Determination of Semivolatile Organic Compounds in Drinking Water Using the Agilent 5977A Series GC/MSD

Application Note

Environmental

Author

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Abstract

A method has been developed on the Agilent 5977A Series GC/MSD for the detection of 30 SVOCs at levels as low as 5 parts per billion (ppb), with excellent linearity ($R^2 > 0.990$) and reproducibility (most relative standard deviations (RSDs) $\leq 3.1\%$).

Introduction

Semivolatile organic compounds (SVOCs) include a variety of chemicals which may have adverse health effects. Many are suspected carcinogens, and some, such as benzo(a)pyrene, are known to be carcinogenic in animals and humans. SVOCs are typically industrial plasticizers, byproducts of incomplete combustion of fossil fuels, medicines, disinfectants, pesticides, and so forth. The pollution of water can happen through contamination of the raw supply, or through leaching from sources such as landfills.

In China, regulation GB5749-2006 governs the allowed limits of SVOCs in drinking water. This application note demonstrates the ability of the 5977A Series GC/MSD to enable sensitive and reproducible detection, in 15 minutes, of 30 SVOCs covered by GB5749-2006, with RSDs that are $\leq 3.1\%$ for most of the 30 compounds tested.

Experimental

Standards and Reagents

Standards for 30 SVOCs and three internal standard compounds were commercially obtained (Table 1). The working calibration standards were prepared in ethyl acetate using the Agilent 7696A Sample Prep WorkBench.

Instruments

The study was performed on an Agilent 7890B gas chromatograph equipped with a Split/Splitless Inlet and coupled to an Agilent 5977A Series GC/MSD, using Synchronous Scan/SIM and Electron Ionization (EI) acquisition modes. Table 2 lists the instrument conditions.

Table 1. 30 SVOC Standards and Three Internal Standards (IS)

No.	Name	CAS	No.	Name	CAS
1	1,3,5-Trichlorobenzene	108-70-3	16	Methyl parathion	298-00-0
2	1,2,4-Trichlorobenzene	120-82-1	17	Heptachlor	76-44-8
3	1,2,3-Trichlorobenzene	87-61-6	18	Malathion	121-75-5
4	Dichlorvos	62-73-7	19	Dursban	2921-88-2
5	2,4,6-Trichlorophenol	88-06-2	20	Parathion	56-38-2
IS-1	Acenaphthene-d10	15067-26-2	21	Bentazone	25057-89-0
6	BHC-*alpha*	319-84-6	22	DDE-o,p'	3424-82-6
7	Hexachlorobenzene	118-74-1	23	DDE-p,p'	72-55-9
8	Dimethoate	60-51-5	24	DDD-o,p'	53-19-0
9	Carbofuran	1563-66-2	25	DDD-p,p'	72-54-8
10	Atrazine	1912-24-9	26	DDT-o,p'	789-02-6
11	BHC-*beta*	319-85-7	27	DDT-p,p'	50-29-3
12	Pentachlorophenol	87-86-5	IS-3	Chrysene-d12	1719-03-5
13	Lindane	58-89-9	28	Di(2-ethylhexyl)phthalate	117-81-7
14	Chlorothalonil	1897-45-6	29	Benzo(a)pyrene	50-32-8
15	BHC-*delta*	319-86-8	30	Deltamethrin	52918-63-5
IS-2	Phenanthrene-d10	1517-22-2			

Table 2. Agilent 7890B GC and Agilent 5977A Series GC/MSD Conditions

GC run conditions	
Analytical column	Agilent DB-8270D UI 20 m × 180 µm, 0.36 µm (p/n 621-9723)
Injection volume	1 µL
Injection mode	Splitless
Inlet temperature	280 °C
Liner	Liner, UI, splitless, single taper, no glass wool (p/n 5190-2292)
Carrier gas	Helium, constant flow, 1.2 mL/min
Oven program	45 °C for 1 minute
	50 °C/min to 100 °C
	0.5 minutes hold
	25 °C/min to 310 °C
	4 minutes hold
Transfer line temperature	280 °C
MS conditions	
Solvent delay	4 minutes
Acquisition mode	Synchronous Scan/SIM
Tune	Etune.u
Gain factor	5.00
Source temperature	250 °C
Quadrupole temperature	150 °C

Acquisition Parameters

Table 3 shows the ions used for acquisition.

Table 3. Acquisition Parameters

Target compounds	RT	Q_0	Q_1	Q_2	Q_3	Target compounds	RT	Q_0	Q_1	Q_2	Q_3
1,3,5-Trichlorobenzene	4.75	180	182	184	145	Methyl parathion	8.67	109	125	263	79
1,2,4-Trichlorobenzene	5.05	180	182	184	145	Heptachlor	8.82	100	272	274	270
1,2,3-Trichlorobenzene	5.26	180	182	184	145	Malathion	8.9	173	127	125	93
Dichlorvos	5.34	109	185	79	187	Dursban	8.99	197	199	314	97
2,4,6-Trichlorophenol	6.06	196	198	97	132	Parathion	9.06	109	97	291	125
BHC-*alpha*	7.88	219	183	181	217	Bentazone	9.15	198	119	161	92
Hexachlorobenzene	7.92	284	286	282	288	DDE-o,p'	9.59	246	248	318	316
Dimethoate	7.95	87	93	125	143	DDE-p,p'	9.84	246	248	318	316
Carbofuran	7.96	164	149	131	123	DDD-o,p'	9.91	235	237	165	212
Atrazine	8.01	200	215	58	173	DDD-p,p'	10.17	235	237	165	212
BHC-*beta*	8.07	219	181	183	109	DDT-o,p'	10.21	235	237	165	212
Pentachlorophenol	8.11	266	264	268	165	DDT-p,p'	10.47	235	237	165	212
Lindane	8.17	219	183	181	111	Di(2-ethylhexyl)phthalate	10.94	149	167	57	70
Chlorothalonil	8.29	266	264	268	270	Benzo(a)pyrene	12.61	252	253	125	126
BHC-*delta*	8.39	219	183	181	217	Deltamethrin	13.29	181	253	251	255

RT – retention time in minutes
Q_0 – quantifier ion
Q_1, Q_2, Q_3 – qualifier ions

Table 4. Calibration Coefficients for the 30 SVOCs

Target compound	R^2	Target compound	R^2
1,3,5-Trichlorobenzene	0.999	Methyl parathion	0.994
1,2,4-Trichlorobenzene	0.999	Heptachlor	0.997
1,2,3-Trichlorobenzene	0.999	Malathion	0.993
Dichlorvos	0.998	Dursban	0.991
2,4,6-Trichlorophenol	0.995	Parathion	0.993
BHC-*alpha*	0.999	Bentazone**	0.991
Hexachlorobenzene	0.999	DDE-o,p'	0.999
Dimethoate	0.995	DDE-p,p'	0.999
Carbofuran	0.993	DDD-o,p'	0.999
Atrazine	0.994	DDD-p,p'	0.996
BHC-*beta*	0.999	DDT-o,p'	0.998
Pentachlorophenol*	0.993	DDT-p,p'	0.993
BHC-*gamma*	0.999	Di(2-Ethylhexyl)phthalate	0.997
Chlorothalonil	0.997	Benzo(a)pyrene	0.998
BHC-*delta*	0.999	Deltamethrin	0.999

*pentachlorophenol: 20–200 ppb
** bentazone: 50–1,000 ppb

Results and Discussion

Linearity

Calibration curves were constructed from 5 to 200 ng/mL ppb for most target compounds, using three internal standards to ensure coverage of all compounds across the entire retention time range. Figure 1 shows the curves for four of the compounds, which had calibration coefficient (R^2) values $\leq$0.997. Pentachlorophenol curves were constructed from 20–200 ng/mL, and bentazone calibration curves were constructed from 50–1,000 ng/mL. The R^2 values for pentachlophenol and bentazone were greater than 0.990.

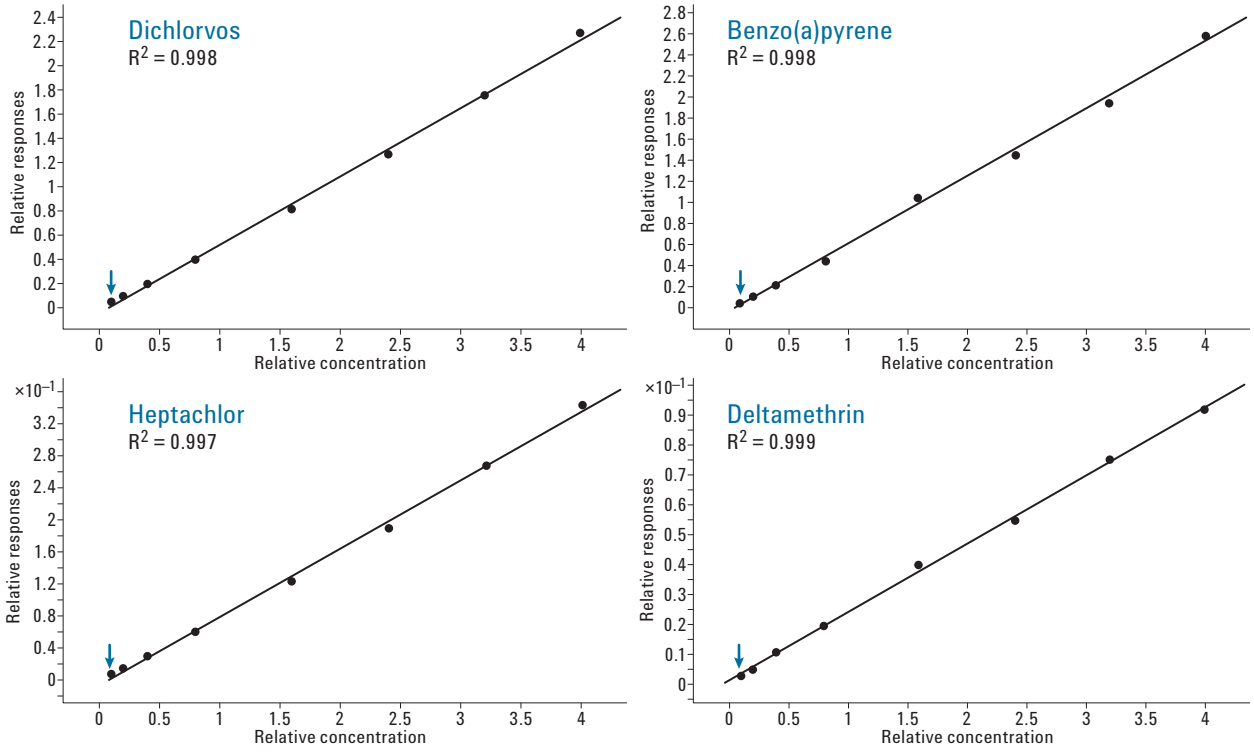

Figure 1. Example calibration curves for four of the SVOCs, from 5 to 200 ng/mL.

Reproducibility

Table 5 illustrates the excellent reproducibility of quantitation obtainable with the 5977A Series GC/MSD. Using the Etune setting provided the lowest RSDs across all 30 SVOC compounds, most of which were ≤3.1% across eight injections, and seven were less than 1%.

*Table 5. Reproducibility (RSD) for a 40 ppb Standards Mix Sample**

Target compound	Average concentration (ppb)	RSD (%)	Target compound	Average concentration (ppb)	RSD (%)
1,3,5-Trichlorobenzene	40.5	0.7	Methyl parathion	39.9	1.5
1,2,4-Trichlorobenzene	40.5	0.5	Heptachlor	37.7	0.8
1,2,3-Trichlorobenzene	40.5	0.7	Malathion	36.6	1.2
Dichlorvos	38.8	4.6	Dursban	36.4	1.4
2,4,6-Trichlorophenol	38.9	1.7	Parathion	35.0	2.2
BHC-*alpha*	38.3	1.1	Bentazone	173.0	2.7
Hexachlorobenzene	40.6	1.0	DDE-o,p'	37.7	0.6
Dimethoate	35.5	3.7	DDE-p,p'	37.4	1.0
Carbofuran	32.8	3.5	DDD-o,p'	36.4	0.9
Atrazine	35.9	1.0	DDD-p,p'	35.0	1.4
BHC-*beta*	38.1	0.7	DDT-o,p'	34.4	1.2
Pentachlorophenol	41.2	3.1	DDT-p,p'	37.1	4.4
BHC-*gamma*	37.8	1.2	Di(2-ethylhexyl)phthalate	37.5	3.1
Chlorothalonil	34.9	1.5	Benzo(a)pyrene	33.5	2.3
BHC-*delta*	38.3	1.5	Deltamethrin	37.5	2.0

*8 consecutive injections were used to calculate the RSDs. The concentration of bentazone was 200 ppb.

The Etune Setting Provides Better Sensitivity

The Extractor Ion Source and tuning protocol (Etune) have increased the sensitivity of the 5977A Series GC/MSD. For example, using Etune versus Atune with a 40 ppb SVOC standards mix provides at least two-fold higher peak heights for every compound in the mix (Figure 2).

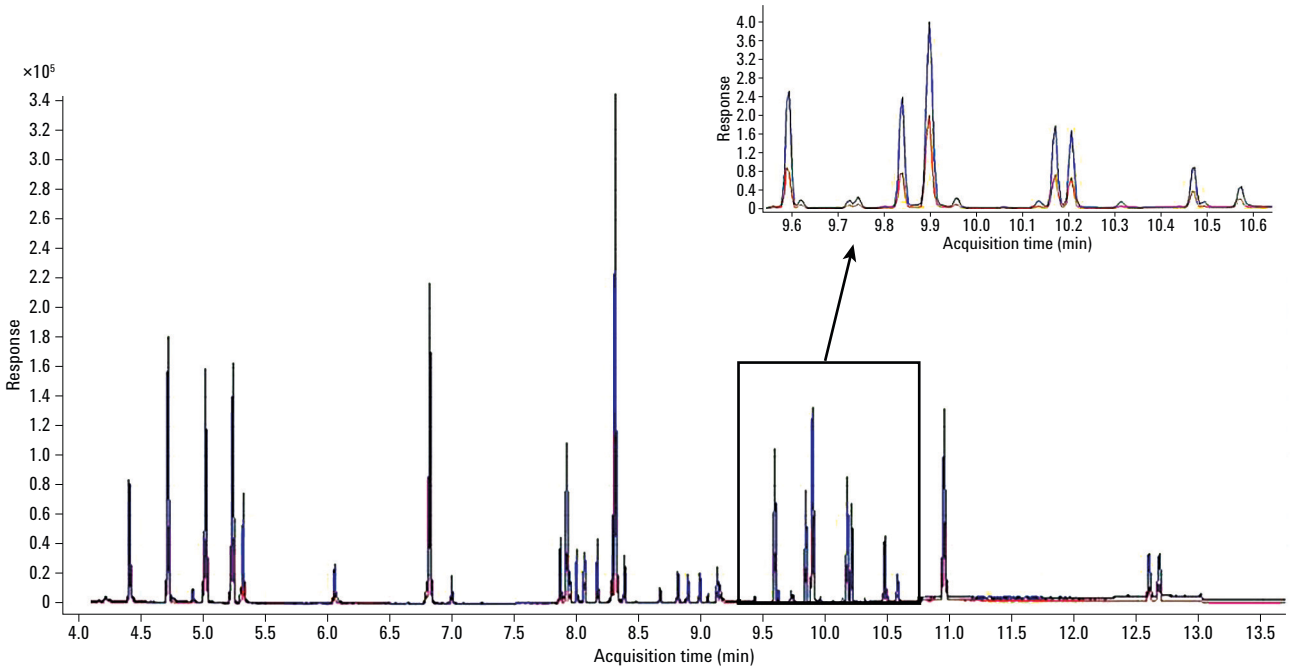

Figure 2. Extracted ion chromatogram for a 40 ppb standards mix solution using the Atune (red) or Etune (blue) tuning protocol, with one region expanded to illustrate the difference in peak heights.

Conclusion

The Agilent 5977A Series GC/MSD provides a stable platform for the sensitive, accurate, and reproducible analysis of SVOCs in drinking water, to meet the Chinese regulation. Use of the Etune tuning protocol provides the highest reproducibility and sensitivity. Using automation such as the Agilent 7696A Sample Prep WorkBench to prepare standards also results in reproducible calibration coefficient (R^2) values.

For More Information

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