Targeted quantitation workflow with Orbitrap GC-MS: PAHs and PCBs in soil extracts

Suresh Seethapathy, Ph.D.
Senior Applications Scientist
Thermo Fisher Scientific
Centers of Excellence – GC/GC-MS

11-Aug 2021

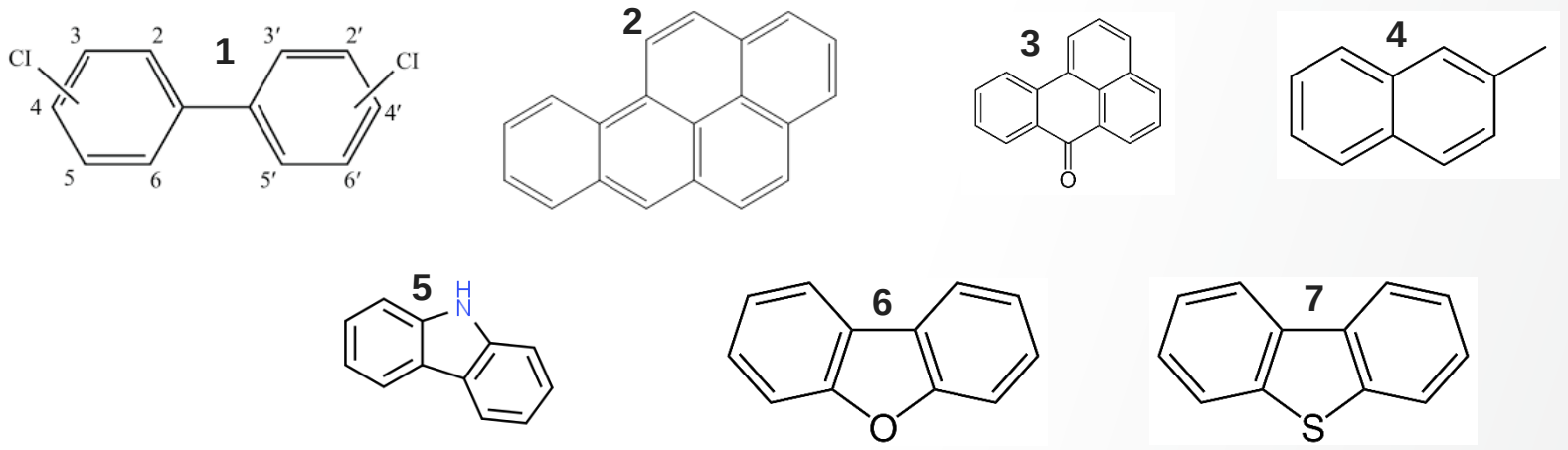
The world leader in serving science

Agenda

1. PAHs and PCBs: Importance, challenges
2. Sample preparation
3. Orbitrap Exploris GC: Schematic and hardware
4. Instrument method, tuning, and calibration
5. Results and discussion
6. Summary

PCBs and PAHs: Importance

- Polychlorinated biphenyls (PCBs)
  - Coolants and lubricants (i.e. transformer oils, capacitors etc.,)
- Polyaromatic hydrocarbons (PAHs)
  - Combustion products (i.e. diesel soot, stack emissions, bushfires)
- Substituted PAHs (oxyPAHs, methylPAHs & polyaromatic (N,S,O) heterocycles (PASHs, PAOHs, PANHs)
  - Combustion products and indirectly from PAHs



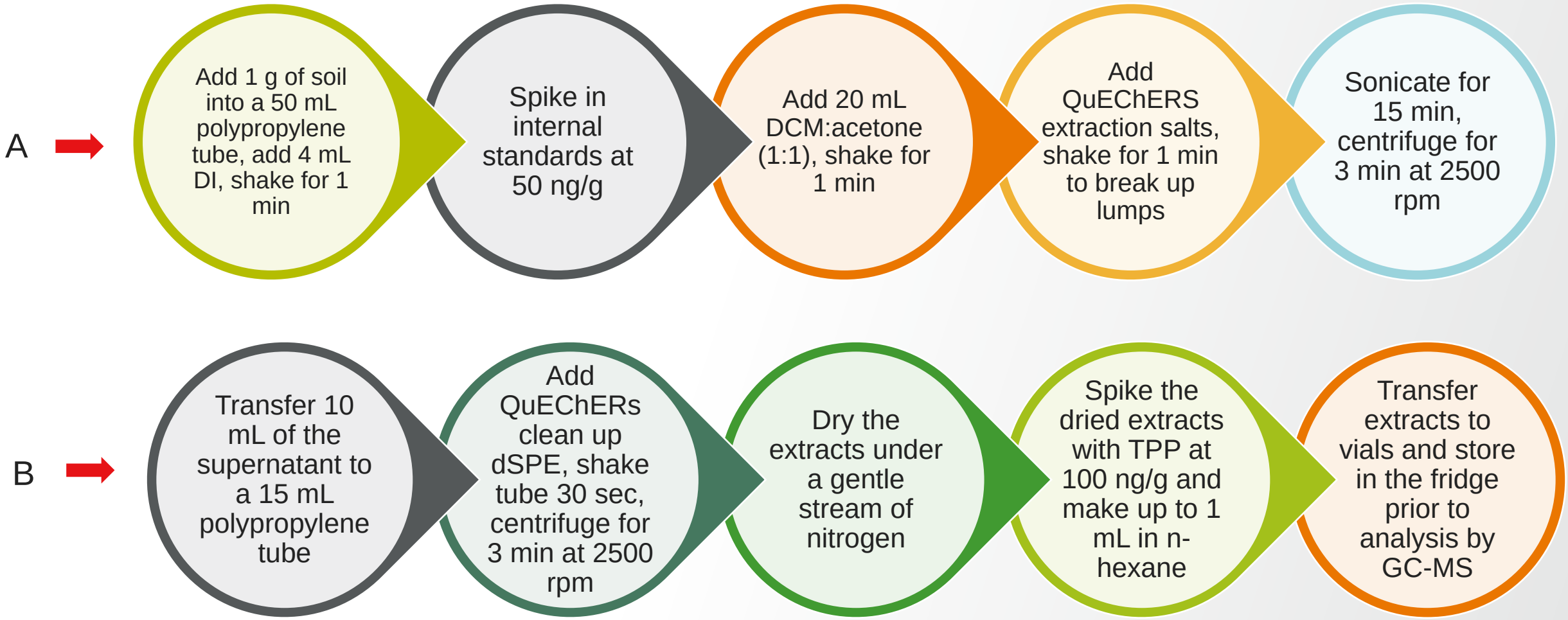
1= PCB (general structure), **2**=Benzo(a)pyrene (PAH), **3**=Benzanthrone (oxyPAH), **4**= 2-methylnaphthalene (methylPAH), **5**=Carbazole (PANH), **6**=Dibenzofuran (PAOH), **7**=Dibenzothiophene (PASH)

suresh.seethapathy@thermofisher.com | 11-August-2021

PCBs and PAHs: Challenges and method considerations

- Gas Chromatography (GC)
  - Mass Spectrometer (MS) - EI/CI
- Multiple chromatographic methods
- Time-consuming sample preparation
  - Soxhlet extraction (slow [~48 hours] consuming large amounts of solvents)
- Chromatographic separation of critical pairs
  - i.e. Benzo(b)fluoranthene/ benzo(k)fluoranthene
- Long run times >40 mins

Sample prep (QuEChERS extraction and dSPE clean-up)



Two hours sample preparation time up to 20X faster vs. Soxhlet extraction

Thermo Scientific Orbitrap Exploris GC series schematic

ExtractaBrite EI/CI ION SOURCE

Robust design, vent free source and column change EI/VeV/CI

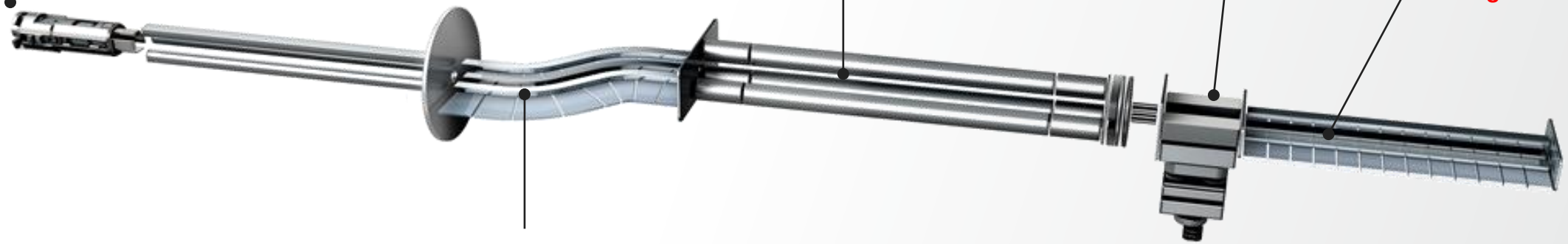
Advanced Quadrupole Technology (AQT)

Isolation widths down to 0.4 Da improves sensitivity and selectivity

C-Trap

Ion Routing Multipole

Facilitates higher energy collisional dissociation (HCD) fragmentation



AdvancedActive Beam Guide (AABG) with axial gradient

Prevents neutrals from entering the quadrupole and improves robustness

High-Field Orbitrap Mass Analyzer

Resolution up to 240,000 at *m/z* 200 and acquisition rates up to 40 Hz

Thermo Scientific Orbitrap Exploris GC Mass Spectrometer: Schematic/hardware

ExtractaBrite EI/CI ION SOURCE

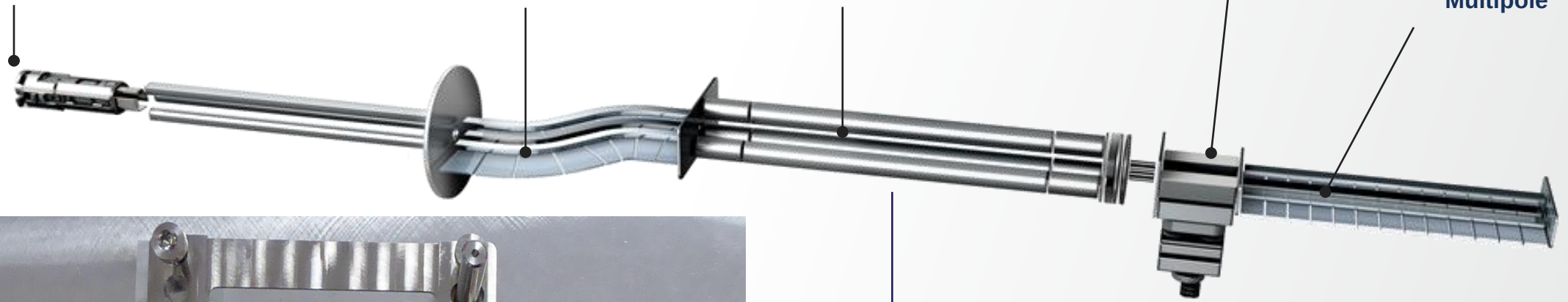
Advanced Active Beam Guide (AABG) with axial gradient

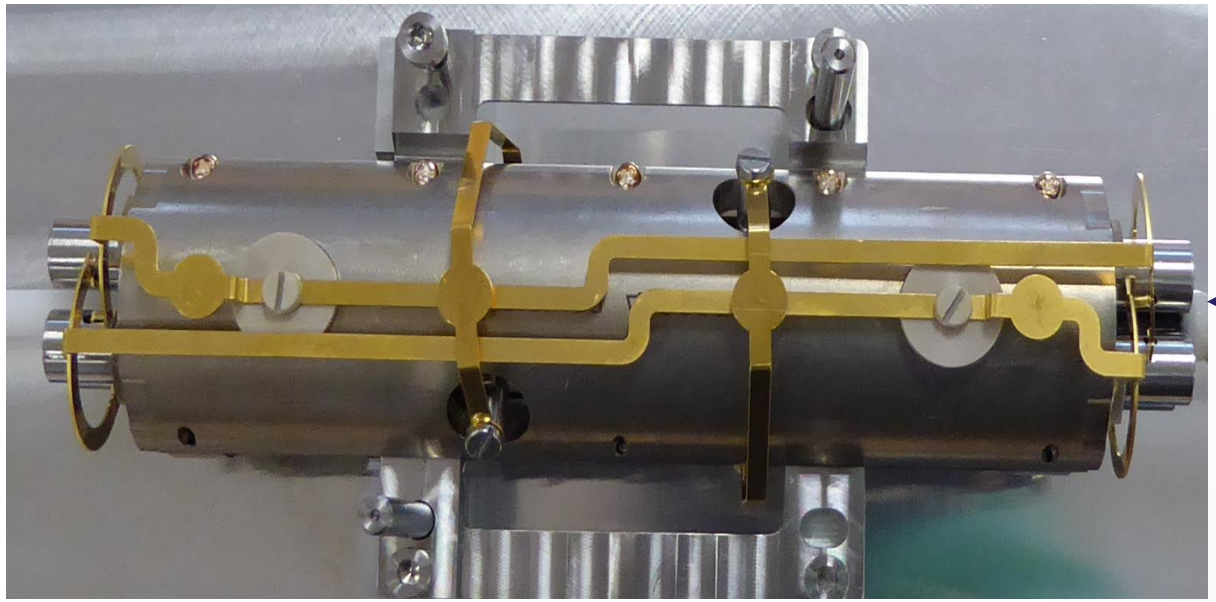
Advanced Quadrupole Technology (AQT)

Isolation widths down to 0.4 Da improves sensitivity and selectivity

C-Trap

Ion Routing Multipole





High-Field Orbitrap Mass Analyzer

Thermo Scientific Orbitrap Exploris GC Mass Spectrometer: Schematic/hardware

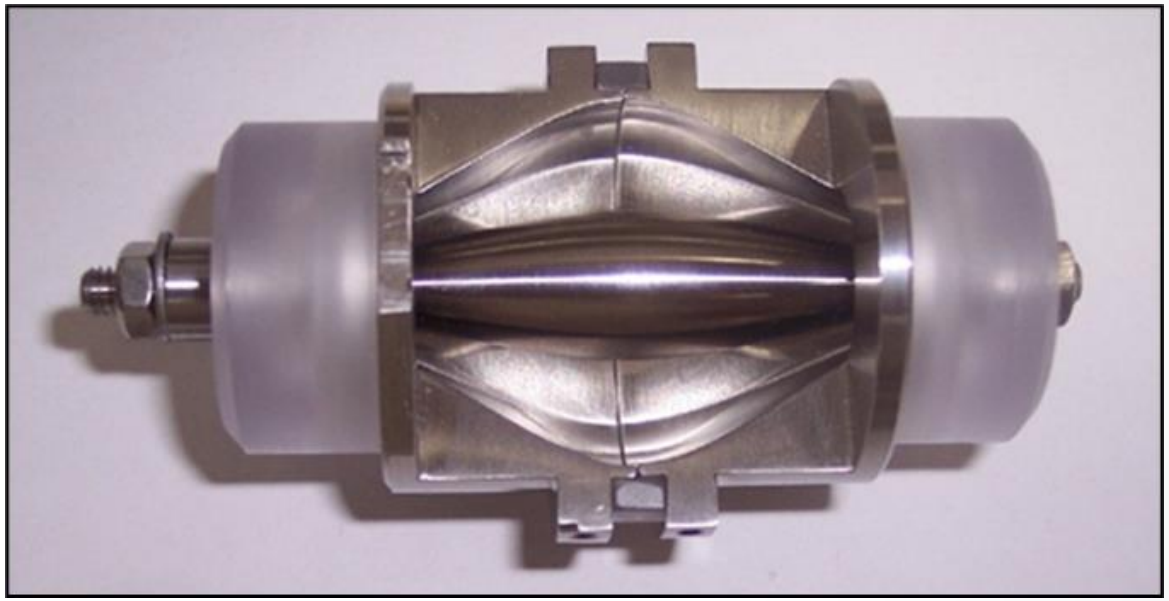
ExtractaBrite EI/CI ION SOURCE

Advanced Active Beam Guide (AABG) with axial gradient

Advanced Quadrupole Technology (AQT)

C-Trap

Ion Routing Multipole



High-Field Orbitrap Mass Analyzer

Instrument method

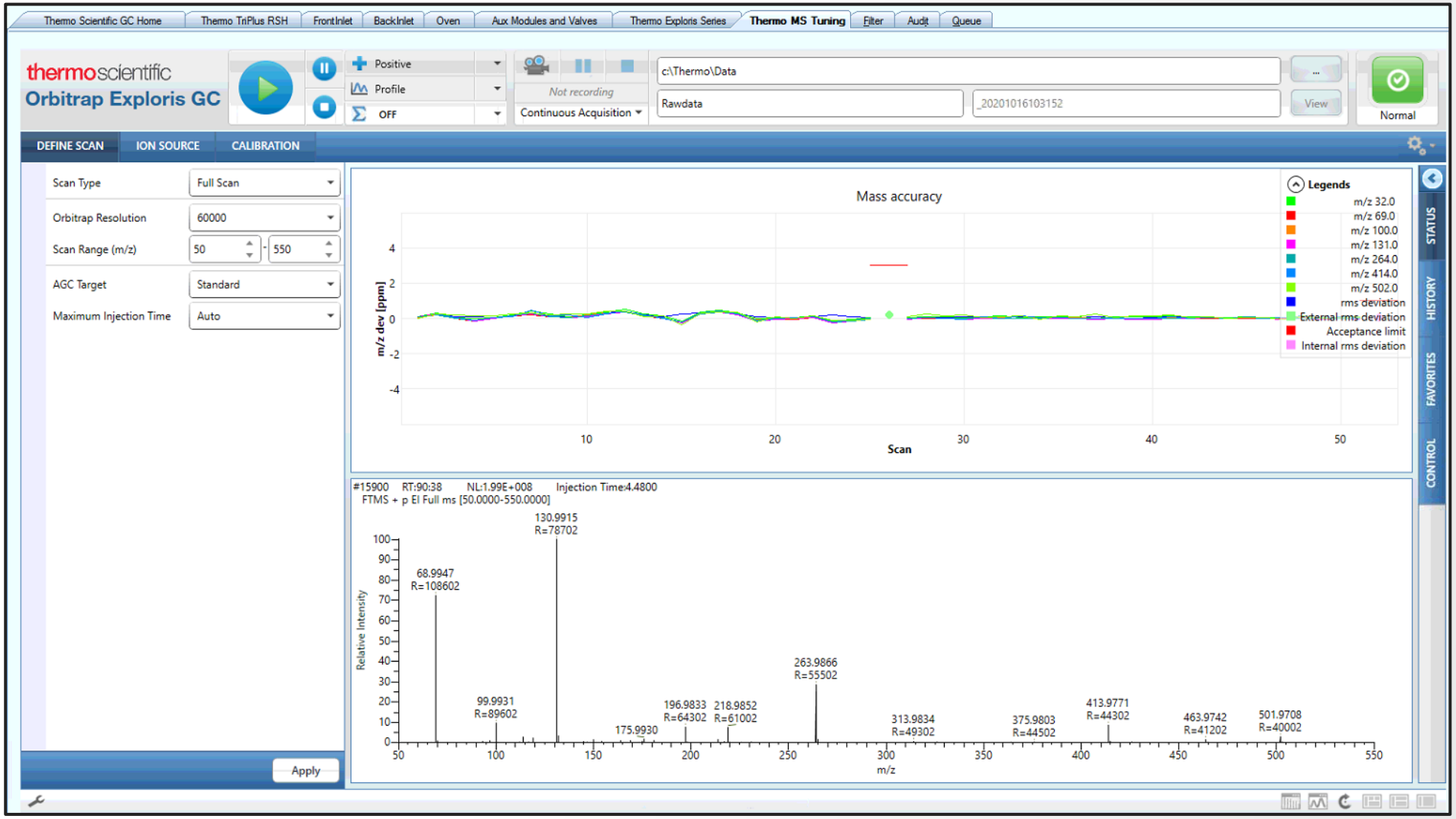
- Column: **Thermo Scientific™ TraceGOLD™ TG-5 Sil MS (30m × 0.25mm, 0.25µm)**
- Inlet and mode: SSL, Splitless
- Flowrate: 1.2 mL/min
- Inject volume: **1 µL**

No	Retention time [min]	Rate [°C/min]	Target value [°C]	Hold time [min]
1	0.000	Run		
2	1.000	0.00	40.0	1.00
3	9.750	28.00	285.0	0.00
4	16.417	3.00	305.0	0.00
5	22.917	30.00	350.0	5.00
6		New Row		
7	22.917	StopRun		

- Thermo Scientific™ Orbitrap Exploris™ GC MS
- Transfer line temperature: 320 ºC
- Source temperature: 350 ºC
- Electron energy (eV): 70
- Acquisition mode: Full scan (FS)
- Mass range *(m/z):* 50-550
- Mass resolution : FS 60,000(FWHM @ *m/z* 200, scan speed 7.4 Hz)
- Lock mass (*m/z*: 207.03235)

Tuning and calibration

Tune and calibrate in under 5 minutes and be confident system is at peak performance for all users

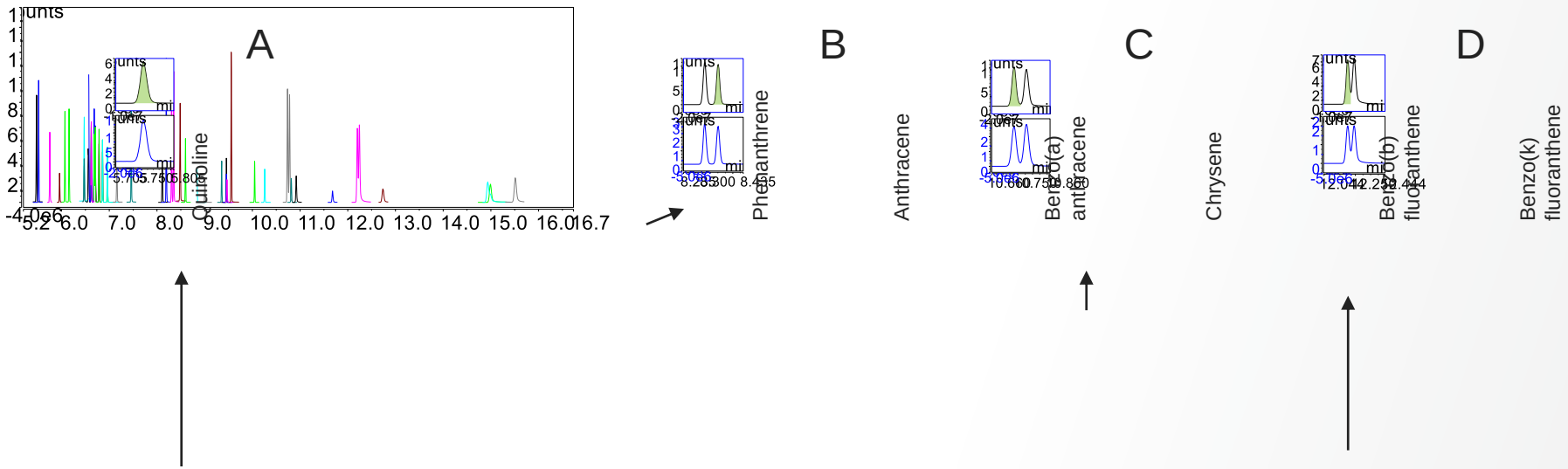


Thermo Scientific™ Chromeleon™ CDS Software

suresh.seethapathy@thermofisher.com | 11-August-2021

Selectivity

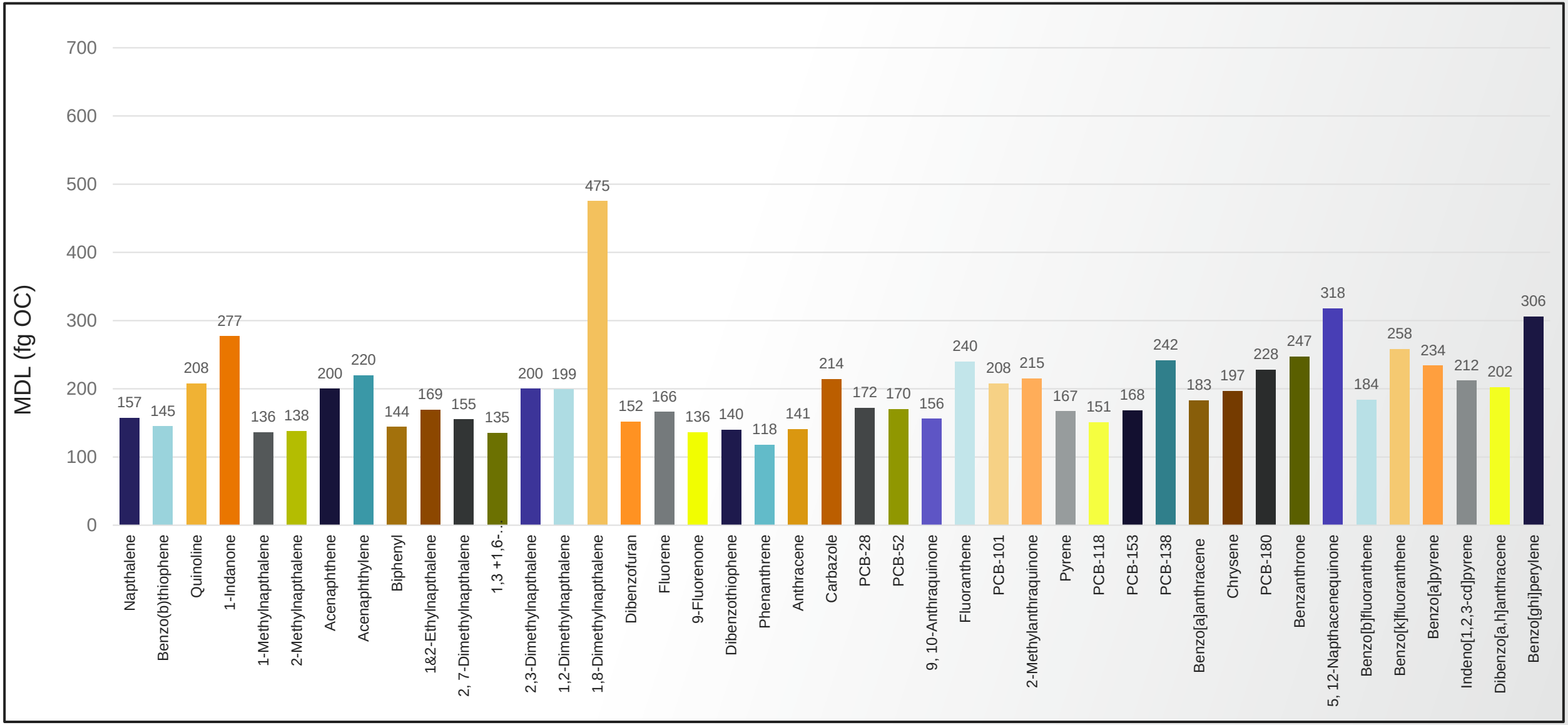
50 pg/uL calibration standard in n-hexane



Retention time (minutes)

suresh.seethapathy@thermofisher.com | 11-August-2021

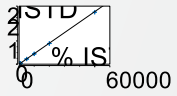
Sensitivity MDLs



Linearity

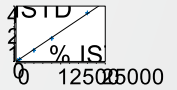
Compound	Compound type	R^2	AVCF % RSD	Compound	Compound type	R^2	AVCF % RSD
Naphthalene	PAH	0.9999	1.6	1,2-Dimethylnapthalene	methylPAH	0.9993	4.5
Acenaphthylene	PAH	0.9987	5.4	1,8-Dimethylnapthalene	methylPAH	0.9998	2.6
Acenaphthene	PAH	0.9995	4.0	PCB-28	PCB	0.9997	2.5
Biphenyl	PAH	0.9998	2.6	PCB-52	PCB	0.9991	2.8
Fluorene	PAH	0.9981	9.0	PCB-101	PCB	0.9998	3.2
Phenanthrene	PAH	0.9995	3.8	PCB-118	PCB	0.9998	3.7
Anthracene	PAH	0.9981	4.3	PCB-153	PCB	0.9998	1.6
Fluoranthene	PAH	0.9998	3.0	PCB-138	PCB	0.9991	2.8
Pyrene	PAH	0.9997	3.2	PCB-180	PCB	0.9997	4.3
Benzo[a]anthracene	PAH	0.9999	1.7	Benzo(b)thiophene	PASH	0.9998	3.2
Chrysene	PAH	0.9997	3.1	Dibenzothiophene	PASH	0.9988	3.7
Benzo[b]fluoranthene	PAH	0.9998	2.6	1&2-Ethylnapthalene	ethylPAH	0.9996	3.7
Benzo[k]fluoranthene	PAH	0.9994	4.5	Quinoline	PANH	0.9988	4.0
Benzo[a]pyrene	PAH	0.9987	5.4	1-Indanone	PAOH	0.9993	4.7
Indeno[1,2,3-cd]pyrene	PAH	0.9964	9.3	Dibenzofuran	PAOH	0.9993	5.3
Dibenzo[a,h]anthracene	PAH	0.9978	7.3	Carbazole	PAOH	0.9980	4.7
Benzo[ghi]perylene	PAH	0.9989	5.1	9, 10-Anthraquinone	PAOH	0.9951	12.9
1-Methylnapthalene	methylPAH	1.0000	1.1	2-Methylanthraquinone	PAOH	0.9981	6.5
2-Methylnapthalene	methylPAH	0.9999	1.8	9-Fluorenone	oxyPAH	0.9997	5.0
2, 7-Dimethylnapthalene	methylPAH	0.9999	1.5	Benzanthrone	oxyPAH	0.9985	6.0
1,3 +1,6-Dimethylnapthalene	methylPAH	0.9999	2.0	5, 12-Napthacenequinone	oxyPAH	0.9963	9.6
2,3-Dimethylnapthalene	methylPAH	0.9999	1.8		**Min**	**0.9951**	**1.1**
					Max	**1.0000**	**12.9**
					Mean	**0.9991**	**4.2**

oxyPAH



R^2=0.9997
% RSD=5.0

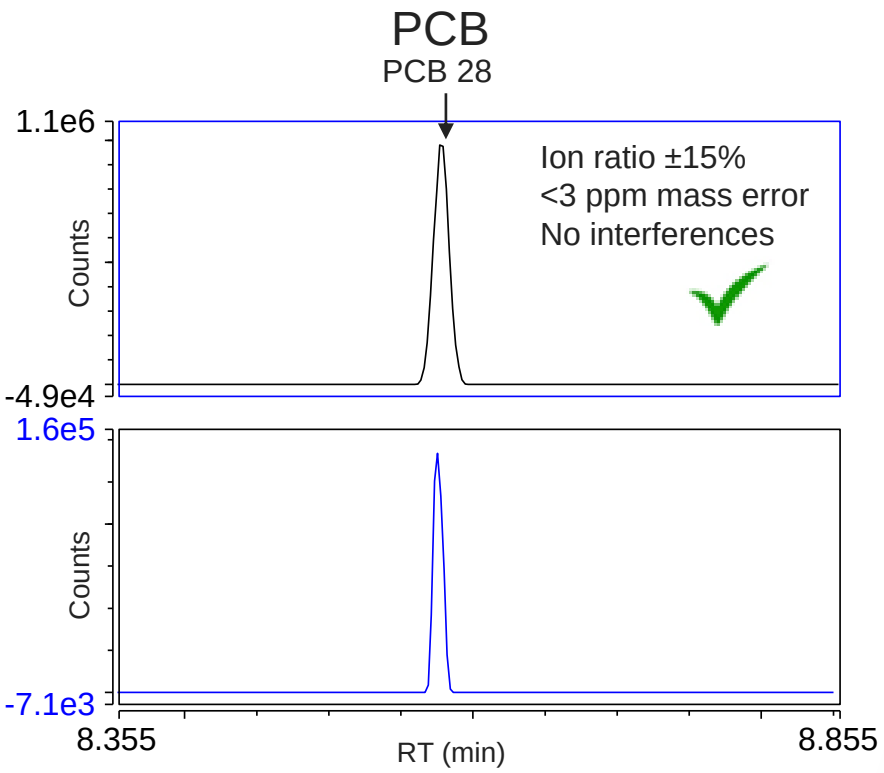
PAH



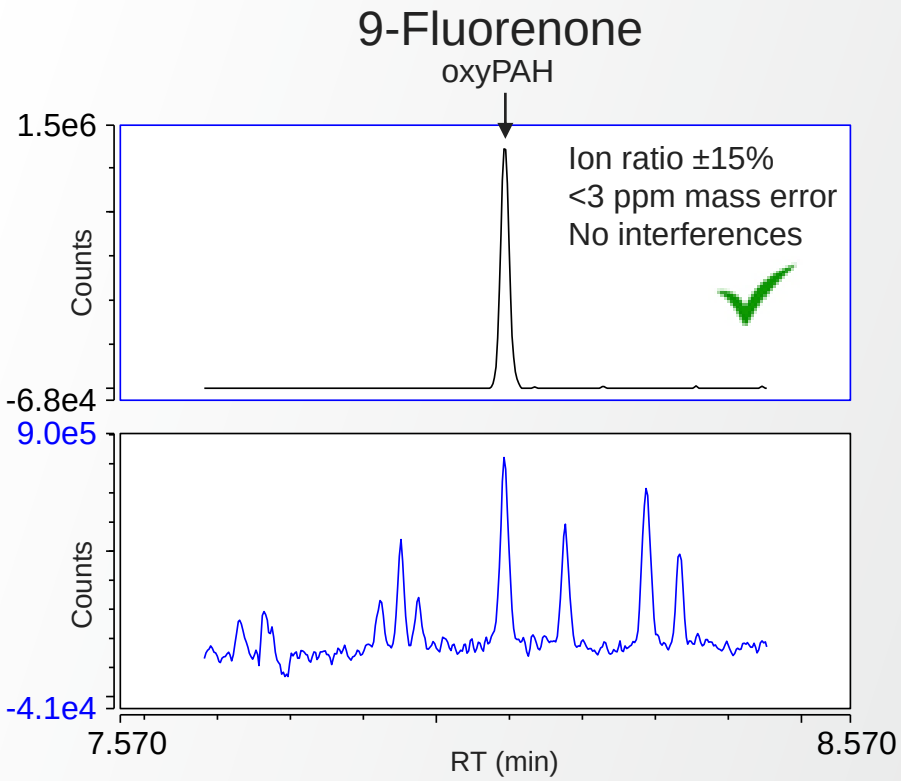
R^2=0.9989
% RSD=4.1

suresh.seethapathy@thermofisher.com | 11-August-2021

Quantification of PAHs and PCBs in soil

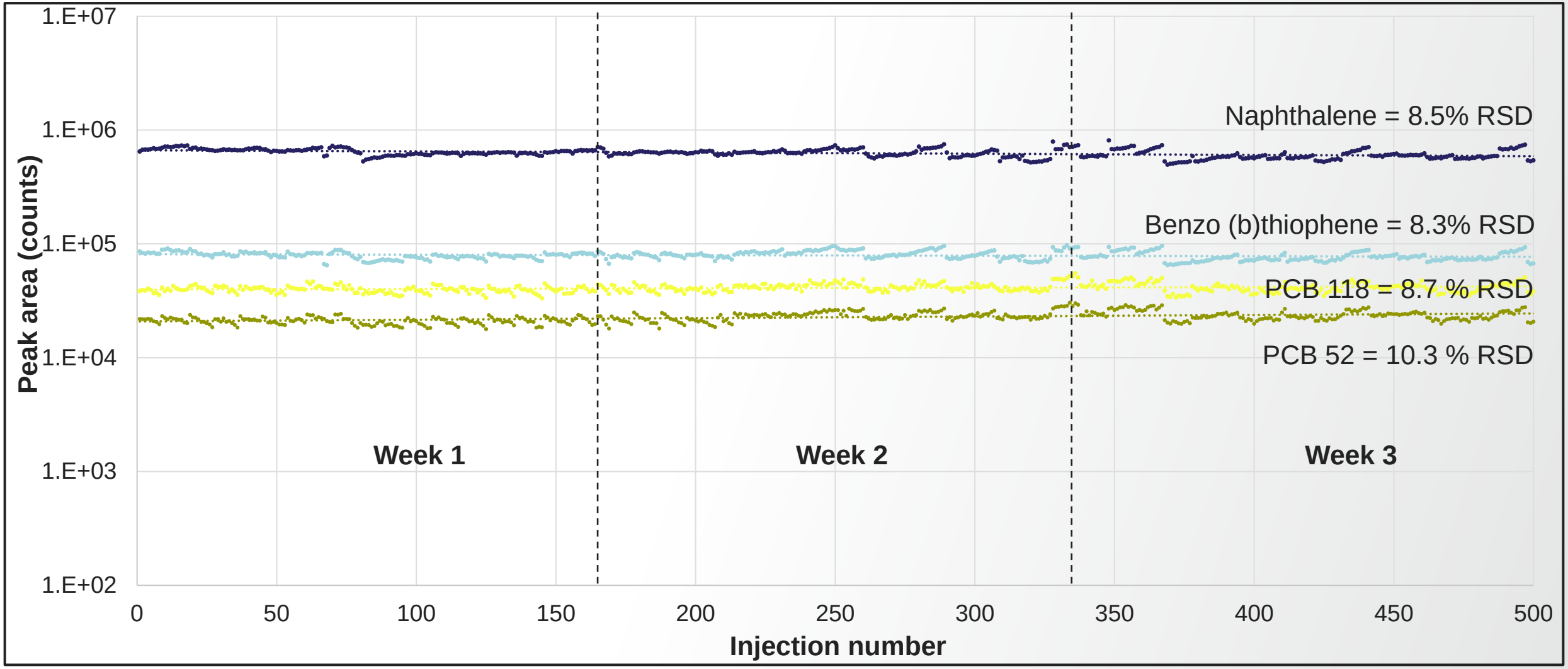


Amount found in sample	0.6 µg/Kg
Ion ratio % deviation	0.7 %
Measured mass (*m/z*)	255.96074
Theoretical mass (*m/z*)	255.96078
Chemical formula	$C_{12}H_7Cl_3$
Mass error (ppm)	0.2



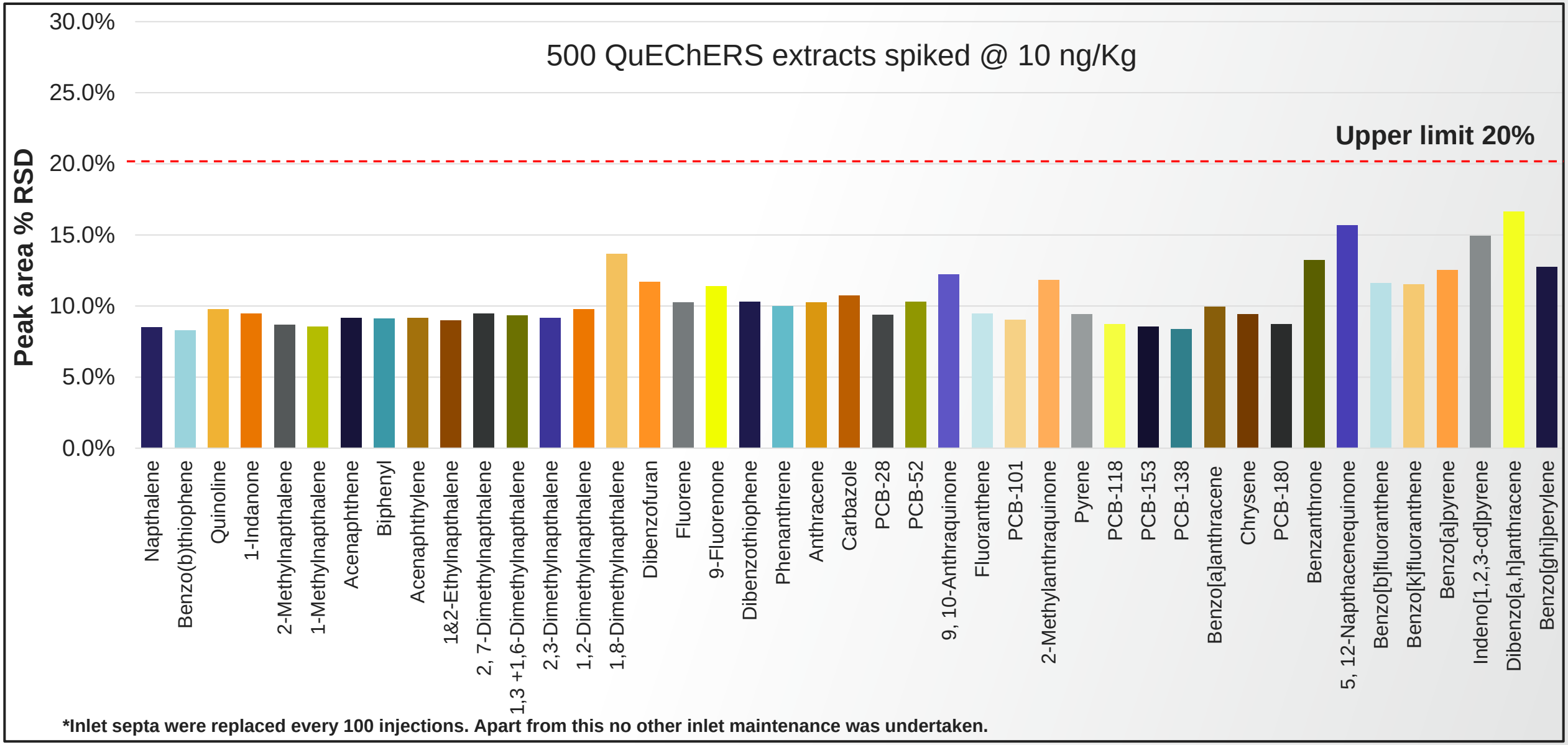
Amount found in sample	0.8 µg/Kg
Ion ratio % deviation	4.8%
Measured mass (*m/z*)	180.05698
Theoretical mass (*m/z*)	180.05697
Chemical formula	$C_{13}H_8O$
Mass error (ppm)	0.1

Robustness: Peak area repeatability



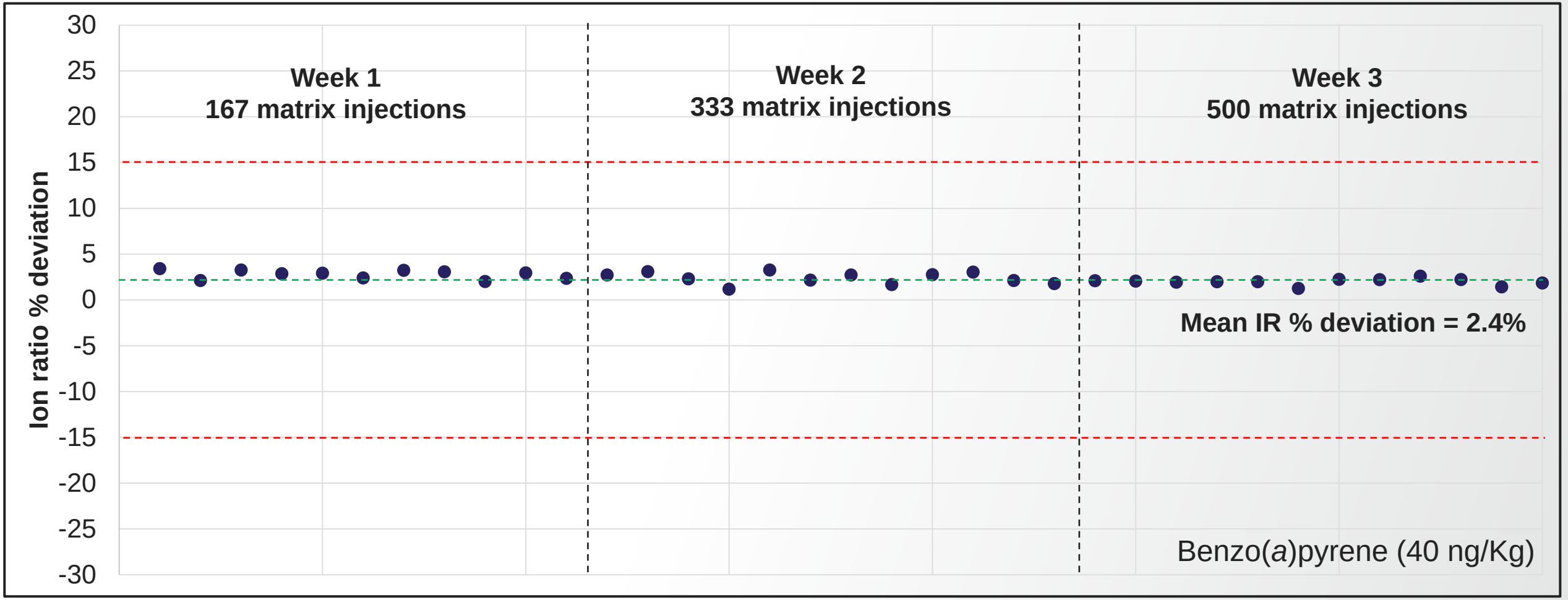
QuEChERS Soil Extract spiked at 10 ng/Kg

Robustness: Peak area repeatability



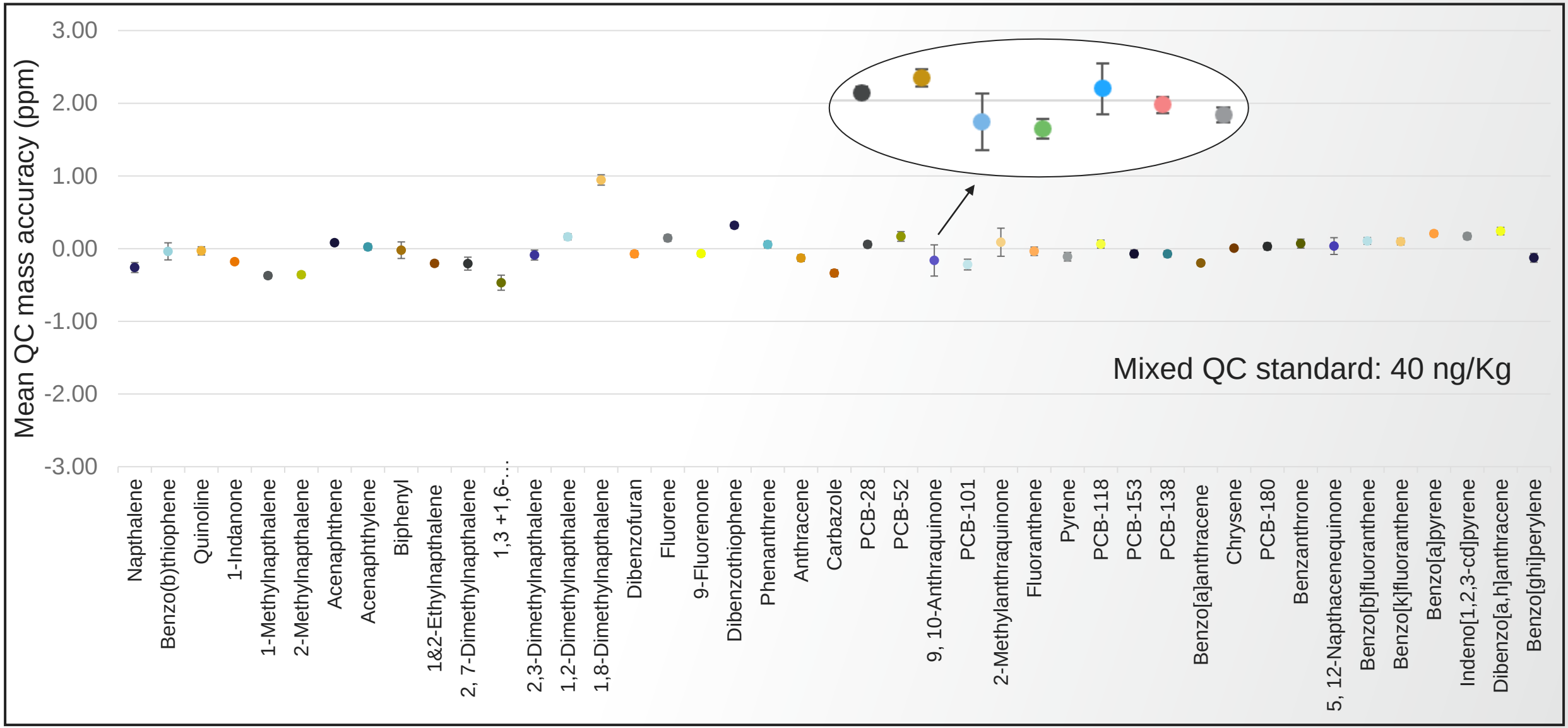
***Inlet septa were replaced every 100 injections. Apart from this no other inlet maintenance was undertaken.**

Robustness: QC standard ion ratio stability



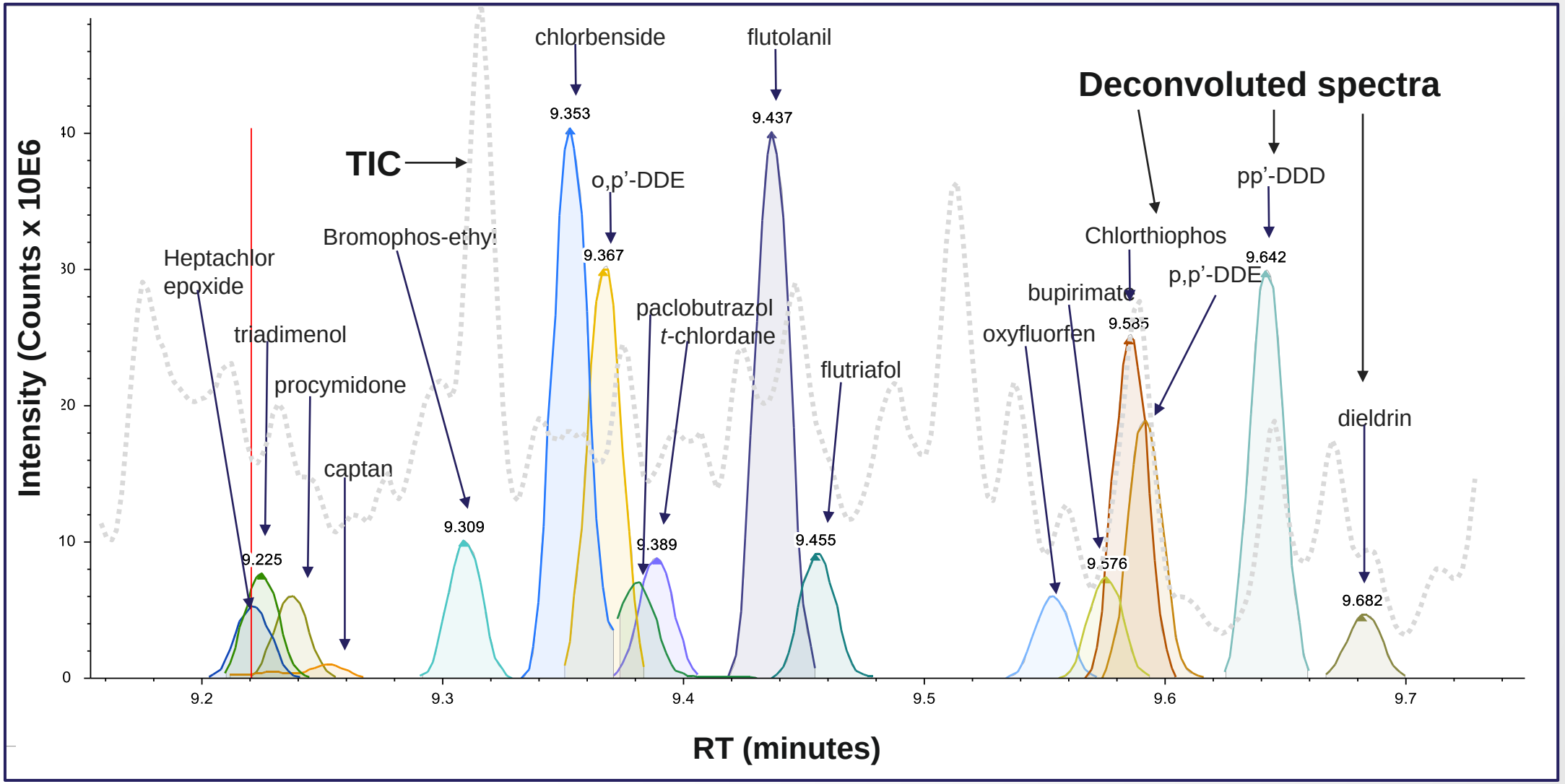
suresh.seethapathy@thermofisher.com | 11-August-2021

Robustness: QC standard mass accuracy stability



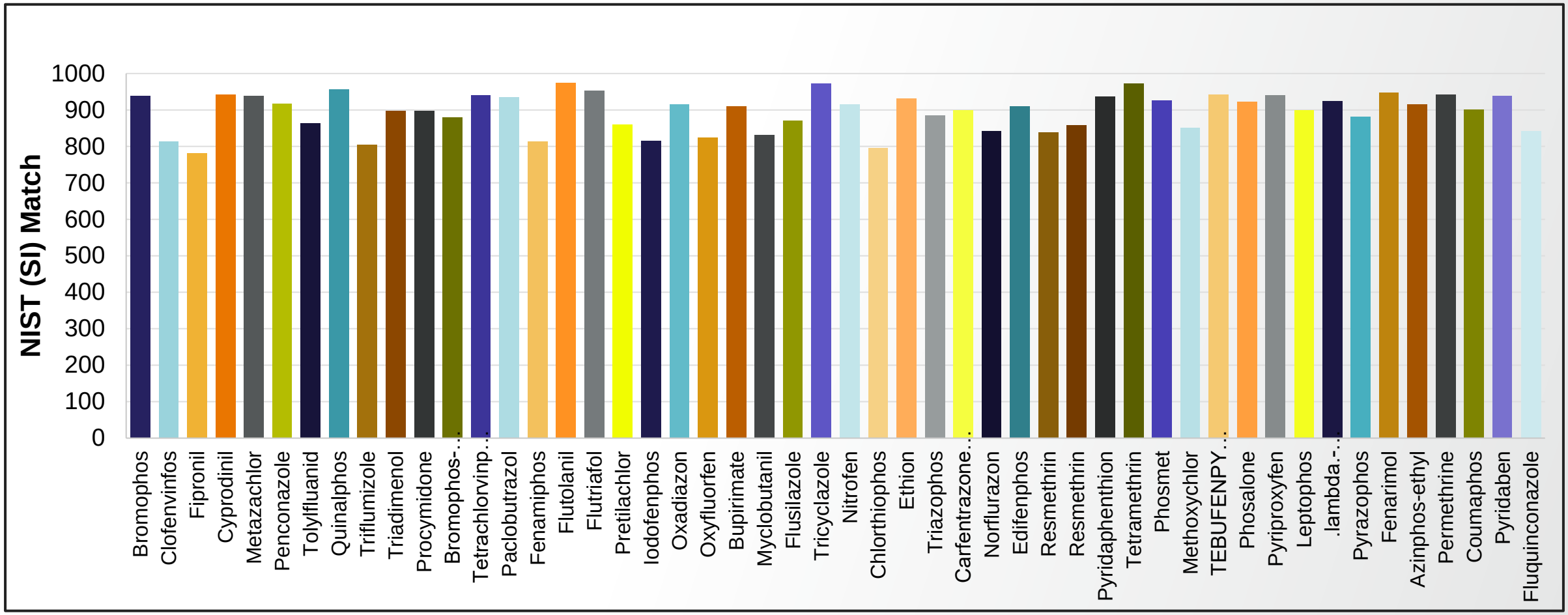
suresh.seethapathy@thermofisher.com | 11-August-2021

Thermo Scientific Compound Discoverer 3.2 Software deconvoluted soil EI spectrum

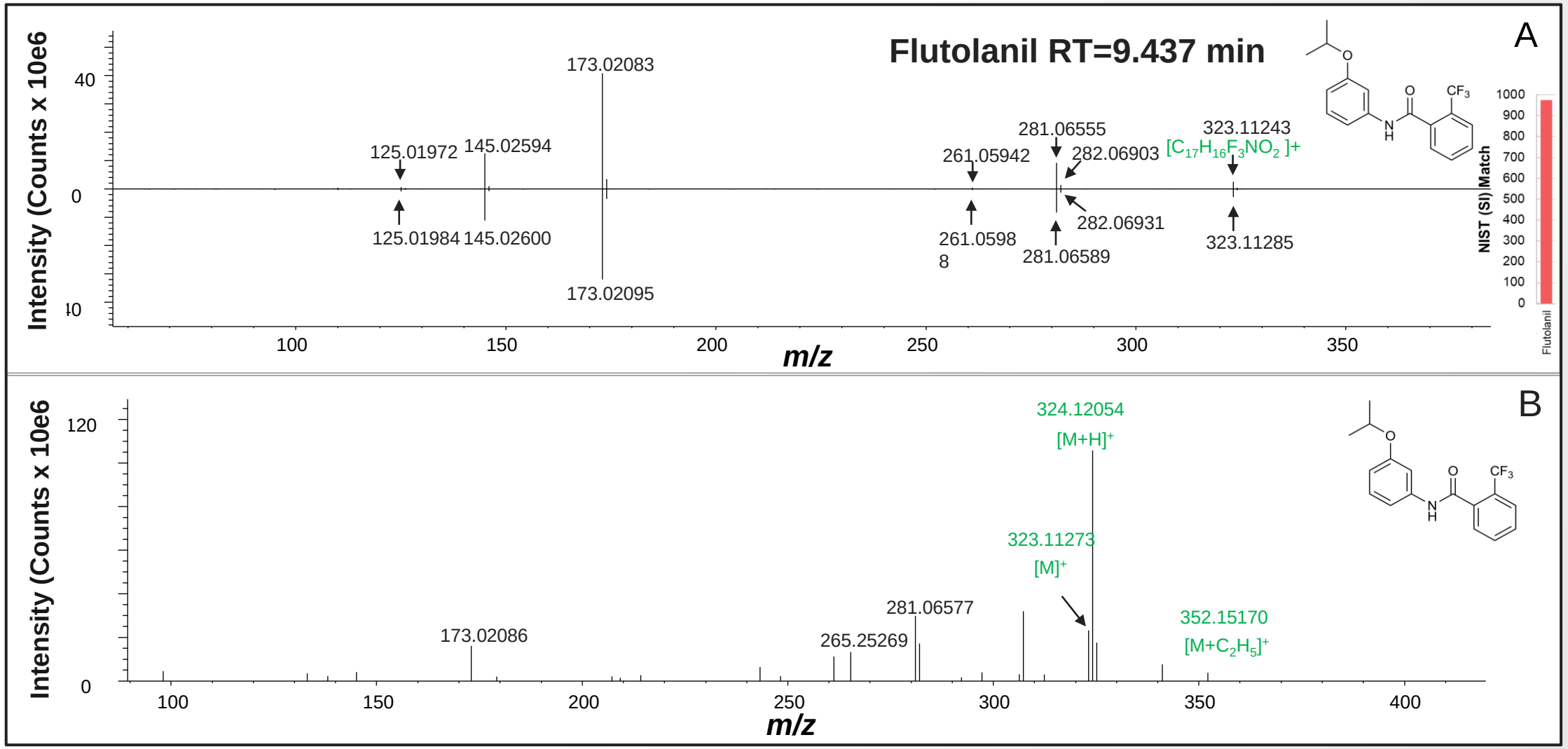


suresh.seethapathy@thermofisher.com | 11-August-2021

NIST search results



Screening for additional contaminants (EI deconvolution and NIST matches)



Summary

- **Orbitrap Exploris GC mass spectrometer**: Best mass accuracy and high resolution leads to easy, reliable, and compliant data generation.
- **Easy full-scan data acquisition**: Retrospective analysis and comprehensive targeted and non-targeted workflow of environmental sample analysis with Thermo Scientific™ Compound Discoverer™ software.
- **Comprehensive method consolidation**: PAHs and PCBs analysis in soil in < 20 min. Up to 20×, realized using modified QuEChERS method compared to tradition Soxhlet extraction methods, saving cost and time.
- **Sensitivity**: MDL values calculated for 45 native compounds ranging from 118 to 475 fg OC (corresponding to 0.1–0.5 µg/kg in sample). LOQs ranged from 0.5 to 5.0 µg/kg in soil as determined.
- **Linear dynamic range**: Better than 6 orders of magnitude.
- **Robustness**: Stable peak area, ion ratios, and mass accuracies were achieved for QuEChERS soil extracts and QC standards, studied over a three week period.
- Overall, an excellent solution for both the chemists running the system and lab managers keeping track of the return on investment.

Thank you

Questions?