Comprehensive & Robust Analysis of Environmental Semivolatile Organic Compounds Using GC-MS/MS

Dale Walker and Rachael Ciotti
Agilent Technologies

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Trusted Answers

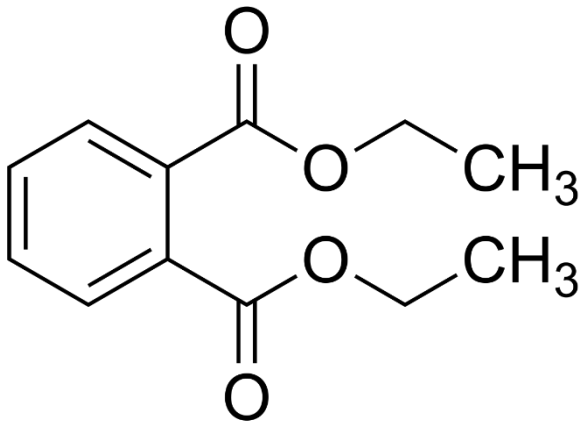
Environmental Protection Agency (EPA) Method 8270E

8270 was previously only single quadrupole only, E revision allows use of a triple quadrupole mass spectrometer in selected reaction monitoring mode (SRM), aka multiple reaction monitoring mode (MRM).

What is MRM?

Multiple **R**eaction **M**onitoring

Diethyl phthalate

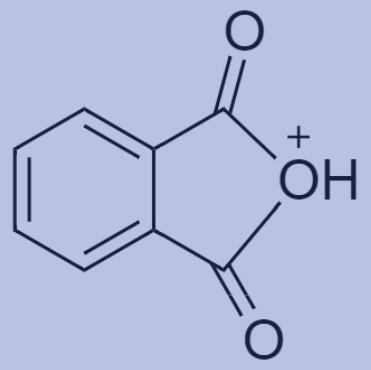


EI to Q1

Q1 only lets *m/z* *149* pass

SIM

Precursor ion



m/z 149

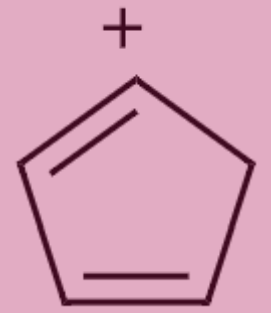
MRM Transition

CID to Q2

N_2

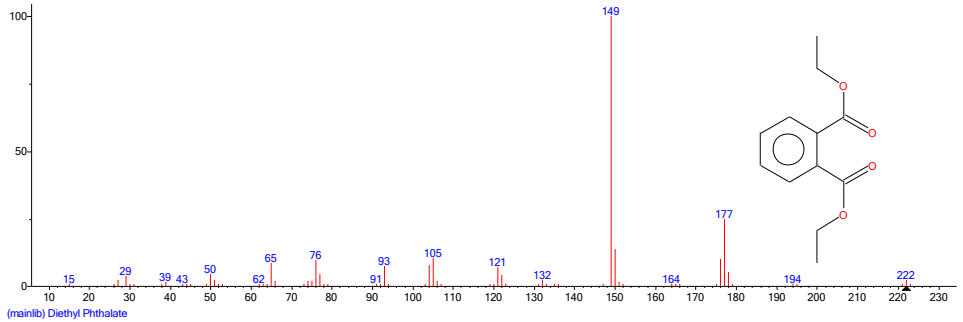
SIM

Product ion



m/z 65

Other fragments



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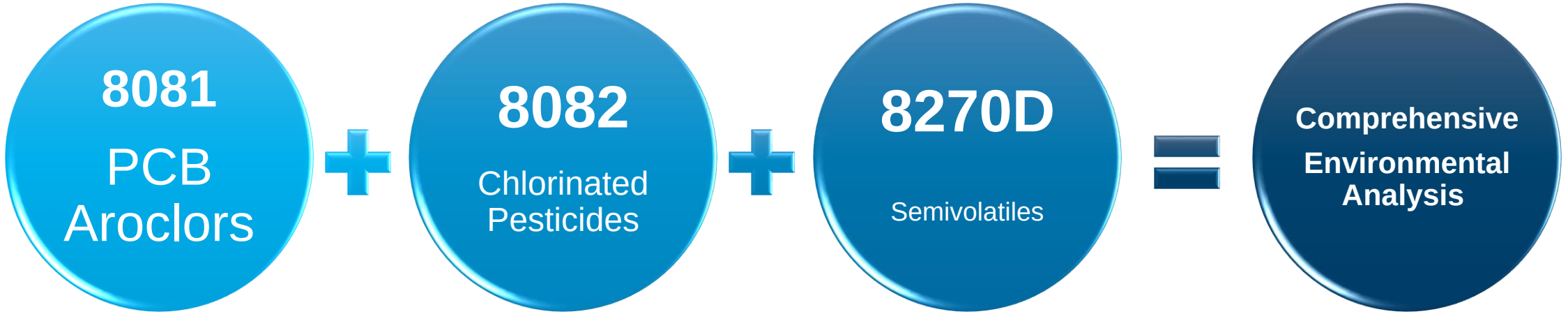
Why GC MS/MS?

Facilitates selective quantitation of target analytes in high chemical background samples

Better S/N in complex matrices as compared to single quad approaches

Femtogram levels of detection and quantification

Goal: Multiple EPA methods on one instrument in a single injection



Dual column
GC- ECD

Dual column
GC- ECD

GC- SQ

GC- TQ

Standards

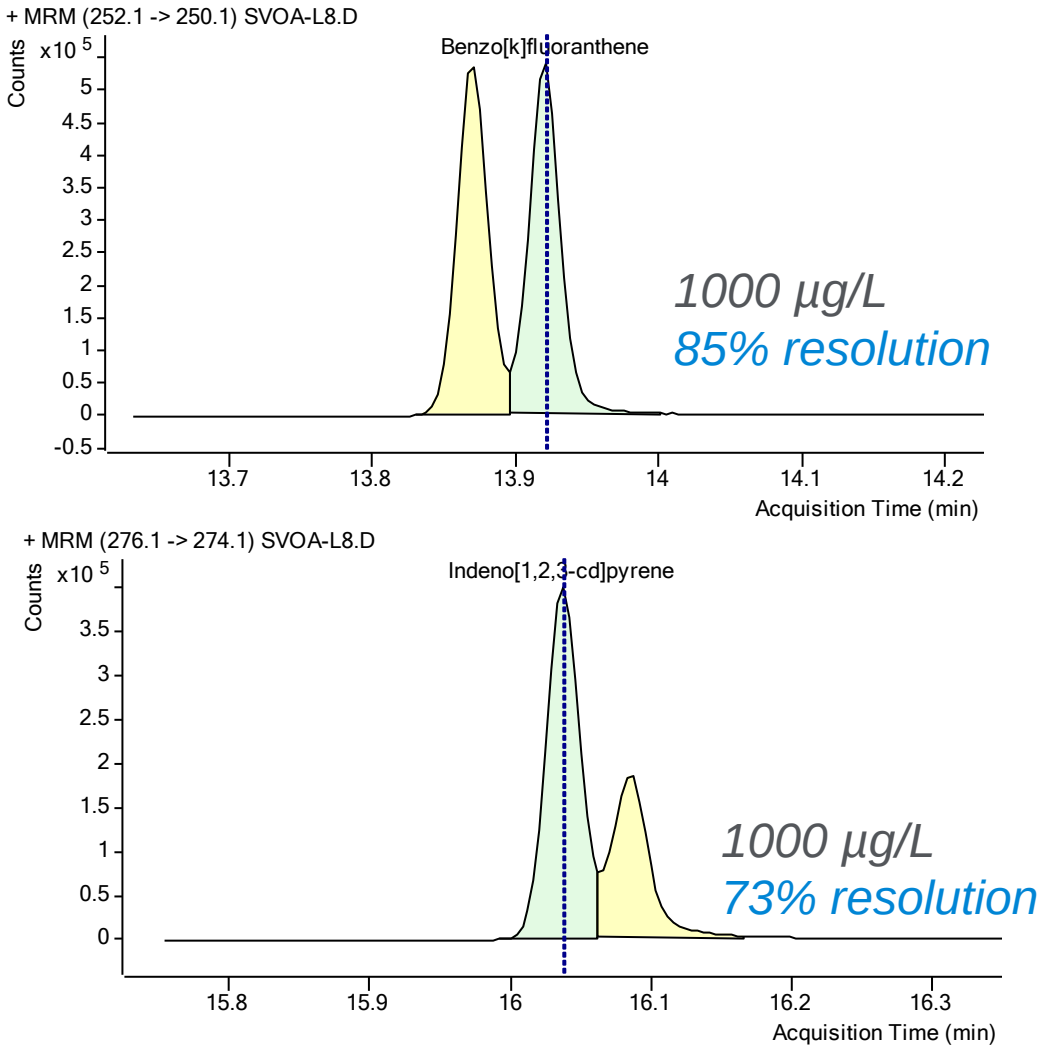
All sourced via Agilent

Aroclors:	1016, 1221, 1232, 1242, 1254, 1260, 1262
Pesticides:	(20): BHCs (alpha, beta, delta, gamma); 4,4'- DDE, 4,4'-DDD, 4,4'-DDT; Aldrin, Dieldrin, cis- and trans-Chlordane, Endosulfan I & II, Endosulfan sulfate, Endrin, Endrin aldehyde, Endrin ketone; Heptachlor, Heptachlor epoxide, Methoxychlor
Semivolatiles:	(76) including acids, bases, PAHs, phthalates, nitrosamines, phenols, etc.
Internal Stds:	1,4-dichlorobenzene-d_4, Naphthalene-d_8, Acenaphthene-d_{10}
	Chrysene-d_{12} Perylene d_{12} 50 µg/L in-vial

Method parameters: GC

<17-minute method

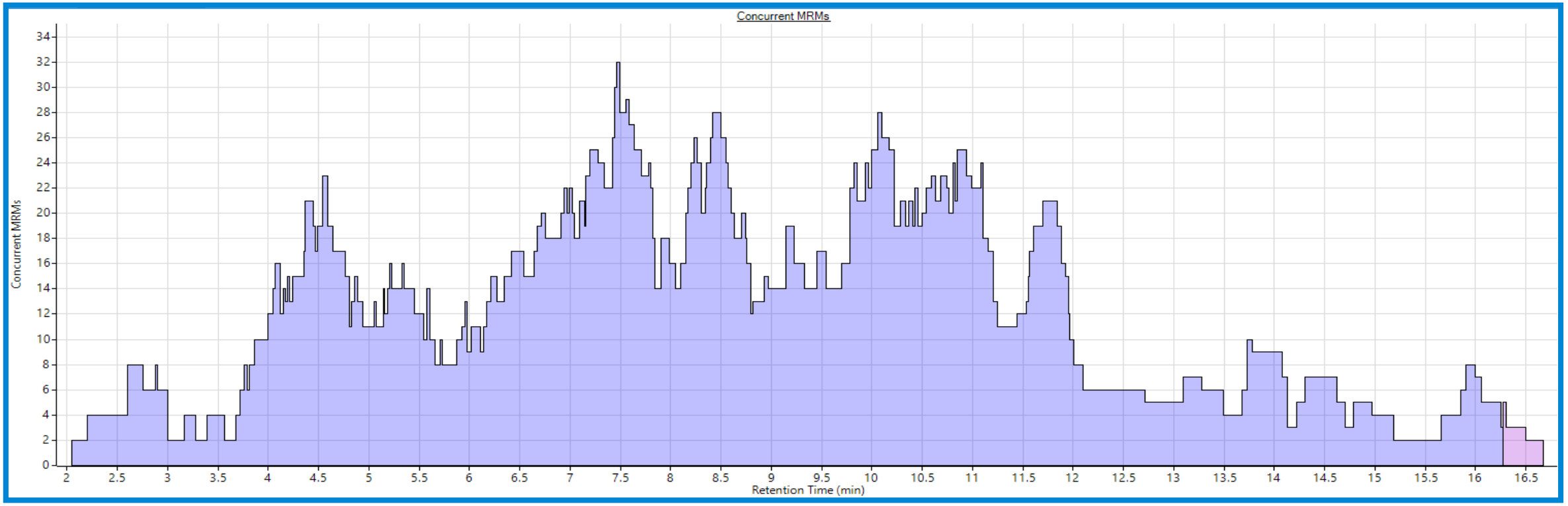
Parameter	Value
Injection Volume	1µL
Inlet	SSL @ 280°Cin pulsed splitless mode 30 psi pulse until 0.6 min Purge 15mL/min at 0.75 min
Liner	Agilent Ultra Inert bottom frit liner
Column	DB-UI 8270D Column 30m x 250µm, 0.25mm
Carrier gas	Helium @ 1.25mL/min constant flow Retention time locked to Acenaphthene-*d10* @7.08 min
Oven	40°C hold 0.5 Ramp 25°C/min → 260 Ramp 5°C/min → 280 Ramp 25°C/min → 320, hold 2 min
MSD Transfer Line	320°C



Method parameters: MS

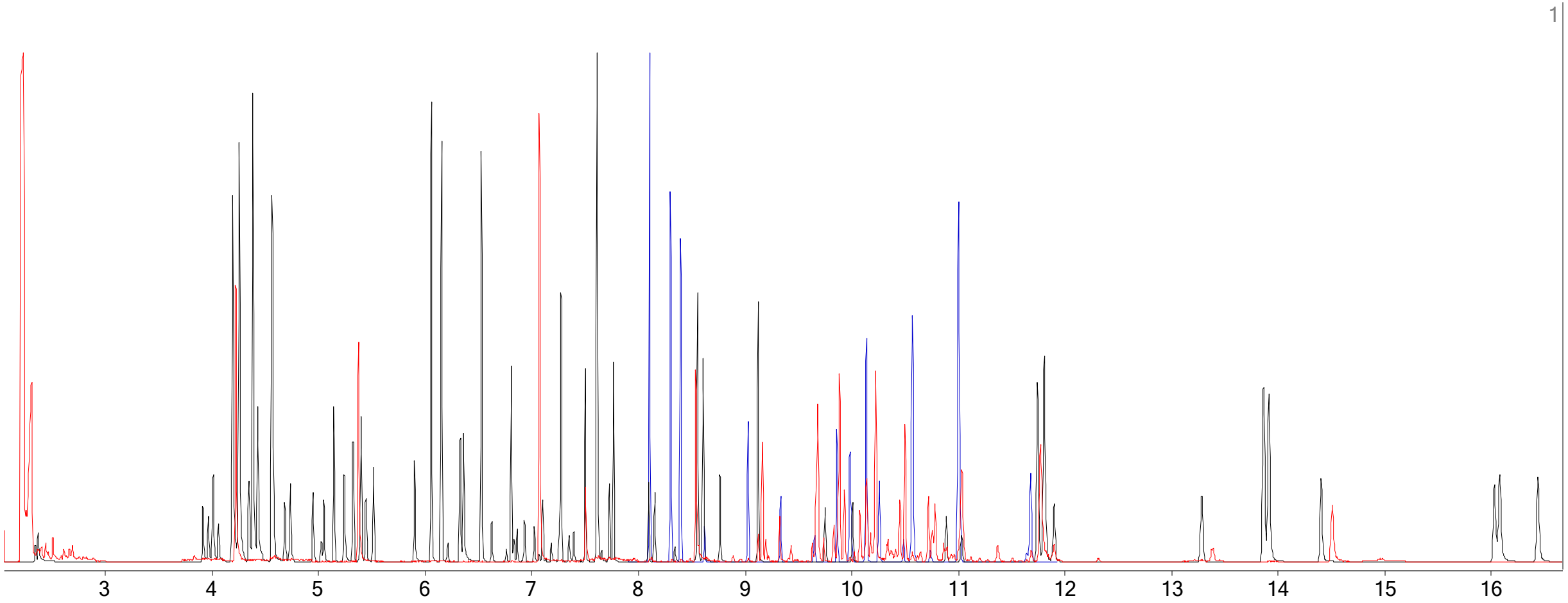
At least 1 quantifier and 1 qualifier transition per analyte

- 292 total MRMs across 219 MRM groups in dynamic MRM mode
- Extractor ion source @ 300°C
- Quadrupoles 1 & 2 @ 150°C
- 2.25mL min Helium quench gas, 1.5 mL/min Nitrogen collision gas



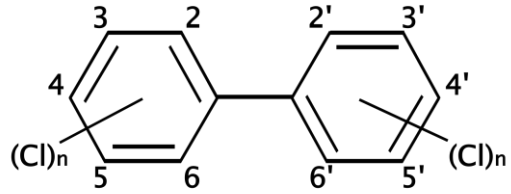
Example chromatogram

8270, Organochlorine pesticides and PCB Aroclors in a single acquisition method



PCBs as Aroclors:

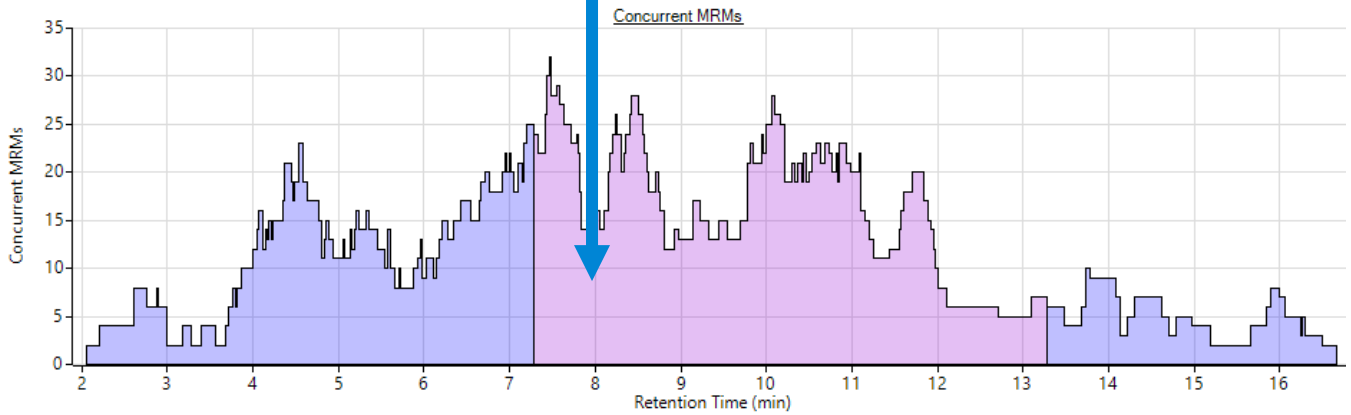
Each homologue group has a unique MRM transition



Homologue Group	Unique Transition	Number of Congeners
Monochlorobiphenyl	188 > 152	3
Dichlorobiphenyl	222 > 152	12
Trichlorobiphenyl	258 >186	24
Tetrachlorobiphenyl	292 > 222	42
Pentachlorobiphenyl	326 > 256	46
Hexachlorobiphenyl	360 > 290	42
Heptachlorobiphenyl	394 > 324	24
Octachlorobiphenyl	428 > 356	12
Nonachlorobiphenyl	462 > 392	3
Decachlorobiphenyl	498 > 428	1
Total Number of Congeners		209

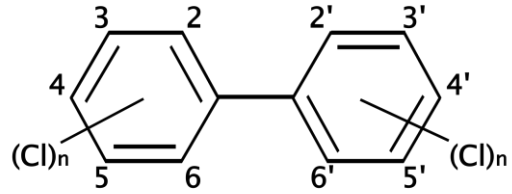
Source: epa.gov

Monitoring window for pentachlorobiphenyl congeners



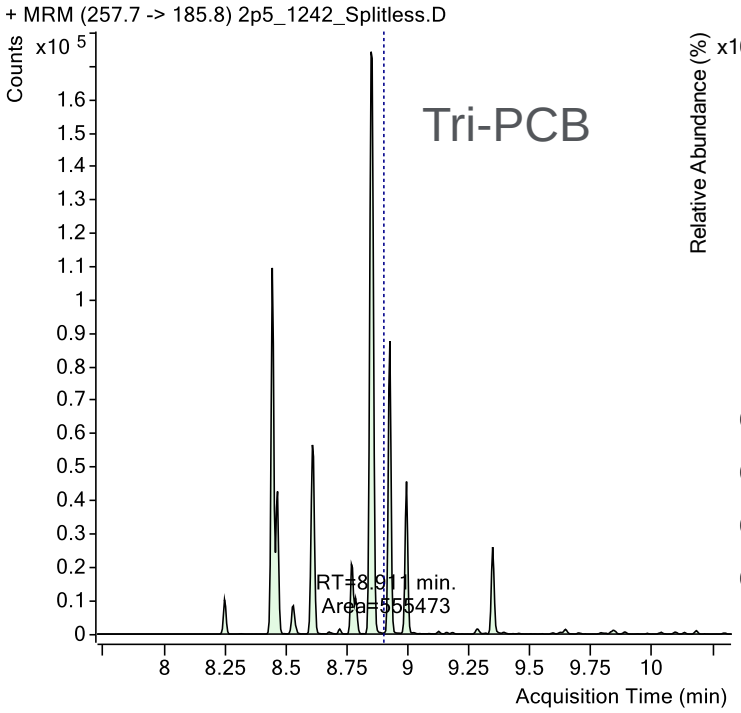
Example Calibration: Aroclor 1242

0.025 – 10 µg/mL



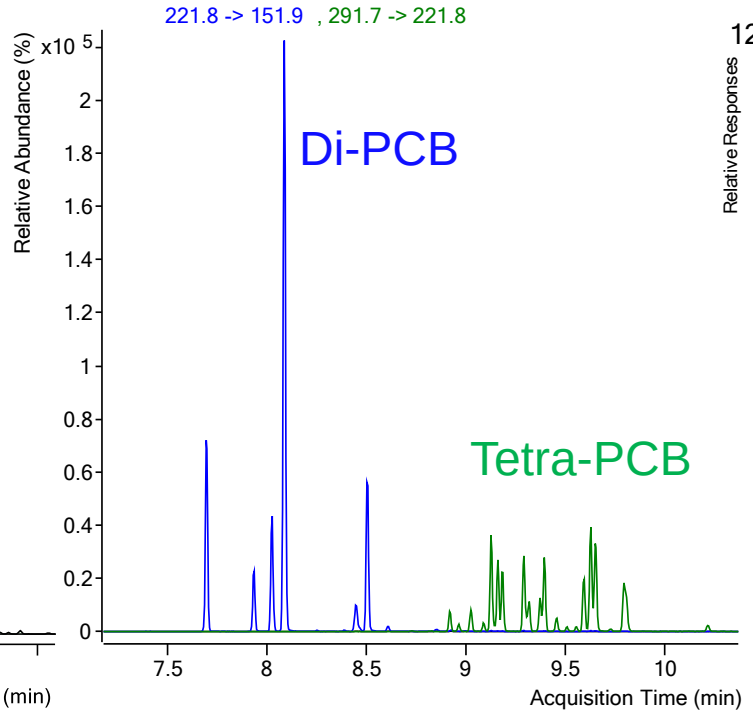
Congener Homologue Level of Chlorination									
Mono	Di	Tri	Tetra	Penta	Hexa	Hepta	Octa	Nona	Deca
0.8%	15%	44.9%	32.6%	6.4%	0.3%	0	0	0	0

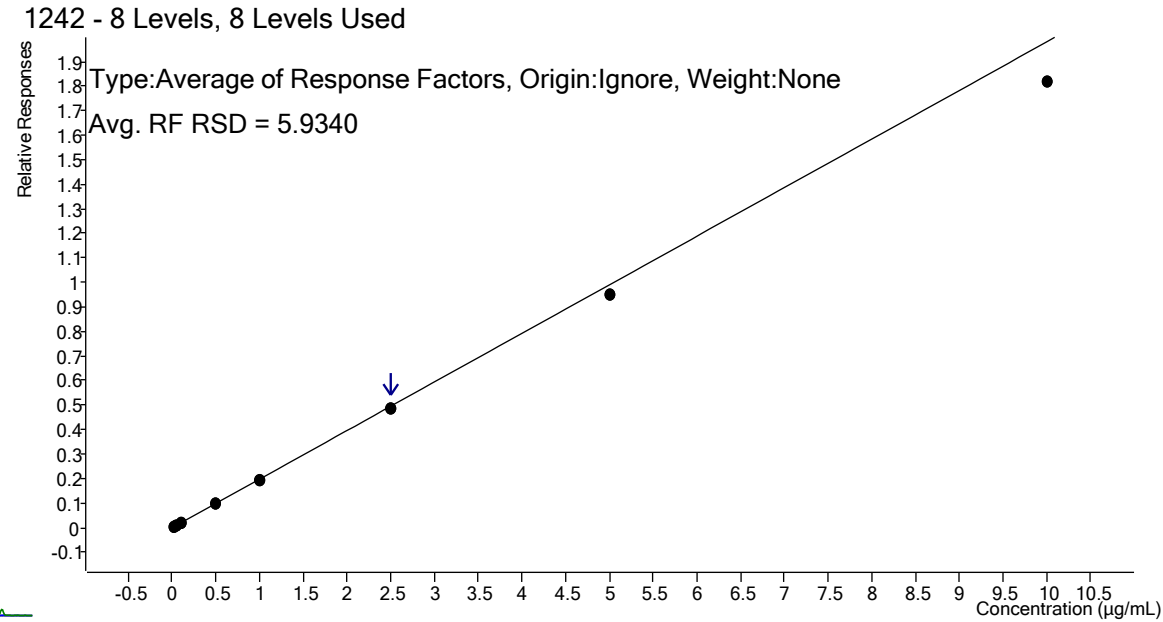
Quantifier MRM



Qualifier MRMs

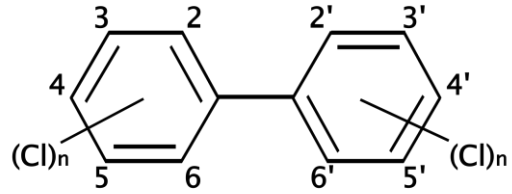
Relative abundance used for pattern matching





Example Calibration: Aroclor 1254

5 – 1000 µg/L

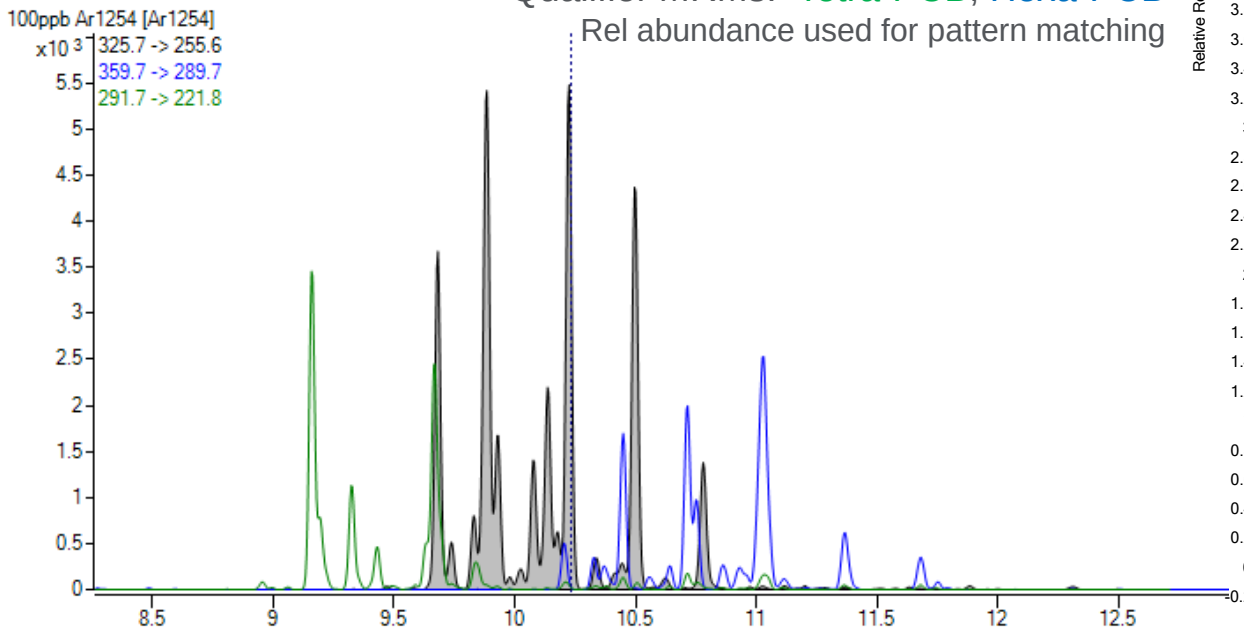


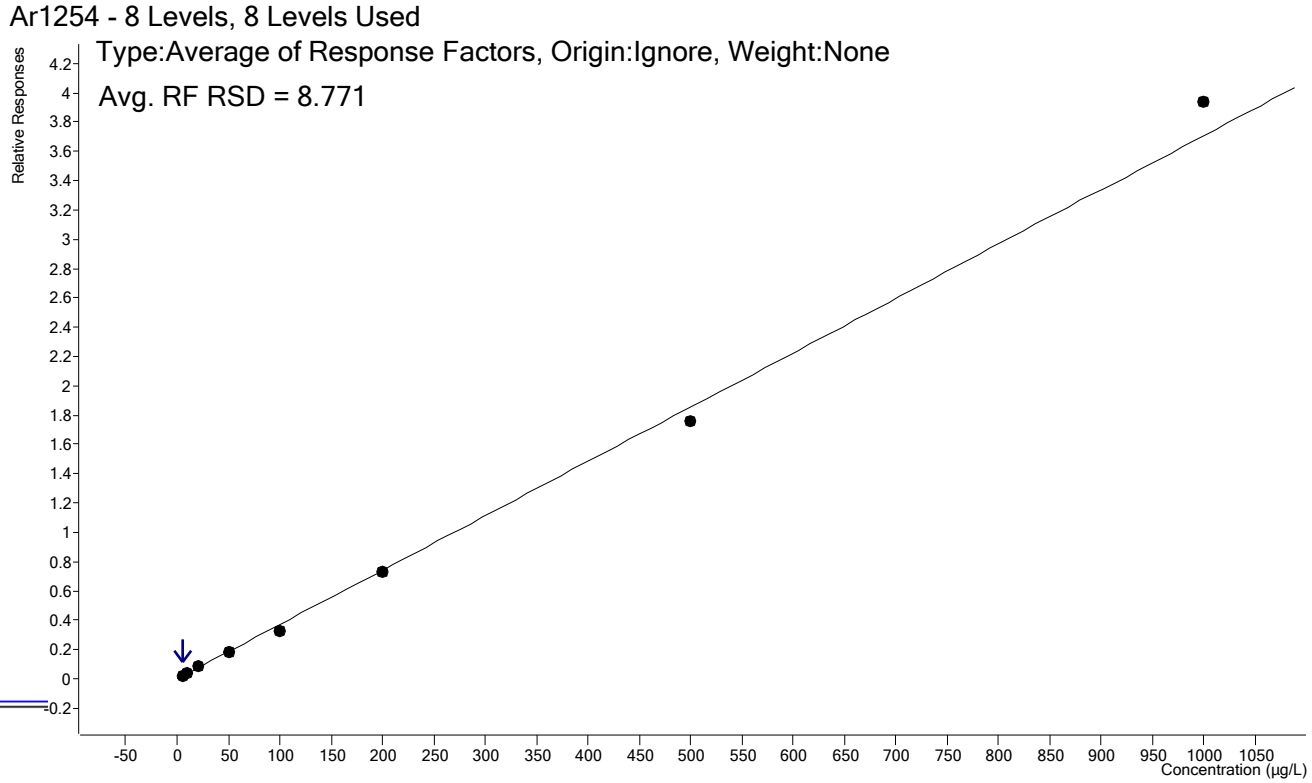
Congener Homologue Level of Chlorination									
Mono	Di	Tri	Tetra	Penta	Hexa	Hepta	Octa	Nona	Deca
0	0.2%	1.3%	16.4%	53%	26.8%	2.7%	0	0	0

Quantifier MRM: Penta-PCB

Qualifier MRMs: Tetra-PCB, Hexa-PCB

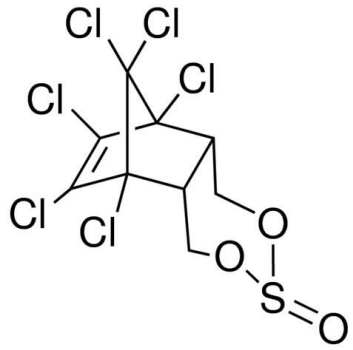
Rel abundance used for pattern matching





Pesticides: Endosulfan I

1 – 1000 µg/L



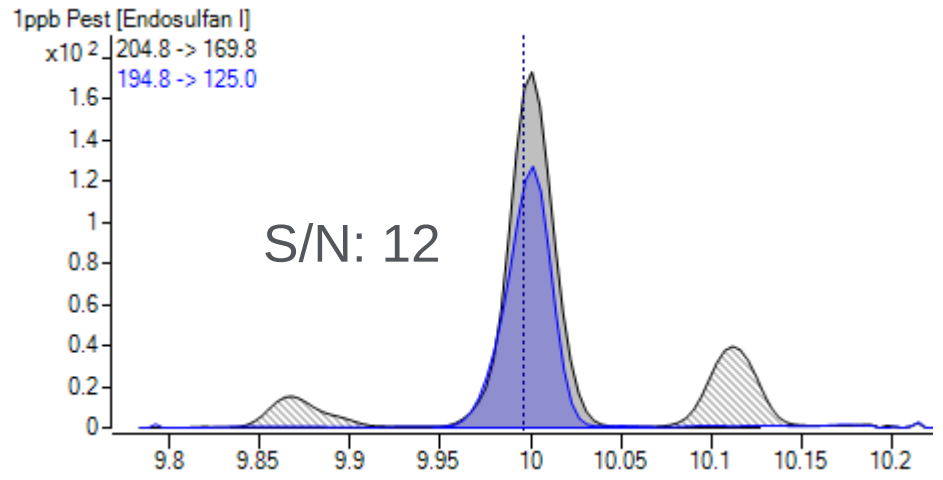
Endosulfan I - 12 Levels, 9 Levels Used

Type:Average of Response Factors, Origin:Ignore, Weight:None

Avg. RF RSD = 6.555

1,000 µg/L accuracy 94%

1 µg/L accuracy 108%

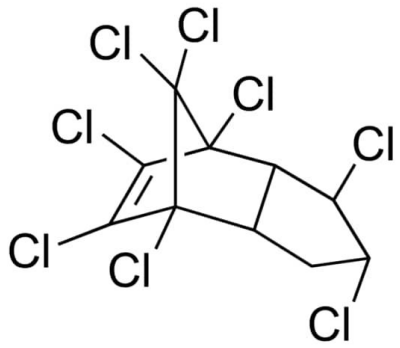


Relative Responses

Concentration (µg/L)

Pesticides: trans-Chlordane

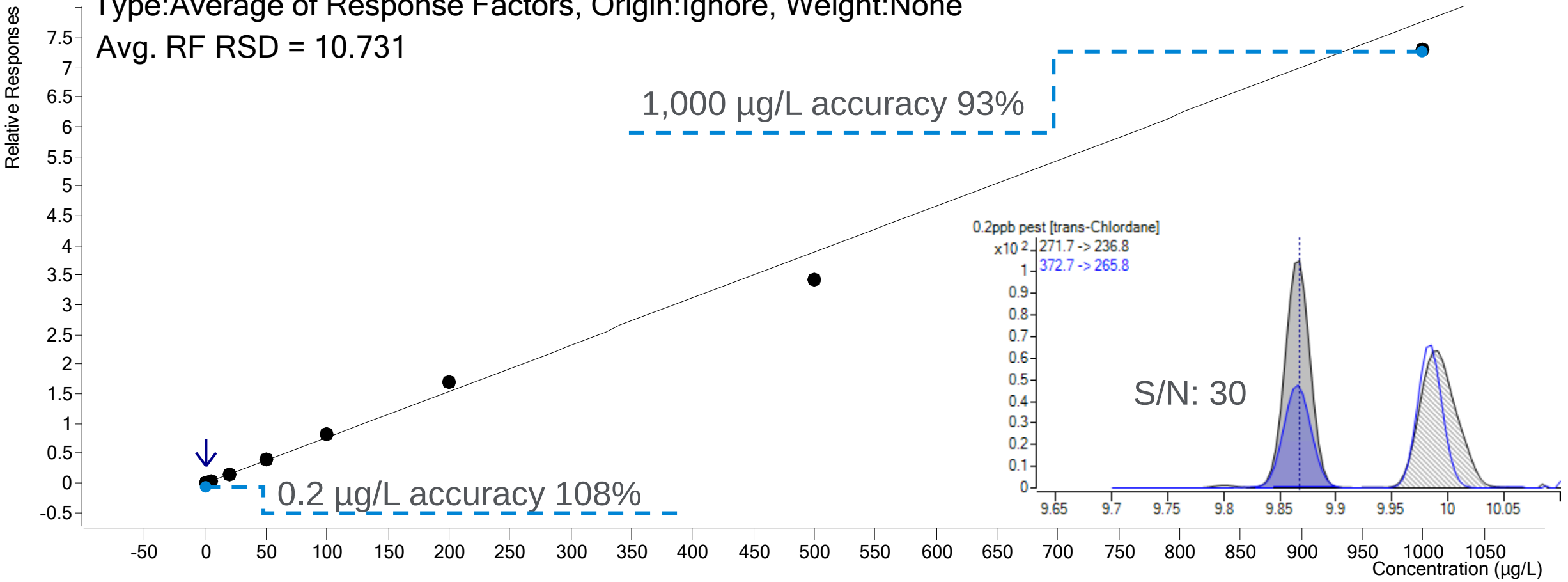
0.2 – 1,000 µg/L



trans-Chlordane - 12 Levels, 11 Levels Used

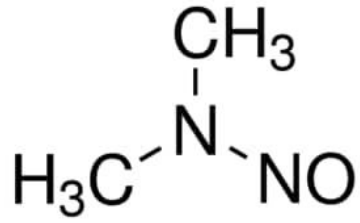
Type:Average of Response Factors, Origin:Ignore, Weight:None

Avg. RF RSD = 10.731



Semivolatiles: N-Nitrosodimethylamine

0.5 – 10,000 µg/L



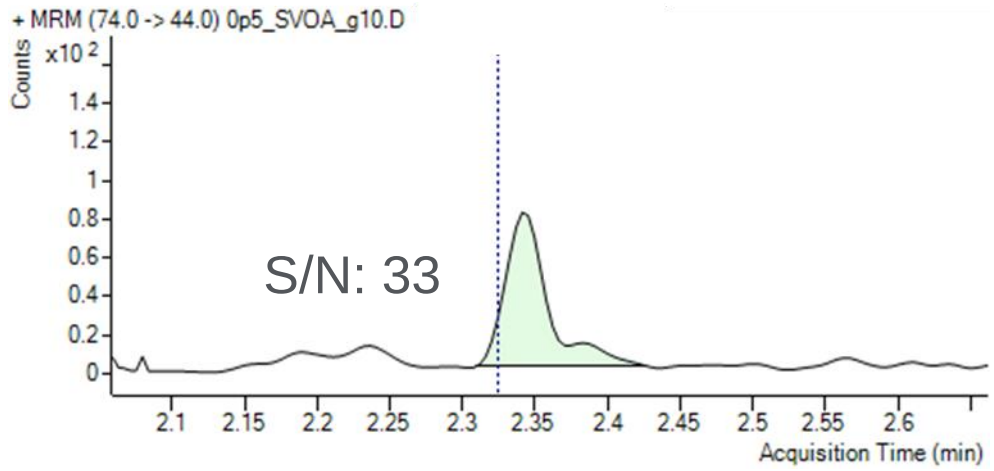
NDMA - 16 Levels, 14 Levels Used

Type:Average of Response Factors, Origin:Ignore, Weight:None

Avg. RF RSD = 5.788

10,000 µg/L accuracy 96.6%

0.5 µg/L accuracy 95.5%

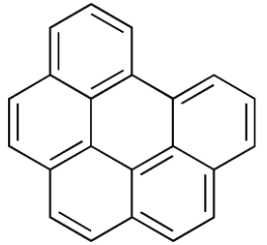


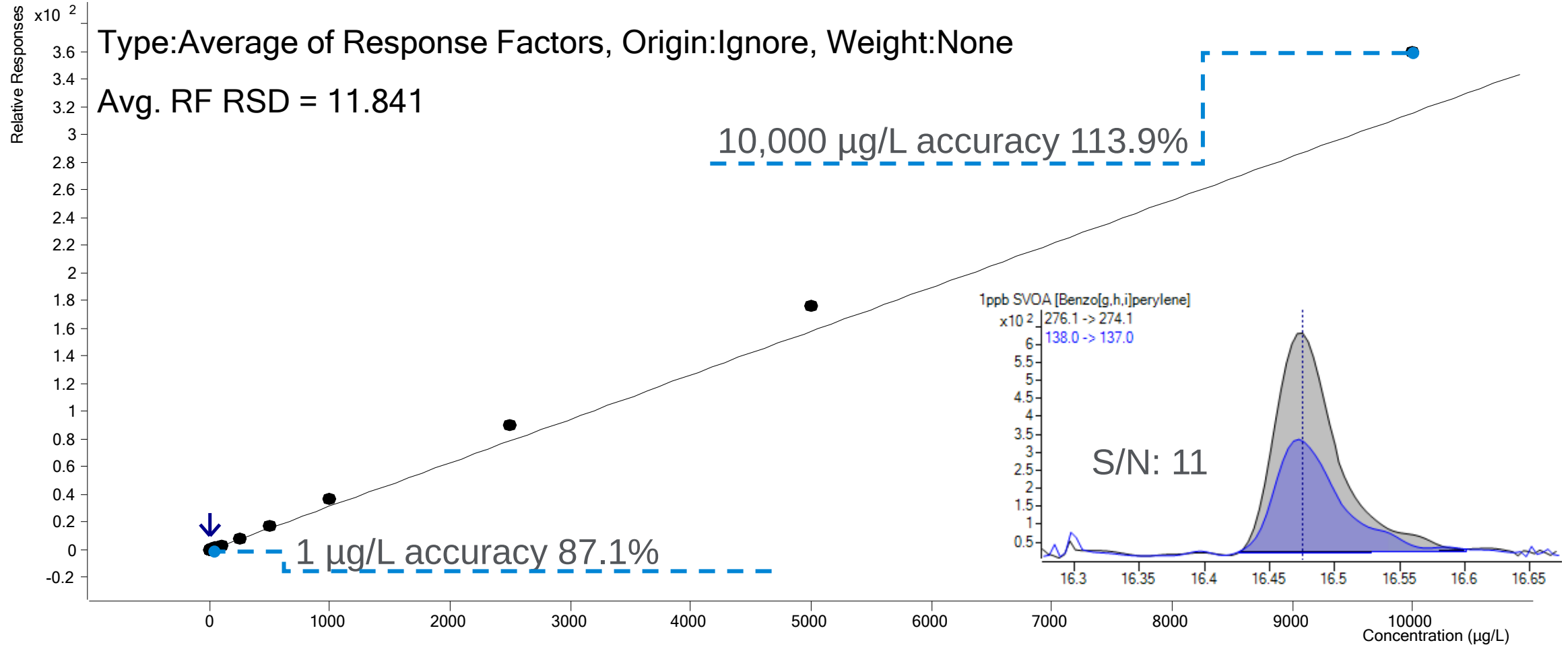
Relative Responses x10 1

Concentration (µg/L)

Semivolatiles: Benzo[g,h,i]perylene

1 – 10,000 µg/L





Show Me The Matrix

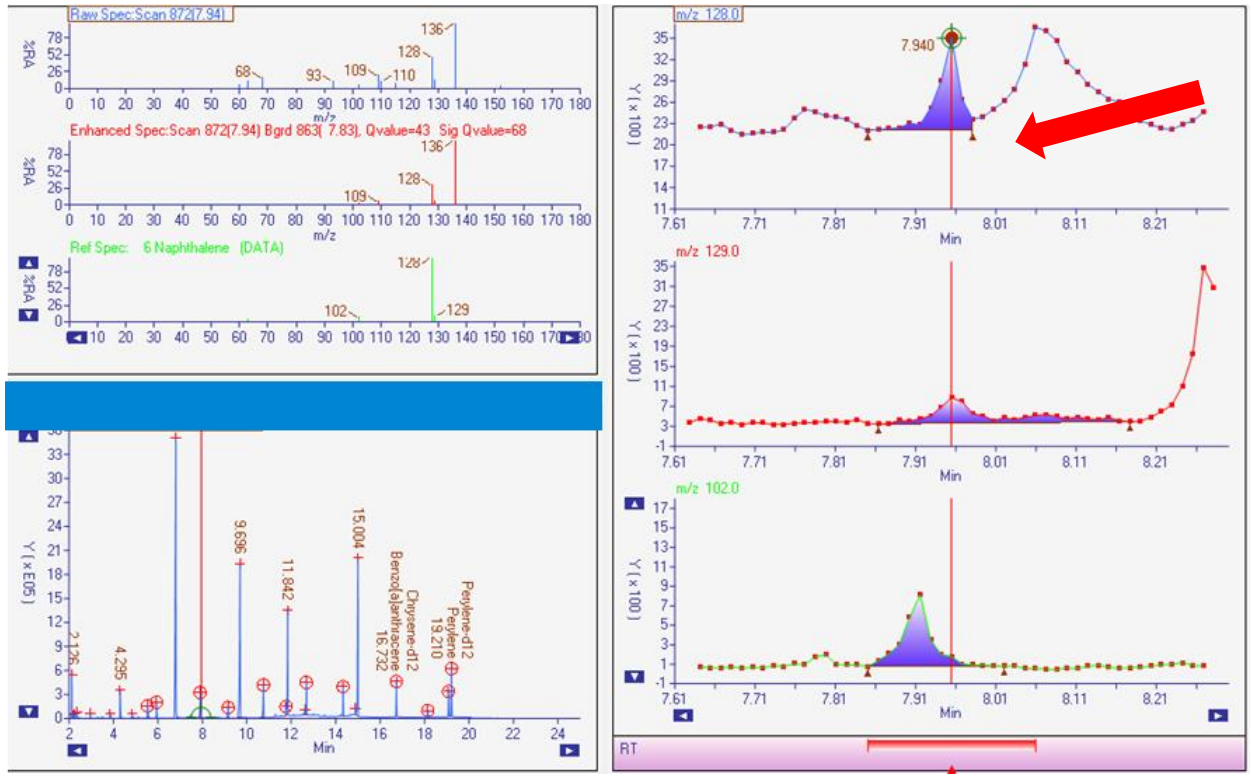
Comparison of SQ vs TQ Results for Ground Water Samples

Naphthalene

SQ SIM

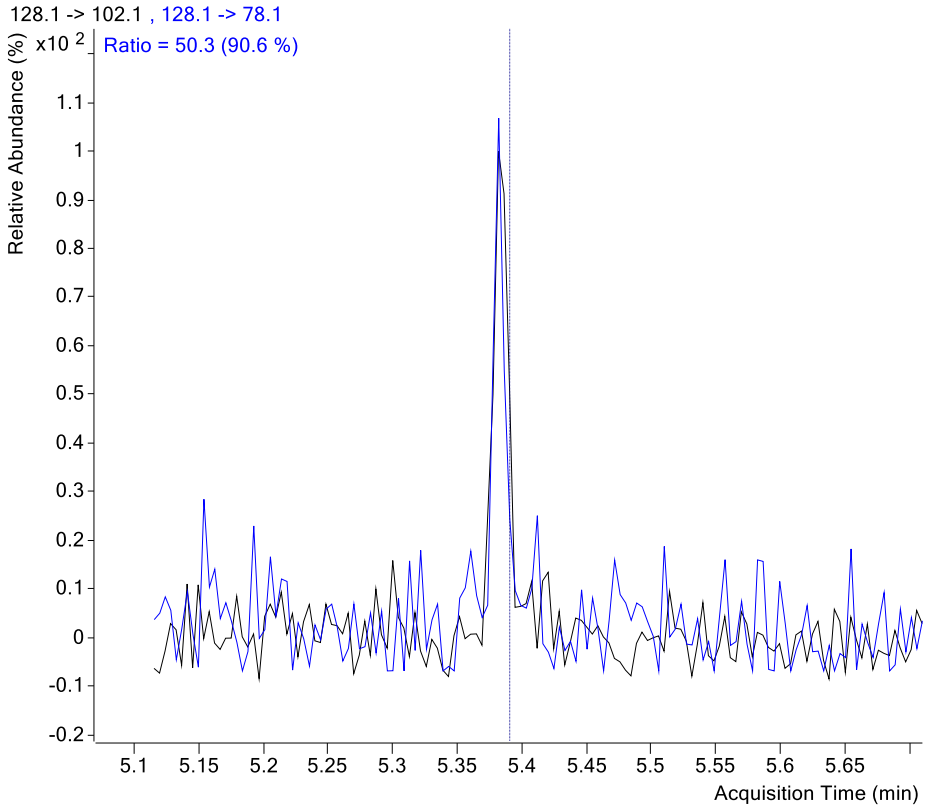
0.0013 µg/mL

Matrix interference in EIC lowers QValue



TQ MRM

0.0011 µg/mL, no matrix interference in MRM

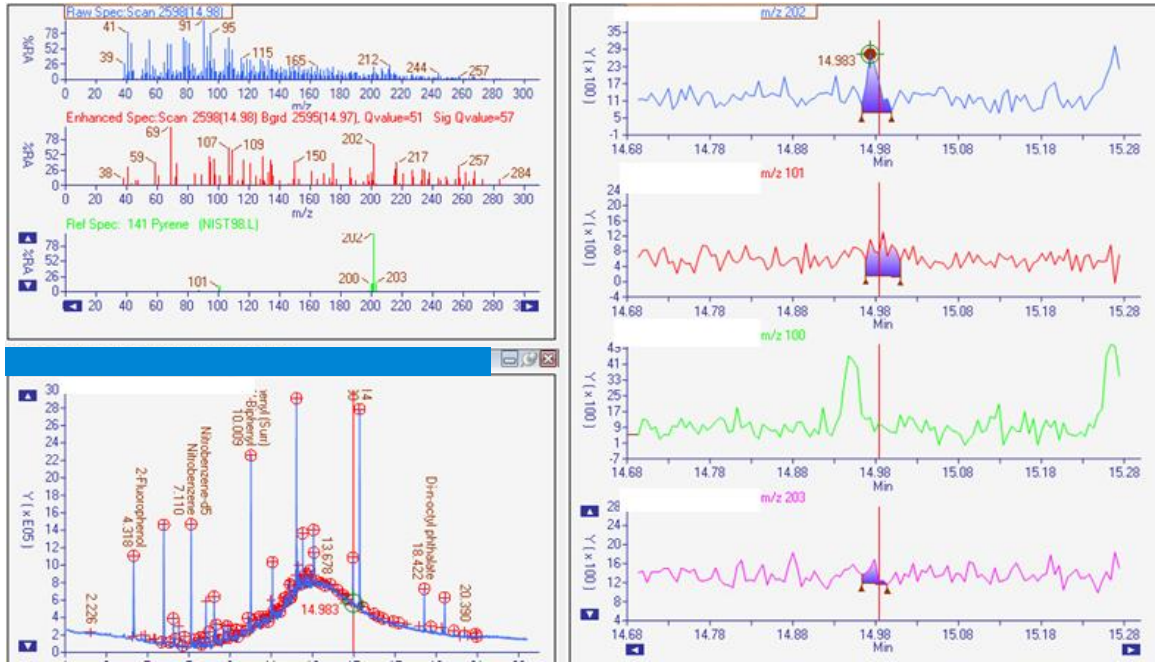


Pyrene

SQ Scan

0.057 µg/mL

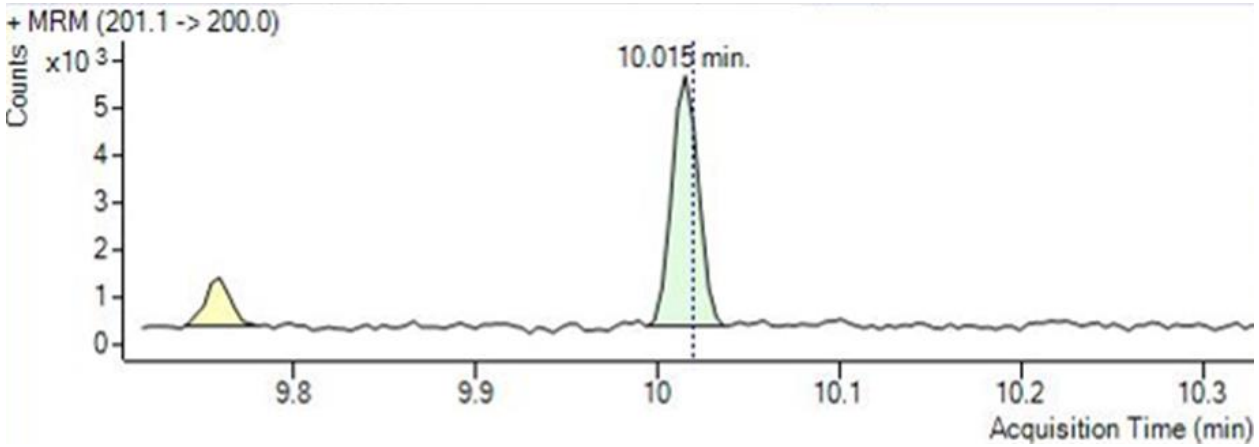
(>MDL; <LOQ)



TQ MRM

0.0304 µg/mL

No issues with SNR



Thoughts and considerations for transitioning to environmental triple quad methods

Increased selectivity comes with a few considerations

DFTPP Tuning

DFTPP tune checks no longer applicable for operation in MRM mode

RTL

TQ methods containing long lists of analytes are best operated while retention time locked to maintain proper transition windows

DFTPP tuning guidance from 8270e: DFTPP system verification not applicable for MS/MS

6.1.3.3 An MS/MS detector may be used if the detector has the necessary pumps, collision cell, collision gases, and high-vacuum system capable of performing transitions in product ion scan mode or the selected reaction monitoring mode (SRM) for the target analytes of interest. Recommendations for specific precursor and product ions in SRM are available for some target analytes from the manufacturers of the equipment. When analysis is performed using product ions for quantitation, it is not an appropriate verification of the system to perform DFTPP analysis and meet the criteria outlined in Sec. 11.3.1. The system, however, must be capable of documenting the performance of both MSs against manufacturer specifications for mass resolution, mass assignment, and sensitivity using the internal calibrant (e.g., Perfluorotributylamine). The performance of the system should be checked at least weekly, or at a frequency appropriate to meet the needs of the project. At a minimum, the performance of the system must be checked just prior to the initial calibration (ICAL).

Agilent Manufacturer's Recommended Tune

Use Tune Check report to satisfy updated 8270E requirement

Triple Quadrupole GC/MS System Verification - Tune

Instrument Name	GCMS_7000D / US1842T101	**MS Model**	7000D
Tune Date & Time	6/23/2020 2:25:55 PM	**Source**	EI with Extractor
Tune File	D:\MassHunter\GCMS\1\7000\atunes.eiex_300.tune.xml Modified		

Air and Water Check	Abundance	Relative Abundance	Limit	Result
PFTBA (69.00)	4402495			
Water	28954	0.66%	<= 20.00%	OK
Oxygen	5616	0.13%	<= 2.50%	OK
Nitrogen	20929	0.48%	<= 10.00%	OK

* Nitrogen values are calculated from oxygen abundance

Automated Tune Check algorithm checks air & water, MS1 and MS2 mass assignments and isotopic abundances; verifies detector suitable for analysis

Triple Quadrupole GC/MS System Verification - Tune

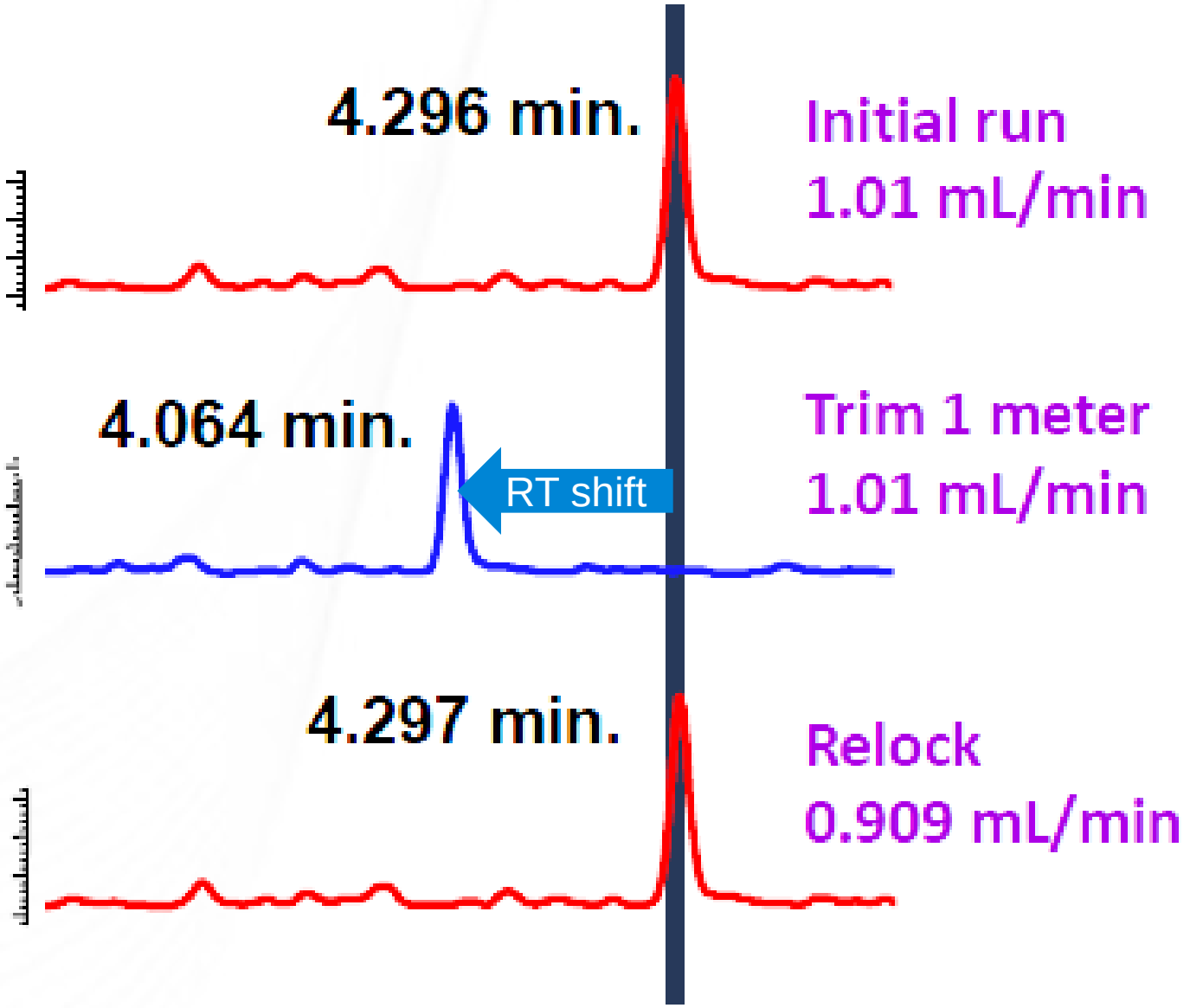
Instrument Name	GCMS_7000D / US1842T101	**MS Model**	7000D
Tune Date & Time	6/23/2020 2:25:55 PM	**Source**	EI with Extractor
Tune File	D:\MassHunter\GCMS\1\7000\atunes.eiex_300.tune.xml Modified		

Instrument Actuals		**Vacuum**	
Ionization mode	EI+	Rough Vac	1.03E+2 mTorr
Source Temp.	301 °C	High Vac	7.52E-5 Torr
MS1 Quad Temp.	151 °C	Turbo 1 Speed	100.0 %
MS2 Quad Temp.	150 °C	Turbo 1 Power	21.2 W
Filament Current	35.0 µA		
GC Gas Flow			
Quench Flow	2.250 mL/min	Column 1	1.500 mL/min
Collision Cell	1.500 mL/min	Column 2	0.000 mL/min

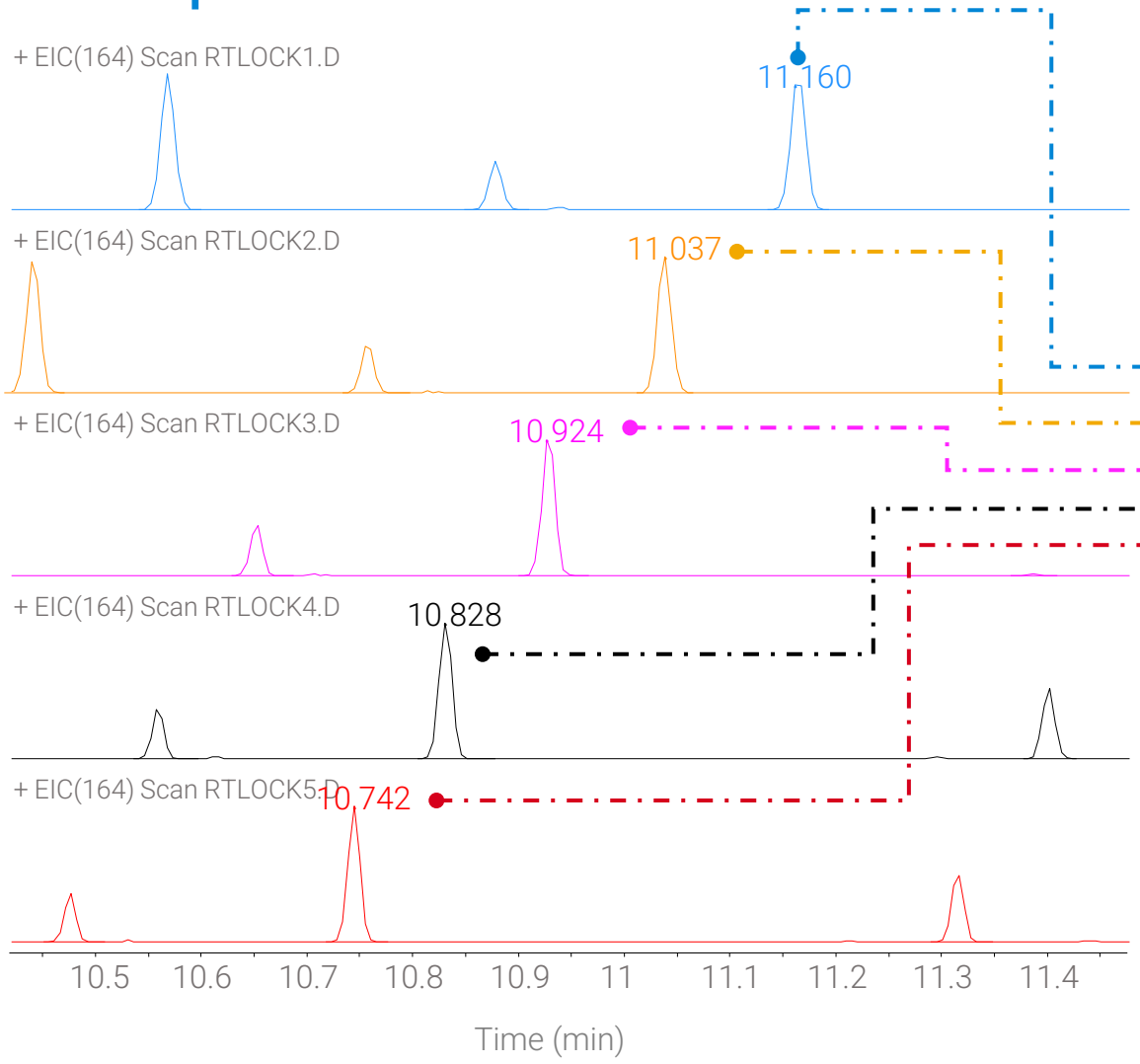
MS1 Checktune Results	Value	Limit	Result
Low mass assignment (target 69.00, actual 69.00)	0.00	<= 0.20	OK
Mid mass assignment (target 264.00, actual 263.90)	0.10	<= 0.20	OK
High mass assignment (target 502.00, actual 502.00)	0.00	<= 0.20	OK
Low mass isotope position (target 70.00, actual 70.10)	0.10	<= 0.20	OK
Mid mass isotope position (target 265.00, actual 265.00)	0.00	<= 0.20	OK
High mass isotope position (target 503.00, actual 503.00)	0.00	<= 0.20	OK
Low mass isotope ratio	1.11%	>= 0.5% and <= 1.6%	OK
Mid mass isotope ratio	5.71%	>= 4.2% and <= 6.9%	OK
High mass isotope ratio	9.91%	>= 7.9% and <= 12.3%	OK
Ratio of mid mass to low mass	34.98%	>= 5.0%	OK
Ratio of high mass to low mass	7.88%	>= 0.8%	OK
Low mass precursor ratio	0.27%	<= 3.00%	OK
Mid mass precursor ratio	0.45%	<= 6.00%	OK

Retention Time Locking premise

RTL is a process to counteract chromatographic changes that alter retention times. Column head pressure is adjusted to modify column flow and deliver desired retention time.



Example RTL calibration



Compound: Acenaphthene-d10

Retention Time Calibration:

File	ml/min Flow	Time min.	Spec Xcor	Deviation Seconds
RTLOCK1.D	0.96	11.160	-NA-	14.130
RTLOCK2.D	1.08	11.037	-NA-	6.744
RTLOCK3.D	1.20	10.924	-NA-	0.000
RTLOCK4.D	1.32	10.828	-NA-	-5.784
RTLOCK5.D	1.44	10.743	-NA-	-10.914

Maximum Deviation: 14.130 seconds

RTL Curve: R = 6.838e-001 A*A - 1.612e+001 A + 9.572e+001

Terms of Curve Fit:

Constant = 9.572e1

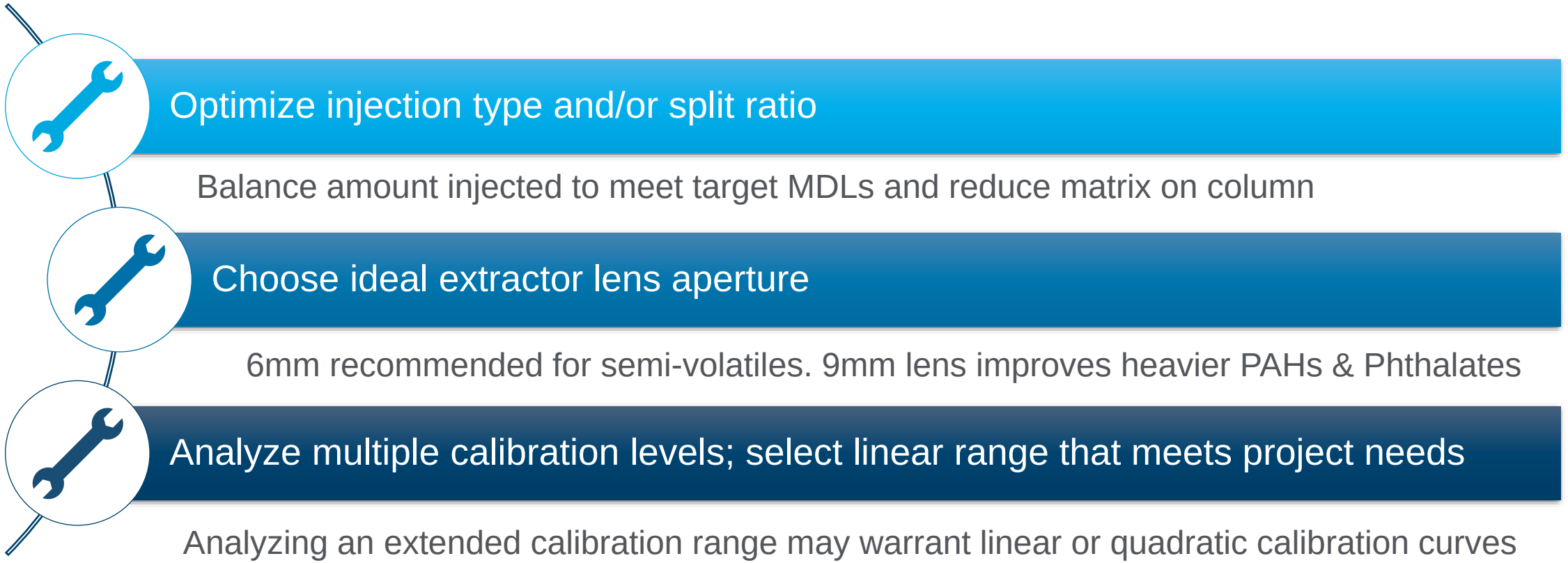
Linear = -1.612e1

Quadratic = 0.684e0

Coefficient = 0.999899 ** Good Fit **

Tools For Optimizing Linear Range

Analyzing for multiple classes of compounds in a single acquisition method warrants special consideration for some analytes. Balance your method's linearity with sensitivity as per project needs.



Summary

Conclusions

- Triple quadrupole EI-MS is well-suited for comprehensive environmental analysis on a single platform
  - Easier data review
  - Excellent sensitivity
  - Eliminate solvent exchange
  - Reduce 8270 water extraction volumes

Acknowledgement

Eurofins TestAmerica

Future Work

Developing simultaneous MRM/Scan method for quantitation and reporting tentatively identified compounds

Questions?

Thank you!

Agilent

Trusted Answers