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Analysis of Semivolatile compounds by EPA 8270 with Shimadzu GCMS Triple Quadrupole Mass Spectrometer

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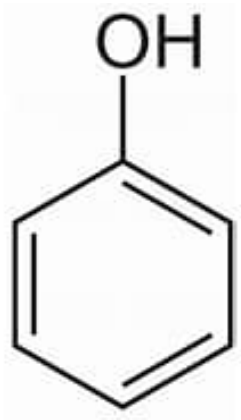
Today’s presentation

- **What are Semivolatile compounds?**
- GC Triple quadrupole Mass Spectrometer
- SVOC application
- Non-Target analysis in Triple quadrupole
- Conclusion
- Q&A

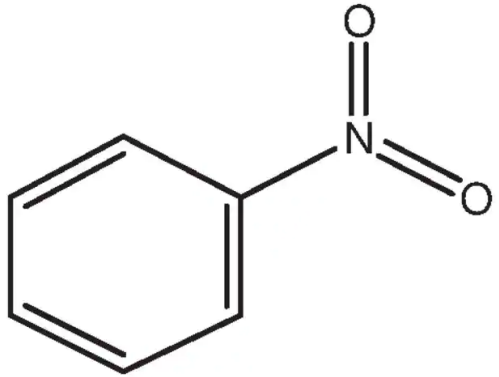
What are Semivolatile compounds?

SVOCs (**S**emi**V**olatile **O**rganic **C**ompounds)

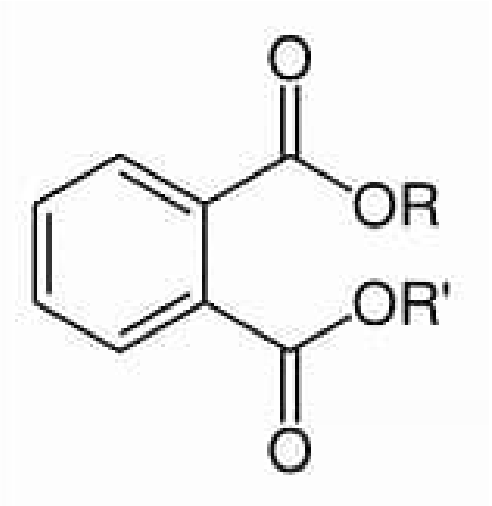
Phenols



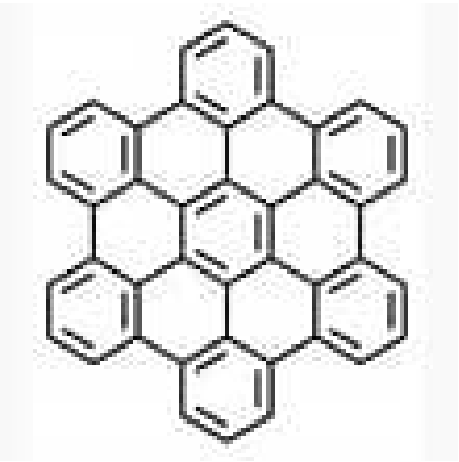
Nitro-Aromaticses



Phthalates



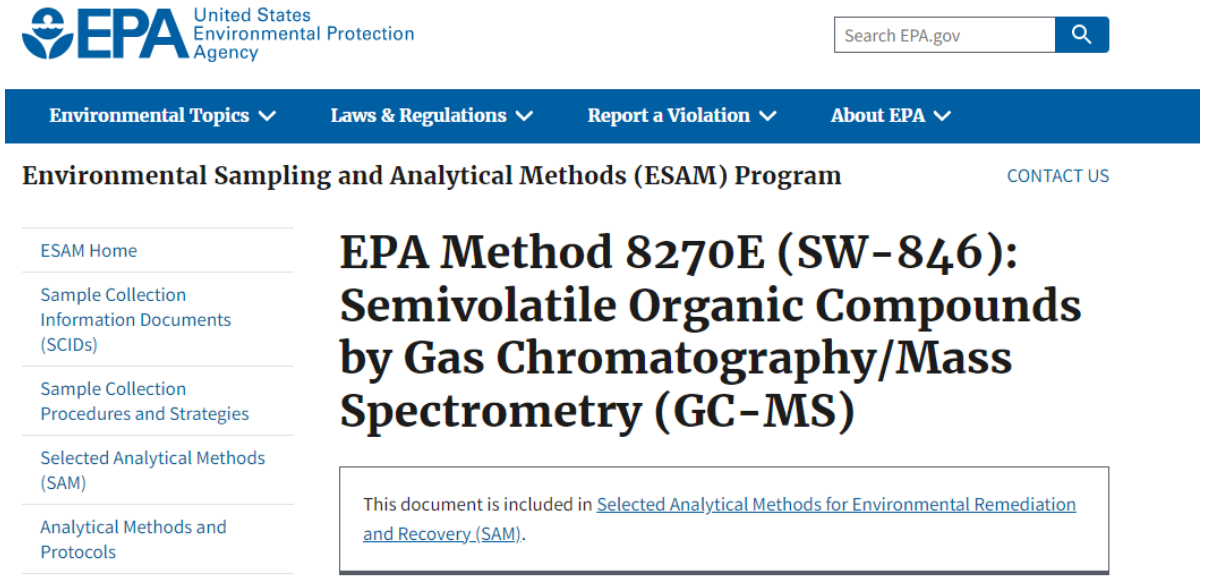
PAHs



Others (Organic acids, Ketones, Amines, etc.)

How to analyze SVOCs?

GC/MS technology is most used to acquire chromatograms, identify and quantitate for SVOCs



EPA methods: Update SW-846

GC-MS/MS detector was allowed to use for the analysis of SVOCs by EPA 8270E, updated in 2018

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).

Today’s presentation

- What are Semivolatile compounds?
- **GC Triple quadrupole Mass Spectrometer**
- SVOC application
- Non-Target analysis in Triple quadrupole
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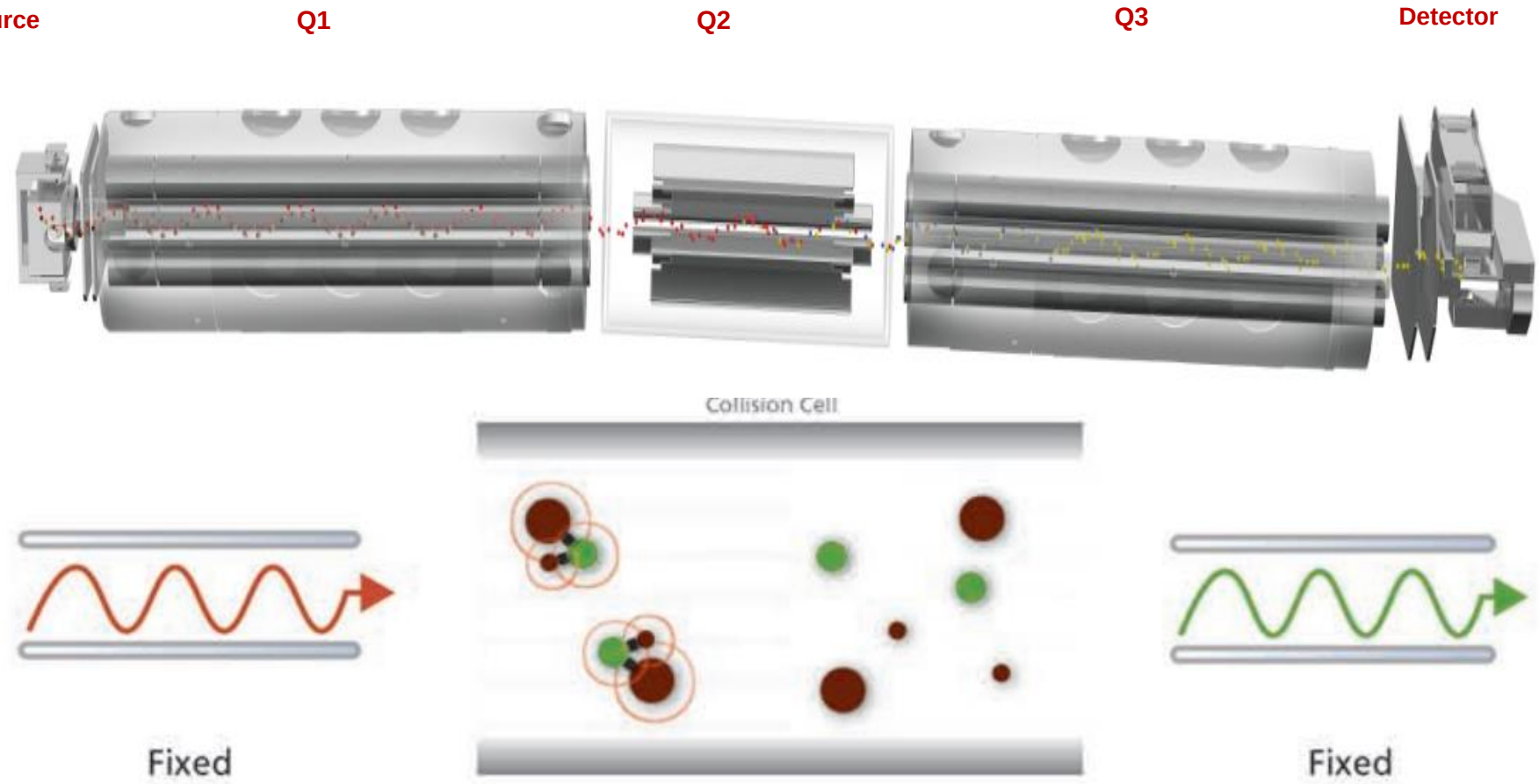
- Q&A

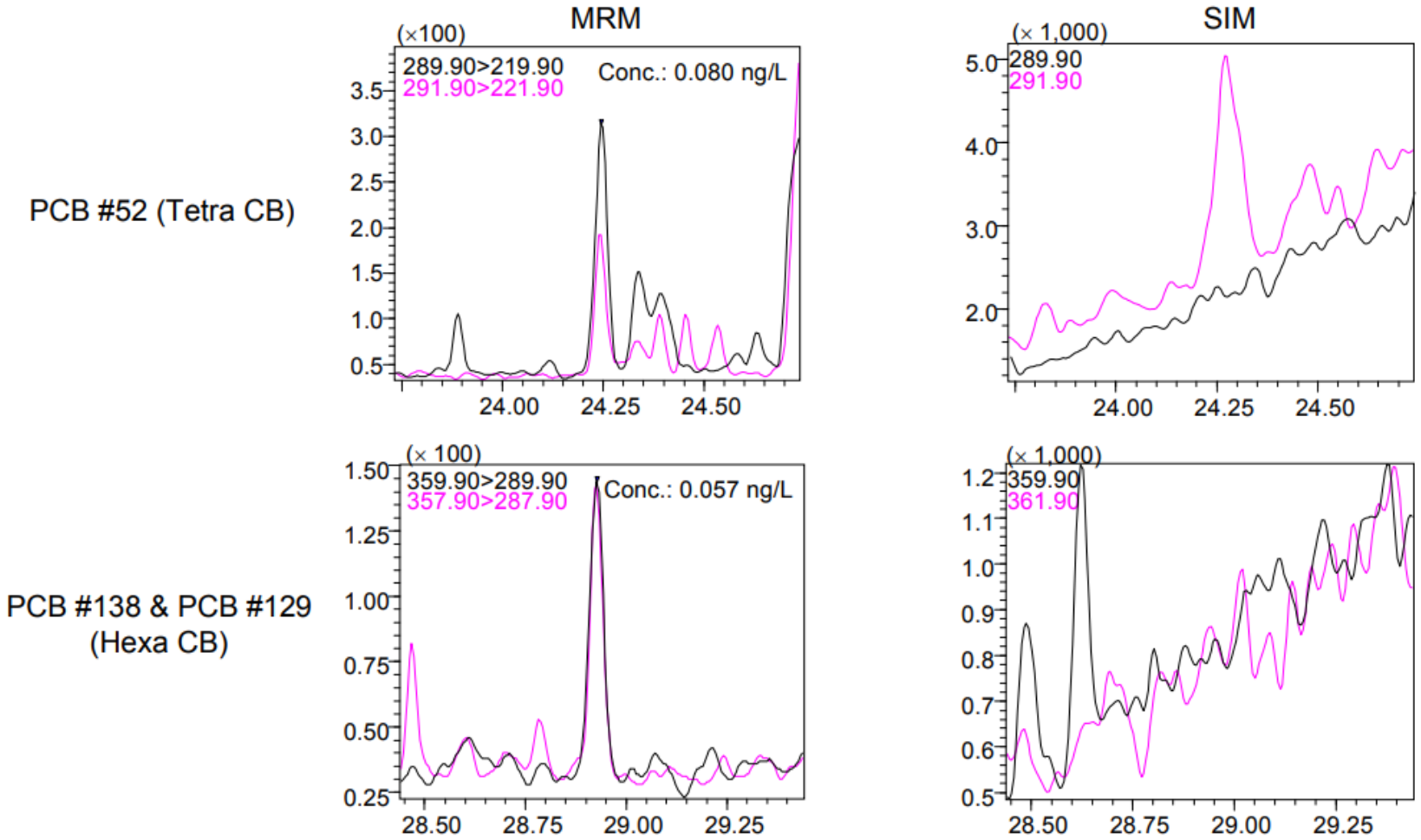
Triple quadrupole GCMS (GC-MS/MS)

GC-MS/MS can achieve great selectivity using Selected Reaction Monitoring, also referred to as Multiple Reaction Monitoring (MRM)



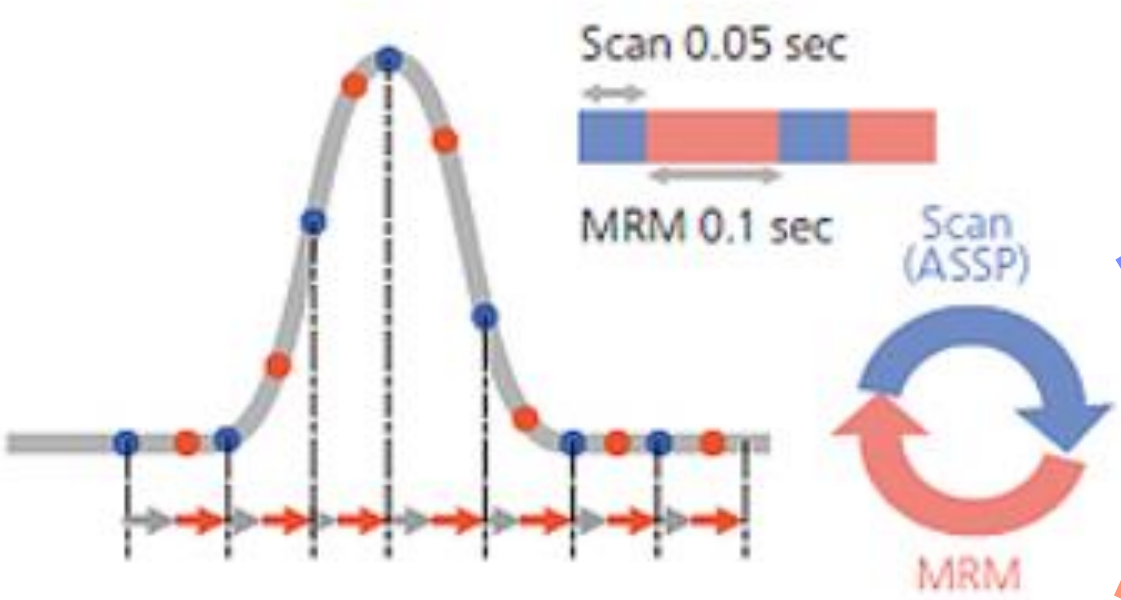
What are the benefits of GC-MS/MS?

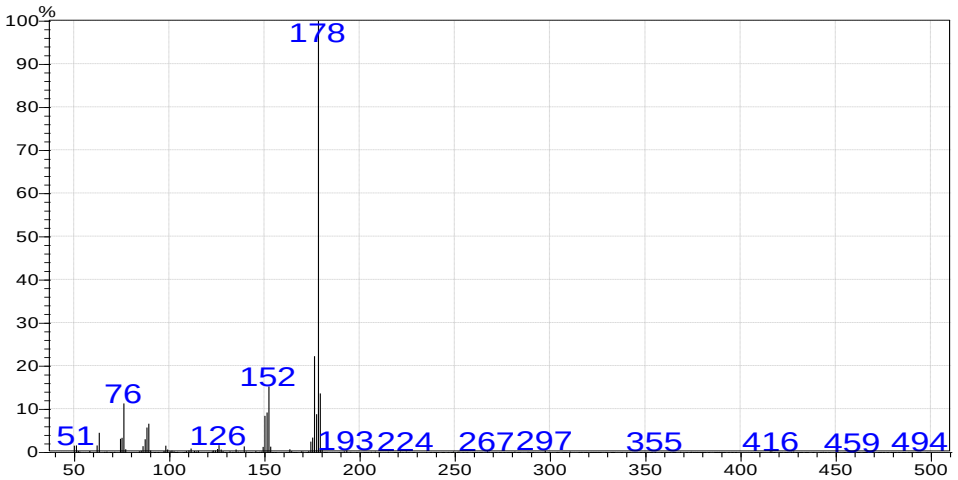
GC-MS/MS can achieve great selectivity using MRM

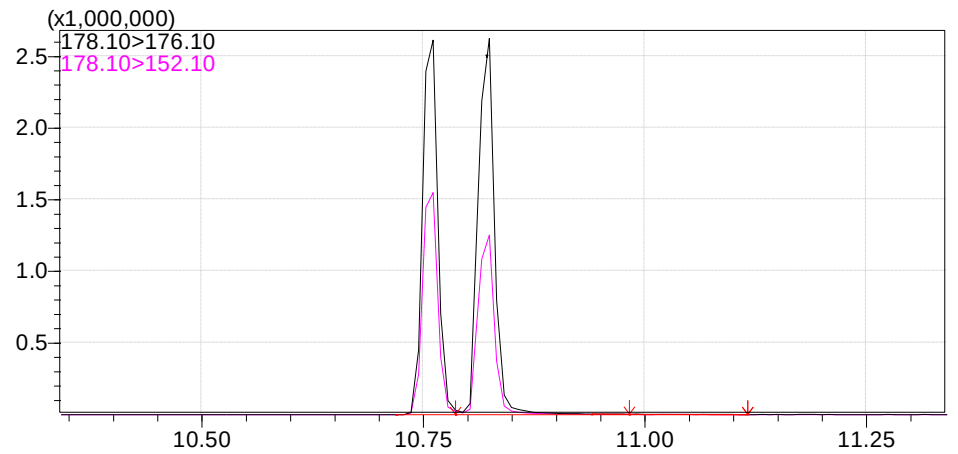


What are the benefits of GC-MS/MS?

GC-MS/MS can perform high sensitivity Scan analysis with MRM analysis







Today’s presentation

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SVOC Application following 8270E

GC and MS conditions

GC conditions	
Injection Temp.	275 ° C
Injection Mode	Split (1:10)
Column Flow	1.2 mL/min
Flow Control Mode	Linear Velocity
Column	Rxi-5MS (30m x 0.25 mm, 0.25 µm)
Oven Temp.	40 ° C (1 min) ->20 ° C/min to 280 ° C -> 5 ° C to 320 ° C (1 min) Total run: 22 min
Carrier Gas	Helium
MS conditions	
Solvent Cut Time	2 min
Ion Source Temp.	200 ° C
Interface Temp.	320 ° C
Detector Voltage	1.3 kV (Absolute)

Compound list and MSMS parameter

Serial#	Type	Acq. Mode	ISTD Group	Level Conc (IS)	Method No.	Compound Name (E)	Ret. Index 1	Ret. Index 2	Ret. Index 3	Ret. Time	C
1	Target	MRM	1		1	1,4-Dioxane	718			2.353	
2	Target	MRM	1		1	N-Nitrosodimethylamine	745			2.603	
3	Target	MRM	1		1	Pyridine	750			2.649	
90	Target	MRM	1		1	2-Fluorophenol	876			3.817	
4	Target	MRM	1		1	Benzaldehyde	970			4.667	
5	Target	MRM	1		1	Phenol	979			4.747	
91	Target	MRM	1		1	Phenol-d6	979			4.747	
6	Target	MRM	1		1	Aniline	983			4.783	
7	Target	MRM	1		1	Bis(2-chloroethyl)ether	990			4.846	
8	Target	MRM	1		1	2-Chlorophenol	997			4.909	
9	Target	MRM	1		1	1,3-Dichlorobenzene	1017			5.078	
10	Target	MRM	1		1	1,4-Dichlorobenzene	1026			5.154	
84	ISTD	MRM	1		1	1,4-Dichlorobenzene-d4	1026			5.154	
11	Target	MRM	1		1	Benzyl Alcohol	1041			5.280	
12	Target	MRM	1		1	1,2-Dichlorobenzene	1046			5.322	
14	Target	MRM	1		1	2-Methylphenol(o-Cresol)	1055			5.397	
13	Target	MRM	1		1	Bis(2-chloro-1-methylethyl) ether	1059			5.431	
15	Target	MRM	1		1	N-nitroso-di-n-propylamine	1076			5.574	
16	Target	MRM	1		1	3-Methylphenol (m-Cresol)/4-Methyl	1076			5.574	
17	Target	MRM	1		1	Hexachloroethane	1091			5.700	
18	Target	MRM	2		1	Nitrobenzene	1099			5.767	
92	Target	MRM	2		1	Nitorobenzene-d5	1099			5.767	
19	Target	MRM	2		1	Isophorone	1134			6.042	
20	Target	MRM	2		1	2-Nitrophenol	1147			6.144	
22	Target	MRM	2		1	2,4-Dimethylphenol	1152			6.183	
21	Target	MRM	2		1	Benzoic Acid	1160			6.246	
23	Target	MRM	2		1	Bis(2-chloromethoxy)methane	1172			6.340	
24	Target	MRM	2		1	2,4-Dichlorophenol	1182			6.418	

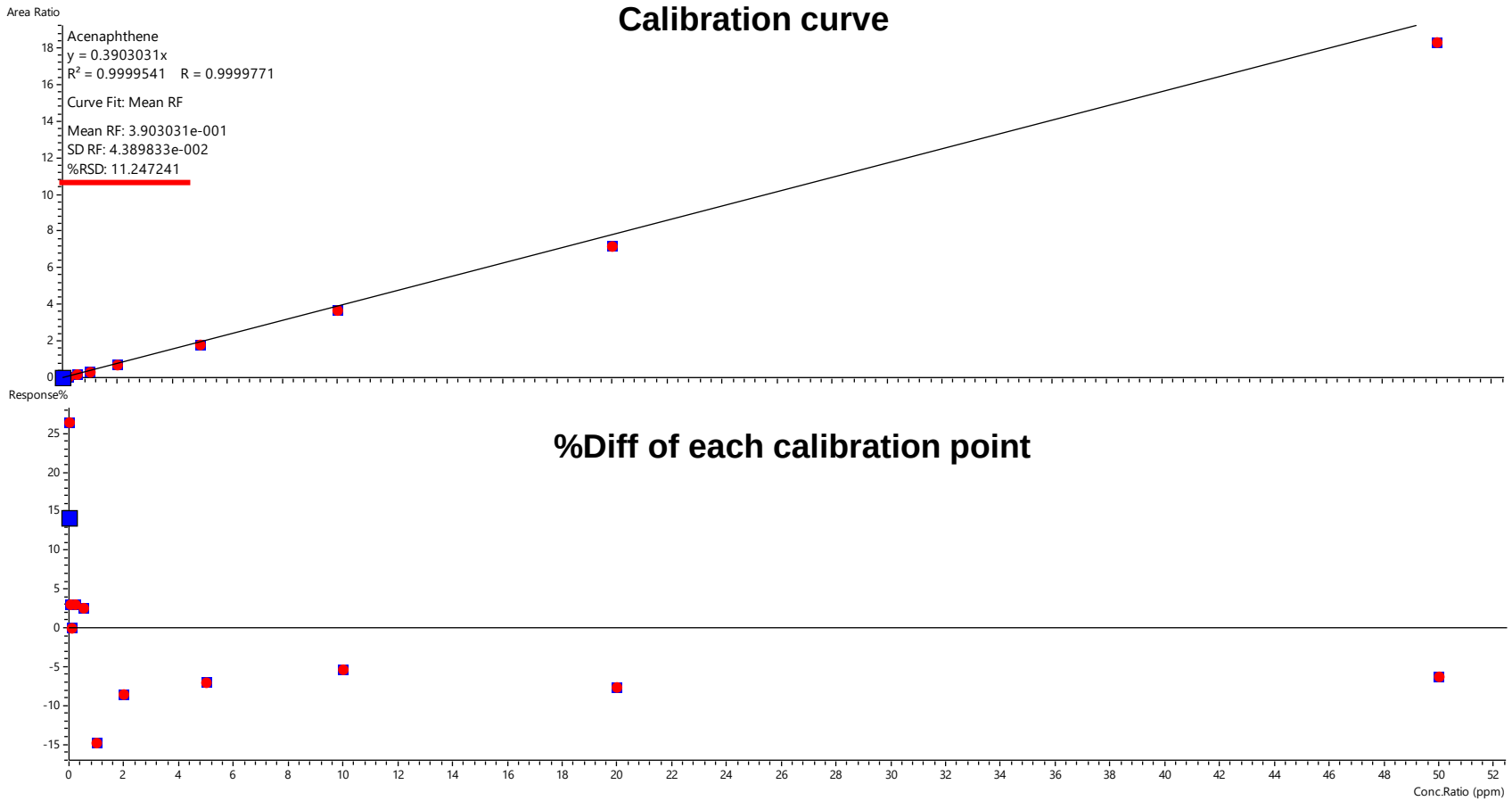
Commercially available libraries or database can accelerate method optimization when new compounds need to be added

Quantitation Result

All 83 compounds passed guidance criteria outlined in EPA 8270E

>60% compounds presented %RSD of RF ≤20% and excellent linearity
with wide calibration ranges (0.01-50ppm or 0.01-20ppm)

Acenaphthene

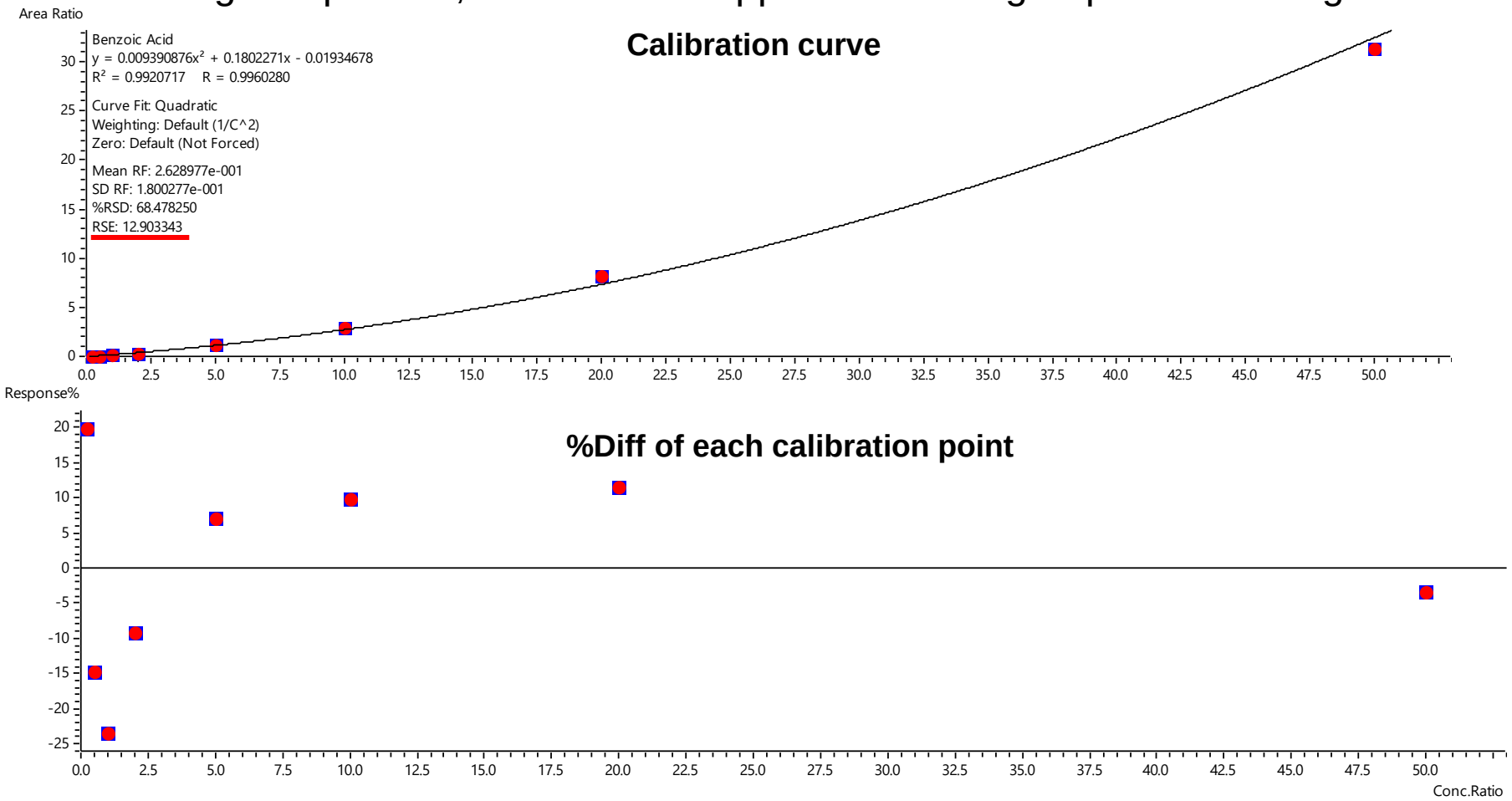


Quantitation Result

All 83 compounds passed guidance criteria outlined in EPA 8270E

Calibration curve criteria was met for challenging compounds, such as benzoic acid and nitro-group containing compounds, from 0.2 to 50 ppm when using a quadratic fitting

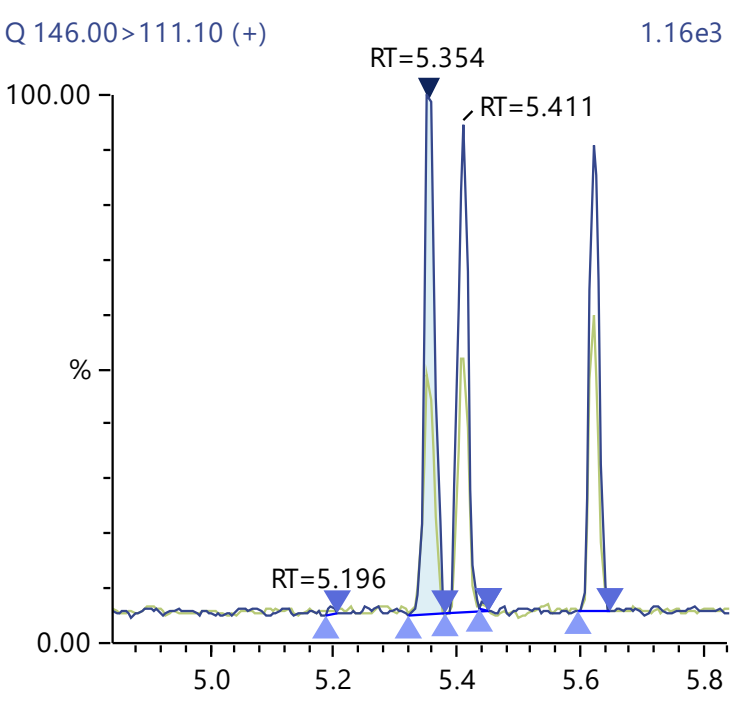
Benzoic Acid



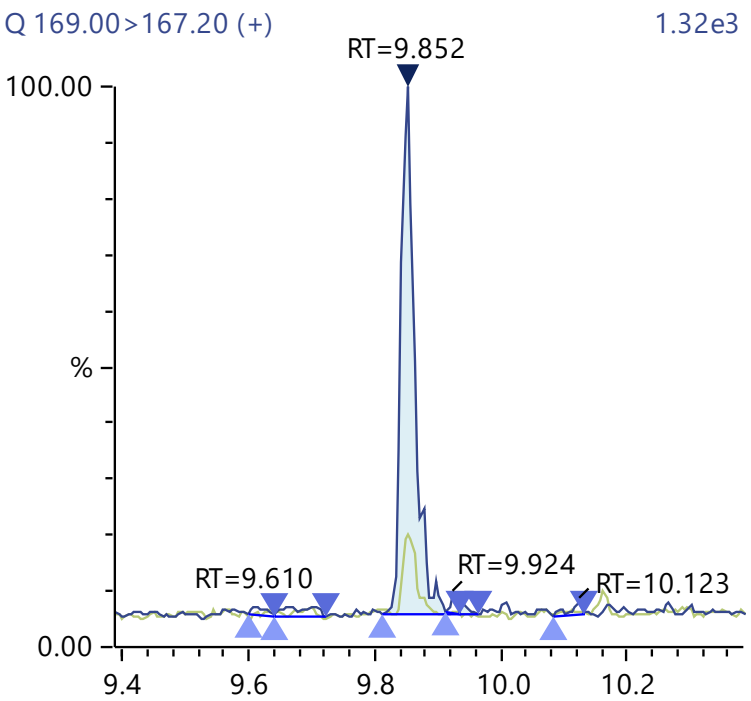
Quantitation Result

At Lowest calibration point good peak shape and good repeatability were obtained

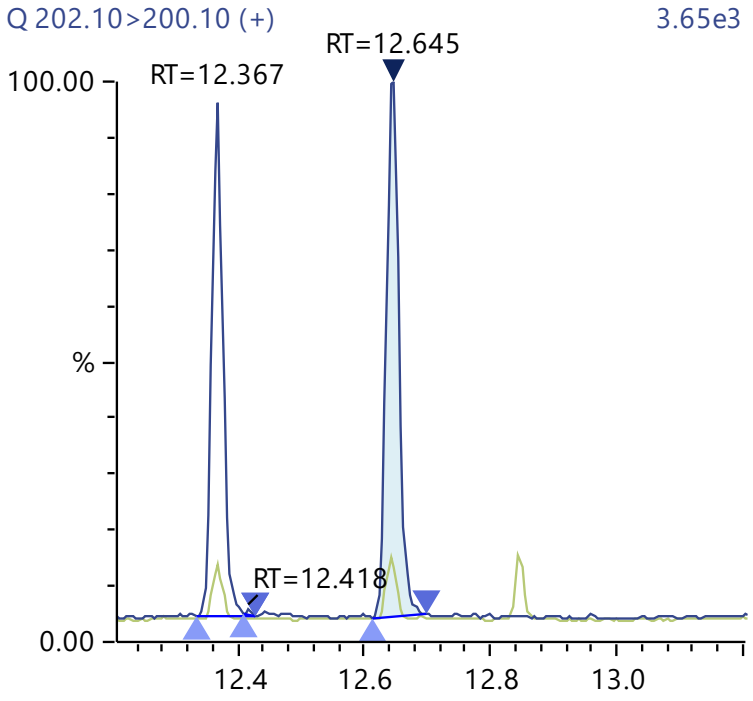
1,3-Dichlorobenzene (%RSD=3.39%)



Diphenylamine (%RSD=4.20%)



Pyrene (%RSD=3.96%)

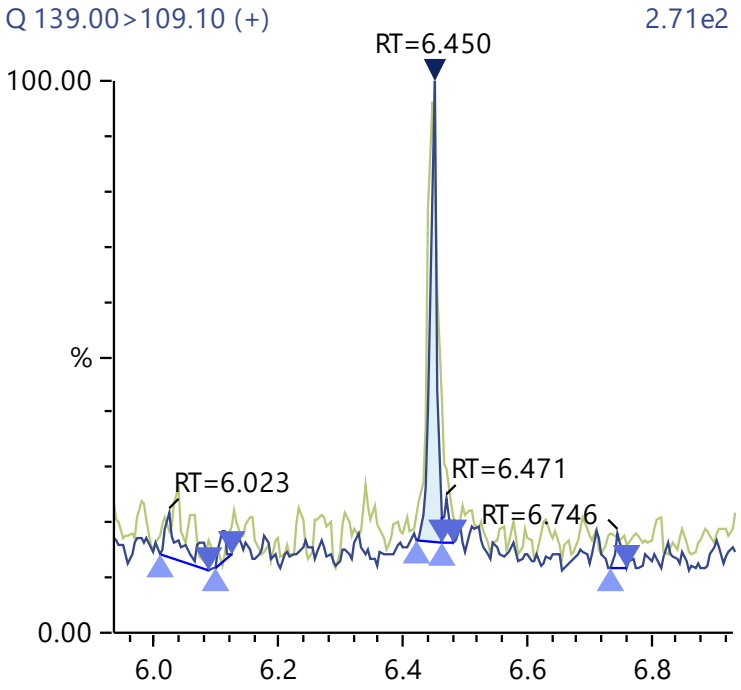


Chromatogram of 10 ppb standard (n=6)

Quantitation Result

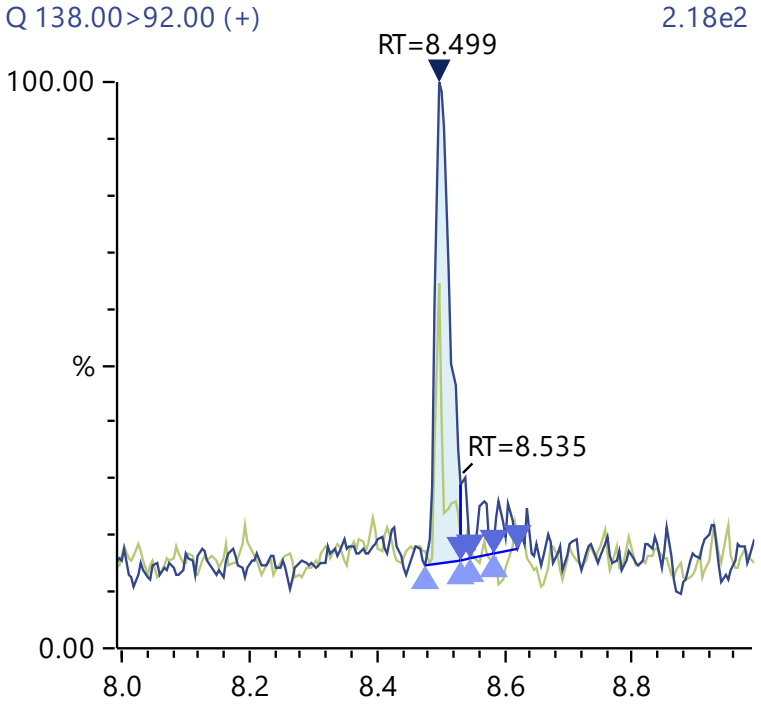
Good repeatability was also achieved for challenging compounds at lowest calibration point

2-Nitrophenol (%RSD=19.67%)



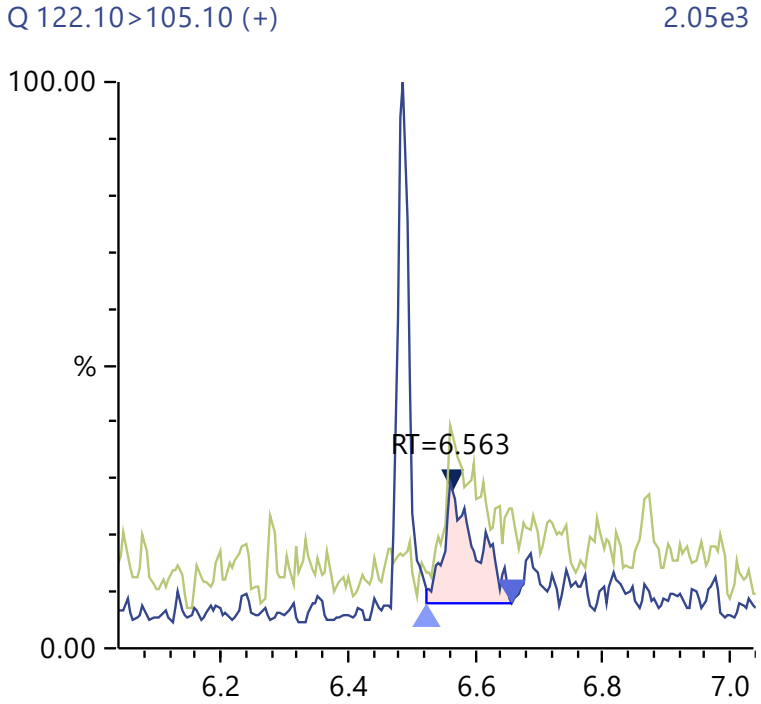
20 ppb Chromatogram (n=6)

2-Nitroaniline (%RSD=12.39%)



20 ppb Chromatogram (n=6)

Benzoic Acid (%RSD=16.9%)

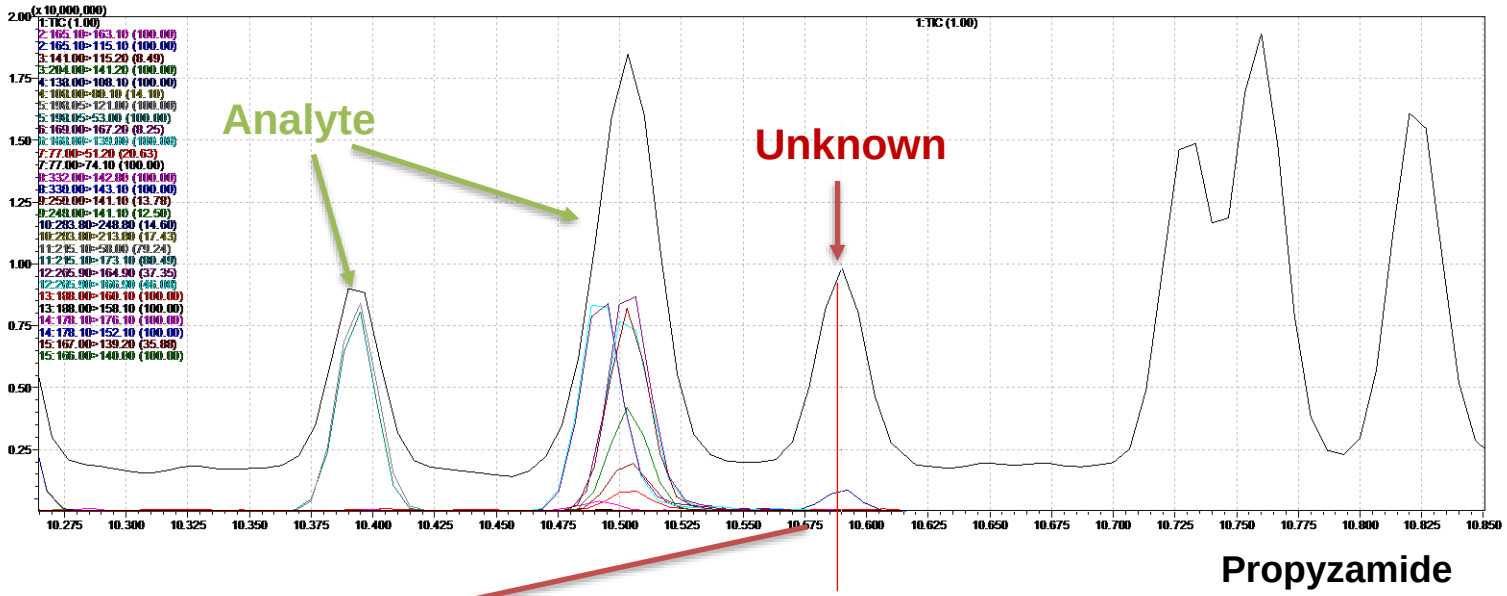


200 ppb Chromatogram (n=6)

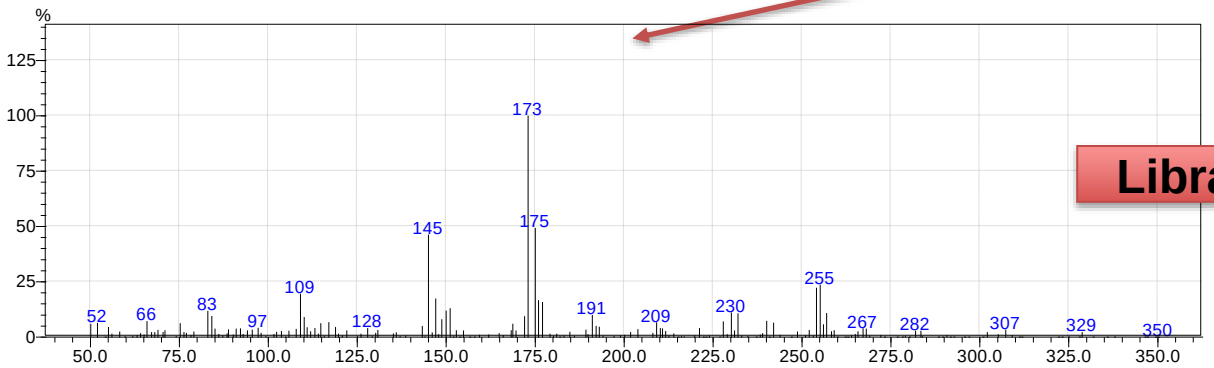
Qualification Result

Scan/MRM simultaneous analysis support unknown compound identification

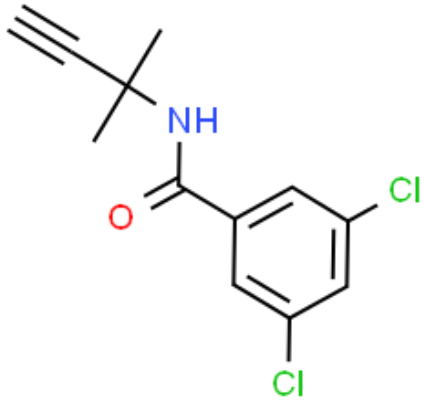
Black:
Total Scan ion chromatogram
Other color:
MRM chromatogram



Propyzamide



Library Search



Application Result

- All 83 compounds pass calibration curve criteria outlined 8270E with wide range
- All 83 compounds show good chromatography and repeatability using MSMS
- Unknown peaks can be identified using library search with MRM analysis

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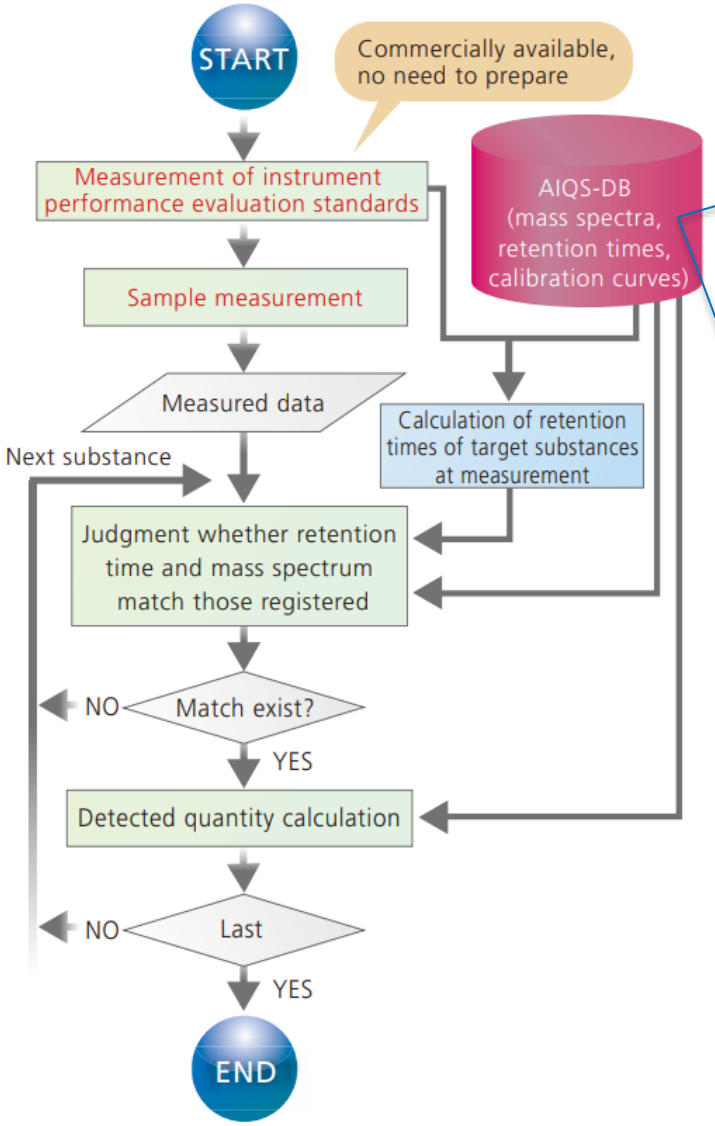
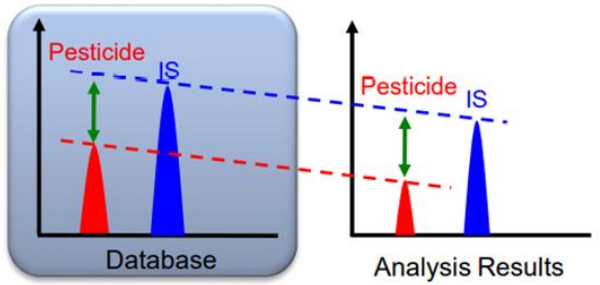
Non-Target analysis in Triple quadrupole



AIQS-DB

(**A**utomated **I**dentification and **Q**uantification **S**ystem)

Theory



Sample prep

Sample 1 L
- ← Phosphate buffer (1 mol/L, pH 7.0, 1 mL)
- ← Sodium chloride (50 g)

Liquid-liquid extraction
- Shaking with 50 mL dichloromethane for 10 min (twice)

Dehydration (anhydrous sodium sulfate)

Concentration (5 mL, rotary evaporator)
- ← 1 mL hexane

Concentration (1 mL, nitrogen gas)
- ← Internal standard solution (10 µg/mL, 100 µL)

Measurement sample

Category 1 Substances	Number of Substances	Category 2 Substances	Number of Substances
CH-containing substances	194	Polycyclic aromatic	79
		PCBs	62
		Other	53
Oxygen-containing compounds	150	Phenols	50
		Other	100
Nitrogen-containing compounds	113	Aromatic amines	43
		Nitrogen compounds	42
		Other	28
Sulfur-containing compounds	12		12
Phosphorus-containing compounds	8		8
PPCPs	14		14
Pesticides	451	Insecticides	184
		Herbicides	118
		Fungicides	116
		Other	33
Total	942		
Internal Standards	8		

Evaluation of AIQS-DB

Using 4 GCMS at 4 location (Column: DB-5ms 30mx0.25mm i.d. 0.25um)

Reproducibility	%RSD (Number of Substances)
Under 10%	41%(47)
10-20%	37%(42)
Over 20%(~70%)	22%(25)

Many of the substances having no or one highly polar functional group.

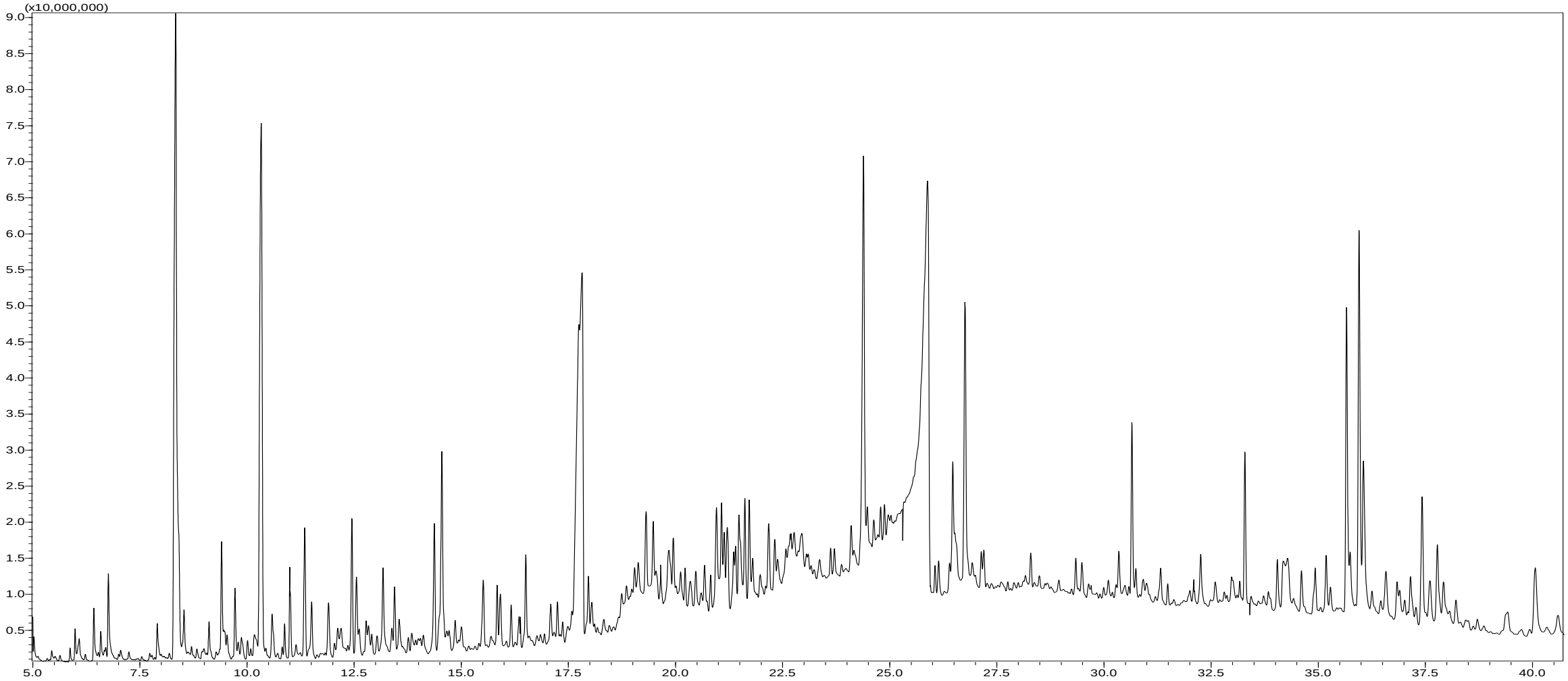
Polycyclic aromatic hydrocarbons with high boiling point, substances with relatively high water solubility containing a high polarity function group

At least 2 high-polarity functional groups such as 2,6-diaminotoluene, m-aminophenol, etc.

When we try to improve those compounds, we should consider about polar column. But as screening purpose, this method is acceptable.

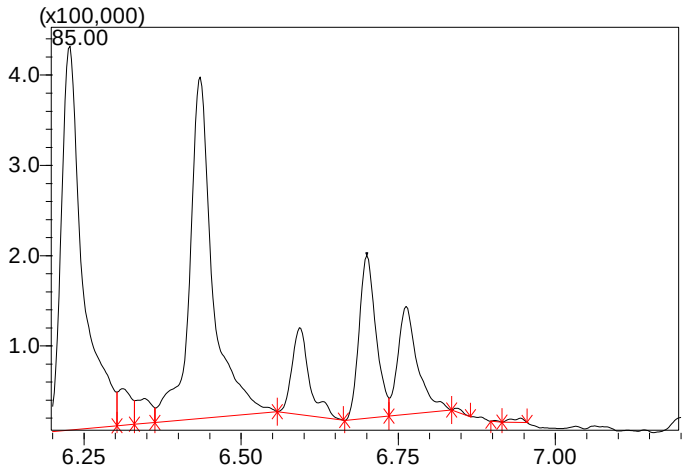
Demonstrate the use of AIQS-DB

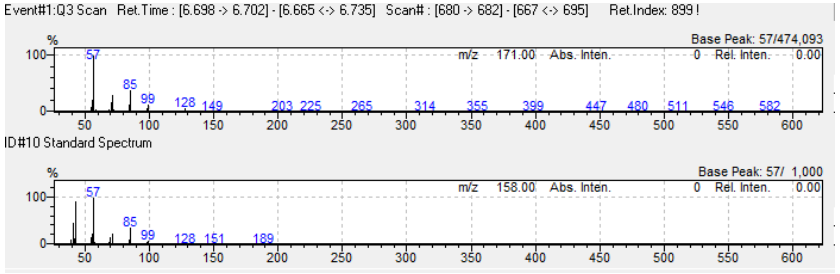
TIC of River water sample (Q3 Scan)



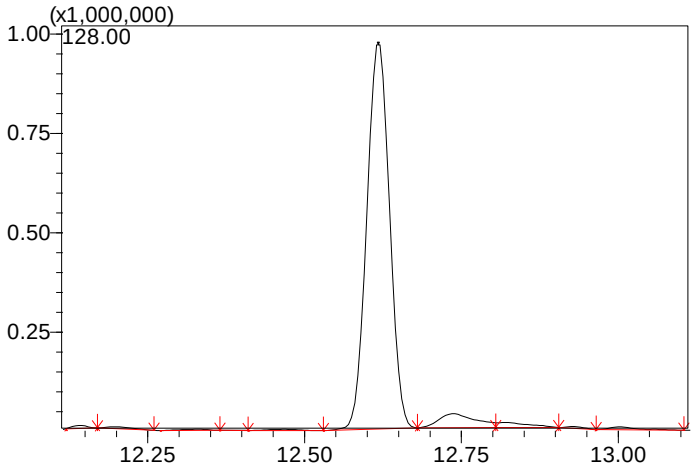
Detected pollutants example

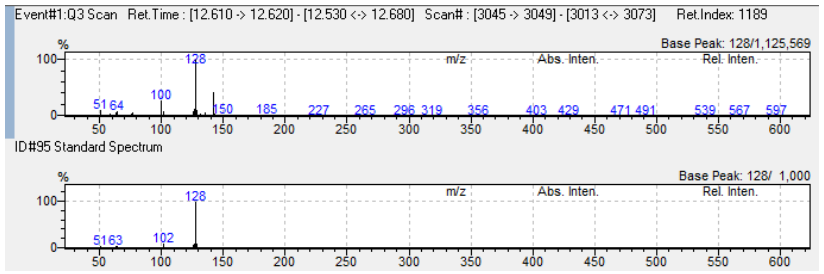
n-C9H20(Nonane)



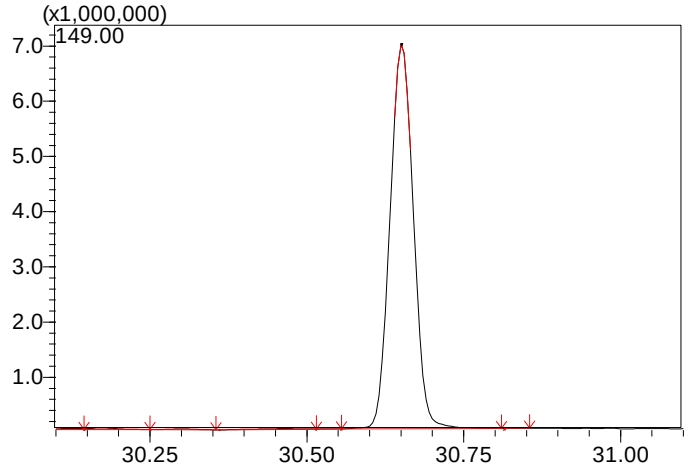


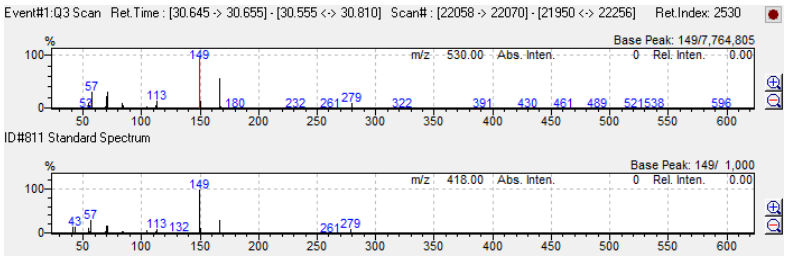
Naphthalene





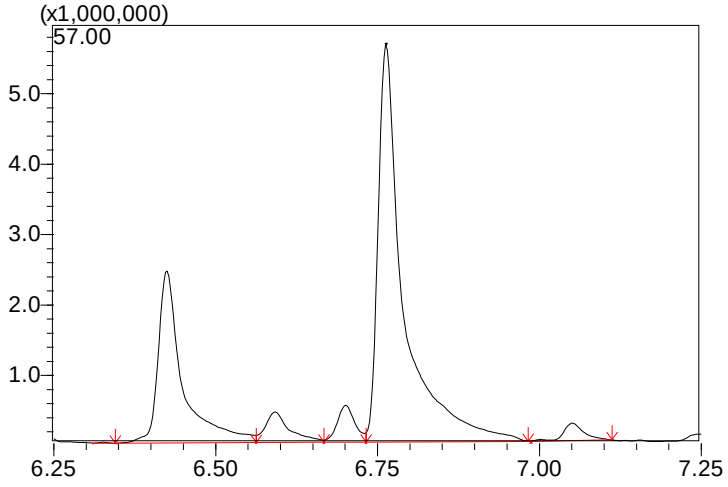
Bis(2-ethylhexyl)phthalate

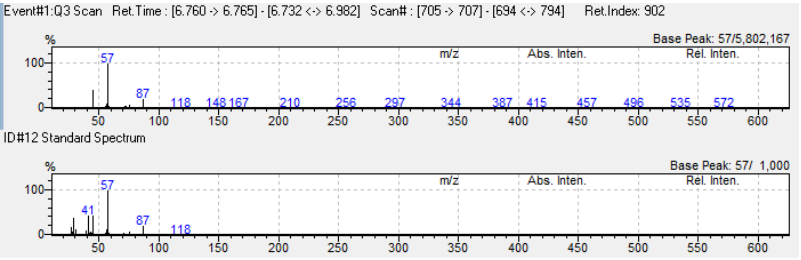




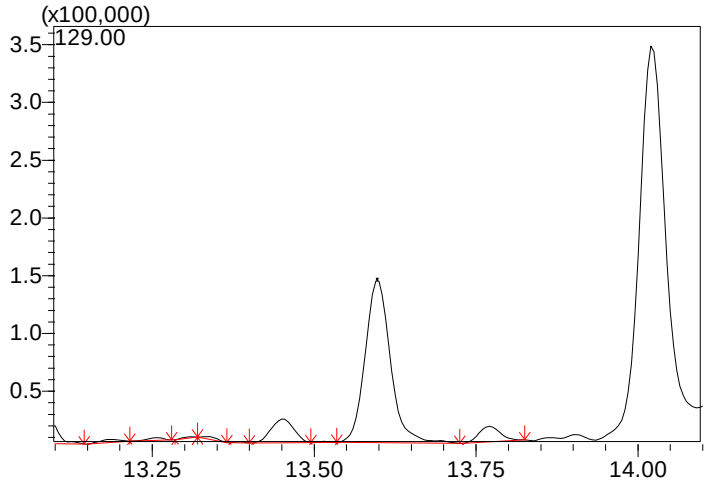
Detected pollutants example

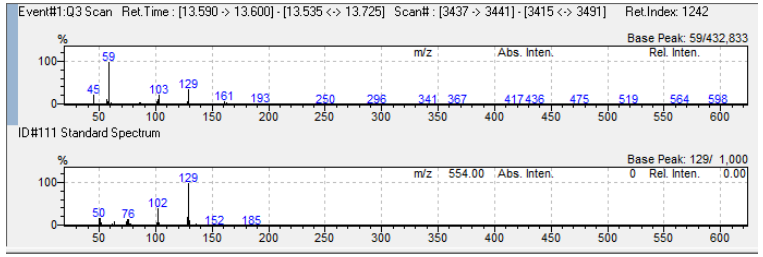
Butoxyethanol



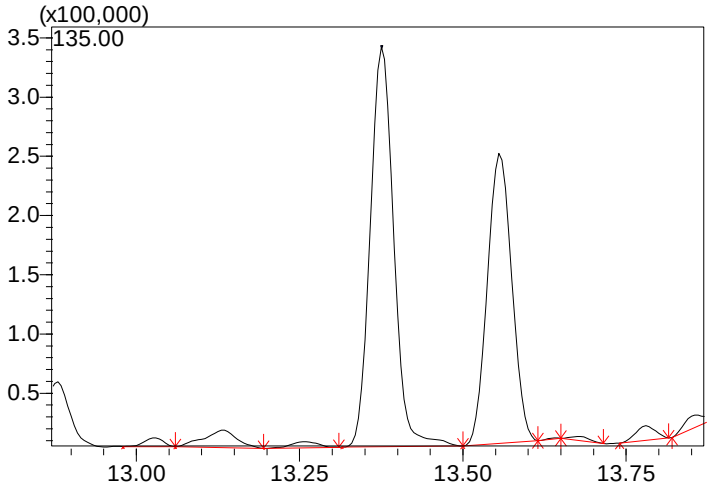


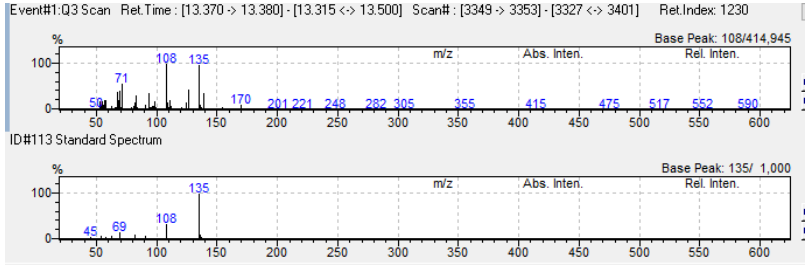
Quinoline





Benzothiazole





Demonstrate Results

Semi-Quantitative Results for detected environmental pollutants using AIQS-DB

Categ	Detected Compounds	Conc. (ng/L in water)	Categ	Detected Compounds	Conc. (ng/L in water)	Categ	Detected Compounds	Conc. (ng/L in water)
1	n-C11H24	62.7	1	Biphenyl	160.7	2	Coprostanol	14121.5
1	n-C12H26	120.1	1	Fluorene	44.6	2	Cyclohexanol	899.7
1	n-C13H28	241.3	1	Naphthalene	270.4	2	Ethanol, 2-phenoxy-	1989.0
1	n-C14H30	190.5	1	Phenanthrene	126.4	2	Phenylethyl alcohol	101.2
1	n-C15H32	188.6	2	Diphenyl ether	213.6	2	Stigmasterol	1697.2
1	n-C16H34	215.3	2	Isophorone	8601.1	2	1,3-Dichloro-2-propanol	304.5
1	n-C17H36	419.8	2	2-Methylphenol	506.7	3	2-Naphthylamine	93.4
1	n-C18H38	420.6	2	2-Naphthol	126.0	3	Acetamide, N-phenyl-	571.0
1	n-C19H40	435.1	2	2-Phenylphenol	52.4	3	2-Chloroaniline	533.5
1	n-C20H42	541.7	2	4-Methyl-2,6-di-t-butylphenol	167.6	3	3,4-Dichloroaniline	959.2
1	n-C21H44	677.3	2	4-tert-Octylphenol	155.4	3	Quinoline	175.4
1	n-C22H46	794.4	2	Bisphenol A	3169.6	4	2(3H)-Benzothiazolone	2544.3
1	n-C23H48	1118.2	2	Nonylphenol	9845.0	4	2-(Methylthio)-benzothiazol	277.7
1	n-C24H50	1505.7	2	2,4,5-Trichlorophenol	38.1	4	2-Acetyl-5-methylthiophene	65.4
1	n-C25H52	2383.4	2	2,4,6-Tribromophenol	3292.6	4	Benzothiazole	177.0
1	n-C26H54	1299.5	2	2,4,6-Trichlorophenol	44.7	5	Tris(1,3-dichloro-2-propyl) phosphate	677.0
1	n-C27H56	1392.3	2	Triclosan	211.3	6	Caffeine	1736.5
1	n-C28H58	966.2	2	Bis(2-ethylhexyl)phthalate	11036.3	6	Diethyltoluamide	345.0
1	n-C29H60	1445.2	2	Diethyl phthalate	2306.6	6	Ibuprofen	1596.3
1	n-C30H62	1625.2	2	Diisobutyl phthalate	914.1	6	L-Menthol	4281.0
1	n-C31H64	2393.8	2	Dimethyl phthalate	261.8	6	Thymol	223.1
1	n-C32H66	979.3	2	Di-n-butyl phthalate	807.1	6	Nicotine	846.2
1	n-C33H68	863.2	2	2-Butoxyethanol	4013.9	7	Fenobucarb	551.5
1	n-C9H20	152.0	2	2-Ethyl-1-hexanol	1628.3	7	Permethrin 1	661.7
1	4-Cymene	351.2	2	alpha-Terpineol	900.9	7	Permethrin 2	114.2
1	1,3-Dimethylnaphthalene	618.1	2	Benzyl alcohol	203.7	7	Piperonyl butoxide	85.7
1	2,6-Dimethylnaphthalene	403.9	2	beta-Sitosterol	3799.5	7	2-Phenylphenol (OPP)	63.9
1	2-Methylnaphthalene	100.9	2	Cholesterol	14408.1	7	Biphenyl	34.6

Non-target and target analysis with GC-MS/MS

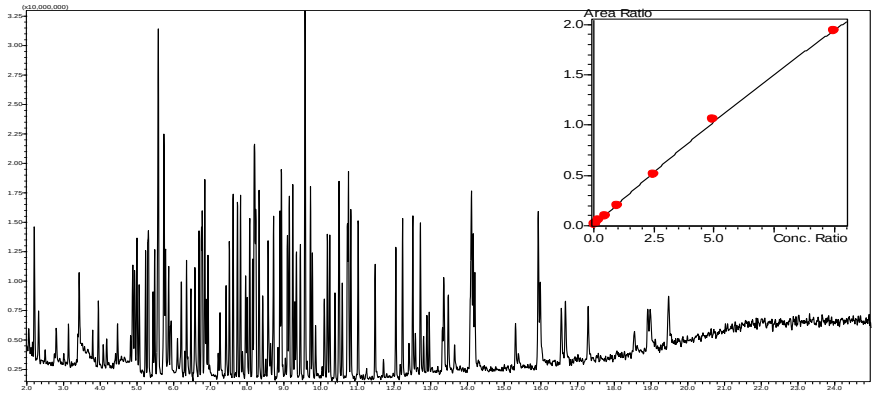
Using 1 method we can acquire both data of non-target result and accurate quant result following 8270E

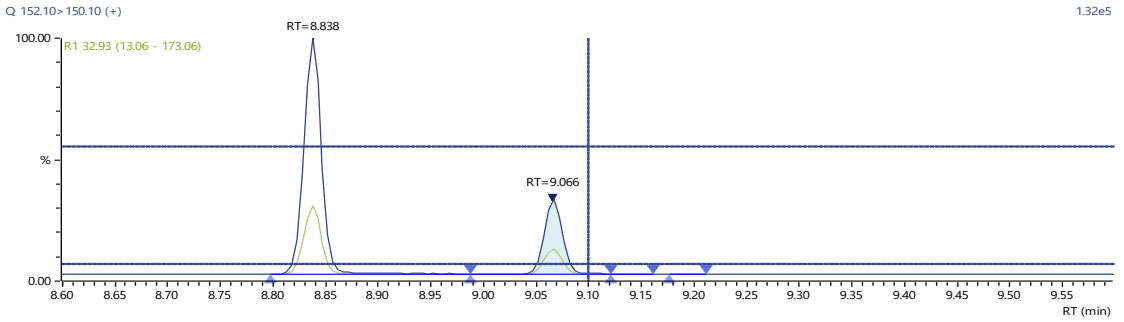
Create Calibration curve for Target analysis using MRM

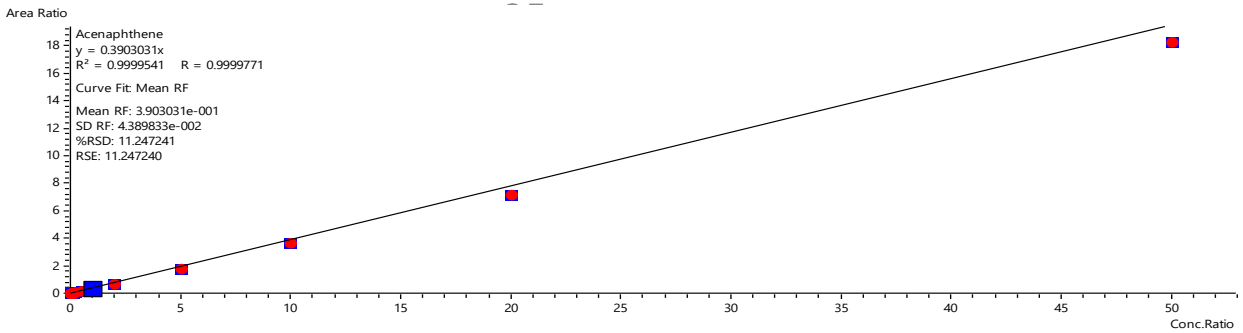
Running sample with Scan/MRM method

Report semi-quant result using Scan Data

Report quant result using MRM data



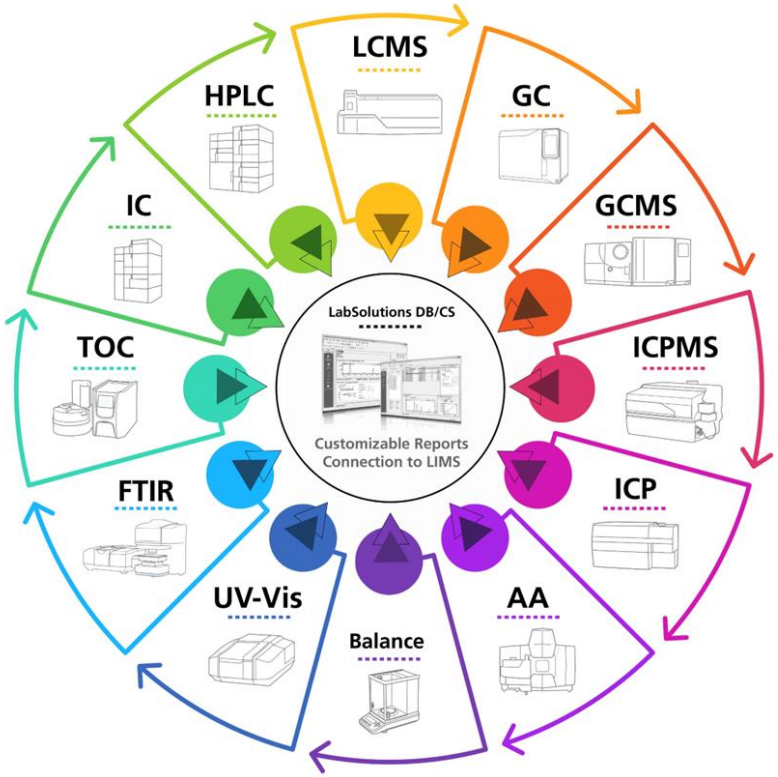




Conclusion

- GC-MSMS is Ready to use solution for SVOC analysis following 8270E guidance
- GC-MSMS can do both quantitation for analyte and qualification for unknown compounds at the same time
- GC-MSMS can do non-target semi-quant and accurate target analysis at the same time

Q&A



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