Analysis of Volatile Organic Compounds in Water Using Static Headspace-GC/MS

Application Note

Environmental

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Abstract

A static headspace (SHS) method was optimized for the determination of volatile organic compounds (VOCs) in water. Analysis was performed by GC/MS in simultaneous scan/SIM mode. Using the trace ion detection mode on a 5975C MSD equipped with triple axis detection, "purge and trap" sensitivities can be obtained, combined with the robustness and ease-of-use of static headspace.

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Introduction

The determination of volatile organic compounds (VOCs) in environmental samples is mostly performed using either static headspace (SHS) or purge and trap (P&T) extraction. Both combine separation by gas chromatography (GC) with detection by mass spectrometry (MS). P&T (also called dynamic headspace) is based on an exhaustive extraction process where, ideally, all solutes present in the sample are extracted completely, concentrated in an adsorbent trap, and then thermally desorbed from the trap to introduce sample to the GC/MS for analysis. In contrast, SHS establishes an equilibrium between the solid or liquid sample and the gas or headspace phase above it in a sealed vial. A portion of the headspace is transferred to the GC/MS for analysis via a valve with a sample loop. In principle, because of exhaustive sampling, P&T is more sensitive than SHS and is preferred for analysis of sub-ppb (ng/L) VOCs in drinking water and surface water. However, P&T autosamplers are more complicated to run and maintain than are SHS autosamplers. SHS offers higher robustness and fewer problems related to carryover, cross-contamination, foam formation (due to the presence of detergents), and water management (trapping problems). In many routine laboratories, there is high interest in efforts to improve instrumentation to the point where SHS analyzes VOCs at the necessary regulatory limits.

Recent developments in GC/MS hardware have resulted in higher sensitivity and lower detection limits, thereby allowing SHS to be considered for drinking and surface water analyses. In addition, faster electronics allow the use of simultaneous scan/SIM methods and fast GC separation, while maintaining enough data points for accurate peak detection and quantification.

In this application note it is shown that by using a state-of-the-art GC/MS system and optimized SHS conditions, P&T sensitivities can be obtained, while maintaining all of the classic advantages of static headspace in terms of ease of use and robustness.

Experimental Conditions

Sample Preparation

Analyses were performed using 10-mL water samples. Samples were placed in a 20-mL headspace vial (P/N 5182-0837) containing 7 g sodium sulfate. The samples were spiked with an internal standard solution. The vials were tightly closed with an aluminum crimp cap with PTFE/silicone septum (P/N 5183-4477) using an electronic crimper (P/N 5184-3572).

An internal standard mixture of three deuterated VOCs was used. The mixture was made from three individual solutions of 1,2-dichloroethane-d4, toluene-d8, and chlorobenzene-d5 (all from Supelco [Bellefonte, PA, USA], 2,000 ppm in methanol). The individual solutions were mixed and diluted in methanol to 800 ng/mL. From this working solution, 10 µL was spiked into each 10-mL sample aliquot, corresponding to an internal standard concentration of 800 ng/L (800 ppt).

In total, 60 target analytes were analyzed and are listed in Table 1. The target list corresponds to EPA Method 524.2 and is also typical of several EU methods.

Calibration was done by analyzing reference water blanks spiked with internal standards and mixtures of the target analytes. Standard mixtures containing all 60 analytes are available from Supelco or Dr Ehrenstorfer (Augsburg, Germany). For reference water, bottled drinking water (Evian) was used with the same salt and internal standards addition as used for the samples. Bottled drinking water often offers better blank values than does HPLC grade water or Milli-Q water.

Calibration levels were between 45 and 1,250 ng/L. These were obtained by spiking 10 µL of VOC standard solutions at 45 to 1,250 ng/mL in methanol.

Instrumental Conditions

The analyses were performed on an Agilent 7890A GC/5975C MSD system. SHS was performed with an Agilent G1888 HS autosampler, equipped with a 1-mL sample loop. The SHS was coupled to a split/splitless injection port. The carrier gas line entering the SSL inlet port was cut close to the inlet and the long leg connected to the carrier gas inlet port on the G1888. The transfer line from the G1888 was connected with a stainless steel zero dead volume union on the tubing end close to the SSL inlet.

The 5975C MSD was operated in simultaneous SIM/SCAN mode with the trace ion detection mode switched on. The MSD was also equipped with the triple axis detector (TAD) option.

The experimental conditions can be summarized as follows:

SHS	Incubation: 10 min at 70 °C, high shake mode
Pressurization:	0.15 min, 20 kPa
Loop:	1 mL, 120 °C, 0.5 min fill time, 0.1 min equilibration time transfer line 120 °C, 0.5 min injection time
GC	
Inlet:	Split/splitless, 250 °C, split 1/10, headspace liner (P/N 5183-4709)
Column:	DB-624, 20 m × 0.18 mm × 1 µm (J & W 121-1324)
Gas:	He, constant pressure (95 kPa)
Oven:	40 °C (5 min) → 180 °C @ 8 °C/min → 250 °C (0.17 min) @ 30 °C/min
Run time:	25-min run

MS (5975C Inert, Agilent)

Transfer line:	300 °C
Scan:	0 to 2 min: 45 to 300 m/z, 2 to 25 min: 33 to 300 m/z
SIM:	See Table 1
Triple Axis Detector (G3392A upgrade kit)	

The method was locked on toluene at 10.42 min. All the data shown correspond to the SIM chromatograms.

Table 1. *SIM Windows, Retention Times, and Ions for Quantification*

Peak no	Name	CAS	RT (min)	Start time window	Dwell time (ms)	IS	Target ion	Qualifiers	
1	Dichlorodifluoromethane	75-71-8	1.31	0.00	70	1	85	87	50
2	Chloromethane	74-87-3	1.45			1	50	52	
3	Vinylchloride	75-01-4	1.55			1	62	64	
4	Bromomethane	74-83-9	1.80	1.80	100	1	94	96	
5	Chloroethane	75-00-3	1.89			1	64	49	
6	Fluorotrichloromethane	75-69-4	2.12	2.10	100	1	101	103	66
7	1,1-dichloroethene	75-35-4	2.62	2.55	100	1	96	61	98
8	Dichloromethane	75-09-2	3.17	3.10	100	1	49	84	86
9	1,2-dichloroethene Z	156-60-5	3.50	3.45	100	1	61	96	98
10	1,1-dichloroethane	75-34-3	4.11	4.00	100	1	63	83	98
11	2,2-dichloropropane	594-20-7	5.07	4.60	70	1	77	41	
12	1,2-dichloroethene E	156-59-2	5.13			1	61	96	98
13	Bromochloromethane	74-97-5	5.55	5.50	70	1	49	130	
14	Trichloromethane	67-66-3	5.75			1	83	47	
15	1,1,1-trichloroethane	71-55-6	6.02			1	97	61	
16	Tetrachloromethane	56-23-5	6.32	6.25	70	1	119	117	82
17	1,1-dichloro-1-propene	563-58-6	6.35			1	75	39	110
IS1	**1,2-dichloroethane d$_4$**		6.72			IS1	65	102	
18	Benzene	71-43-2	6.73	6.55	70	2	78	52	
19	1,2-dichloroethane	107-06-2	6.79			1	98	62	
20	Trichloroethene	79-01-6	7.98	7.40	100	1	132	95	130
21	1,2-dichloropropane	78-87-5	8.40	8.30	100	1	63	76	112
22	Dibromomethane	74-95-3	8.61			1	174	93	79
23	Bromodichloromethane	75-27-4	8.97	8.85	100	1	83	47	129
24	1,3-dichloropropene Z	542-75-6	9.82	9.50	100	1	75	39	110
IS2	**Toluene d$_8$**		10.30	10.10	70	IS2	98	100	70
25	Toluene	108-88-3	10.42			2	91	92	65
26	1,3-dichloropropene E	542-75-6	10.93	10.68	100	1	75	39	110

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Peak no	Name	CAS	RT (min)	Start time window	Dwell time (ms)	IS	Target ion	Qualifiers	
27	1,1,2-trichloroethane	79-00-5	11.25	11.10	100	1	97	83	61
28	Tetrachloroethene	127-18-4	11.44	11.36	70	1	166	131	94
29	1,3-dichloropropane	142-28-9	11.55			1	76	41	78
30	Dibromochloromethane	124-48-1	11.96	11.75	70	1	129	127	79
31	1,2-dibromoethane	106-93-4	12.12			1	107	109	27
IS3	**Chlorobenzene d$_5$**		13.00	12.50	70	IS3	117	82	54
32	Chlorobenzene	108-90-7	13.09			3	112	51	77
33	1,1,1,2-tetrachloroethane	630-20-6	13.29	13.21	70	1	131	117	95
34	Ethylbenzene	100-41-4	13.35			2	91	106	51
35	m-xylene	108-38-3	13.59			2	91	106	51
36	p-xylene	106-42-3	13.59	13.47	100	2	91	106	51
37	o-xylene	95-47-6	14.34	14.00	80	2	91	106	51
38	Styrene	100-42-5	14.38			2	104	78	
39	Tribromomethane	75-25-2	14.70	14.54	100	1	173	252	91
40	Cumene	98-82-8	15.08	14.88	100	2	105	120	77
41	Bromobenzene	108-86-1	15.59	15.35	50	3	77	156	
42	1,1,2,2-tetrachloroethane	79-34-5	15.72			1	83	85	
43	1,2,3-trichloropropane	96-18-4	15.76			1	75	77	110
44	n-propylbenzene	103-65-1	15.89			2	120	91	
45	2-chlorotoluene	95-49-8	16.01			3	91	126	
46	4-chlorotoluene	106-43-4	16.23	16.12	80	3	126	91	63
47	1,2,4-trimethylbenzene	95-63-6	16.26			2	105	120	
48	*tert*-butylbenzene	98-06-6	16.88	16.60	80	2	134	119	91
49	1,3,5-trimethylbenzene	108-67-8	16.98			2	105	120	
50	*sec*-butylbenzene	135-98-8	17.31	17.15	70	2	105	134	91
51	1,3-dichlorobenzene	541-73-1	17.46			3	146	111	75
52	Cymene	99-87-0	17.62	17.55	80	2	119	134	
53	1,4-dichlorobenzene	106-46-7	17.65			3	146	111	75
54	1,2-dichlorobenzene	95-50-1	18.36	18.00	70	3	146	111	75
55	n-butylbenzene	104-51-8	18.43			2	91	134	92
56	1,2-dibromo-3-chloropropane	96-12-8	19.93	19.00	100	1	157	75	153
57	1,2,4-trichlorobenzene	120-82-1	21.55	20.80	100	3	180	145	109
58	Hexachloro-1,3-butadiene	87-68-3	21.93	21.75	80	1	225	190	260
59	Naphthalene	91-20-3	22.01			2	128	102	
60	1,2,3-trichlorobenzene	87-61-6	22.49	22.28	100	3	180	145	109

Method Development

Column Selection and Chromatographic Conditions

For the analysis of VOCs, a column with low phase ratio (relatively thick film) is normally used. In this work, a 20 m × 180 µm id column coated with 1 µm DB-624 was used. This column (or a 0.25 mm id version) has recently become preferred for EPA Methods 524 or 624 compared to larger diameter columns used when the methods were originally developed. The narrow id allows one to speed up the analysis while maintaining resolution. Most of the target analytes were well separated using the temperature program indicated above. In cases of coelution, solutes could be effectively quantified using unique MS ions. Only p-xylene and m-xylene were not separated at all. In addition, the quantification ion may need to be changed if both 1,2-dichloroethene (E) and 2,2-dichloropropane (t_R = 5.1 minutes) or 1,1,2,2-tetrachloroethane and 1,2,3-trichloropropane (t_R = 15.7 minutes) are found to be present in samples.

Another critical aspect in the analysis of VOCs by SHS or P&T coupled to GC/MS is the focusing of the most volatile
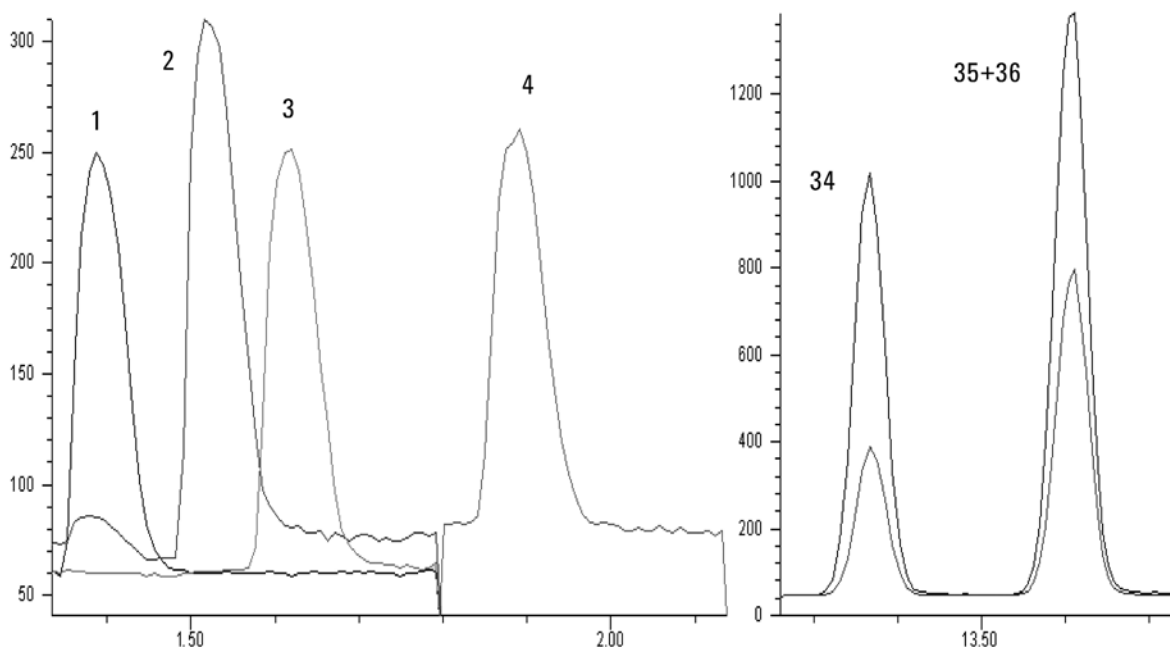
Figure 1. Peak shape of very volatile compounds compared to less volatile compounds – Extracted Ion Chromatograms at m/e 85 (1. CCL_2F_2), m/e 50 (2. chloromethane), m/e 62 (3. vinylchloride), m/e 94 (4. bromomethane), and ions at m/e 91 and 106 (34. ethylbenzene and 35/36. m/p xylene).

(gaseous) solutes (first six eluters). If the transfer from the sampler (SHS or P&T) is too slow, their bandwidths are large or distorted. Transfer and injection speeds can be increased by increasing the split ratio, but the sensitivity decreases as a consequence. A good compromise was found using a 1:10 split ratio. The resulting peak widths obtained for a water sample spiked at the 300 ppt level are shown in Figure 1. The peaks for early peaks difluorodichloromethane, chloromethane, vinylchloride, and bromomethane are broader than for the later-eluting (focused) analytes, such as ethylbenzene and xylenes, but were still acceptable for good quantification at the required detection limits.

Effect of Salt Addition

The sensitivity of an SHS method is limited by the concentration of the VOC in the headspace. This concentration depends on the initial concentration in the water, the phase ratio between liquid phase and gas phase, and the water/air distribution constant. The last depends on solute characteristics (vapor pressure, water solubility), temperature, pressure, pH, and salt concentration.

To normalize the salt concentration (same concentration in calibration solutions and samples), a high concentration of salt (sodium chloride, sodium sulfate) is typically added to saturate the sample.

The effect of salt addition is demonstrated in Figure 2 by comparing the responses of the VOCs obtained by analyzing a water sample spiked at 300 ppt level with and without salt addition. An average gain in sensitivity by a factor 2.2 was obtained by addition of salt. The "salting-out effect" drives the VOCs into the headspace. For some solutes, such as 1,2-bromo-3-chloropropane, which has a lower response in MS, the gain was almost a factor of 4.

Figure 2 shows overlaid SIM chromatograms for some early-eluting (highly volatile) solutes (Figure 2a) and mideluting ones (Figure 2b). The gain factor for the most volatile solutes (gases: chloromethane to vinylchloride) is small for some (= 1.5), but is larger for the mideluters (gain is a factor < 2.5).
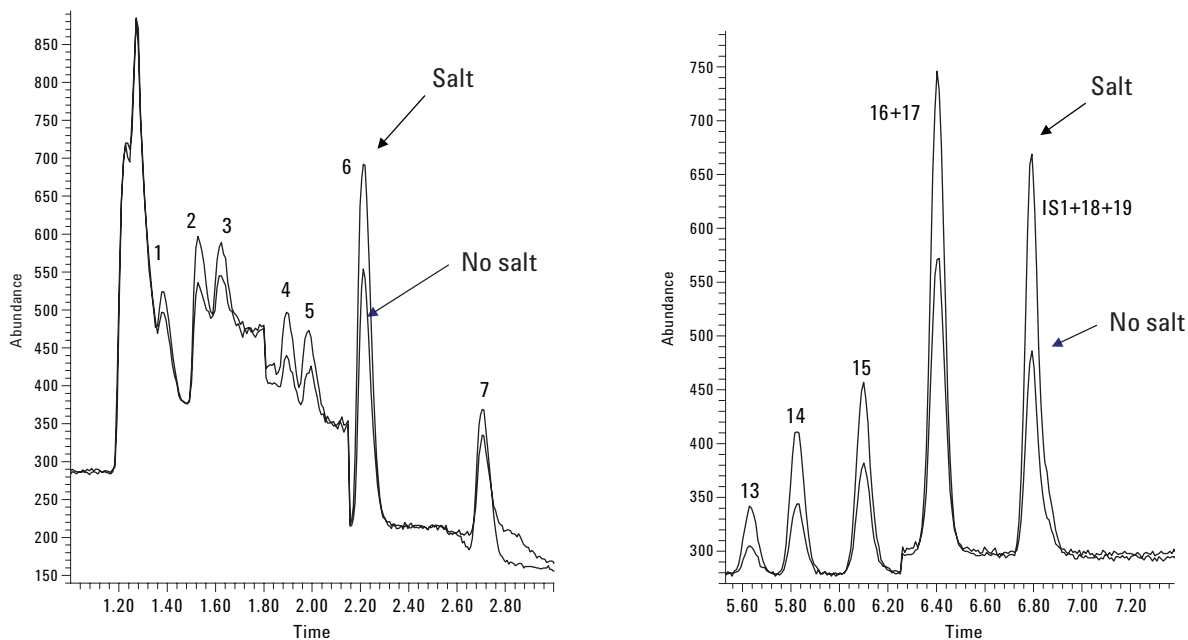
Figure 2.   Effect of salt addition on response, water spiked at 300 ppt. See Tables 1 and 2 for peak identification.

SHS Conditions

Incubation Time

Since SHS is an equilibrium technique, the equilibration time plays an important role. Maximum sensitivity is obtained if equilibrium is reached between the concentration of the solutes in the sample and in the headspace gas phase. Tests were made using a 10-mL water sample spiked at 300 ppt level. Headspace injections were performed after equilibration times between 10 and 60 minutes (using 80 °C equilibration temperature, high shaking).

No significant difference in peak areas was observed for the different VOCs, indicating that equilibrium is reached for the 10-mL sample using the high-shaking mode on the G1888 in less than 10 minutes. Therefore, an equilibration time of 10 minutes was selected for further work.

Incubation Temperature

The sample-headspace equilibrium is also influenced by the temperature. Seven experiments with increasing incubation temperature from 40 to 100 °C in 10 °C increments were performed (10-minute equilibration time, vial pressure: 48 kPa).

In general it is expected that a higher temperature will increase the concentration of the solutes in the headspace and consequently will increase the response in GC/MS analysis.

From the experiments, however, some interesting observations can be made. The responses (peak areas) for some selected solutes are plotted versus equilibration temperature in Figure 3. Vinylchloride was selected as representative for the high-volatility (early-eluting) VOCs, benzene was selected as representative for a medium-volatility (mideluting) VOC, and 1,2,3-trichlorobenzene as a representative for the late-eluting, low-volatility VOCs.

As can be seen from the plots, the high-volatility solutes behave slightly differently from the others. Between 40 and 70 °C, the response obtained for vinylchloride is nearly constant. At temperatures higher than 70 °C, the response drops. The same behavior was observed for the other early-eluting solutes (for example, dichlorodifluoromethane, chloromethane, bromomethane, chloroethane and fluorotrichloromethane). For these solutes, static headspace extraction at low equilibration temperatures is already efficient.

For medium- and low-volatility solutes, the analytical sensitivity maximized at 70 °C. For all solutes, including the high-volatility analytes, responses decreased by 50 to 60 percent as the equilibrium temperature increased from 70 to 100 °C. This is probably caused by increased vial pressure leading to higher dilution during sample loading (decompression) in the headspace sampler.
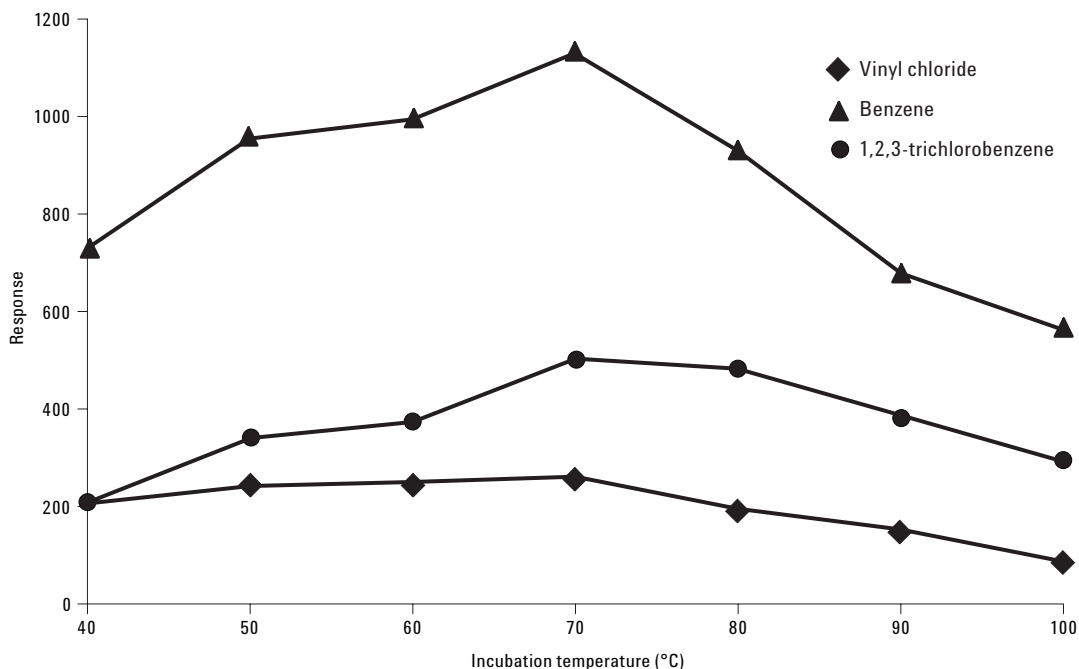
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Incubation temperature influence

Figure 3.   Influence of SHS incubation temperature on response for vinylchloride (early eluter), benzene (mideluter), and 1,2,3-trichlorobenzene
(late eluter).

The higher response obtained at 70 °C in comparison to equilibration at 40 °C is illustrated for the solutes eluting in the 2.5- to 9-minute elution window (eluting between dichloroethene and bromodichloromethane) in Figure 4a. In Figure 4b, the chromatograms obtained at 70 and 100 °C (similar elution window as in Figure 4a) are compared. The decrease in response at 100 °C is clear and, moreover, an increase in background level is observed. This is probably due to the introduction of a higher amount of water (as vapor) during headspace injection.

For these reasons, 70 °C was selected as the optimum equilibration temperature.
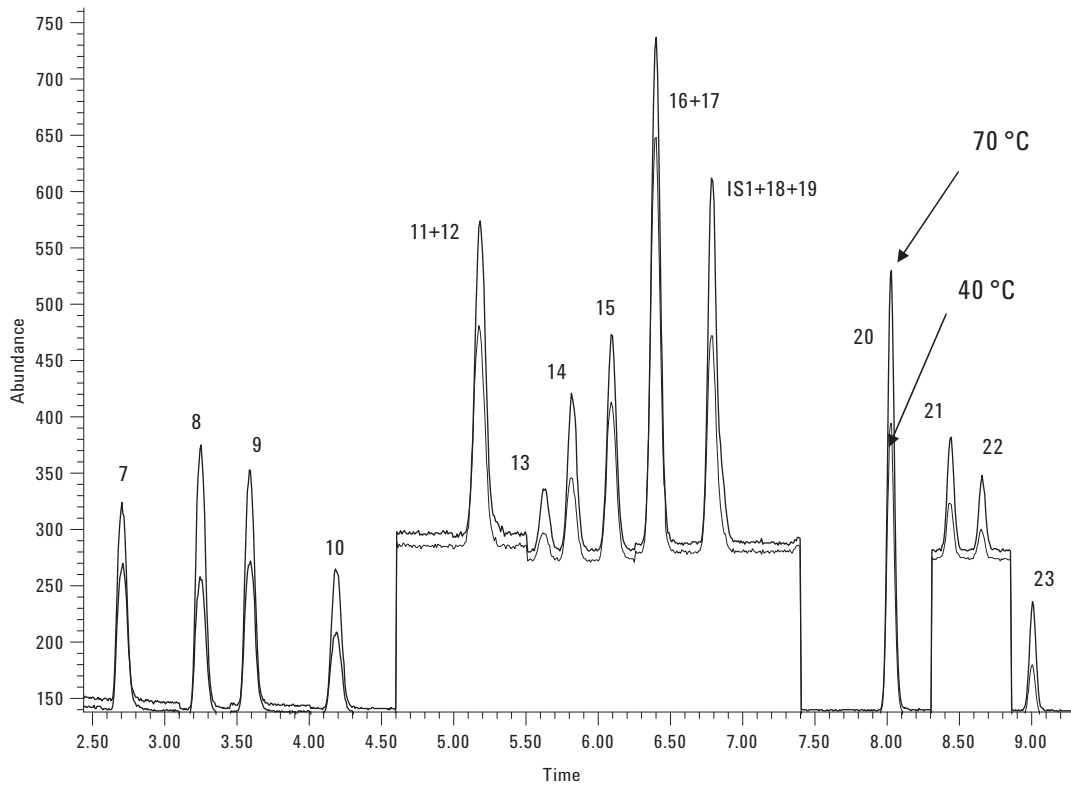
Figure 4a.   Overlay of SIM chromatograms obtained by SHS GC/MS using incubation temperatures of 40 and 70 °C. See Tables 1 and 2 for peak identification.
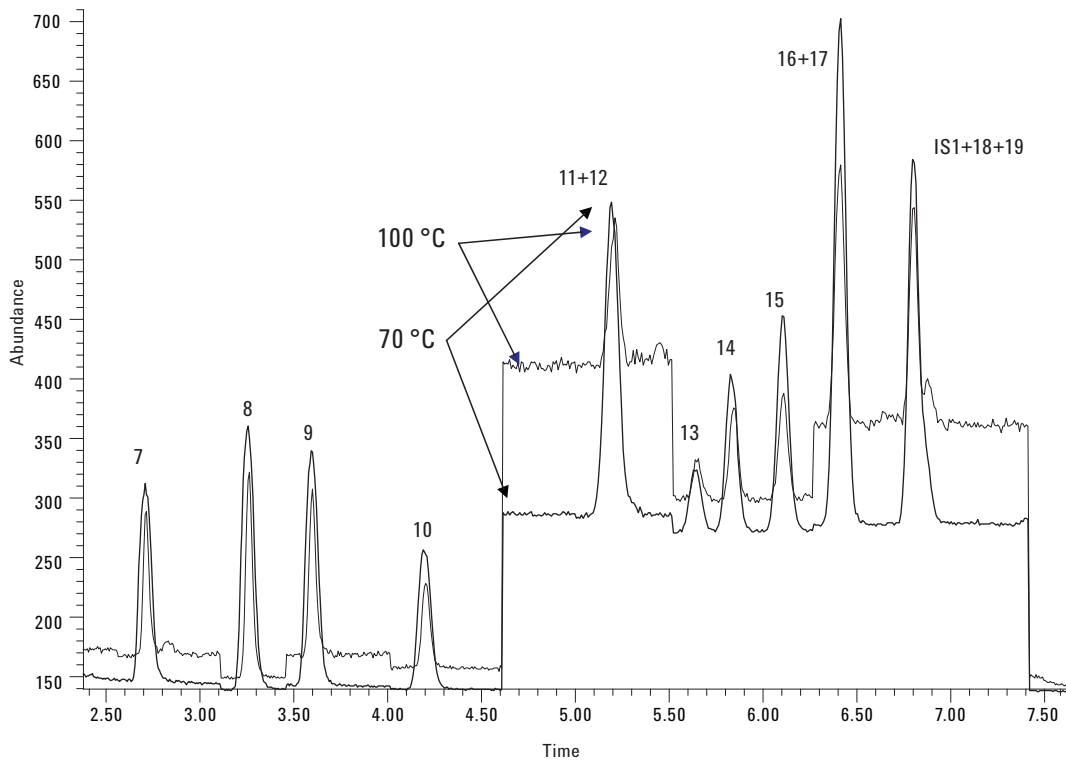

Figure 4b.   Overlay of SIM chromatograms obtained by SHS GC/MS using incubation temperatures of 70 and 100 °C. See Tables 1 and 2 for peak identification.

Vial Pressure

After equilibrium, the vial is pressurized with carrier gas. The pressurized headspace is vented to a gas sampling valve with sample loop for subsequent injection into the GC/MS for analysis. The pressure provides a reproducible driving force to move sample to the loop. Too little pressure will prevent a representative sample from filling the sample loop. Too much pressure will result in excessive dilution of headspace, lowering the concentration of analytes and reducing analytical sensitivity. Since the optimal vial pressure is a function of several variables, such as vial size, sample temperature, and sample loop volume, it should be optimized.

Six experiments were performed at 70 °C equilibrium temperature and 10-minute equilibrium time with increasing vial pressures from 0 to 100 kPa in 20-kPa increments. No significant difference in analyte sensitivity was observed for vial pressure settings between 0 and 40 kPa. At higher vial pressures, however, the response of all analytes dropped (response at 100 kPa was 30 percent lower than at 20 kPa vial pressure). A vial pressure of 20 kPa was selected as optimum.

Final Chromatogram

An example of a blank water sample spiked at 1,250 ppt level with all 60 solutes and the three internal standards (at 800 ppt) is shown in Figure 5.
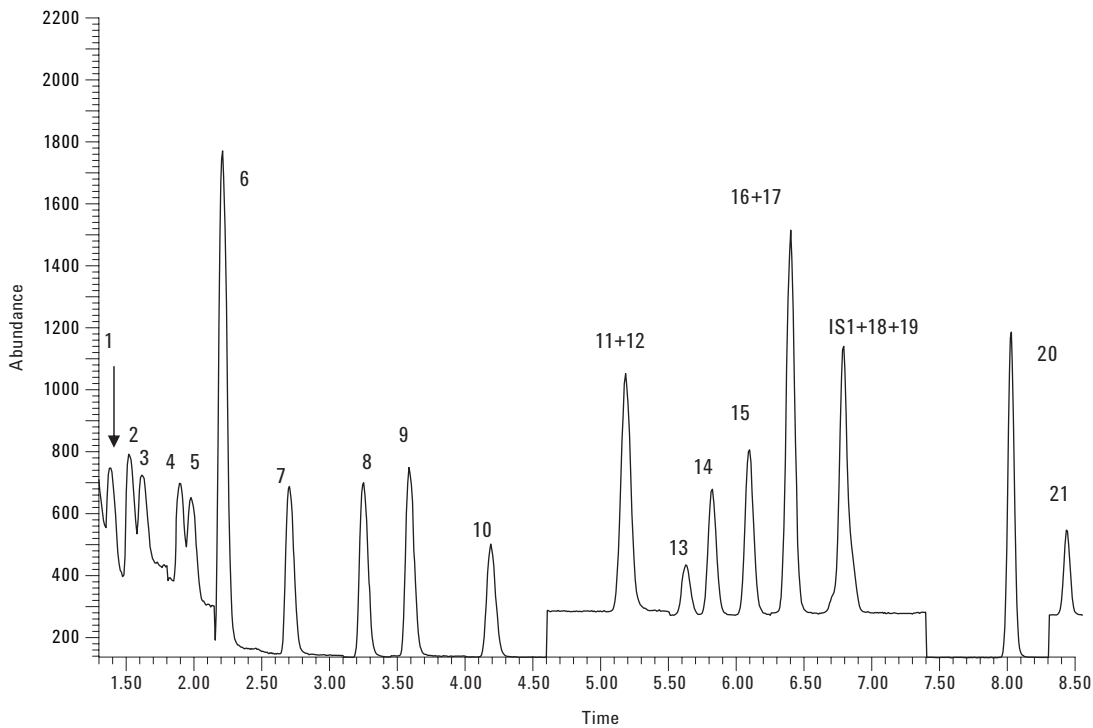

Figure 5a.   SIM chromatogram obtained by SHS GC/MS of water sample spiked at 1.25 ppb with VOCs. See Tables 1 and 2 for peak identification.
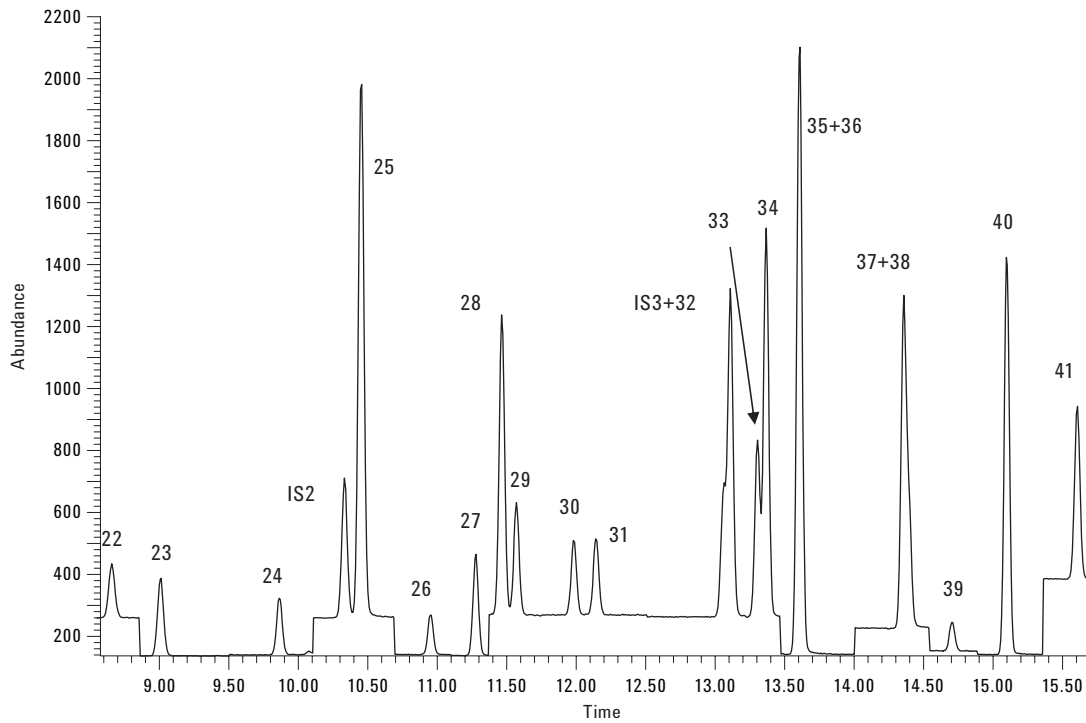
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Figure 5b. SIM chromatogram obtained by SHS GC/MS of water sample spiked at 1.25 ppb with VOCs. See Tables 1 and 2 for peak identification.

Figure 5c. SIM chromatogram obtained by SHS GC/MS of water sample spiked at 1.25 ppb with VOCs. See Tables 1 and 2 for peak identification.
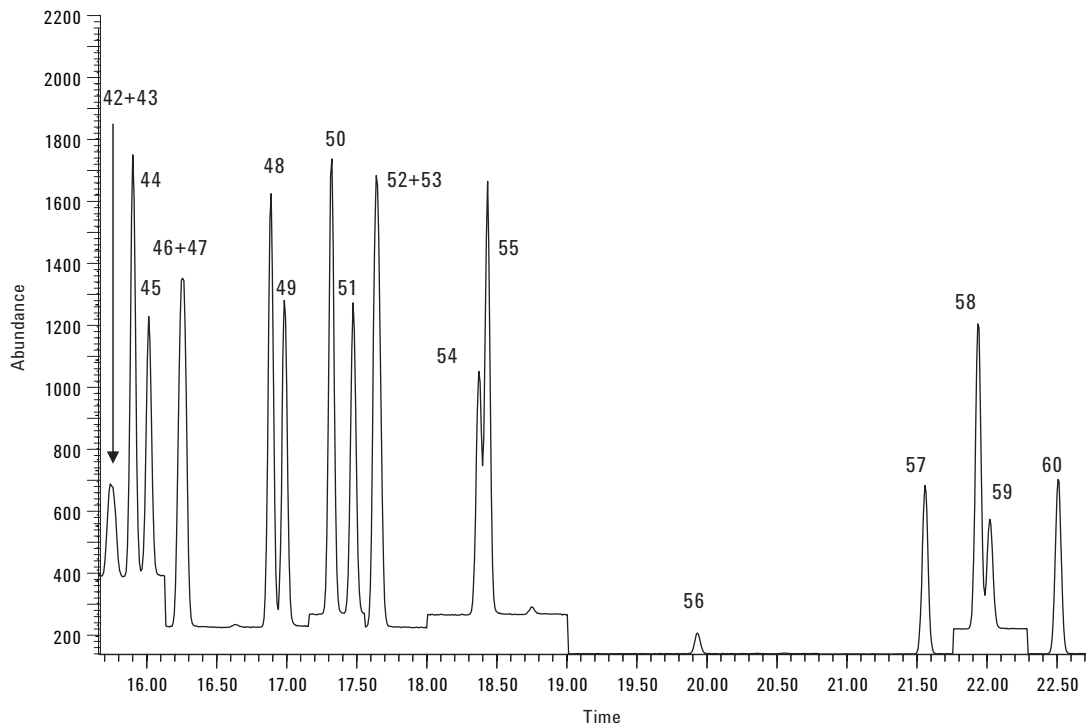
Validation

Linearity

Linearity was tested on five levels (+ blank) between 45 and 1,250 ppt. The correlation coefficients of the external standard calibration curve were 0.99 on average. The correlation coefficients for the internal standard method (plot of relative areas versus relative concentration) for all solutes are given in Table 2.

The linearity was better than 0.990 in all cases (average 0.996), except for 1,2-dibromo-3-chloropropane (r² = 0.966), which gives a lower response in MS.

The linearity was also calculated as %RSD in relative response factors over the entire calibration range. The RSD values obtained in this range are also listed in Table 2. For three solutes, namely dichloromethane, trichloromethane (chloroform), and toluene, the lowest calibration points were not taken into account, since in the blank analyses also some traces of these solutes were present (due to lab contamination).

On average, the RSDs are around 10 to 15 percent (mean = 13.6 percent), well below the 20 percent requirements specified in EPA Method 524.2 (for P&T GC/MS).

Repeatability

Repeatability (n = 6) was tested at the 150-ppt level. The average %RSD was 5.4 percent. For most solutes, even for the high-volatility analytes, the RSDs at this level were well below 10 percent. For some haloalkanes, which have lower MS responses, higher values were observed, but still meet method requirements and are close to those achieved with P&T. For low-volatility solutes, such as aromatics (BTEX) and chloroaromatics, RSDs were excellent.

Limits of Detection (LODs)

Using trace ion detection (TID) mode (selected in method setup) in combination with a triple-axis detector (hardware upgrade), improved signal-to noise values can be obtained as illustrated in Figure 6. A subset of the chromatogram is shown for a blank water sample spiked at 45 ppt, comparing standard mode (Figure 6a) and TID ON (Figure 6b). Using TID, noise is reduced, resulting in better S/N ratio.

LODs were calculated for each compound at the 45-ppt level. Results are listed in Table 2. Typically, the LODs were ≤ 20 ppt. For most aromatics and chloroaromatics, LODs were ≤ 10 ppt. For some haloalkanes and haloalkenes, the LOD was between 20 and 50 ppt. 1,2-dichloroethane had the highest value at 136 ppt.

Regulatory limits, as included in EU Directive 98/83/EC on drinking water, are 1 µg/L (1 ppb) for benzene, 10 µg/L (10 ppb) for trichloroethylene, and 0.5 µg/L (500 ppt) for vinylchloride. It is clear that the LODs obtained by this SHS GC/MS method are more than adequate to meet the EU method requirements (we achieved one to two orders of magnitude better LODs).
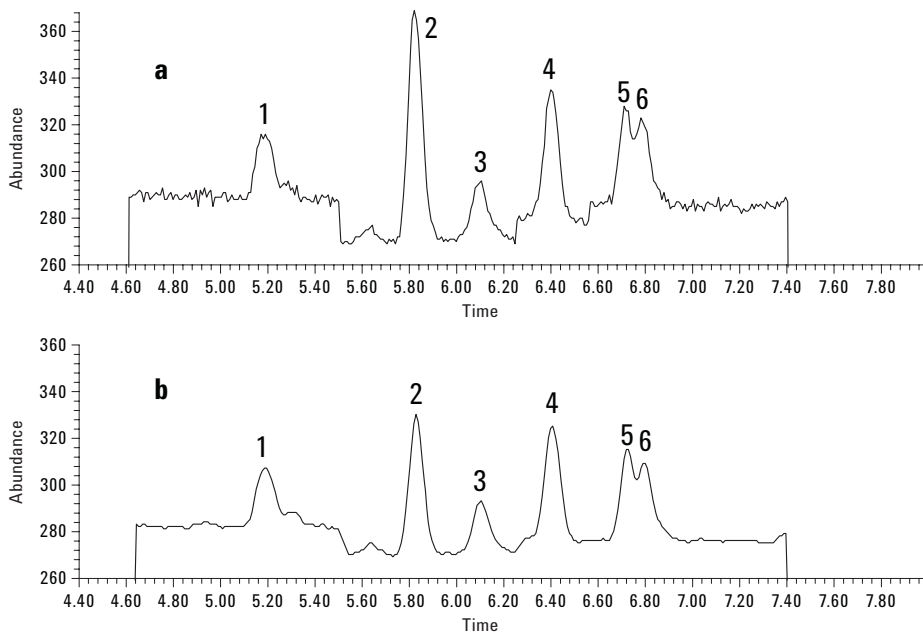

Figure 6.   SIM chromatogram with MS in normal mode (top) or in TID ON mode (bottom) (water sample spiked at 45 ppt level).
            Peaks: 1. 2,2-dichloropropane+1,2-dichloroethene; 2. trichloromethane, 3. trichloroethane (1,1,1);
            4. tetrachloromethane+1,1-dichloropropene; 5. benzene; and 6. dichloroethane.

Table. 2   Figures of Merit for VOC Analysis Using the New SHS GC/MS Method

Peak no	Compounds	RT	Q Ion	r^2 45 – 1250	RSD 150 ppt (n = 6)	RSD 45-1250	LOD (ppt)
IS1	**1,2-dichloroethane d₄**	6.72	65	/	3.3	/	/
1	Dichlorodifluoromethane	1.31	85	0.996	2.6	13.5	**24**
2	Chloromethane	1.45	50	0.995	3.8	10.7	**45**
3	Vinyl chloride	1.55	62	0.998	5.7	6.4	15
4	Bromomethane	1.80	94	0.999	6.8	6.2	**45**
5	Chloroethane	1.89	64	0.999	2.4	5.7	**27**
6	Fluorotrichloromethane	2.12	101	0.998	1.8	18.5	6.3
7	1,1-dichloroethene	2.62	96	0.999	7.2	3.5	18
8	Dichloromethane	3.17	49	0.996	5.6	**10.7***	20
9	1,2-dichloroethene trans	3.50	61	0.999	2.9	12.5	14
10	1,1-dichloroethane	4.11	63	0.999	0.7	9.5	12
11	2,2-dichloropropane	5.07	77	0.998	4.1	14.1	15
12	1,2-dichloroethene cis	5.13	61	1.000	4.2	8.4	**23**
13	Bromochloromethane	5.55	49	0.997	**15.0**	4.0	**38**
14	Trichloromethane	5.75	83	0.994	3.8	16.2*	10
15	1,1,1-trichloroethane	6.02	97	0.997	3.5	15.1	9.0
16	Tetrachloromethane	6.32	119	0.997	1.6	14.6	9.0
17	1,1-dichloro-1-propene	6.34	75	0.999	2.8	5.3	15
19	1,2-dichloroethane	6.79	98	0.992	**11.2**	5.2	**136**
20	Trichloroethene	7.98	132	0.997	5.0	6.9	10
21	1,2-dichloropropane	8.40	63	0.998	4.4	9.9	20
22	Dibromomethane	8.61	174	0.996	**11.3**	8.2	20
23	Bromodichloromethane	8.97	83	0.999	6.7	4.9	**21**
24	1,3-dichloropropene cis	9.82	75	0.999	3.6	8.3	**23**
26	1,3-dichloropropene trans	10.93	75	0.999	**19.3**	13.4	**28**
27	1,1,2-trichloroethane	11.25	97	0.995	9.0	13.5	15
28	Tetrachloroethene	11.44	166	0.998	0.8	11.5	5.9
29	1,3-dichloropropane	11.55	76	0.994	5.1	13.5	11
30	Dibromochloromethane	11.96	129	0.998	9.0	6.5	17
31	1,2-dibromoethane	12.12	107	0.994	7.6	12.0	20
33	1,1,1,2-tetrachloroethane	13.29	131	1.000	7.9	10.9	14
34	Tribromomethane	14.70	173	0.997	9.9	13.8	**23**
42	1,1,2,2-tetrachloroethane	15.72	83	0.992	9.3	12.9	14
43	1,2,3-trichloropropane	15.76	75	0.990	**14.7**	12.5	14
56	1,2-dibromo-3-chloropropane	19.93	157	**0.966**	**19.4**	9.5	**47**
58	Hexachloro-1,3-butadiene	21.93	225	0.993	3.7	16.7	5.9
IS2	**Toluene d₈**	10.30	98	/	2.9	/	/
18	Benzene	6.73	78	0.995	1.1	10.8	4.7
25	Toluene	10.42	91	0.991	2.5	**8.8***	3.8
34	Ethylbenzene	13.35	91	0.999	2.8	7.5	4.5
35+36	p-xylene + m-xylene	13.59	91	0.998	2.3	16.4	3.0
37	o-xylene	14.34	106	0.999	7.9	13.1	13
38	Styrene	14.38	104	0.997	6.7	12.1	12
40	Cumene	15.08	105	0.999	3.2	15.4	4.2
44	n-propylbenzene	15.89	120	0.999	3.9	14.0	15
47	1,2,4-trimethylbenzene	16.26	105	0.999	3.8	10.1	7.9

Peak no	Compounds	RT	Q Ion	r² 45 – 1250	RSD 150 ppt (n = 6)	RSD 45-1250	LOD (ppt)
48	*tert*-butylbenzene	16.88	134	0.998	3.8	10.7	14
49	1,3,5-trimethylbenzene	16.98	105	0.998	4.1	10.8	7.6
50	*sec*-butylbenzene	17.31	105	0.997	4.2	6.1	4.1
52	Cymene	17.62	119	0.997	4.3	17.9	5.3
55	n-butylbenzene	18.43	91	0.998	3.8	16.5	5.8
59	Naphthalene	22.01	128	0.993	4.5	11.2	14
IS3	**Chlorobenzene d$_5$**	**13.00**	**117**	/	**2.5**	/	/
32	Chlorobenzene	13.09	112	0.995	1.5	16.2	6.4
41	Bromobenzene	15.59	77	0.995	6.8	13.5	17
45	2-chlorotoluene	16.01	91	0.999	4.5	17.7	7.6
46	4-chlorotoluene	16.23	126	0.999	2.5	14.3	9.4
51	1,3-dichlorobenzene	17.46	146	0.998	2.9	15.2	7.1
53	1,4-dichlorobenzene	17.65	146	0.999	3.3	9.8	7.9
54	1,2-dichlorobenzene	18.36	146	0.997	1.1	14.6	9.0
57	1,2,4-trichlorobenzene	21.55	180	0.998	6.1	13.2	11
60	1,2,3-trichlorobenzene	22.49	180	0.997	5.3	11.3	10
	AVERAGE			**0.996**	**5.4**	**13.6**	

*Contamination at lowest (45 ppt) level. RSDs listed are in the range of 150 to 1,250 ppt.

Simultaneous Scan/SIM Mode

In the proposed method, the MS was operated in simultaneous scan/SIM mode. The SIM mode resulted in high sensitivity, while the scan mode can be used for confirmation of solute identity at 1-ppb or higher concentration levels (for some solutes even at the 0.1-ppb level).

If needed, the scan data can also be used for identification of nontarget sample components at levels above 1 ppb.

For SIM, dwell times of 50 to 100 ms were used and for scan mode, the sample rate was set at 2[1]. This corresponds to about 9 scans/s. In this way, more than five spectra are collected across the peak. This is illustrated in Figures 7a and 7b, showing the data points obtained for three late-eluting (focused) peaks (sec. butylbenzene, 1,3-dichlorobenzene, and cymene+1,4-dichlorobenzene) for a scan trace at 1-ppb level and a SIM trace at 45-ppt level, respectively. (AMDIS was used to highlight the data points).
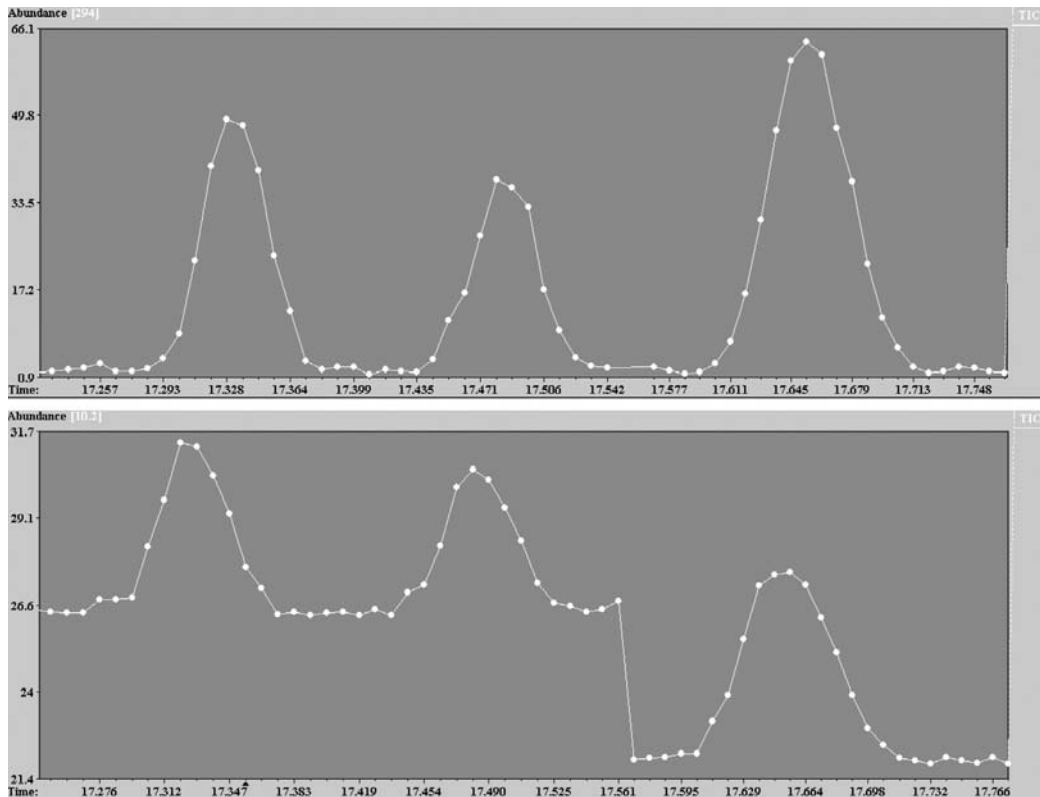
Figure 7. *Demonstration of number of data points per peak for scan chromatogram at 1.25-ppb level (top) and SIM chromatogram at 45-ppt level (bottom) using 5075C in scan/SIM mode (scan: 2^1 sampling).*

Examples

An example of an SHS GC/MS analysis of tap water sample is shown in Figure 8. In the chromatogram, several solutes are detected. Most of these solutes are identified as chlorinated hydrocarbons, originating from the chlorination process. It is interesting to note that in this sample, trichloromethane (peak 2) is only present at trace level, while in other tap-water samples, it is often present as the most abundant peak. Here the brominated halocarbons are more abundant, probably indicating a different water treatment procedure.

The concentrations of the detected VOCs were determined using the internal standard method. The following concentrations were found:

1. 1,2-cis-dichloroethene (3 ppb)
2. Trichloromethane (0.1 ppb)
3. 1,1,1-trichloroethane (0.4 ppb)
4. Trichloroethylene (0.8 ppb)
5. Bromodichloromethane (1 ppb), IS2 (d8-toluene)
6. Toluene (49 ppt)
7. Tetrachloroethylene (0.3 ppb)
8. Dibromochloromethane (6.4 ppb), IS3 (d5-chlorobenzene)
9. Tribromomethane (14 ppb)

A river-water sample was also analyzed. In this sample, chlorinated hydrocarbons were not detected. However, it was interesting to observe that some aromatic hydrocarbons were present. These aromatic hydrocarbons could originate from gasoline spillage.
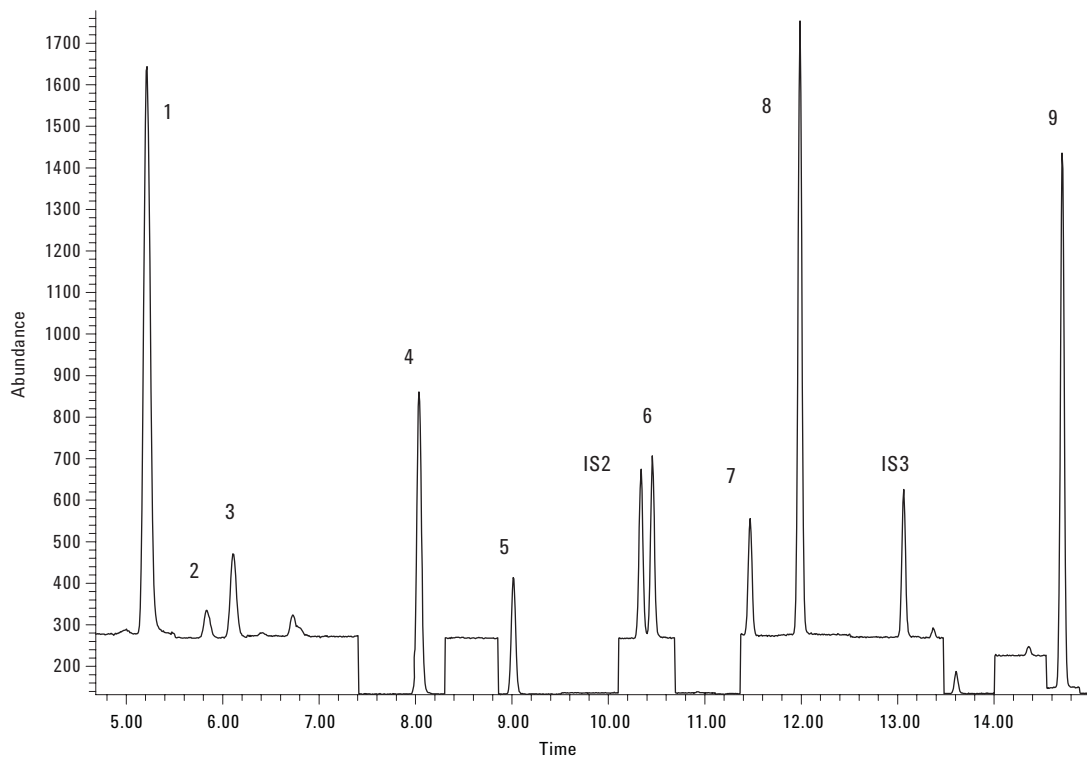
14

Figure 8.   *Analysis of tap water using SHS GC/MS. Peaks: 1. 1,2-cis-dichloroethene (3 ppb); 2. 1,1,1-trichloroethane (0.4 ppb); 3. trichloromethane (0.1 ppb); 4. trichloroethylene (0.8 ppb); 5. bromodichloromethane (1 ppb), IS2 (d8-toluene); 6. toluene (49 ppt); 7. tetrachloroethylene (0.3 ppb); 8. dibromochloromethane (6.4 ppb), IS3 (d5-chlorobenzene); and 9. tribromomethane (14 ppb).*
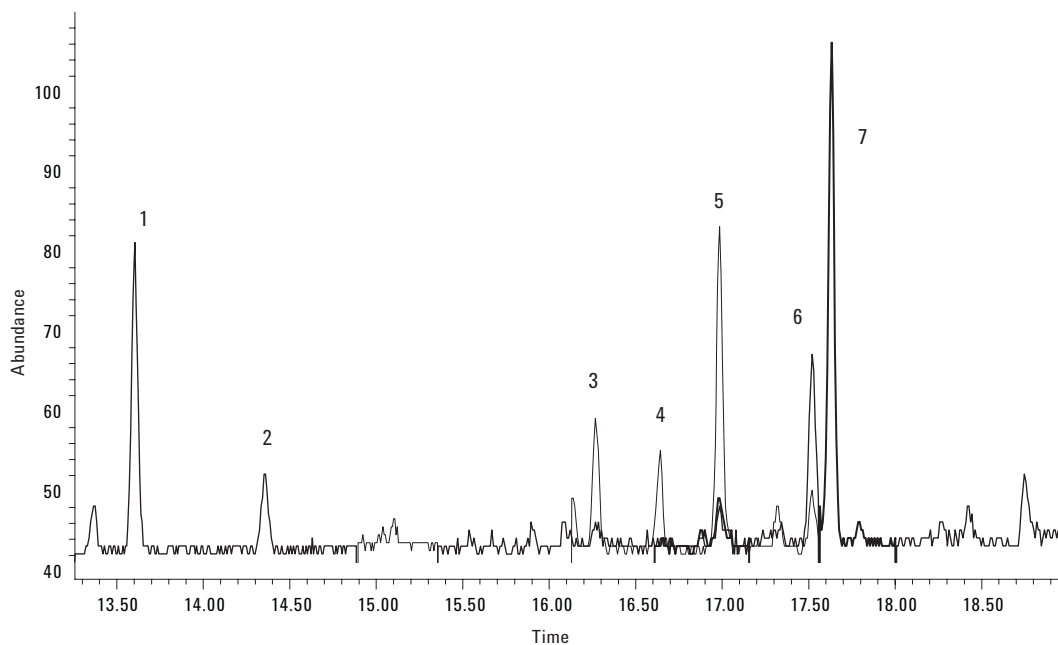

Figure 9.   *Extracted ion chromatograms obtained on river-water sample analyzed by SHS GC/MS. Peaks: 1. m/p xylene (13 ppt); 2. o. xylene (4 ppt); 3. 1,2,4-trimethylbenzene (39 ppt); 4. t.butylbenzene (5 ppt); 5. 1,3,5-trimethylbenzene (81 ppt); 6. C3-benzene isomer; and 7. cumene (88 ppt).*

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Conclusions

A fast SHS GC/MS method was developed and validated for analysis of low-level VOCs in water. Using the 5975C MSD with triple-axis detector, trace ion detection mode, and simultaneous SIM/scan mode, LODs were one to two orders of magnitude better than required by U.S. EPA and EU directives. Excellent repeatability and robustness can be obtained.

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