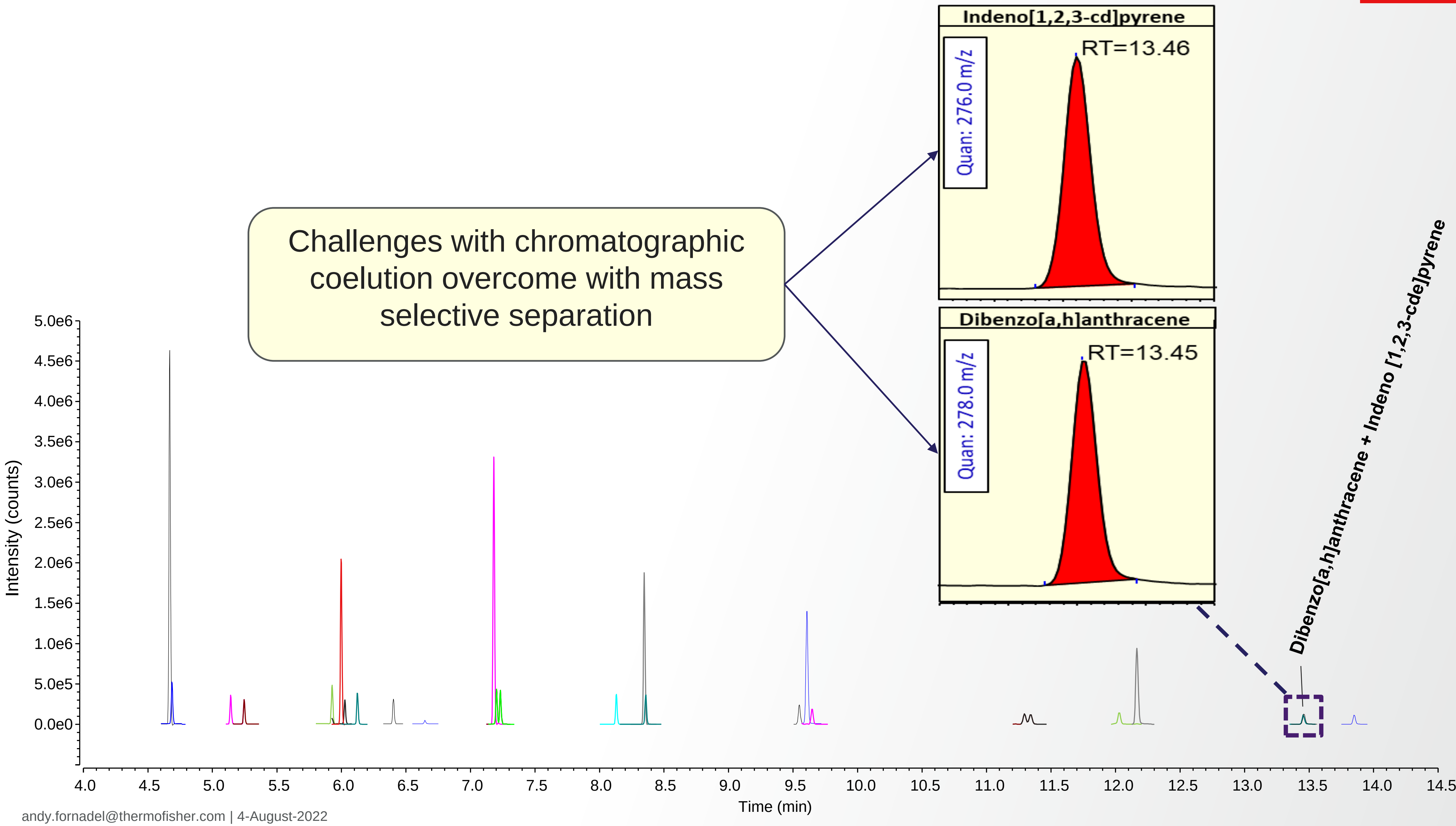
Chromatographic separation and isomer resolution

Challenges with chromatographic coelution overcome with mass selective separation



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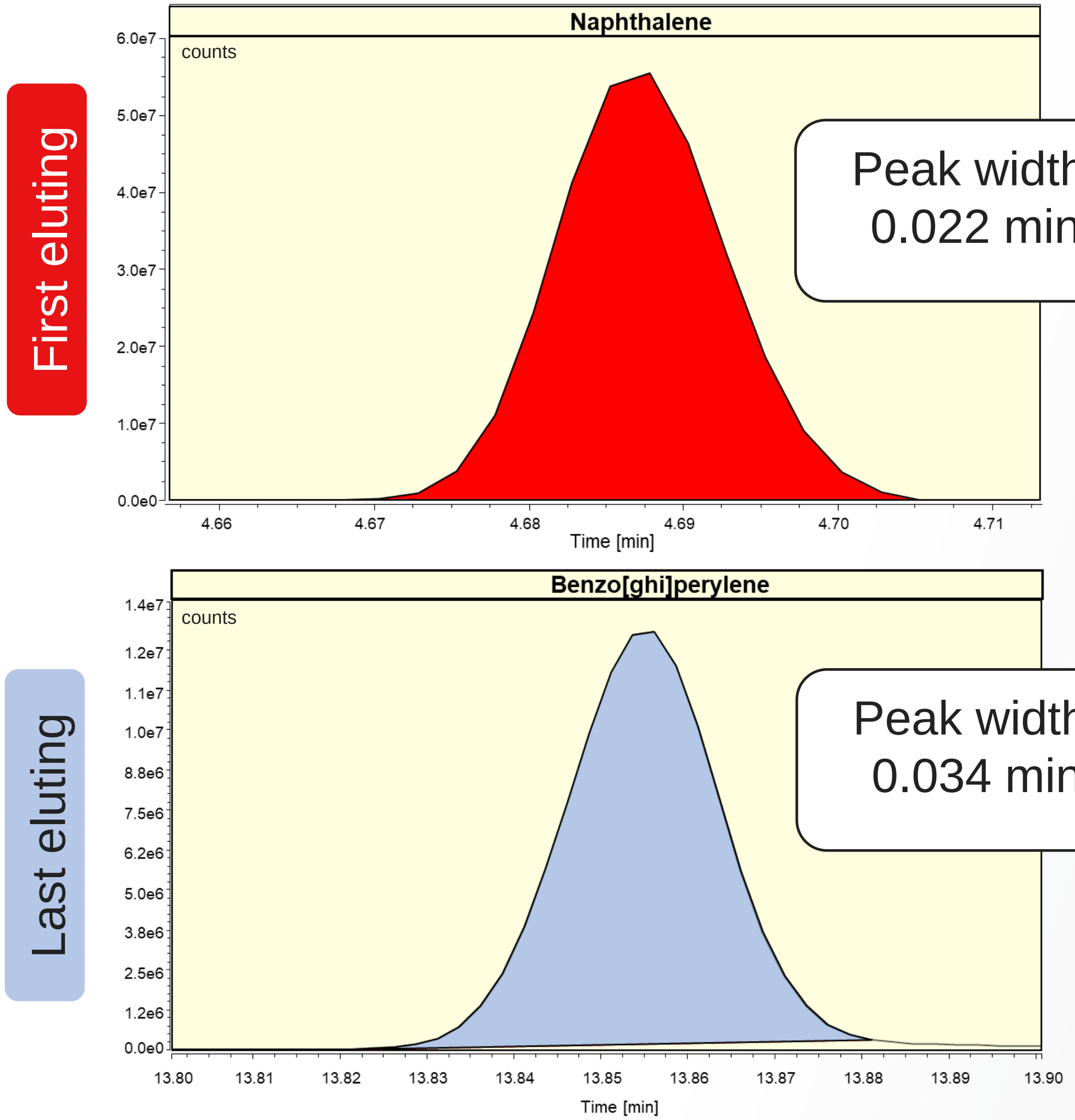
Chromatography

EPA Method 8270E criteria – Peak broadening



Peak width: 0.022 min

Peak width: 0.034 min

Minimal peak broadening observed between early and late eluting compounds

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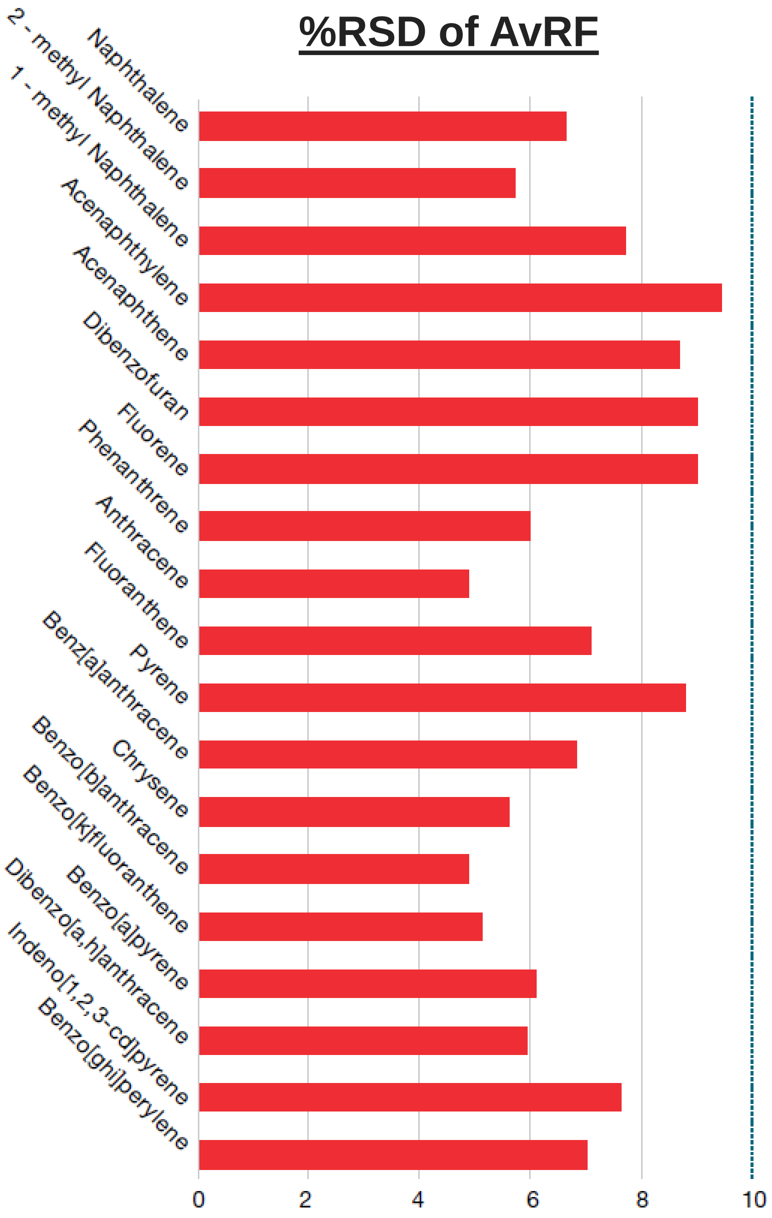
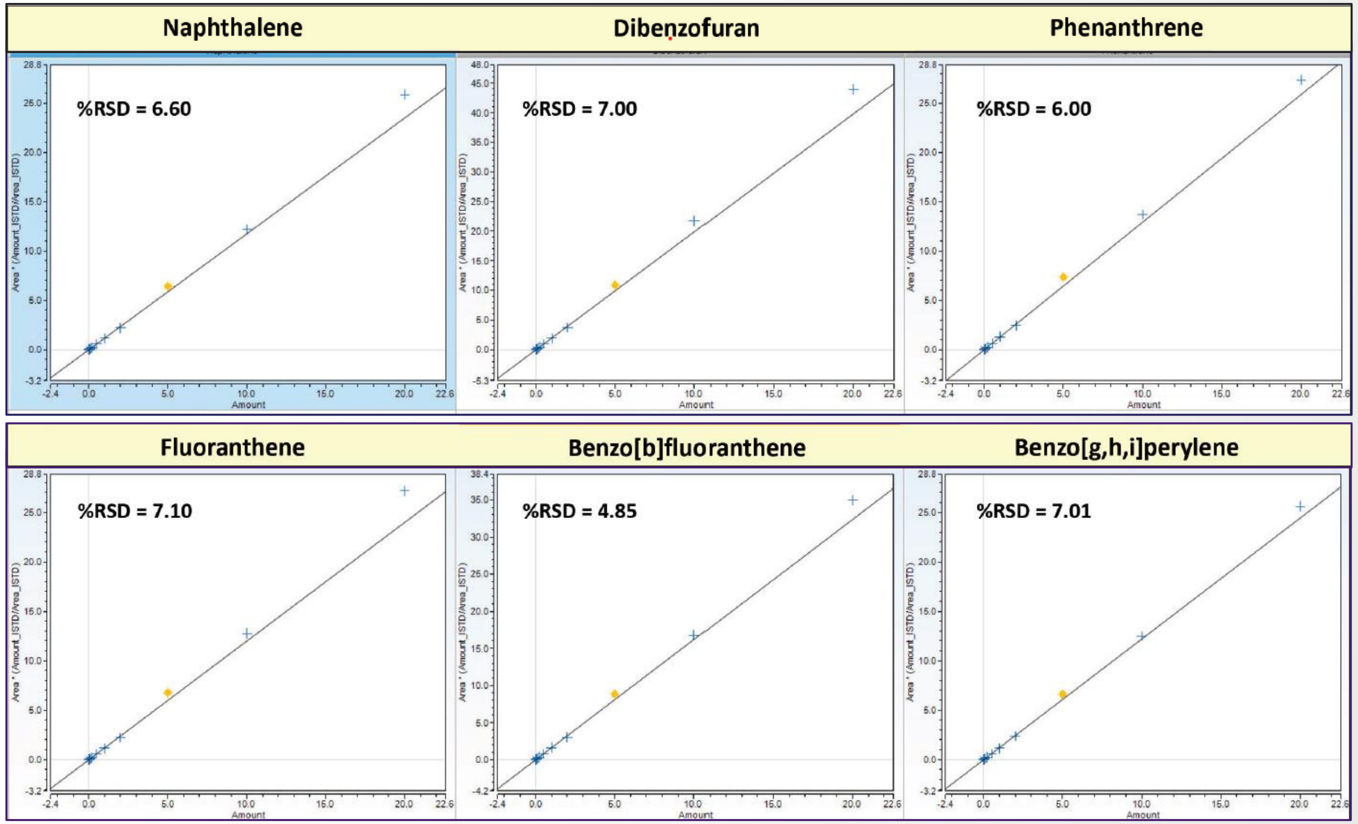
Response linearity



Calibration range: 2.5 – 20,000 ng/ml



- Average relative response factor (AvRF) calibration variation below EPA Method 8270E criteria (%RSD < 15%)
- Quantitation possible at trace levels and high contamination levels with single calibration curve

Performance towards PAH analysis in water and soil

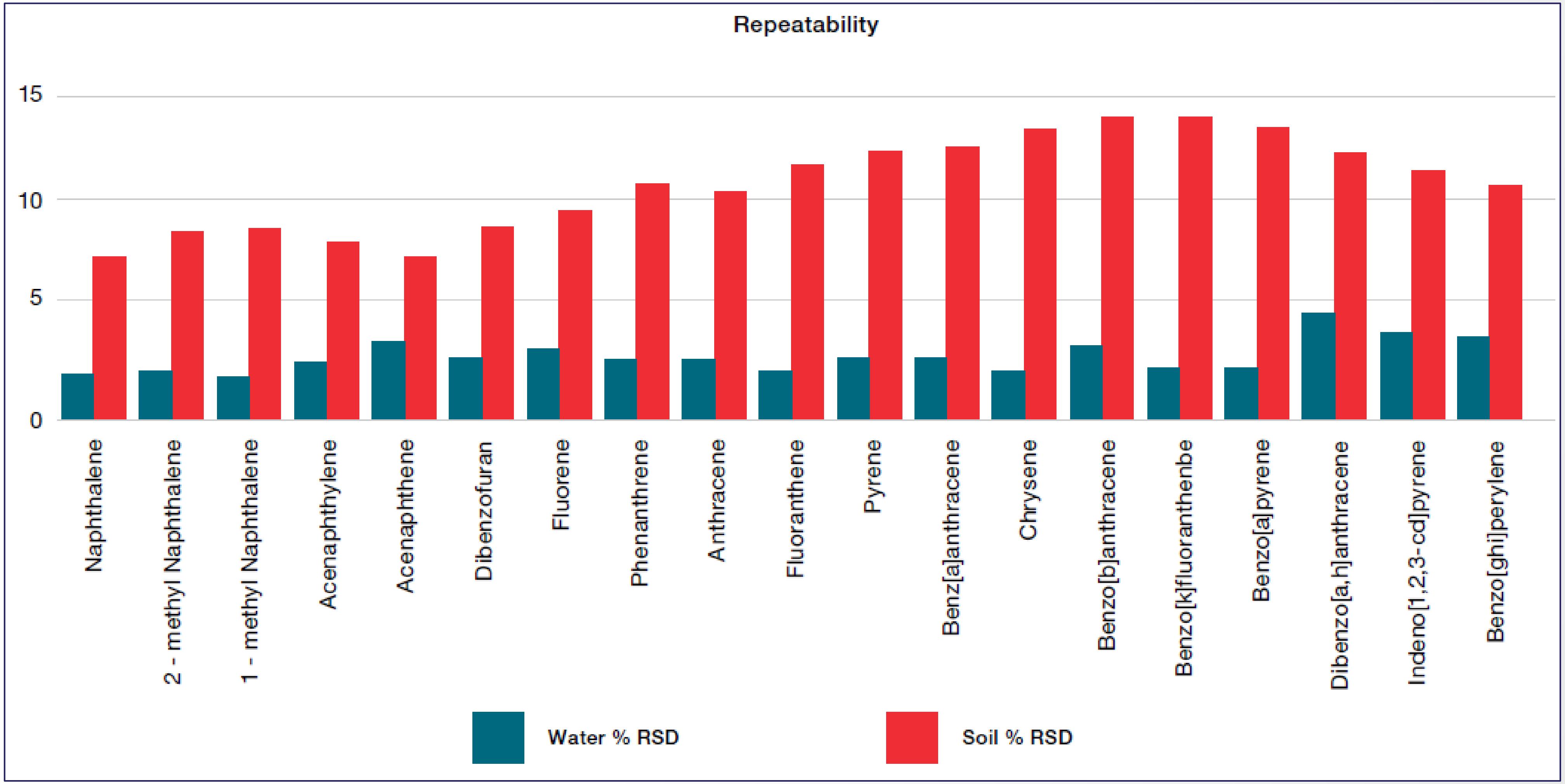
1 Repeatability in sample matrices

2 Instrument robustness using EPA method 8270E

3 In sequencing tune and calibration checks

Repeatability

- 20 ng/mL spiked in blank water and soil QC matrices (n = 10)

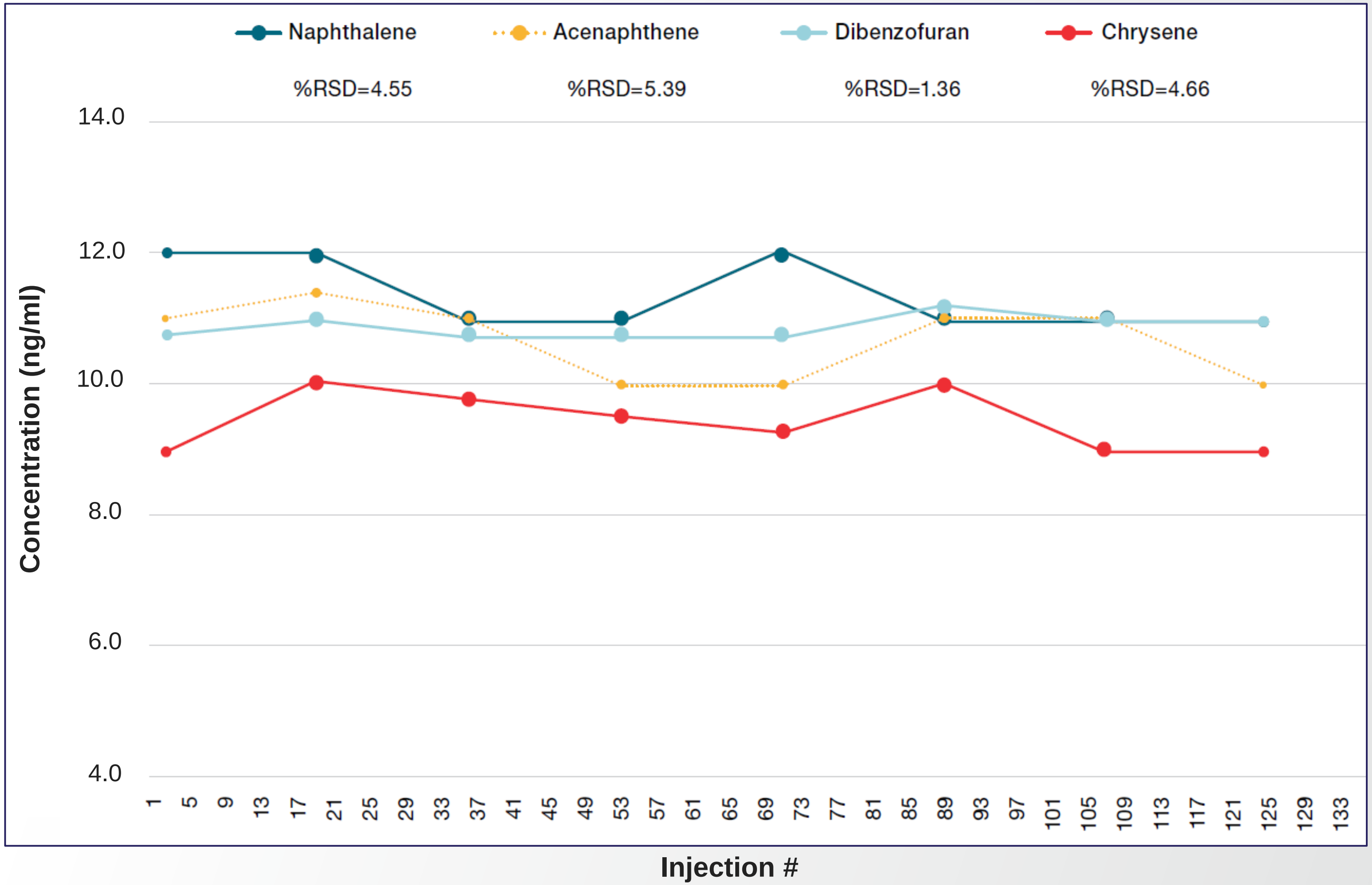


Reproducibility – Water analysis

Water QC sample at 10 ng/ml

%RSD < 10% after 133 consecutive injections (52 hours) without any GC or MS maintenance:

- Liner change
- Column trimming
- MS cleaning



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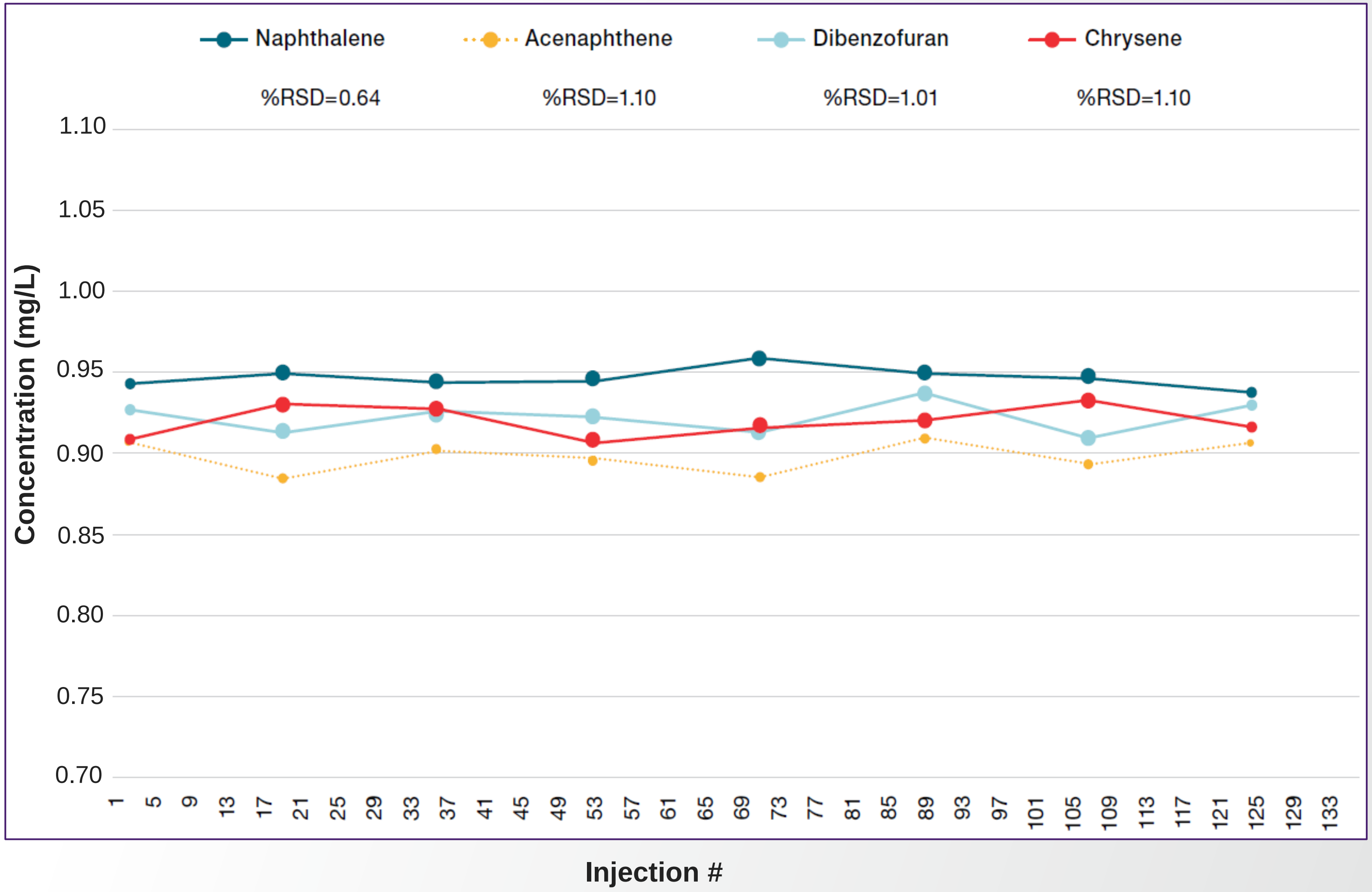
Reproducibility – Soil analysis

Soil QC sample at 1.0 mg/L

%RSD < 10% after 133 consecutive injections (52 hours) without any GC or MS maintenance:

- Liner change
- Column trimming
- MS cleaning



In sequence tuning, calibration and QC checks

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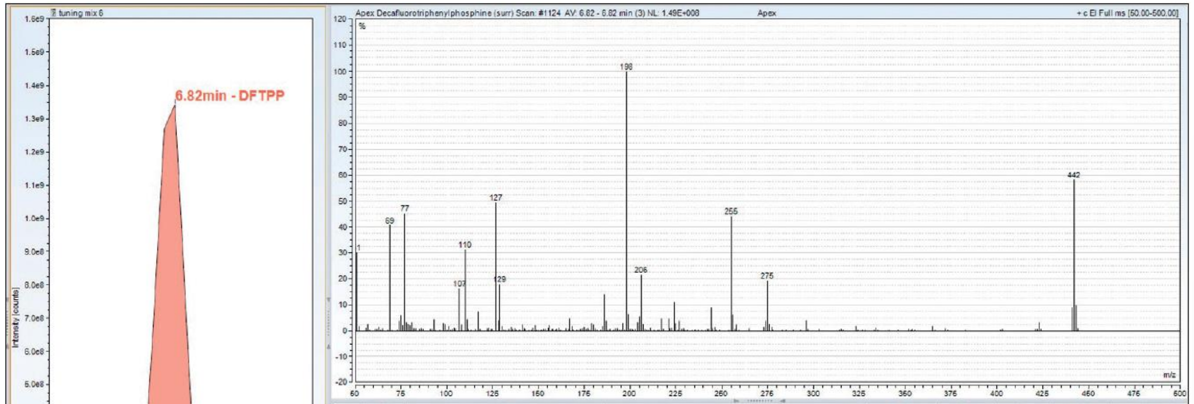
MS tuning verification every 6 hours with DFTPP in full scan with report automatically generated



	A	B	C	D	E	F	G	H
1	Number	Name	Tested Injections	Test Result	Eval. Result	Operator	Ref. Value (1)	Ref. Value (2)
2	1	m/z 51 - 10 to 80% of the base peak	(injection.customVar("Analysis_Type")="MS Tune Check")	Passed	30	between	10	80
3	2	m/z 68 - Less than 2% of m/z 69	(injection.customVar("Analysis_Type")="MS Tune Check")	Passed	0	<	2	
4	3	m/z 70 - Less than 2% of m/z 69	(injection.customVar("Analysis_Type")="MS Tune Check")	Passed	0	<	2	
5	4	m/z 127 - 10 to 80% of the base peak	(injection.customVar("Analysis_Type")="MS Tune Check")	Passed	49	between	10	80
6	5	m/z 197 - Less than 2% of m/z 198	(injection.customVar("Analysis_Type")="MS Tune Check")	Passed	0	<	2	
7	6	m/z 198 - Greater than 50% of m/z 442	(injection.customVar("Analysis_Type")="MS Tune Check")	Passed	172	>	50	
8	7	m/z 199 - 5 to 9% of m/z 198	(injection.customVar("Analysis_Type")="MS Tune Check")	Passed	6	between	5	9
9	8	m/z 275 - 10 to 60% of the base peak	(injection.customVar("Analysis_Type")="MS Tune Check")	Passed	19	between	10	60
10	9	m/z 365 - Greater than 1% of m/z 198	(injection.customVar("Analysis_Type")="MS Tune Check")	Passed	2	>	1	
11	10	m/z 441 - Present	(injection.customVar("Analysis_Type")="MS Tune Check")	Passed	13,406,901	>	0	
12	11	m/z 441 - Less than 24% of m/z 442	(injection.customVar("Analysis_Type")="MS Tune Check")	Passed	16	<	24	
13	12	m/z 442 - Greater than 50% of m/z 198	(injection.customVar("Analysis_Type")="MS Tune Check")	Passed	58	>	50	
14	13	m/z 443 - 15 to 24% of m/z 442	(injection.customVar("Analysis_Type")="MS Tune Check")	Passed	17	between	15	24
15		Number of executed test cases:	13	Passed				
16								

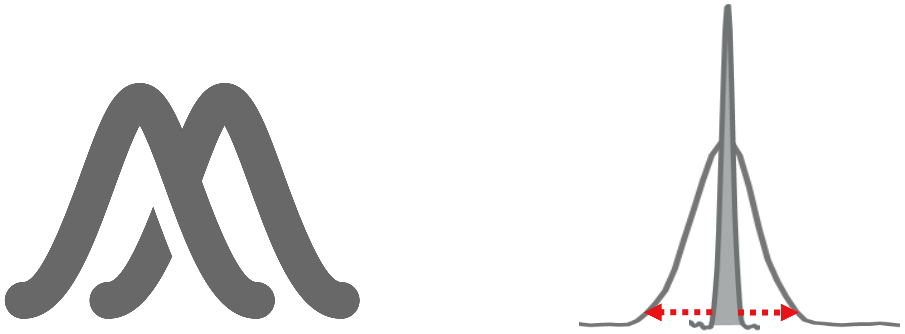
Summary View | Peak Results | Library Search | System Suitability Tests | Calibration | Audit Trail

#	TIC	Name	Type	Position	Instrument Method	Status	Analysis_Type
1		DCM	Unknown	54	PAHs SIM - 10uA - SPLIT 10to1	Finished	Field Sample
2		tuning mix 1	Unknown	53	PAHs SIM - 10uA - SPLIT 10to1 - FS	Finished	Field Sample
3		QC low water	Unknown	1	PAHs SIM - 10uA - SPLIT 10to1	Finished	Field Sample
4		QC low soil	Unknown	2	PAHs SIM - 10uA - SPLIT 10to1	Finished	Field Sample
5		QC middle water	Unknown	3	PAHs SIM - 10uA - SPLIT 10to1	Finished	Field Sample
6		QC middle soil	Unknown	4	PAHs SIM - 10uA - SPLIT 10to1	Finished	Field Sample
7		QC high water	Unknown	5	PAHs SIM - 10uA - SPLIT 10to1	Finished	Field Sample
8		QC high soil	Unknown	6	PAHs SIM - 10uA - SPLIT 10to1	Finished	Field Sample
9		Cali check 0.0025	Unknown	10	PAHs SIM - 10uA - SPLIT 10to1	Finished	Field Sample
10		s1	Unknown	55	PAHs SIM - 10uA - SPLIT 10to1	Finished	Field Sample
11		s2	Unknown	56	PAHs SIM - 10uA - SPLIT 10to1	Finished	Field Sample
12		s3	Unknown	57	PAHs SIM - 10uA - SPLIT 10to1	Finished	Field Sample
13		s4	Unknown	58	PAHs SIM - 10uA - SPLIT 10to1	Finished	Field Sample
14		s5	Unknown	59	PAHs SIM - 10uA - SPLIT 10to1	Finished	Field Sample
15		s6	Unknown	60	PAHs SIM - 10uA - SPLIT 10to1	Finished	Field Sample
16		s7	Unknown	61	PAHs SIM - 10uA - SPLIT 10to1	Finished	Field Sample
17		s8	Unknown	62	PAHs SIM - 10uA - SPLIT 10to1	Finished	Field Sample
18		s9	Unknown	63	PAHs SIM - 10uA - SPLIT 10to1	Finished	Field Sample
19		tuning mix 2	Unknown	53	PAHs SIM - 10uA - SPLIT 10to1 - FS	Finished	Field Sample
20		Cali check 0.005	Unknown	11	PAHs SIM - 10uA - SPLIT 10to1	Finished	Field Sample
21		QC low water 2	Unknown	1	PAHs SIM - 10uA - SPLIT 10to1	Finished	Field Sample
22		QC low soil 2	Unknown	2	PAHs SIM - 10uA - SPLIT 10to1	Finished	Field Sample
23		QC middle water 2	Unknown	3	PAHs SIM - 10uA - SPLIT 10to1	Finished	Field Sample
24		QC middle soil 2	Unknown	4	PAHs SIM - 10uA - SPLIT 10to1	Finished	Field Sample
25		QC high water 2	Unknown	5	PAHs SIM - 10uA - SPLIT 10to1	Finished	Field Sample
26		QC high soil 2	Unknown	6	PAHs SIM - 10uA - SPLIT 10to1	Finished	Field Sample
27		s10	Unknown	64	PAHs SIM - 10uA - SPLIT 10to1	Finished	Field Sample
28		s11	Unknown	65	PAHs SIM - 10uA - SPLIT 10to1	Finished	Field Sample

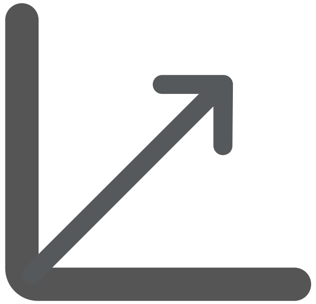
Routine calibration and sample QC checks at different concentrations to ensure analysis accuracy

- Calibration accuracy: ± 10%
- Spiked recovery: 80 – 120 %

Conclusions



Efficient chromatographic separation within 14.5 min with minimal peak broadening by late eluting compounds and isobaric interferences avoided



Linear dynamic range over 4 orders of magnitude allowing multiple sample types to be analyzed on a single calibration curve.

Robust analysis of PAHs was demonstrated with %RSD < 10% for sample QCs after 133 consecutive injections with no GC or MS maintenance

Spike recoveries of sample QC range from 80-120% with method detection limits ranging from 0.5 – 7.6 pg on column

In sequence tuning and report generation automatically provides compliance requirements for EPA method 8270E and allowing for maximum instrument up time

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Thank you

The line has been unmuted for questions.