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Application News

GCMS-QP2050 Gas Chromatograph Mass Spectrometer

Analysis of Semivolatile Organic Compounds by Single Quadrupole GCMS-QP2050 Following EPA 8270E

User Benefits

- The GCMS-QP2050 meets quality control criteria for the instrument and initial calibration curve as outlined in EPA 8270E.
- Excellent sensitivity was demonstrated for the Semivolatile Organic Compounds targeted, including early eluting 1,4-Dioxane to later eluting Benzo(g,h,i)perylene
- Scan/SIM capability supports quantitative analysis and identification of unknown compounds in samples through library searches.

■ Abstract

This application note evaluates the performance of the GCMS-QP2050 single quadrupole gas chromatography mass spectrometer for the analysis of semivolatile organic compounds (SVOCs) listed in EPA 8270E. All compounds met the calibration criteria determined in EPA 8270E (reference 1), with an average detection limit 10 times lower than those normally reported as vial concentration.

■ Introduction

Semivolatile Organic Compounds (SVOCs) are routinely analyzed in multiple environmental matrices by environmental laboratories. SVOCs listed in 8270E contain various classes of compounds such as Phenols, Phthalates, and PAHs. In this study, the performance of Shimadzu's GCMS-QP2050 system for the simultaneous analysis of SVOCs included in EPA 8270E was evaluated. The fast scan speed of the GCMS-QP2050 allows for simultaneous Scan/SIM analysis. Using Scan, spectrum information with accurate quantitative results was acquired.

■ Experimental

Standard Solutions

Commercially available analytical standards were mixed to prepare a stock analyte solution, Internal Standard (IS) solution, and surrogate solution. The standards purchased are listed in Table 1.

Calibration Range and Method Conditions

Calibration standards were prepared to cover a wide calibration range (0.01 ppm to 20 ppm) with 11 calibration levels. This instrument was installed with a 30m Restek Rxi-SVOCms column with 0.25mm and a 0.25um film thickness.

This column is designed specifically for SVOCs analysis and achieves good peak shape and resolution for isomers. Constant linear velocity mode was chosen as GC flow control to get better peak separation.

Table 1: Standard products used in this study.

Type	Vendor	P/N	Product name
Analyte	Restek	31850	8270 MegaMix Standard (76 compounds)
Analyte	Restek	31834	Benzidine Mix (2 comp.)
Analyte	o2si	110903-01	CLP 4.2 Additional Comp.
Analyte	Millipore Sigma	CRM48367	1,4-Dioxane solution
Analyte	Millipore Sigma	CRM47508	Benzoic Acid Solution
IS	Millipore Sigma	CRM48902	EPA 8270 Semivolatile Internal Standard Mix
Surrogate	Millipore Sigma	CRM47960	EPA 8270 Surrogate Standard

Table 2: GC and MS conditions.

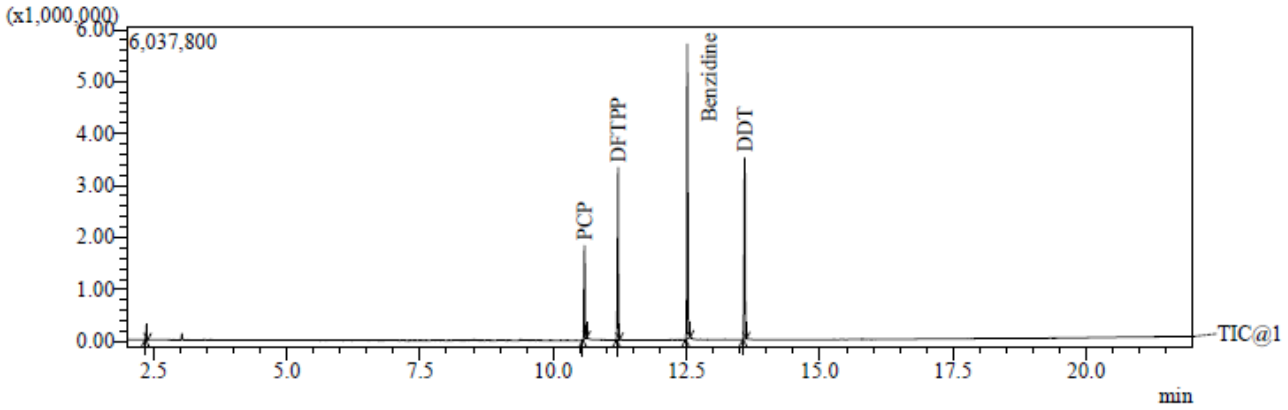
GC conditions	
Injection Temp.	275 °C
Injection Mode	Split (1:10)
Column Flow	1.2 mL/min
Flow Control Mode	Linear Velocity
Column	Rxi-SVOCms (30m x 0.25 mm, 0.25 µm)
Oven Temp.	40 °C (1 min) ->20 °C/min to 280 °C -> 5 °C to 320 °C Total run: 21 min
Carrier Gas	Helium
MS conditions	
Solvent Cut Time	2 min
Ion Source Temp.	230 °C
Interface Temp.	320 °C
Detector Voltage	+0.15 kV (relative to Tuning)
Analysis Type	Scan/SIM simultaneous
TMP Speed	255 L/sec

■ Results and Discussion

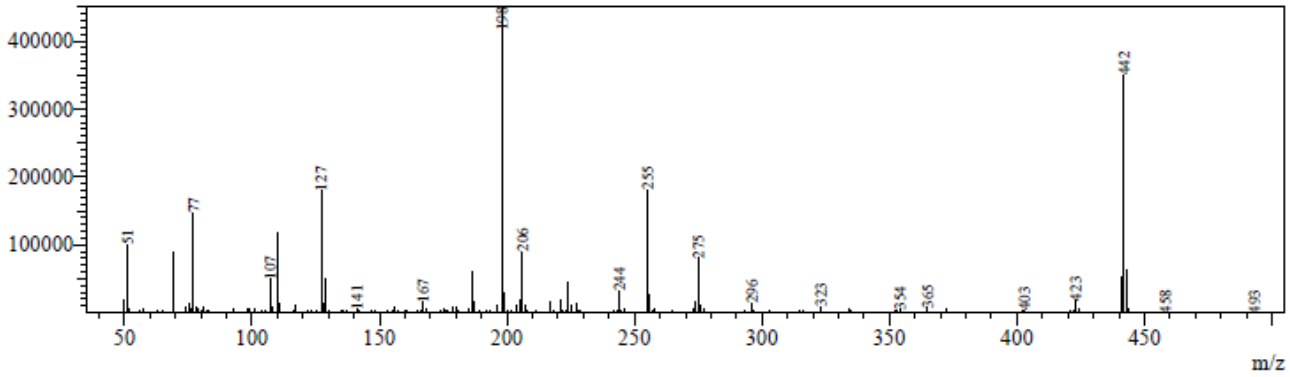
System Validation before Analysis

Before injecting the calibration standards, EPA 8270E requires confirming the status of the instrument through a DFTPP spectrum pattern check for assessing the MS condition (Figure 1) and evaluating the tailing factor of Benzidine and Pentachlorophenol for checking the column condition (Figure 2).

Inertness of the injection port, evaluated by checking the degradation of DDT, was not included in this study because reactive compounds (e.g., organochloride pesticides) were not included in this study. As a result, GCMS-QP2050 passed all criteria outlined by 8270E.



ID#:1 R.Time:11.210(Scan#:1843)
MassPeaks:451
Spectrum Mode:Averaged 11.210-11.220(1843-1845)
BG Mode:Calculated from Peak Segment 1 - Event 1



Comp. Name : DFTPP Ret. Time : [11.210->11.220]-[11.180<->11.285]

m/z	Criteria	Rel. Int.	Abs. Int.	Status
68	< 2% of mass 69	1.22	1072	Pass
69	Present	19.57	88105	Pass
70	< 2% of mass 69	0.56	489	Pass
197	< 2% of mass 198	0.25	1125	Pass
198	Base peak or present	100.00	450208	Pass
199	5 - 9% of mass 198	6.55	29500	Pass
365	> 1% of the base peak	1.54	6941	Pass
441	< 150% of mass 443	82.00	52358	Pass
442	Base peak or present	77.59	349315	Pass
443	15 - 24% of mass 442	18.28	63853	Pass

Figure 1: DFTPP spectrum pattern check result: Pass

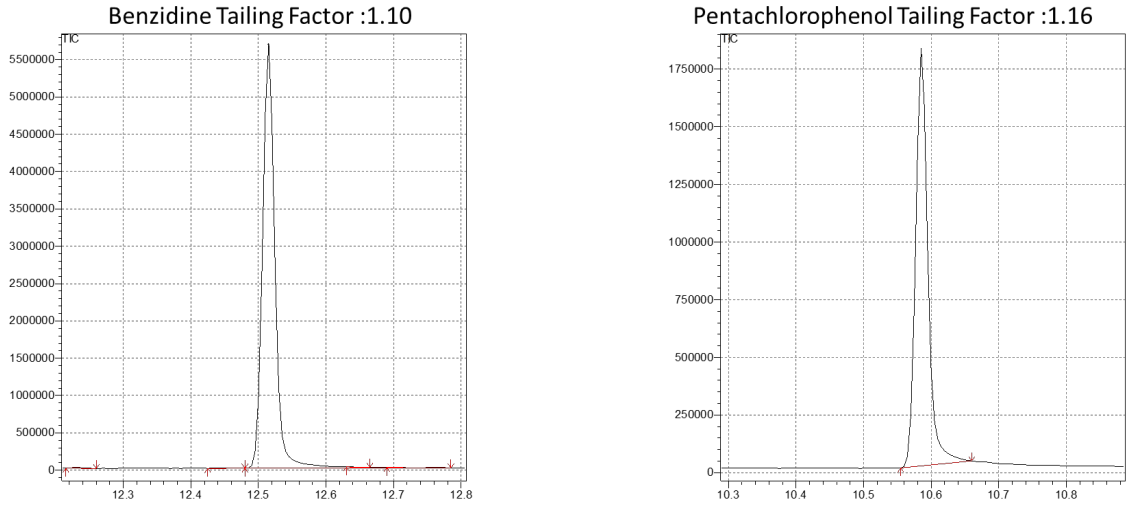


Figure 2: Benzidine and Pentachlorophenol tailing factor check result: Pass (Criteria is 2.0).

Validation of Resolution

During calibration data acquisition, resolution of isomers was confirmed with the Benzo(b)fluoranthene and Benzo(k)fluoranthene pair. As shown in Figure 3, the resolution was 25%, exceeding acceptance criteria from EPA 8270E (50%) (Figure 3).

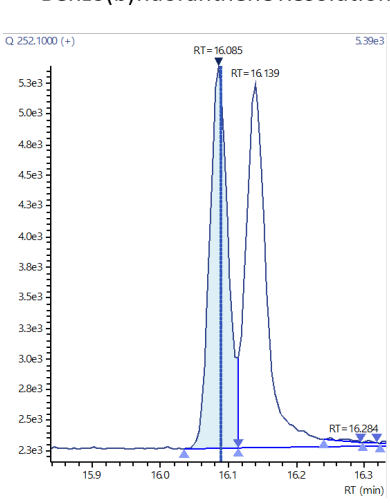


Figure 3: 0.01ppm resolution result: Pass

Validation of Calibration Curve

1) Calibration points are recommended to be within ±30% of the true value when recalculated with the calibration curve, except the lowest standard, for which the acceptance criteria is ±50%.
2) For the average RF calibration model, Relative Standard Deviation (RSD) of Response Factors (RFs) must be less than 20%
3) For linear and quadratic[1] calibration curves, R2 must be ≥0.99 and Relative Standard Error (RSE) must be <20%.

[1]Use of a quadratic calibration curve requires at least 6 calibration levels. Acceptable calibration curves must meet criteria #1, and either criteria #2 or #3.

For some of the targeted compounds, like 2,4-Dinitrophenol and Benzoic acid, which are problematic compounds, a weighted calibration curve (using as weight: $1/x^2$) provides better results for meeting criteria #1. This approach is acceptable and recommended in EPA 8000D (Determinative Chromatographic Separations). Calibration standards with a calculated value that exceeded criteria #1 were omitted from the final calibration curve of each compound. Table 3 is result for this application. As shown, all compounds meet the criteria.

Table 3: Validation and Accuracy result of each calibration curve

	Curve fit	Lowest point (ppm)	Highest point (ppm)	RSE	R2	%Accuracy at lowest point
1,4-Dioxane	Average RF	0.01	20	8.3	----	111
N-Nitrosodimethylamine	Average RF	0.02	20	8.9	----	87
Pyridine	Quadratic	0.1	20	5.2	0.9974	101
2-Fluorophenol	Average RF	0.01	20	6.3	----	105
Benzaldehyde	Average RF	0.01	20	6.4	----	108
Phenol-d5	Average RF	0.01	20	4.9	----	100
Phenol	Average RF	0.01	20	5.8	----	109

Aniline	Average RF	0.01	20	11.6	----	79
Bis(2-chloroethyl)ether	Quadratic	0.01	20	9.4	0.9913	109
2-Chlorophenol	Average RF	0.01	20	5.3	----	103
1,3-Dichlorobenzene	Average RF	0.01	20	7.7	----	109
1,4-Dichlorobenzene	Average RF	0.01	20	7.7	----	110
Benzyl Alcohol	Average RF	0.01	20	6.6	----	101
1,2-Dichlorobenzene	Average RF	0.01	20	7.9	----	109
2-Methylphenol(o-Cresol)	Average RF	0.01	20	5.1	----	101
Bis(2-chloro-1-methylethyl) ether	Average RF	0.01	20	8.8	----	118
3-Methylphenol (m-Cresol)/4-Methylphenol(p-Cresol)	Average RF	0.01	20	7.5	----	99
N-nitroso-di-n-propylamine	Average RF	0.01	20	6.5	----	95
Hexachloroethane	Average RF	0.01	20	11.9	----	125
Nitrobenzene-D5	Average RF	0.01	20	7.9	----	104
Nitrobenzene	Average RF	0.01	20	14.2	----	91
Isophorone	Average RF	0.01	20	8.8	----	96
2-Nitrophenol	Average RF	0.01	20	15.2	----	91
2,4-Dimethylphenol	Average RF	0.01	20	6.6	----	99
Benzoic Acid	Quadratic	0.1	10	8.2	0.9916	98
Bis(2-chloromethoxy)methane	Average RF	0.01	20	5.9	0.9998	108
2,4-Dichlorophenol	Average RF	0.01	20	7.3	----	116
1,2,4-Trichlorobenzene	Average RF	0.01	20	10.1	----	117
Naphthalene	Average RF	0.01	10	7.7	----	111
4-Chloroaniline	Average RF	0.01	20	5.5	----	96
Hexachlorobutadiene	Average RF	0.01	20	12.1	----	121
Caprolactam	Quadratic	0.1	20	7.2	0.9952	104
4-Chloro-3-methylphenol	Average RF	0.01	20	8.7	----	100
2-Methylnaphthalene	Average RF	0.01	20	7.0	----	107
1-Methylnaphthalene	Average RF	0.01	20	7.2	----	108
Hexachlorocyclopentadiene	Average RF	0.01	20	5.8	----	94
2,4,6-Trichlorophenol	Average RF	0.01	20	8.8	----	102
2,4,5-Trichlorophenol	Average RF	0.01	20	11.8	----	89
2-Fluorodiphenyl	Average RF	0.01	20	8.7	----	109
1,1'-Biphenyl	Average RF	0.01	10	8.3	----	110
2-Chloronaphthalene	Average RF	0.01	20	8.0	----	111
2-Nitroaniline	Average RF	0.01	10	15.1	----	104
1,4-Dinitrobenzene	Quadratic	0.01	10	9.7	0.9913	105
Dimethyl phthalate	Average RF	0.01	20	9.0	----	117
1,3-Dinitrobenzene	Quadratic	0.02	2	9.3	0.9926	102
2,6-Dinitrotoluene	Quadratic	0.05	5	10.1	0.9926	102
1,2-Dinitrobenzene	Quadratic	0.02	5	8.8	0.9935	104
Acenaphthylene	Average RF	0.01	20	10.0	----	110
3-Nitroaniline	Quadratic	0.1	10	10.3	0.9935	105
Acenaphthene	Average RF	0.01	20	10.6	----	116
2,4-Dinitrophenol	Quadratic	0.2	20	9.7	0.9913	105
4-Nitrophenol	Quadratic	0.2	20	9.3	0.9931	87
2,4-Dinitrotoluene	Quadratic	0.02	2	8.0	0.9945	101
Dibenzofuran	Average RF	0.01	10	8.3	----	112
2,3,5,6-Tetrachlorophenol	Average RF	0.01	20	16.6	----	136
2,3,4,6-Tetrachlorophenol	Average RF	0.01	20	13.4	----	120
Diethyl Phthalate	Average RF	0.1	20	12.2	----	124
Fluorene	Average RF	0.01	10	9.5	----	116
4-Chlorophenyl-phenyl ether	Average RF	0.01	20	12.1	----	113
4-Nitroaniline	Average RF	0.01	20	17.9	----	95
4,6-Dinitro-2-methylphenol	Quadratic	0.1	10	9.5	0.9931	107
Diphenylamine	Average RF	0.01	20	7.7	----	108
Azobenzene	Average RF	0.01	20	12.0	----	91
2,4,6-Tribromophenol	Average RF	0.02	20	8.6	----	112
4-Bromophenyl phenyl ether	Average RF	0.01	20	9.0	----	111
Hexachlorobenzene	Average RF	0.01	20	13.5	----	121
Atrazine	Average RF	0.01	20	8.6	----	94
Pentachlorophenol	Average RF	0.05	20	15.7	----	125
Phenanthrene	Average RF	0.01	10	7.8	----	112
Anthracene	Average RF	0.01	10	5.8	----	100

Carbazole	Average RF	0.01	10	6.2	----	102
Di-n-butyl phthalate	Average RF	0.01	10	10.4	----	96
Fluoranthene	Average RF	0.01	10	5.6	----	103
Benzidine	Quadratic	0.05	10	10.1	0.9914	105
Pyrene	Average RF	0.01	10	6.0	----	101
p-Terphenyl-d14	Average RF	0.01	10	6.8	----	100
Butyl benzyl phthalate	Average RF	0.01	10	15.6	----	97
Bis(2-ethylhexyl) adipiate	Quadratic	0.01	2	7.7	0.9942	104
3,3'-Dichlorobenzidine	Average RF	0.01	20	9.6	----	100
Benzo[a]anthracene	Average RF	0.01	20	12.6	----	125
Chrysene	Average RF	0.01	20	10.9	----	118
Bis(2-ethylhexyl) phthalate	Quadratic	0.01	2	10.4	0.9944	104
Di-n-octyl phthalate	Quadratic	0.01	10	10.4	0.9912	105
Benzo(b)fluoranthene	Average RF	0.01	10	5.2	----	107
Benzo(k)fluoranthene	Average RF	0.01	10	12.8	----	123
Benzo(a)pyrene	Average RF	0.01	10	8.8	----	119
Indeno(1,2,3-cd)pyrene	Average RF	0.01	20	12.2	----	132
Dibenzo(a,h)anthracene	Average RF	0.01	20	16.20	----	142
Benzo(g,h,i)pyrelene	Average RF	0.01	20	15.97	----	131

Validation of Scan Result

In this study, the Scan/SIM simultaneous method setting was used to obtain qualification information without losing SIM sensitivity. The total ion chromatograph is shown in Figure 4. Accurate Mass Spectrum information was obtained at the same time with SIM accurate quantification analysis.

As examples, Figure 5 shows the mass spectrum of representative compounds with different boiling points (low: 1,4- dioxane, middle: 3-Nitroaniline, high: Benzo(g,h,i)pyrelene). The excellent score demonstrates the suitability of Scan/SIM despite the complexity of the chromatogram.

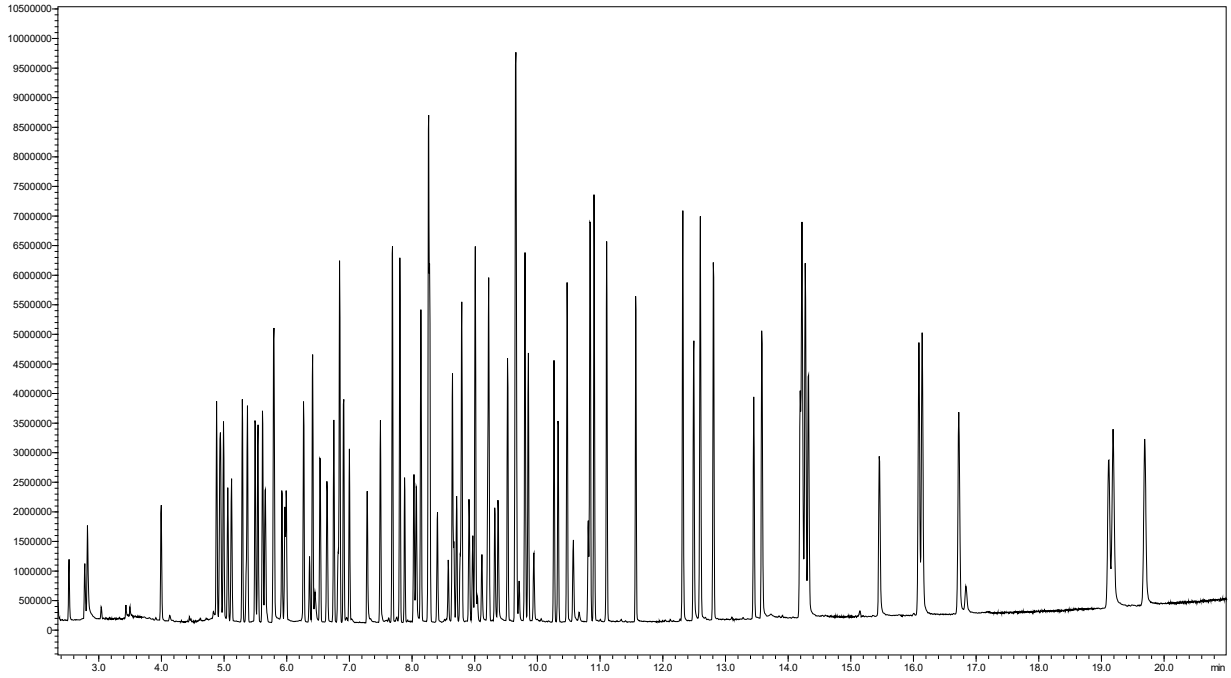
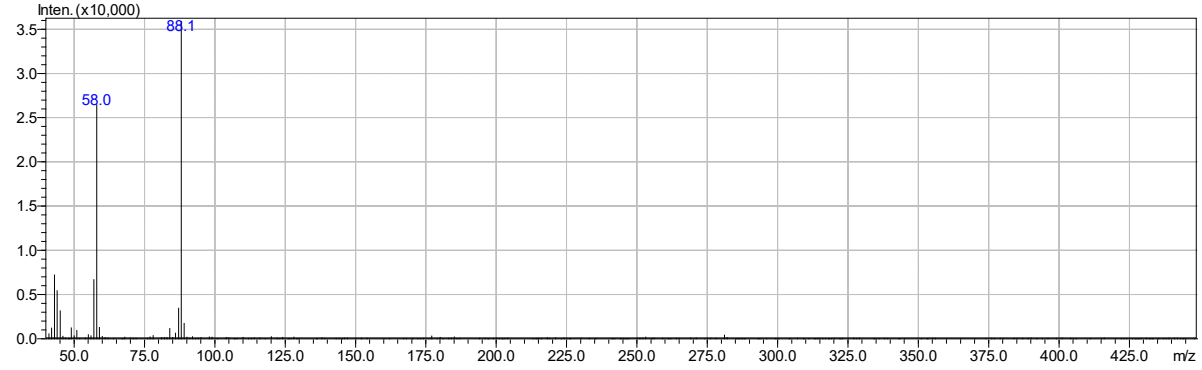
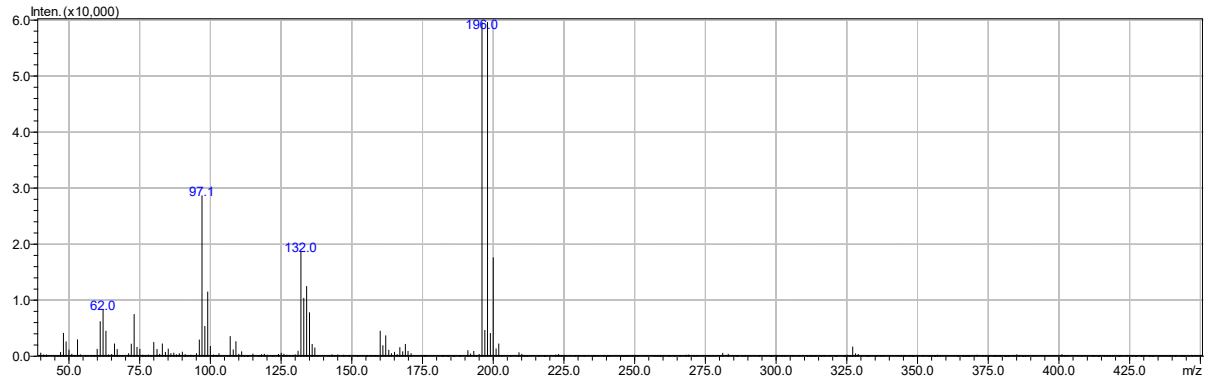


Figure 4: Scan Total ion chromatogram (TIC)

1,4 Dioxane (Similarity Score: 93)



3-Nitroaniline (Similarity Score: 90)



Benzo(g,h,i)perylene (Similarity Score: 95)

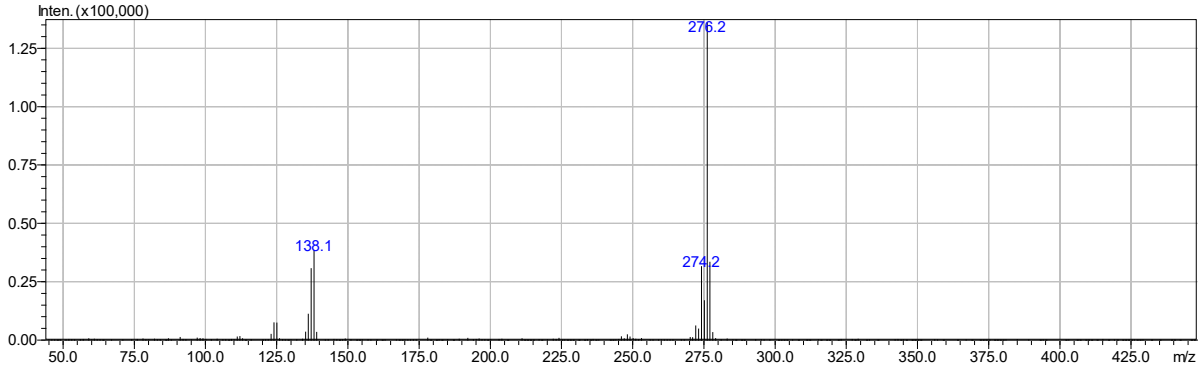


Figure 5: Mass Spectrum example (100 pg on column)

■ Conclusion

This study demonstrates the capabilities of Shimadzu's GCMS-QP2050 for the analysis of SVOCs. The GCMS-QP2050 meets routine system check and initial calibration requirements as specified by USEPA method 8270E. Because of the high performance of this single quadrupole instrument, a calibration range (0.01 ppm to 20 ppm), 10 times lower than commonly reported concentrations (0.2 ppm to 200 ppm), can be analyzed. This enables environmental laboratories to modify their sample preparation workflow by using a higher split ratio, reducing the initial sample volume or injection volume, while maintaining desired performance and reducing maintenance frequency.

Moreover, simultaneous Scan/SIM data acquisition can be performed with the GCMS-QP2050 without loss of sensitivity in SIM mode. With a single injection, accurate quantitative analysis can be done at the same time as the tentative identification of the sample components as outlined in EPA 8270E.

■ Reference

1) USEPA 8270E 8270e_revised_6_june_2018.pdf (epa.gov)

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