

# Application News

## No. M267

### Gas Chromatography Mass Spectrometry

## Ultra-Fast Analysis of Volatile Organic Compounds in Water By Headspace-GC/MS/MS

### Introduction

Volatile organic compounds (VOCs) in environmental water and tap water are typically analyzed by headspace-GC/MS or by purge-and-trap-GC/MS. Because many of these VOCs exhibit low solubility in water and vaporize easily, analyses must be conducted as soon as possible following collection of the sample, and sample holding times are kept short to minimize losses of the volatile target compounds. Additionally, the analysis time for an individual sample should be as short as possible so the maximum number of samples can be analyzed before the holding times expire, preventing low bias in the results.

Analysis on a short, narrow-bore capillary column can shorten analysis times significantly without sacrificing chromatographic separation. However, some compounds co-elute and background interference from environmental matrices can increase when using short columns, potentially obstructing identification and quantitation of target compounds at low concentrations. Using a triple quadrupole GC/MS/MS, operated in the Multiple Reaction Monitoring (MRM) mode can improve overall sensitivity of the target compounds, while simultaneously improving selectivity when peaks co-elute, or in the presence of a complex matrix.

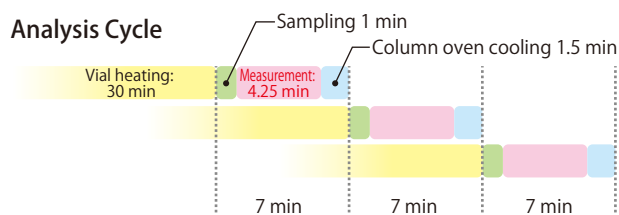
This study presents analysis conditions for 25 VOCs covering a range of volatility, using static headspace as the sample introduction technique, with GC/MS/MS operated in the MRM mode for detection and quantitation. Use of a short, narrow-bore capillary column permitted analysis of 8 samples per hour, or approximately one sample every 7 minutes.

### Experimental Instrumentation

The study was conducted using the Shimadzu HS-20 Loop Model headspace sampler, operated in the static headspace mode, with separation and compound identification using the Shimadzu GCMS-TQ8030 triple quadrupole mass spectrometer. Samples were also run in the SIM mode for comparison, to illustrate how the MRM mode can be used to provide selectivity when peaks co-elute, and to improve selectivity in a dirty matrix. Instrument configuration and operating conditions are shown in Table 1. Fig. 1 illustrates the HS-20 and GCMS-TQ8030 analysis cycle times.

**Table 1 Instrument Configuration and Operating Conditions for Analysis of VOCs by Headspace-GC/MS/MS**

Headspace Instrument	Shimadzu HS-20 Loop Model
Operation Mode	Loop mode Loop volume = 1 mL
Sample Equilibration	70 °C for 30 minutes Agitation level: Off Sample preparation overlap enabled
Sampling Conditions	Vial pressurization: 0.5 min, 50 kPa, equilibration 0.05 min Loop loading: 0.25 min, equilibration 0.05 min Sample injection = 0.1 min
Needle Flush	2 minutes
Heated Zones	Sample pathway = 200 °C Transfer line = 200 °C
GCMS Instrument	Shimadzu GCMS-TQ8030
Injection Mode	Split injection, 30:1 split ratio
Column	Rxi-624Sil MS, 20 m x 0.18 mm I.D., x 1 µm
Carrier Gas	Helium Constant linear velocity mode, 50 cm/sec
Oven Program	70 °C, 40 °C/min to 220 °C, 0.5 min hold Oven cooling 1.5 min Sample-to-sample injection interval 7 minutes
MS Analysis Mode	GC/MS in SIM mode, 2 ions per compound GC/MS/MS in MRM mode, 2 transitions per compound Event (loop) time = 0.15 sec
Heated Zones	Ion source = 200 °C GC-to-MS interface = 230 °C



**Fig. 1 HS-20 and GCMS-TQ8030 Analysis Cycle Times with One Sample Injected Approximately Every 7 Minutes.**

### Calibration Standards

Calibration standards were prepared by adding 3 grams of sodium chloride (pre-cleaned by heating to 300 °C, followed by cooling to room temperature) to five 20 mL headspace vials each containing 10 mL of VOC-free mineral water. Each 10-mL aliquot was spiked with 24 of the 25 target compounds to generate final concentrations of 0.1, 0.5, 1.0, 5.0, and 10 µg/L (parts-per-billion, ppb). The 1,4-dioxane was spiked at a concentration 10-fold higher than the other compounds because of its relatively higher solubility in water and lower sampling efficiency. Each calibration standard solution was also spiked with 4 internal standards (IS): vinyl chloride-d3 (4 ppb), p-bromofluorobenzene (2 ppb), fluorobenzene (2 ppb), and 1,4-dioxane-d8 (20 ppb). All calibration standards were analyzed using the conditions shown in Table 1.

## Results and Discussion

Fig. 2 shows the total ion current chromatogram (TIC) acquired from analysis of a 5 µg/L (ppb) calibration standard using the conditions shown in Table 1. From the chromatogram, it is evident that there are several co-eluting pairs, for example MTBE (#5) and *trans*-1,2-dichloroethylene (#6), or 1,2-dichloroethane (#11) and benzene (#12). In the case of vinyl chloride-d3 (#1) and vinyl

chloride (#2), the compounds also elute in the portion of the chromatogram subject to disruption from the early-eluting water peak. Careful selection of appropriate MRM transitions can provide sufficient selectivity to properly identify and integrate the individual co-eluting compounds, as well as those compounds affected by matrix interference, in this case water.

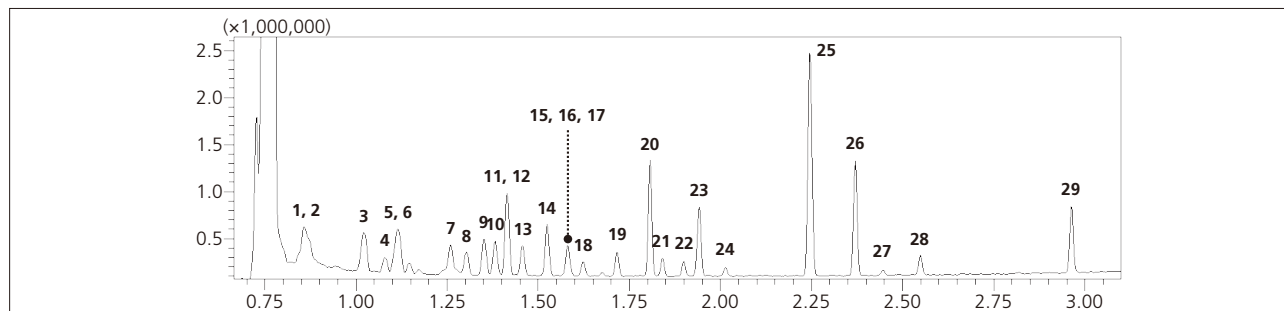


Fig. 2 Total Ion Current Chromatogram (TIC) of the 5 µg/L VOC Calibration Standard

Fig. 3 illustrates how the MRM mode can be used to selectively separate individual co-eluting peaks, and to eliminate background interference from the matrix. Vinyl chloride-d3 and vinyl chloride not only co-elute with one another, they elute on the tail of the large, early-eluting water matrix peak which makes unambiguous peak integration difficult when data are acquired in the SIM mode (top of Fig. 3). Using the MRM mode

(bottom of Fig. 3), interference from the water matrix peak is completely eliminated, and the two peaks are easily integrated for calibration or quantitation. Comparative SIM and MRM chromatograms of 1,4-dioxane-d8 (#15) and 1,2-dichloropropane (#16) provide an example of how the MRM mode is used to selectively separate co-eluting peaks from one another when they have similar mass spectral fragments.

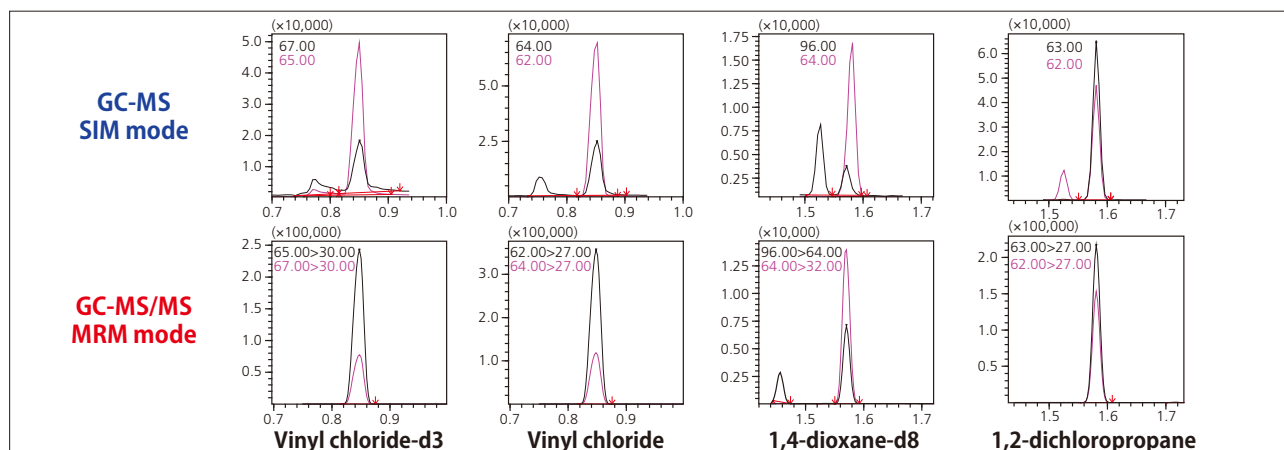


Fig. 3 SIM Chromatogram (Top) and MRM Chromatogram (Bottom) of Selected VOCs

Statistical results of the calibration are shown in Table 2. Relative Standard Deviation (RSD) of concentrations from n=5 analyses was 10.6 % or better for all compounds, and correlation coefficients (R) were 0.999 or higher, indicating linearity across the calibration range of 0.1 to 10.0 µg/L.

Table 2 Calibration Statistics for VOCs

Peak No.	Compound Name	%RSD	Correlation Coefficient (R)
1	Vinyl chloride-d3 (ISTD)	-	-
2	Vinyl chloride	2.13	0.9997
3	1,1-dichloroethylene	4.28	0.9998
4	Dichloromethane	5.57	0.9997
5	Methyl-t-butyl ether (MTBE)	5.02	0.9997
6	<i>Trans</i> -1,2-dichloroethylene	5.53	0.9996
7	<i>Cis</i> -1,2-dichloroethylene	5.17	0.9996
8	Trichloromethane	9.47	0.9995
9	1,1,1-trichloroethane	3.63	0.9995
10	Carbon tetrachloride	1.32	0.9997
11	1,2-dichloroethane	8.71	0.9993
12	Benzene	6.13	0.99976
13	Fluorobenzene (ISTD)	-	-
14	Trichloroethylene	3.81	0.9996
15	1,4-dioxane-d8 (ISTD)	-	-

Peak No.	Compound Name	%RSD	Correlation Coefficient (R)
16	1,2-dichloropropane	6.77	0.9997
17	1,4-dioxane	9.71	0.9999
18	Bromodichloromethane	6.34	0.9996
19	<i>Cis</i> -1,3-dichloropropene	4.51	0.9995
20	Toluene	7.21	0.9996
21	<i>Trans</i> -1,3-dichloropropene	4.23	0.9994
22	1,1,2-trichloroethane	4.91	0.9994
23	Tetrachloroethylene	5.36	0.9996
24	Dibromochloromethane	8.08	0.9996
25	<i>m</i> -, <i>p</i> -xylene	4.06	0.9997
26	<i>o</i> -xylene	2.76	0.9997
27	Bromoform	10.6	0.9996
28	4-bromofluorobenzene	-	-
29	1,4-dichlorobenzene	1.22	0.9998

## Conclusion

Operating conditions for the Shimadzu HS-20 Loop Model headspace sampler and the Shimadzu GCMS-TQ8030 triple quadrupole mass spectrometer have been optimized for analysis of up to 8 VOC samples per hour. The triple quadrupole Multiple Reaction Monitoring mode provided sensitivity to detect and quantitate VOC compounds at 0.1 ppb, and to selectively analyze compounds which co-elute with one another, or which are subject to interference from the matrix.

## Materials Used

The VOC-free mineral water was from Volvic. All analytical standards were acquired from Wako Pure Chemical Industries, Ltd., as shown below.

- VOC compound mixture, Code No. 224-01581
- Vinyl chloride, Code No. 515-01081
- 1,4-dioxane, Code No. 049-28791
- Vinyl chloride-d3, Code No. 512-36141
- *p*-bromofluorobenzene + fluorobenzene, Code No. 029-15021
- 1,4-dioxane-d8, Code No. 042-29021