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

Andy Fornadel, PhD

Product Marketing Manager – Americas

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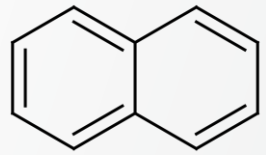
# Agenda

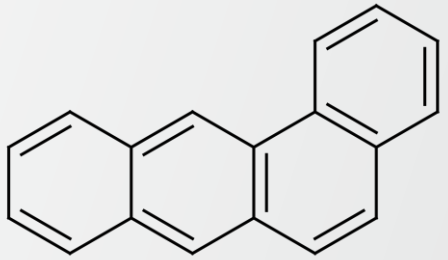
1. Introduction to polycyclic hydrocarbons
2. Challenges in GC-MS analysis using EPA method 8270E
3. Analysis of PAHs in water and soil
4. Conclusions

# Introduction – Polycyclic Aromatic Hydrocarbons (PAHs)

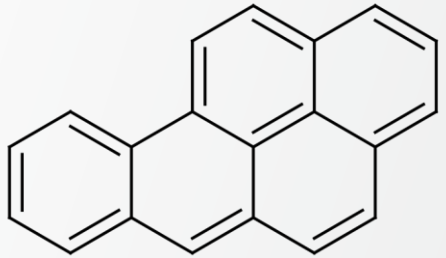
- Organic compounds consisting of 2 or more aromatic rings
- Sources:
  - Naturally occurring in fossil fuels
  - Anthropogenically produced form the incomplete combustion of organic matter (i.e., fossil fuels, wood, garbage)
- Over 100 PAH compounds identified in environmental samples



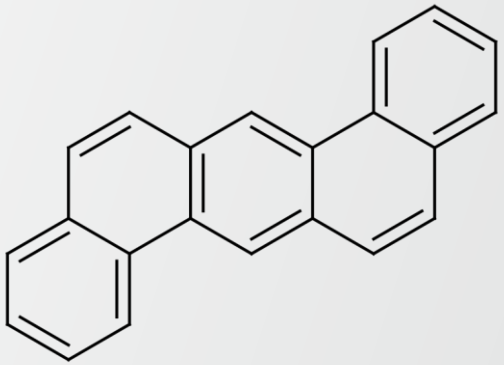
**Napthalene**



**Benz[*a*]anthracene**



**Benzo[*a*]pyrene**



**Dibenz[*a,h*]anthracene**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# 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

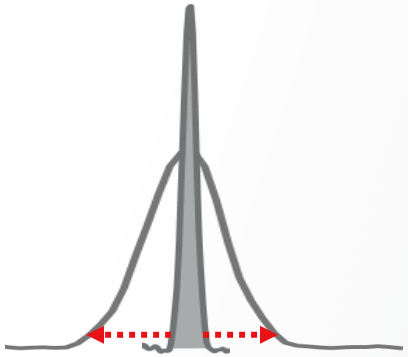
Environment and Human health hazard

# 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

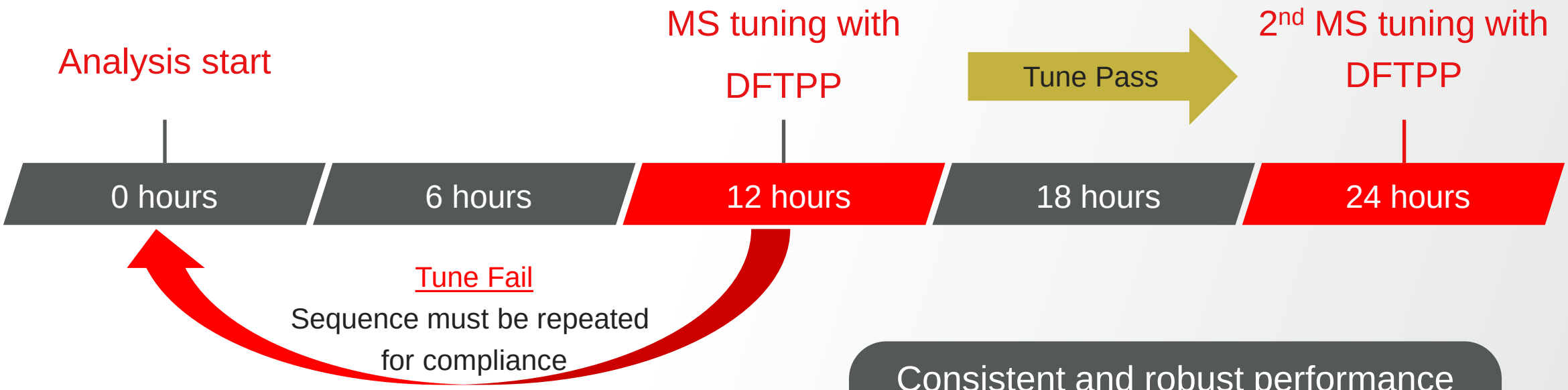


- Compounds with high boiling points prone to peak broadening and carryover between injections

- 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

# Analytical Configuration

| 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 |

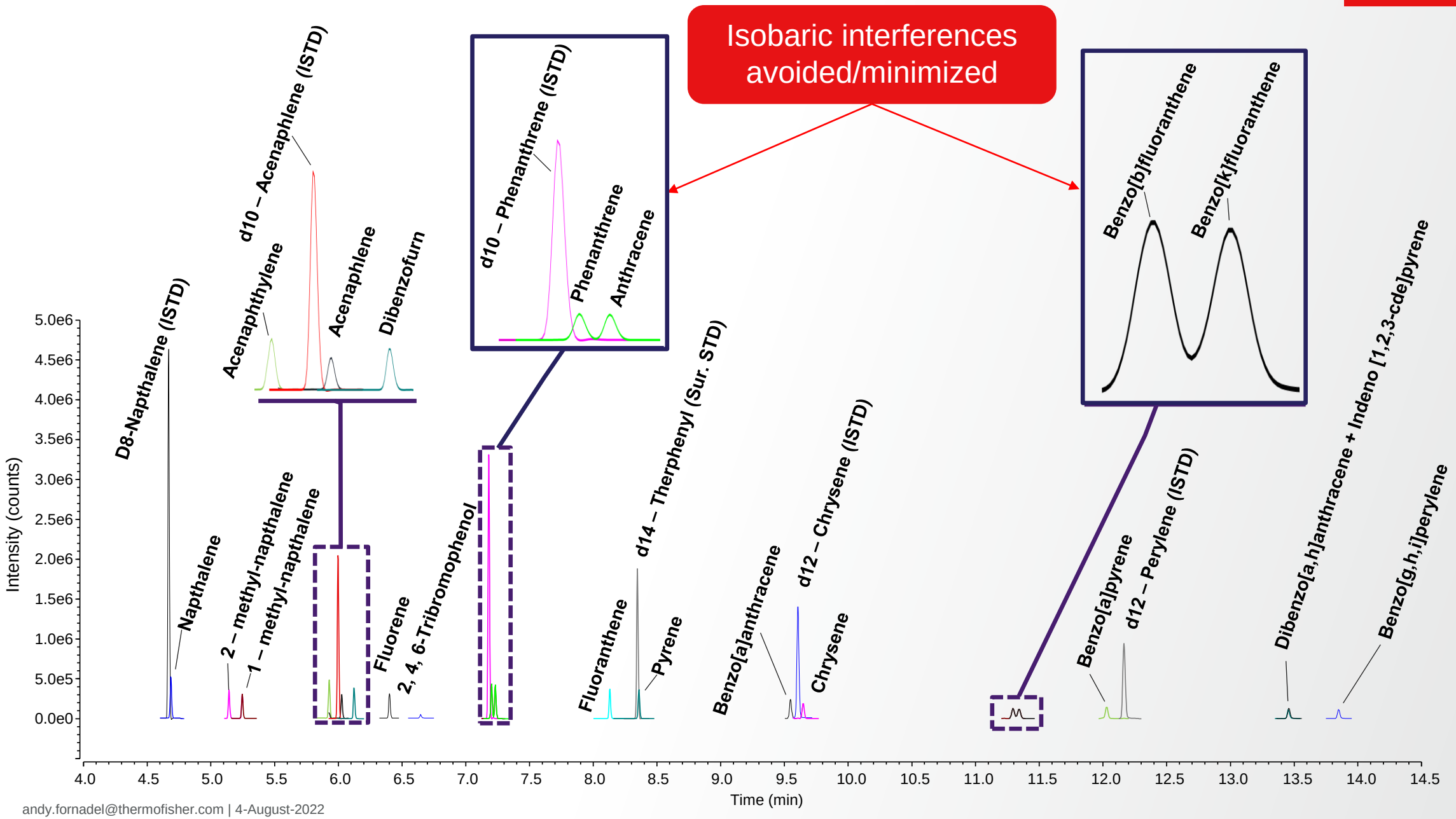
| Chromatographic column | |
|---|---|
| Thermo Scientific™ TraceGOLD™ TG-PAH | P/N 26055-0470 |
| Column dimensions | 30 m × 0.25 mm i.d. × 0.10 µm |

| 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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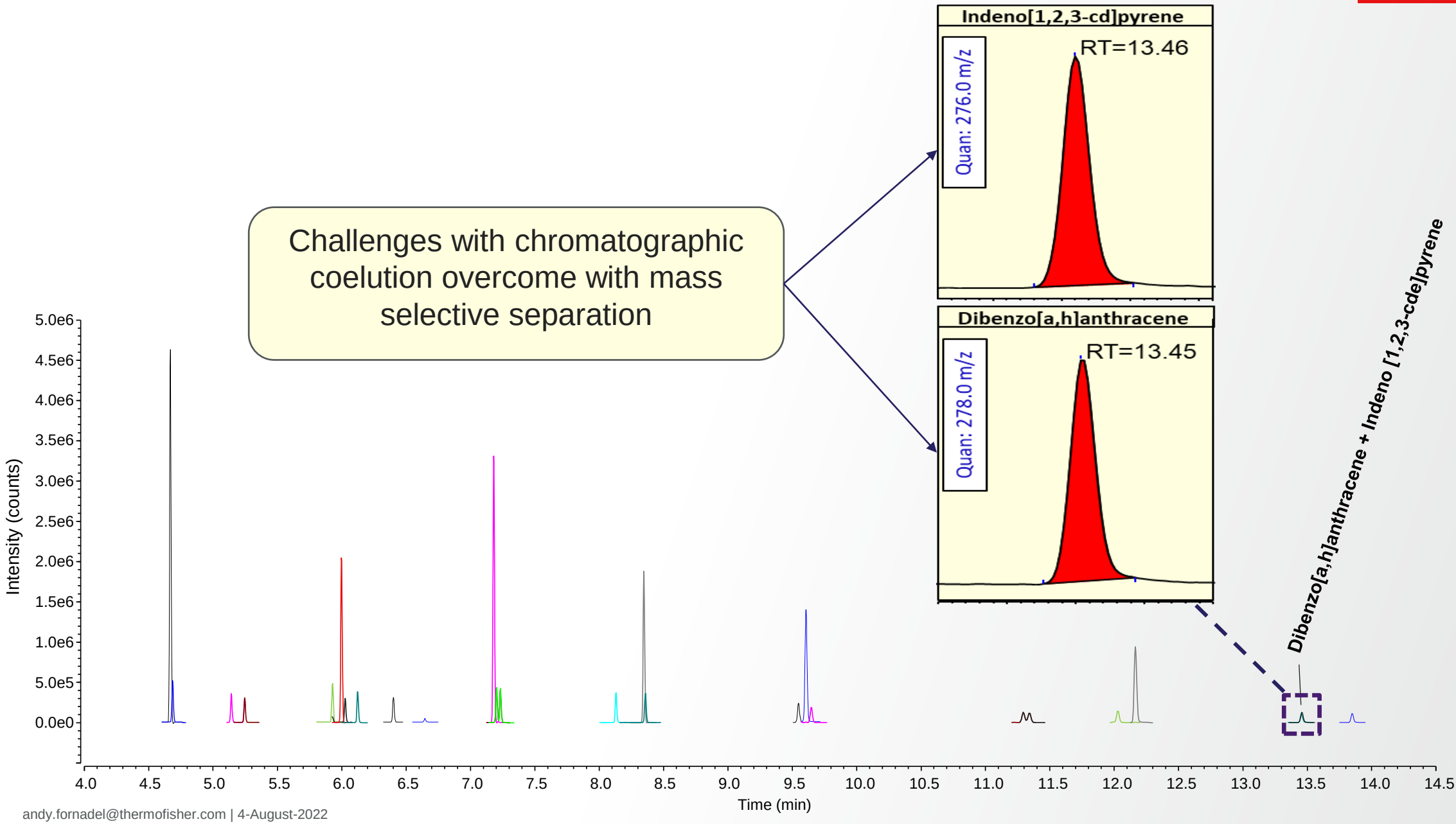
# Chromatographic separation and isomer resolution

Challenges with chromatographic coelution overcome with mass selective separation





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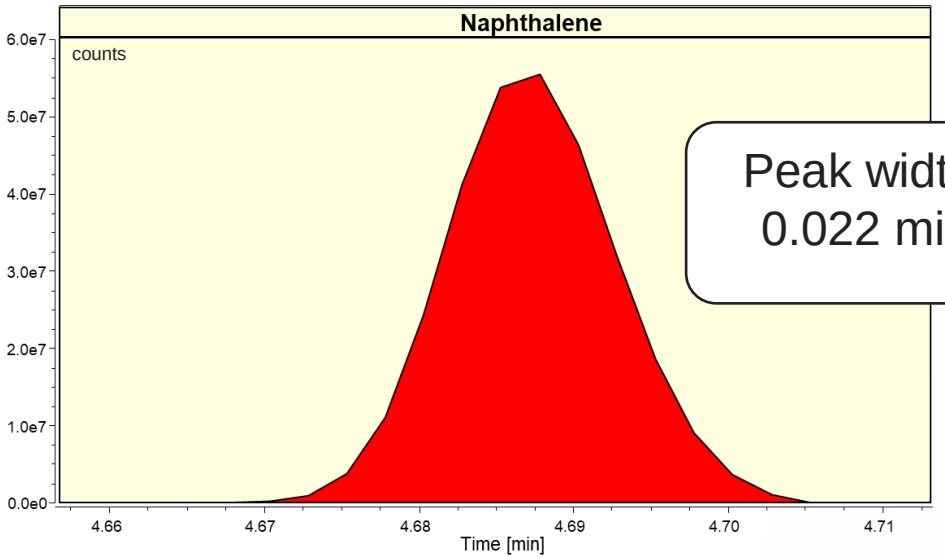
# Chromatography

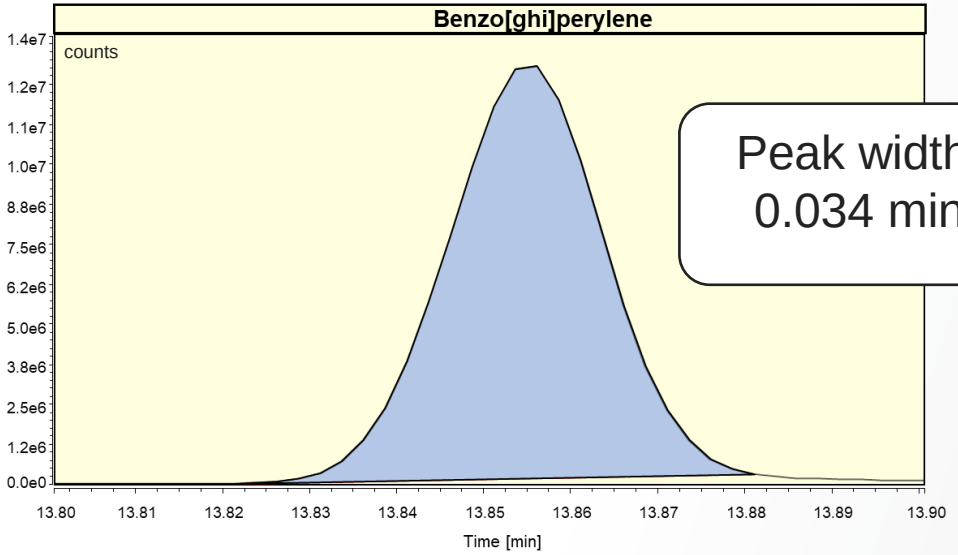
## EPA Method 8270E criteria – Peak broadening

First eluting




Peak width: 0.022 min

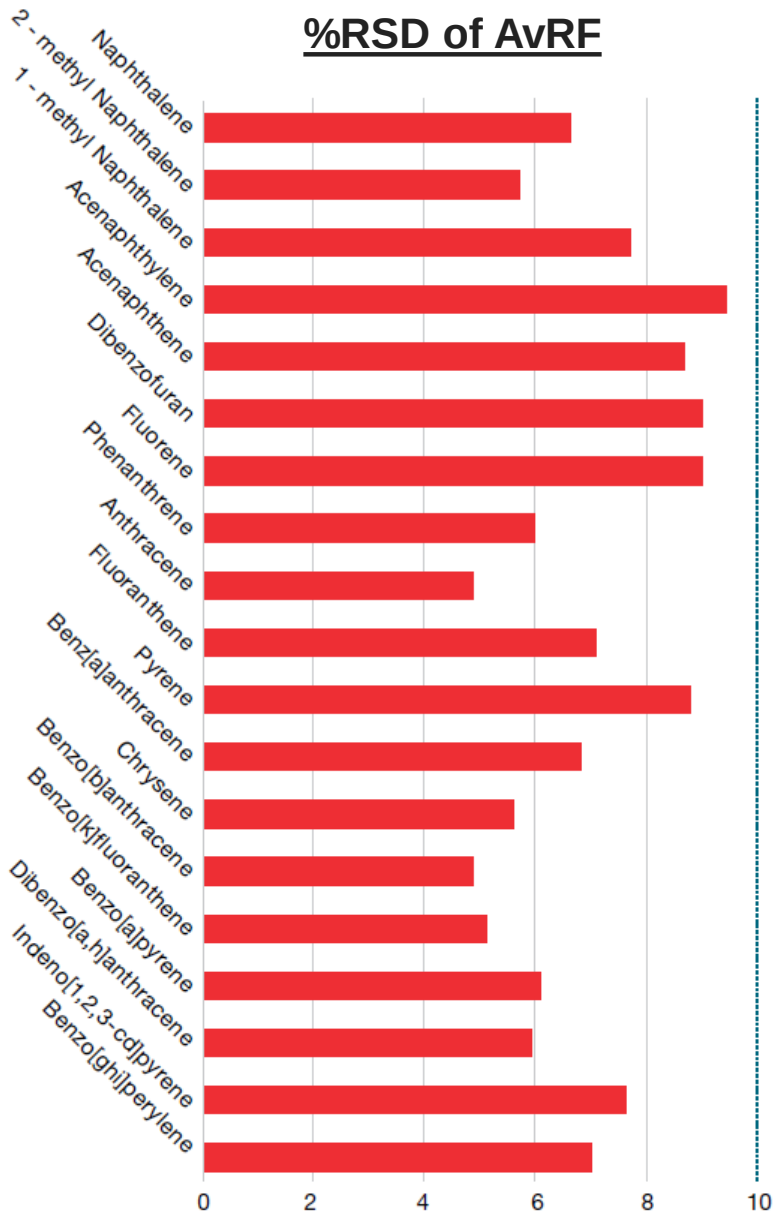
Last eluting



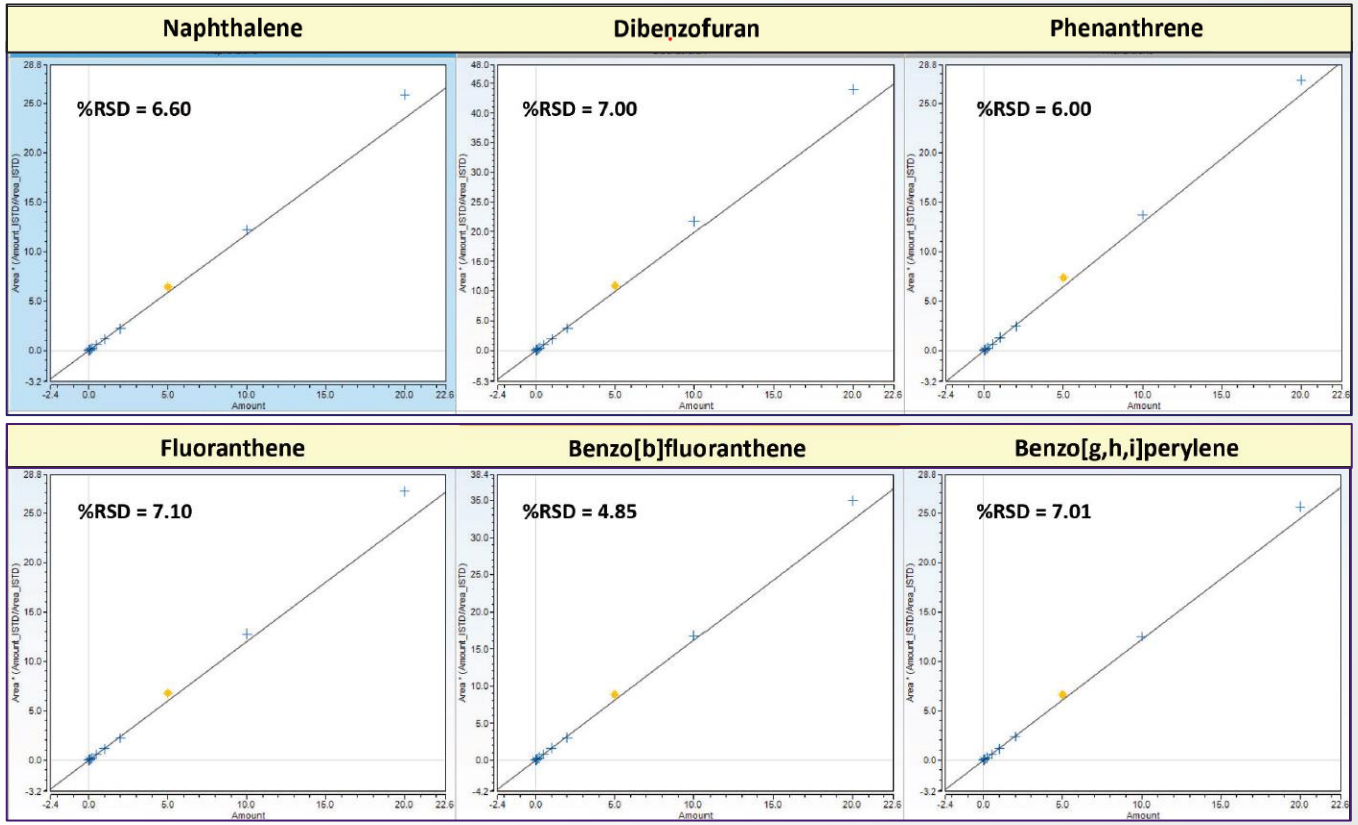

Peak width: 0.034 min

Minimal peak broadening observed between early and late eluting compounds

# Response linearity




## Calibration range: 2.5 – 20,000 ng/ml



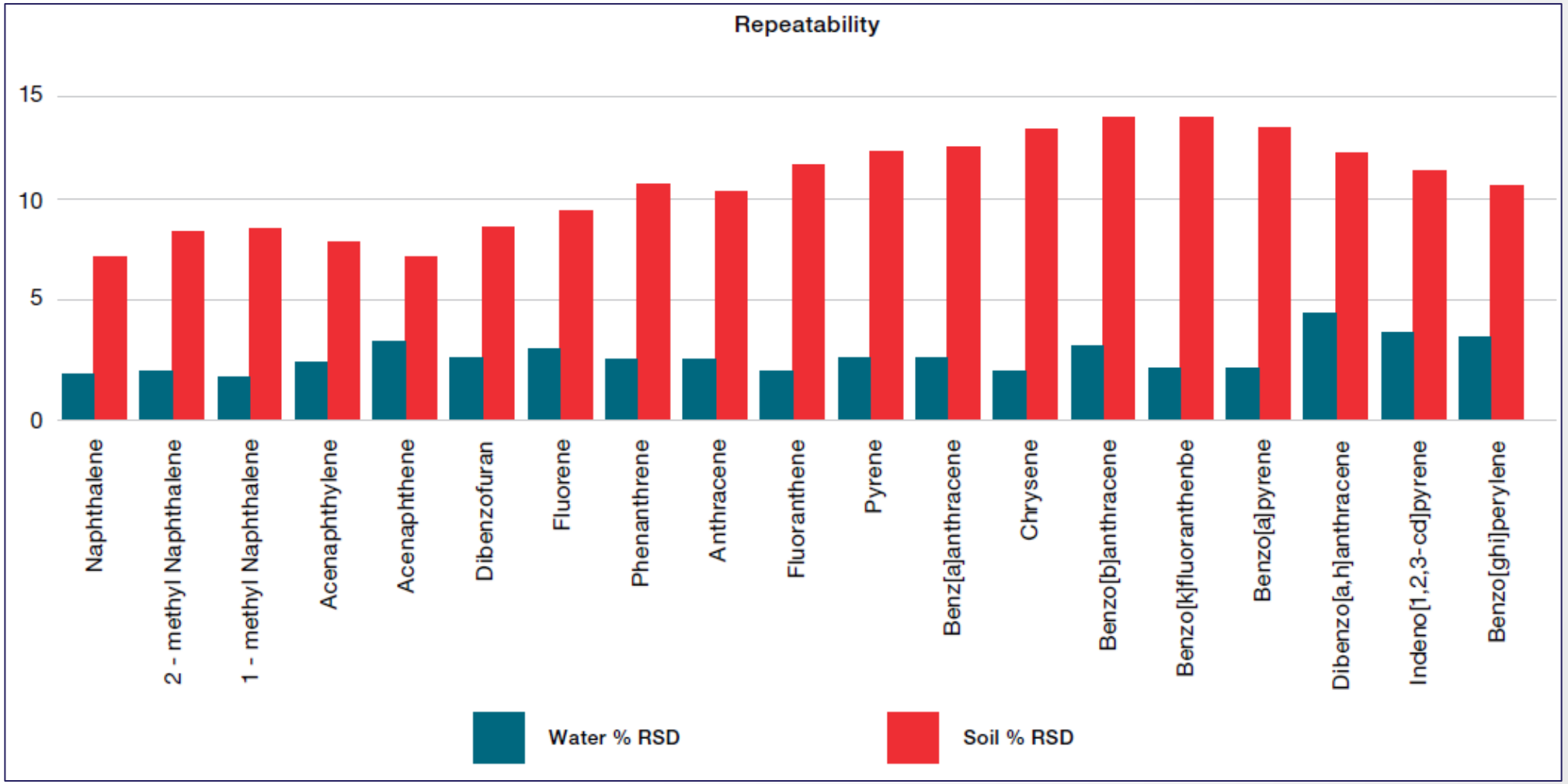

- Average relative response factor (AvRF) calibration variation below EPA Method 8270E criteria (%RSD < 15%)
- Quantitation possible at trace levels and high contamination levels with single calibration curve

# 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)

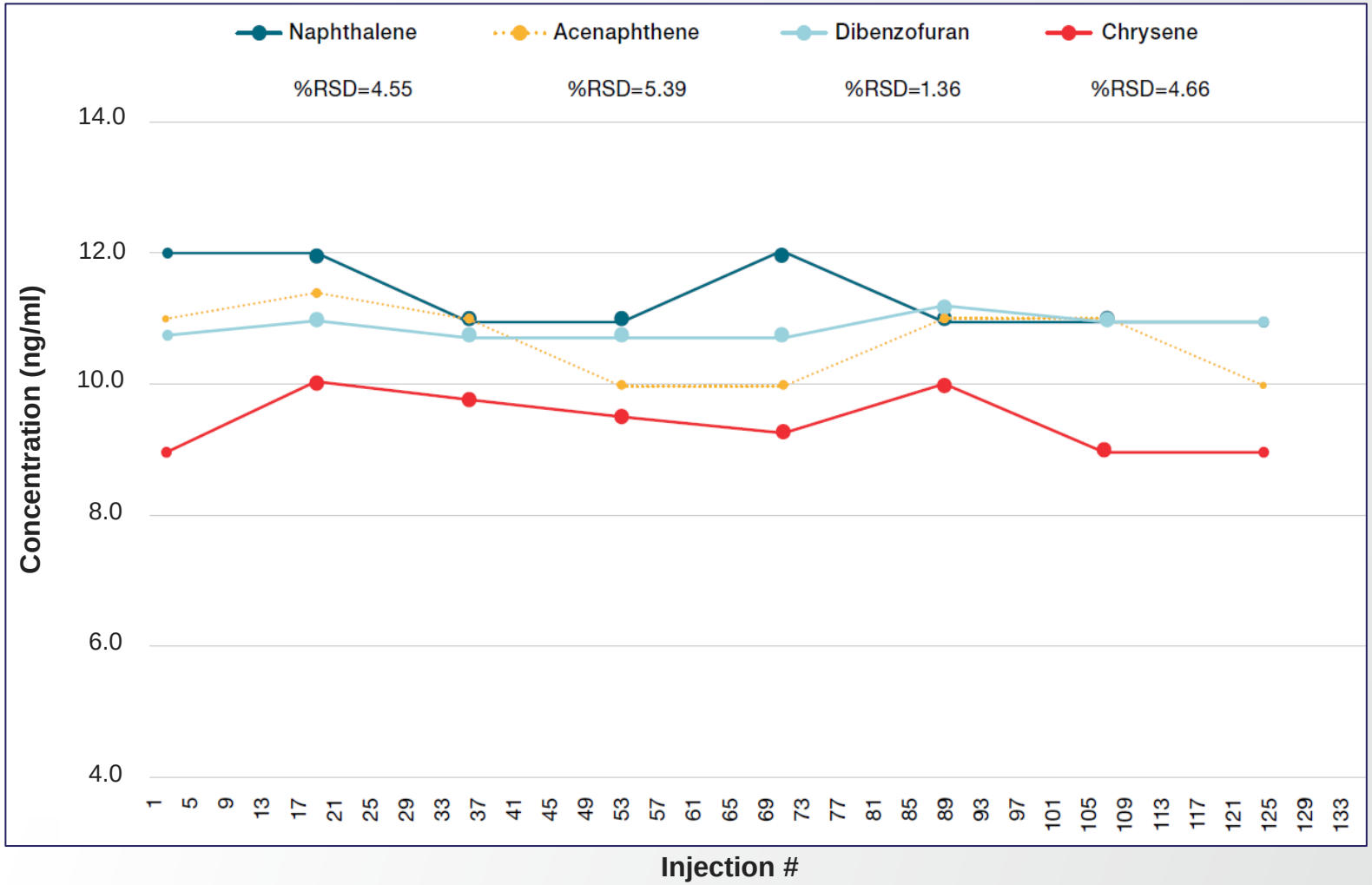


# Reproducibility – Water analysis

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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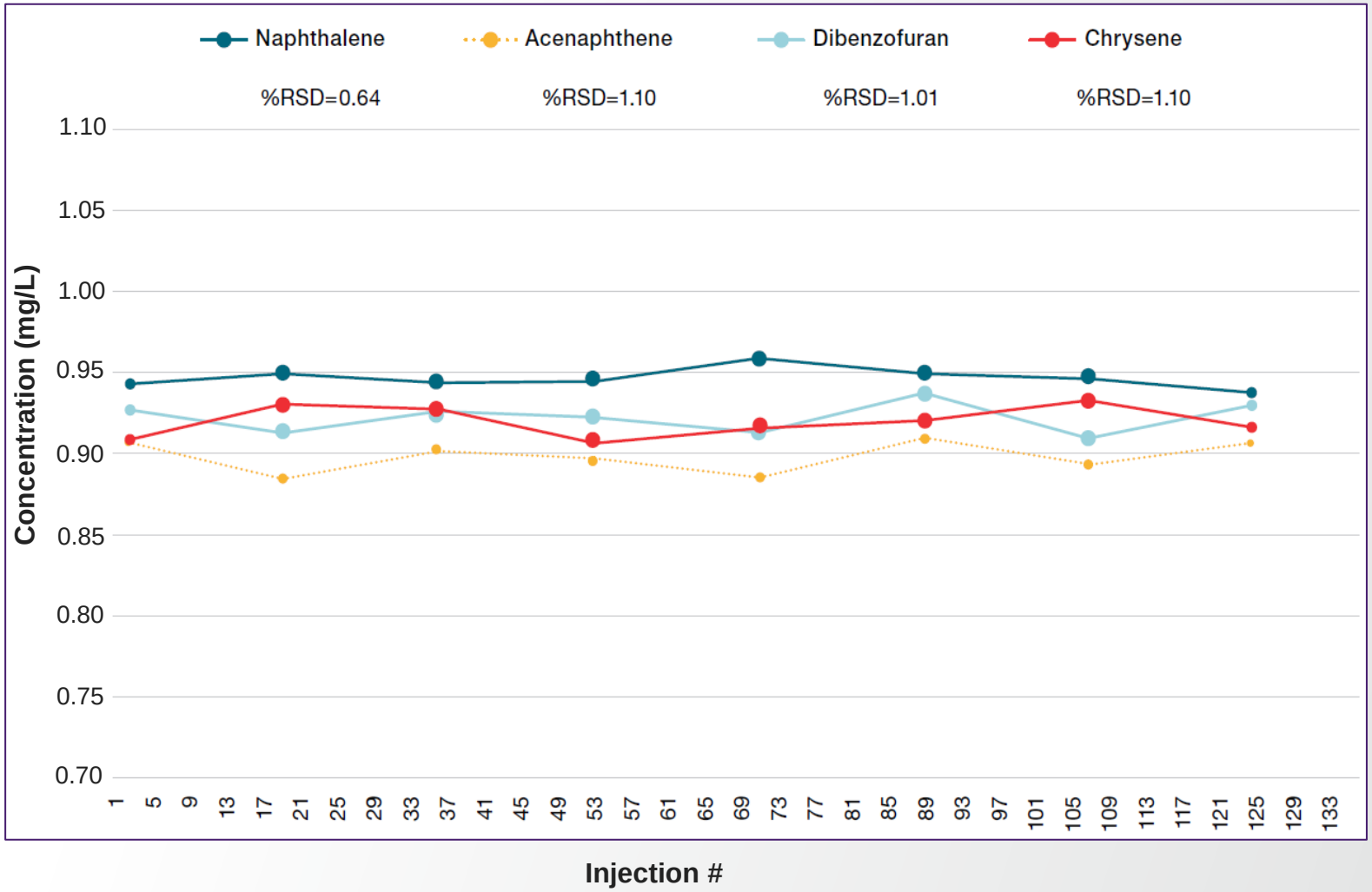
# Reproducibility – Soil analysis

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





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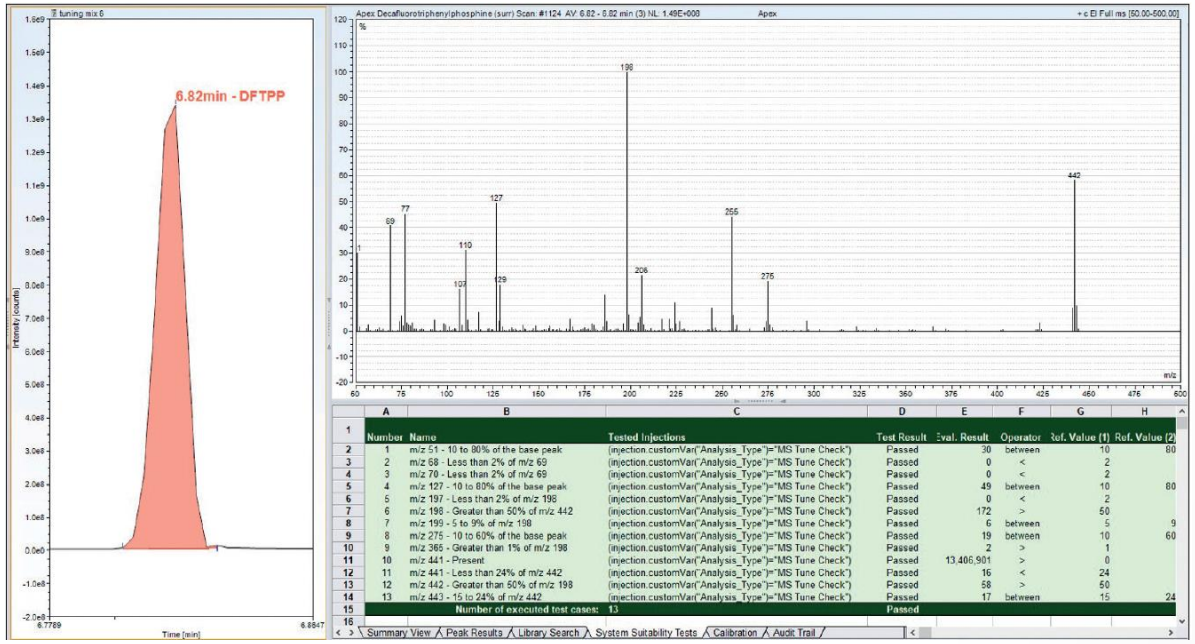
# In sequence tuning, calibration and QC checks

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

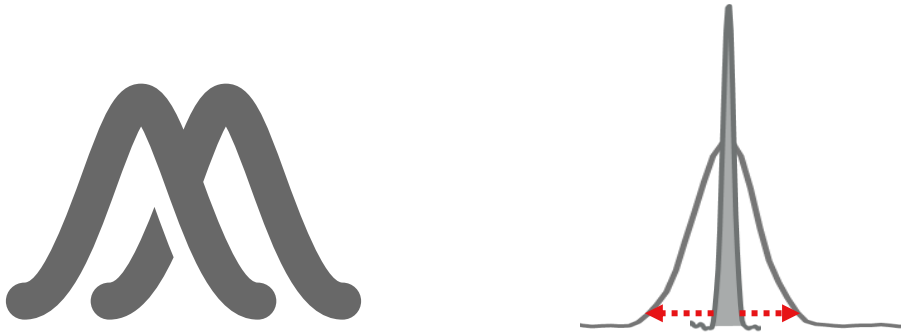



| # | TIC | Name | Type | Position | Instrument Method | Status | *Analysis_Type |
|---|---|---|---|---|---|---|---|
| 1 | | DCM | Unknown | 54 | PAHs SIM - 10uA - SPLIT 10to1 | Finished | Field Sample |
| 2 | | tuning mix 1 | Unknown | 53 | PAHs SIM - 10uA - SPLIT 10to1 - FS | Finished | Field Sample |
| 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 |

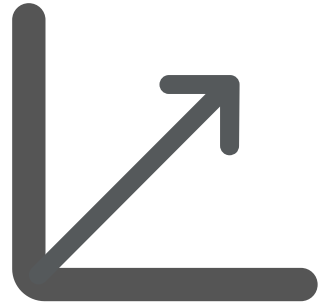
Routine calibration and sample QC checks at different concentrations to ensure analysis accuracy

- 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



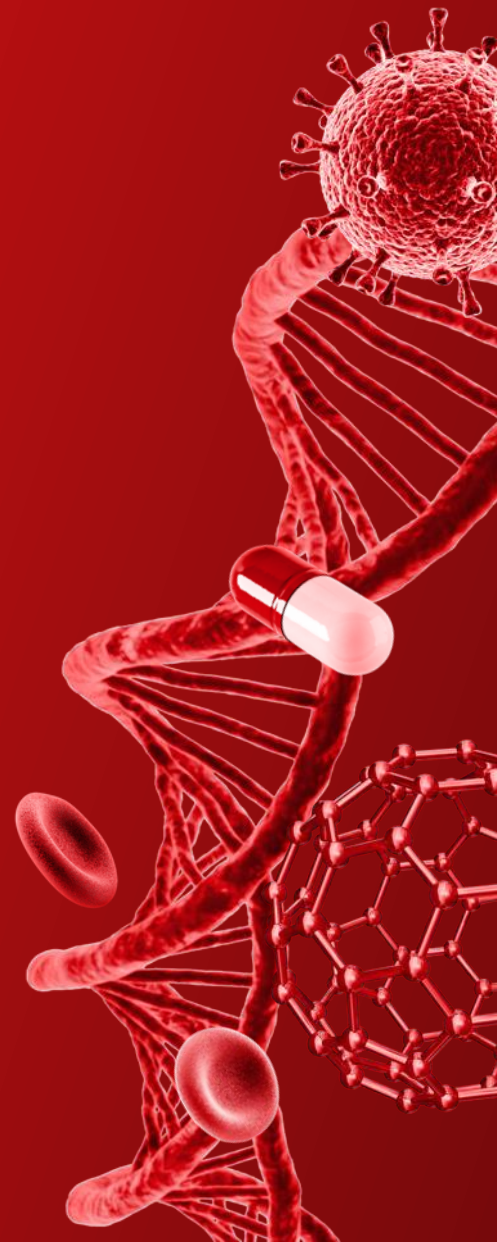
Linear dynamic range over 4 orders of magnitude allowing multiple sample types to be analyzed on a single calibration curve.

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

# Thank you

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